AIS-066

AUTOMOTIVE INDUSTRY STANDARDS

Guidelines for Analysis of Automotive Rubbers by Fourier Transform Infra-red Spectrometry (FTIR) and Thermogravimetry (TGA) Techniques

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UNDER

CENTRAL MOTOR VEHICLE RULES - TECHNICAL STANDING COMMITTEE

SET-UP BY

MINISTRY OF ROAD TRANSPORT & HIGHWAYS
GOVERNMENT OF INDIA

July 2004

Status chart of the Standard to be used by the purchaser for updating the record

Sr. No.	Corr-igenda.	Amend-ment	Revision	Date	Remark	Misc.

General remarks :

Introduction

The Government of India felt the need for a permanent agency to expedite the publication of standards and development of test facilities in parallel when the work on the preparation of the standards is going on, as the development of improved safety critical parts can be undertaken only after the publication of the standard and commissioning of test facilities. To this end, the Ministry of Surface Transport (MOST) has constituted a permanent Automotive Industry Standard Committee (AISC) vide order No. RT-11028/11/97-MVL dated September 15, 1997. The standards prepared by AISC will be approved by the permanent CMVR Technical Standing Committee (CTSC). After approval, the Automotive Research Association of India, (ARAI), Pune, being the Secretariat of the AIS Committee, has published this standard. For better dissemination of this information ARAI may publish this document on their Web site.

The present automotive standard is prepared to provide guidelines to the users for incorporating Fourier Transform Infra-red (FT-IR) Spectrometer and Thermogravimetry (TGA) techniques in general practice for quality control, material screening and related problem solving where a composition can be made with a known material of the same type. It is recommended for identification of polymeric material, UV degradation additives, etc used in the construction of safety related components.

Considerable assistance has been taken from the following International standards.

1. BS 4181, Part 1-1985; ISO 4650:1985 “Identification of Rubbers by Infra-red Spectrometry” Part 1 – Method for identification of hydrocarbon, chloroprene, nitrile and chlorosulphonated polyethylene rubbers.
2. ASTM D 3677:90; “Rubber Identification by Infra-red Spectrometry”.
3. ASTM E 1131:93; “Composition Analysis by Thermogravimetry”.

The Automotive Industry Standards Committee (AISC) responsible for preparation of this standard is given in Annexure :II

Guidelines for Analysis of Automotive Rubbers by Fourier Transform Infra-red Spectrometry (FTIR) and Thermogravimetry (TGA) Techniques

1. SCOPE

1.1 The test method described in the standard is a guideline technique for identification and composition analysis of automotive rubbers. It includes rubbers in the raw state and, when compounded, both in the cured & uncured state.

Limitation : For the cured rubber, it is advisable to do extraction with solvent like Acetone / MEK before doing FT-IR test, as the chemicals and blends of two or more rubber may interfere the spectra and mislead the conclusion.

1.2 The standard specifies Infrared spectrometry (FTIR) and Thermogravimetry (TGA) instrumental techniques to examine both pyrolysis products (pyrolysates) and of films cast from solutions.

1.3 The FTIR spectrophotometer technique is intended to provide qualitative identification of rubber polymer, while, TGA method to determine the amounts of volatile matters, combustible materials and ash content of rubber compounds.

2. REFERENCES

FT-IR Spectrometer Technique

- BS 4181, Part 1-1985; ISO 4650:1985 "Identification of Rubbers by Infra-red Spectrometry" Part 1 – Method for identification of hydrocarbon, chloroprene, nitrile and chlorosulphonated polyethylene rubbers.
- ASTM D 3677:90; "Rubber Identification by Infra-red Spectrometry".

TGA Technique

- ASTM E 1131:93; "Composition Analysis by Thermogravimetry".

3. SIGNIFICANCES & USES

3.1 The guidelines in the standard are intended for research, development, quality control, material screening and related problem solving where compositional analysis is desired or a comparison can be made with known materials of the same type utilizing an Infra-red and thermo-gravimetric techniques.

3.2 The techniques should be used for identification and composition analysis of the automotive rubbers and their blends (Table-1) used for the construction of vehicles.

3.3 The standard should be used by raw material manufacturers, rubber compounders, moulders, auto manufacturers to have consistency in quality of rubber products to meet desired performance and life expectancy in the field. To meet desired mechanical strength and stability in some of the elastomeric components it is essential to maintain specific carbon-to-polymer ratio ranges. In some cases control on specific inert content (for example, ash, filler, reinforcing agent, etc.) is required to meet performance specifications.

4. SUMMARY OF TEST METHOD

4.1 FTIR Spectrometer Technique

4.1.1 Identification from Pyrolyzates

4.1.1.1 A small quantity of extracted and dried rubber is pyrolzed in a stream of nitrogen in a test tube held in a small electric furnace at 450 to 500^{0}C, or alternatively, rapidly pyrolyzed in a small test tube in the hot zone of a gas flame.

4.1.1.2 A Congo Red paper Test for chlorine is conducted during pyrolysis.

4.1.1.3 A few drops of the pyrolyzate are transferred to a salt (KBr) plate and an infrared spectrum recorded over the 4000 – 400 cm^{-1} wave number region (2.5 – 0.25 µm wavelength).

4.1.1.4 The rubber is identified by comparison to the standard reference spectra and by the reference table of diagnostic absorptions (Ref. Annex-I).

Table 1

Commonly used Automotive Rubbers and analyzed by FTIR Spectrometer & TGA Techniques

Abbreviations	*Rubber Polymer*
NR	Natural Rubber (NR) – Natural isoprene rubber
NBR	Nitrile Butadiene Rubber
H - NBR	Hydrogenated Nitrile Butadiene Rubber
SBR	Styrene Butadiene Rubber
BR	Polybutadiene Rubber
IIR	Butyl Rubber
EPDM	Ethylene Propylene Terpolymer
CR	Polychloroprene (Neoprene) Rubber
CO / ECO	Epichlorohydrene
CSM	Chlorosulphonated Polyethylene
ACM	Acrylic Elastomer
Q	Silicones
FKM / FPKM	Fluoro Elastomers
FVMQ	Fluorosilicone elastomer
TPV	Polyurethanes
EVM	Ethylene Vinyl Acetals
Commonly used Rubber Blends	
NR + BR	Natural rubber + Butadiene rubber blend
NR + SBR	Natural rubber + Styrene Butadiene rubber
SBR + BR	Styrene Butadiene rubber + Butadiene rubber blend
NR + CR	Natural rubber + Polychloroprene rubber
NBR + PVC	Nitrile Butadiene rubber + Poly Vinylchloride
EPDM + NR	Ethylene Propylene Diene monomer + Natural rubber

4.1.1.5 Each laboratory employing this standard must prepare spectra of all rubbers they may 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.

4.1.2 Identification from films

4.1.2.1 A small quantity of extracted and dried rubber is dissolved in 1,2-dichlorobenzene, filtered, and a film cast on a salt (KBr) plate. This film is used as in 4.1.1.4.

4.1.2.2 A small quantity of extracted and dried rubber is subjected to mild thermal degradation at 200 ± 5^{0}C for a short time. The degraded is dissolved in trichloroethylene then chloroform, and a film cast on a salt (KBr) plate. This film is used as in 4.1.1.4.

4.2 Thermogravimetry (TGA) Technique

4.2.1 This method is an empirical technique using Thermogravimetry in which the mass of the rubber, heated at a controlled rate in an appropriate environment, is recorded as a function of time or temperature. Mass losses over specific temperature range and in a specific atmosphere provide a compositional analysis of the rubber.

5 APPARATUS

5.1 FTIR Spectrophotometer

5.1.1 Double beam high resolution FTIR spectrophotometer capable of recording a spectrum over the 4000 –400 cm-1 and complying with the requirement of resolution of 4 cm-1 max. should be used. An experienced analyst according to the manufacturer's directions for optimum performance shall operate the equipment.

5.2 Thermogravimetry Analyzer

5.2.1 The instrument capable of continuously weighing a sample under atmospheric control over selected temperature range or over a selected time period. The instrument should work along with:

- Electrobalance, sensitive to 2 µg
- Specimen holder constructed of material that will not decompose within the anticipated temperature range and that will not react with the specimen rubber material.
- Temperature sensor
- Furnace, to hold the specimen and temperature sensor, controllable from 25 to at least 1000^{0}C
- Temperature programmer or computer interface controller
- Output device, such as monitor, plotter, printer or analog recorder, with sufficient sensitivity to measure a 25 µg mass change per 1 cm of chart deflection minimum. The capability to measure the first derivative of the signal may be useful.
- Gas flow control device, with the capability of switching between inert and reactive gases.

6. SAMPLE PREPARATION

6.1 Temperature controlled Pyrolysis (Preferred Method) For Infrared spectrometry

6.1.1 Method samples are prepared by using Extraction Apparatus as shown in Fig.-1 and then dried sample is pyrolyzed in the Temperature controlled Pyrolysis Apparatus as shown in Fig.-2.

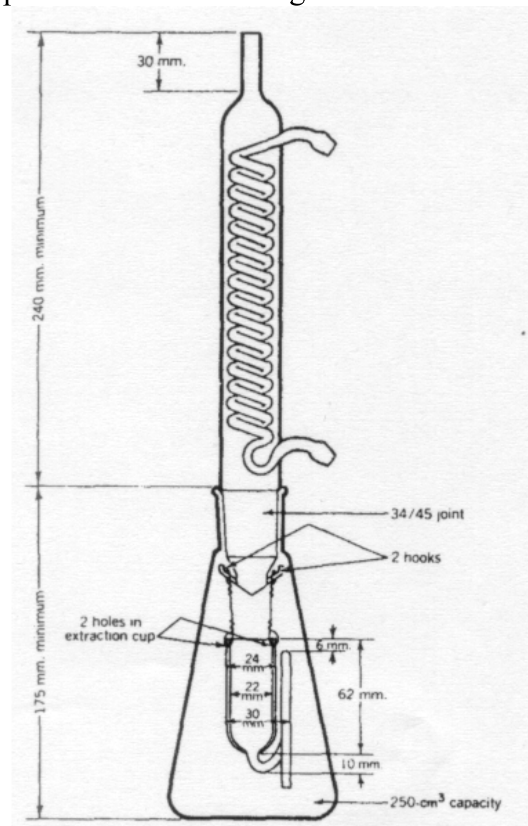


Fig. 1 Extraction Apparatus with Glass Condenser and Ground Glass Joint

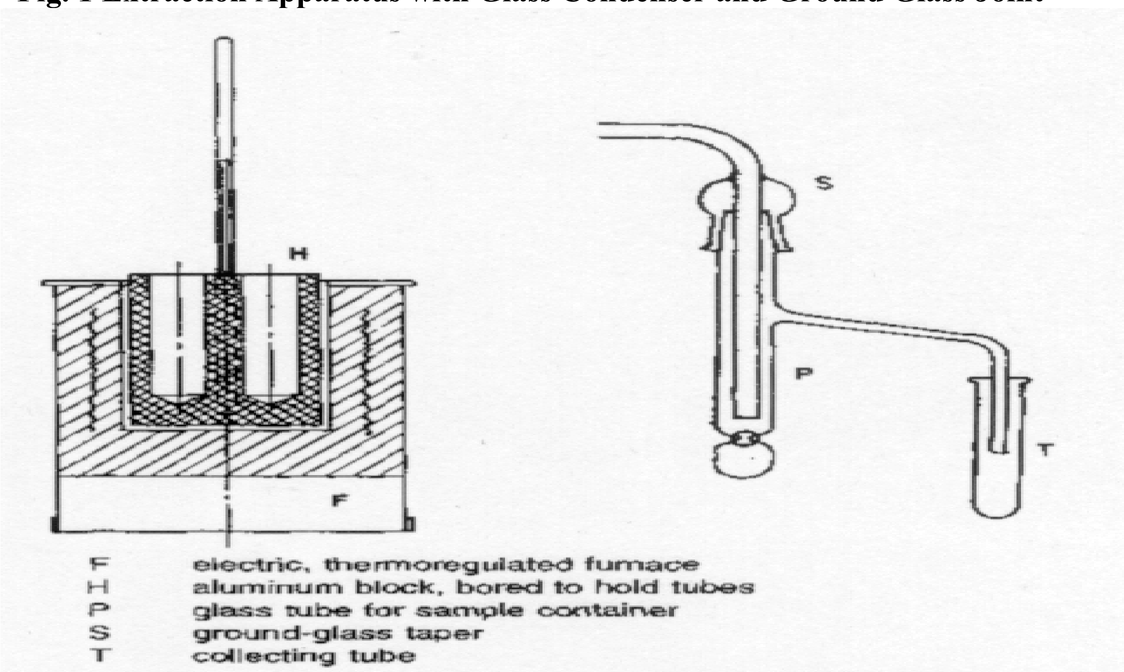


Fig. 2 Temperature Controlled Pyrolysis Apparatus

6.1.1.2 Prepare the test portion of rubber part by milling into a thin sheet on a laboratory mill or cut cubes of 2 mm wide and wrap around 0.5 gm in filter paper or nylon cloth. Then extract the test specimen in Extraction Apparatus in accordance with IS: 3400; Part 22; Annex I; clause A 1.1.1 for a minimum of 4hrs with methanol, ethanol, or 2-propanol. A vulcanizate may be extracted with acetone or 2-butanone, in addition to above alcohols. Alternatively, the rapid reflux procedure may be used for 1 hr in accordance with section 25 of test method ASTM D 297.

6.1.1.3 Remove the extracted rubber from the apparatus and dry at 100^0C and fee of solvent for 2 hrs max.

6.1.1.4 Introduce small dried sample in pyrolysis tube (Fig.-2; P). Adjust the electric regulated furnace (Fig.-2; F) to 400 – 4500C. Attach nitrogen gas inlet to the pyrolysis tube (P). Place the tube inside the aluminium block (H) bored to hold the tube. Introduce a small amount of anhydrous sodium sulphate and Congo red paper into collecting tube (T). Purge the nitrogen gas in the pyrolysis tube and collect pyrolyzate in collecting tube (T).

6.1.1.5 Place few drops of pyrolyzate on salt plate (KBr window) using capillary pipette. Place the spacer in position and close the cell with another salt plate (KBr). Mount the cell in the infrared spectrophotometer.

6.1.1.6 Record the spectrum over the IR range from 4000 – 400cm^{-1}.

6.1.2 Gas Flame Pyrolysis (Alternative Method)

6.1.2.1 Prepare extracted rubber as per 6.1.1.1 and 6.1.1.2. Dry 2 gm of sample portion as per 6.1.1.3. Place 0.1 to 0.2 gm in the bottom of small glass test tube. Place moistened Congo red paper across the mouth of tube. Hold the tube horizontally and quickly heat lower end of the tube containing test sample on the gas burner, so that the rubber is rapidly pyrolyzed and charring is kept to a minimum. Note the colour change in the Congo red paper from red to blue indicating the presence of chlorine. Maintain the heating until the pyrolyzate condenses in the cool end of the tube, withdraw the test tube from the flame and cool it while holding horizontally.

6.1.2.2 Record the infrared spectrum after preparing the sample as per 6.1.1.5.

6.1.3 Sample Preparation for Raw Rubbers

6.1.3.1 Prepare the test portion in accordance 6.1.1.1 and 6.1.1.2 pyolyze and test for chlorine.

6.1.3.2 Place 1 gm of prepared rubber (6.1.1.1 and 6.1.1.2) and 50 cm^3 of chloroform in a 100 cm^3 flask fitted with a reflux condenser. Boil until the rubber dissolves.

6.1.3.3 Cool and transfer to a beaker.

6.1.3.4 Concentrate the solution to a small volume in a stream of nitrogen.

6.1.3.5 Cast a film on a salt plate (KBr) and record the infrared spectrum taking care that film has a thickness sufficient to give approximately 10 to 20% transmittance at 1450 cm^{-1}.

6.2 Sample Preparation for Thermogravimetry Method.

6.2.1 Rubber samples are measured in as received conditions.

7 CALIBRATION

7.1 FTIR Spectrometer

7.1.1 The polystyrene thin film supplied along with the FTIR spectrometer by the manufacturer is used for routine calibration of the instrument.

7.1.2 Periodically the instrument is purged with inert nitrogen gas to remove moisture and CO_2 levels in the instrument.

7.1.3 During non-working hours and when the humidity in atmosphere is more it is recommended to keep zero watt bulb in the sample compartment to protect FTIR source lamp.

7.2 Thermogravimetry Analyzer

7.2.1 Calibrate the TGA according to the prescribed procedures or appropriate operating manual at the heat and purge gas flow rates to be used.

8 INTERPRETATION OF FTIR SPECTRA

8.1 It is recommended to prepare set of reference spectra of rubber polymers that are frequently required in routine work on the same instrument on which unknown samples are analyzed. It is always better to have “finger print spectra” of reference sample to control quality of rubber products.

8.2 The other way is to have proprietary spectral library software like Hummel spectral polymer library which helps to identify unknown rubber polymer.

9 TGA CALCULATIONS

9.1 The thermogram of rubber compounds is plotted using appropriate sample size (normally 20 mg), flow rate (normally 50 mL / min) of reactive (air or oxygen) or inert (nitrogen) gases, programming gas purging time & temperature, heating rate (normally 10^{o}C / min) and controlling gas switch temperature in ^{o}C. All these parameters depend upon type of rubber mix / blend is analyzed. From the typical thermogram plot as shown in Fig.-3, Highly / medium volatile matter, combustible materials and ash content in rubber compounds are determined using following equations.

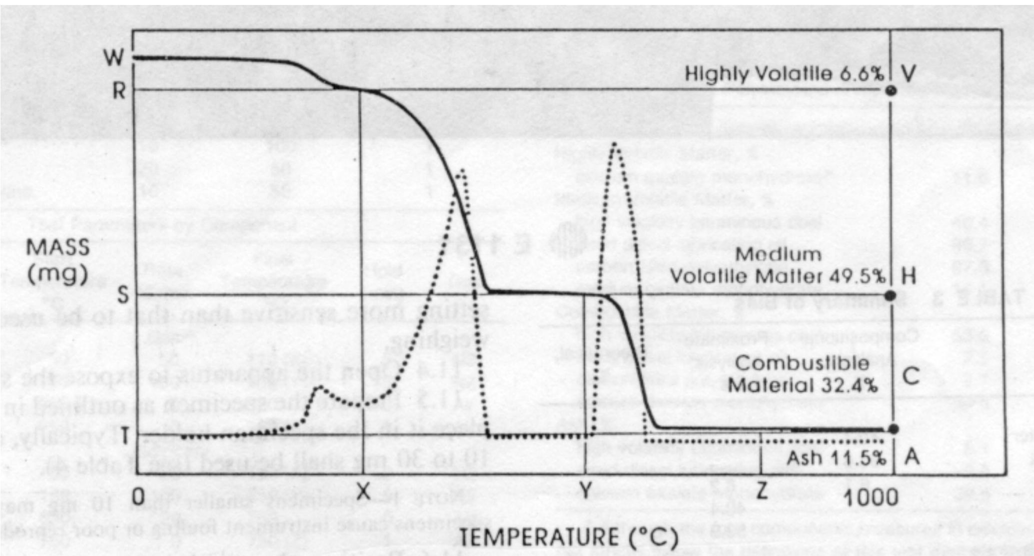


Fig. 3 Sample Thermogravimetric Curve

9.2 Highly volatile matters

$$V = \frac{W - R}{W} \times 100\%$$

9.3 Medium volatile matter (Polymer / rubber content)

$$O = \frac{R - S}{W} \times 100\%$$

9.4 Combustible material (Carbon content)

$$C = \frac{S - T}{W} \times 100\%$$

9.5 Ash content

$$A = \frac{T}{W} \times 100\%$$

Where,
V = Highly volatile matter, %
W = Original sample mass, mg
R = Mass measured at temperature X, mg
O = Medium volatile matter content;%
S = Mass measured at temperature Y, mg
C = Combustible material content;%
T = Mass measured at temperature Z, mg
A = Ash content;% Sample : Rubber

10 FTIR spectrometer and Thermogravimetry (TGA) method, thus combined together are complementary and supplementary powerful tools in qualitative and quantitative analysis of automotive rubbers to meet the required performance.

Annexure : I

Diagnostic Absorptions for FTIR Spectrophotometer analysis for the automotive rubbers

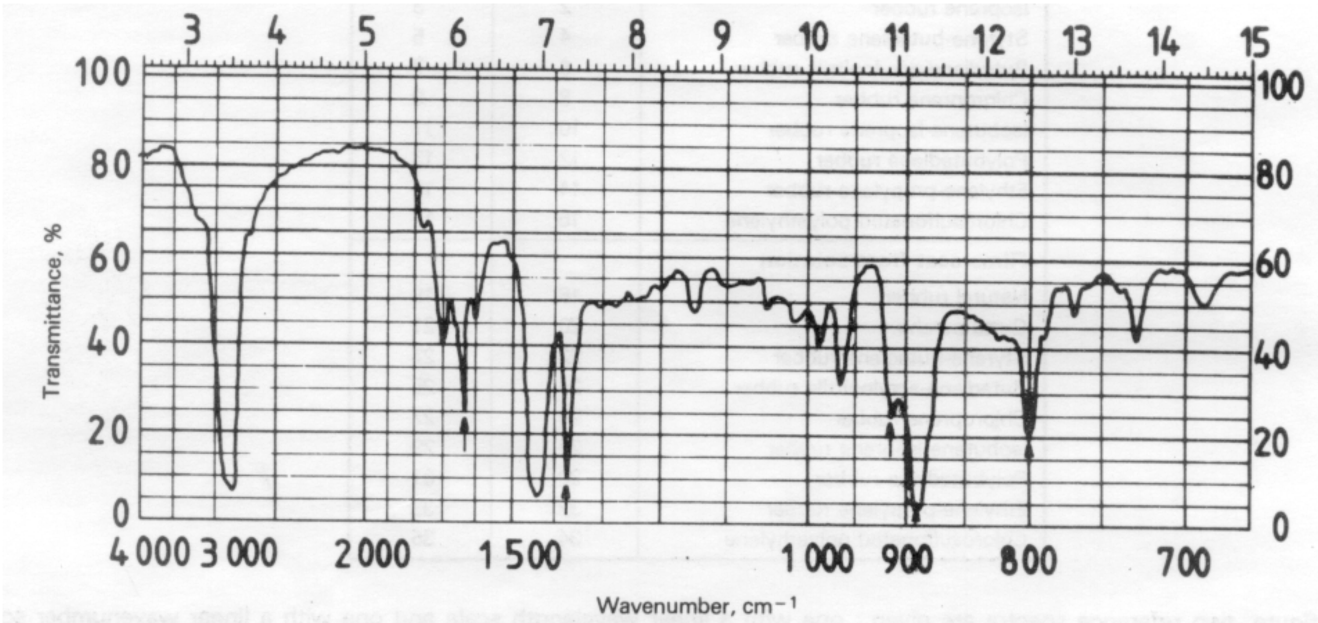
Rubber Polymer	Abb.	Wave number, cm^{-1}	Wave length, μm	Intensity	Ref. Spectra	
					Raw Rubber	Vulcanizate
Natural Rubber (NR) – Natural isoprene rubber	NR	885 1370 800 1640 909	11.3 7.3 12.5 6.1 11.0	Very strong Strong Medium Medium Shoulder	1	2
Nitrile Butadiene Rubber	NBR	2220 962 1610 1590 909	4.5 10.4 6.2 6.3 11.0	Medium / Strong Medium Medium Medium Medium	3	4
Hydrogenated Nitrile Butadiene Rubber	H-NBR	2225-2220 2240-2236 909 962	4.49-4.5 4.46-4.47 11.0 10.4	Medium (with split) Medium Medium Medium	NA	5
Styrene Butadiene Rubber	SBR	699 775 909 990 1490 962	14.3 12.9 11.0 10.1 6.7 10.4	Very strong Strong Strong Fairly Strong Medium Medium	6	7
Polybutadiene Rubber	BR	909 962 990 813 695	11.0 10.4 10.1 12.3 14.4	Strong Strong Medium Weak Weak	8	9
Butyl Rubber	IIR	1370 1390 885 1250-1220 725	7.3 7.2 11.3 8.0-8.2 13.8	Strong Strong Strong Medium Doublet, sometimes absent Very weak or sometimes absent	10	11

Rubber Polymer	Abb.	Wave number, cm^{-1}	Wave length, µm	Intensity	Ref. Spectra	
					Raw Rubber	Vulcani zate
Ethylene Propylene Terpolymer	EPDM	1370 909 885 962 725	7.3 11.0 11.3 10.4 13.8	Strong Strong Strong Medium Medium	12	13
Polychloroprene (Neoprene) Rubber	CR	820 747 769 885 699	12.2 13.4 13.0 11.3 14.3	Medium Weak, sometimes absent Weak, sometimes absent Medium Medium	14	15
Epichlorohydrene	CO / ECO	1430 1300 1120 836 746	7.0 7.7 9.0 12.0 13.4	*	*	16
Chlorosulphonated Polyethylene	CSM	909 962 990 741 813 720 695	11.0 10.4 10.1 13.5 12.3 13.9 14.4	Strong Medium Medium Medium Weak Weak Weak	17	18
Acrylic Elastomer	ACM	1733 1380 1175 1100 740	5.8 7.3 8.5 9.1 13.6	Strong Medium Strong Medium Medium	*	*
Fluoro Elastomers	FKM / FPKM	1398 1205 885 835 503	7.2 8.3 11.3 12.0 20.0	*	*	19
Silicones	Q	1260 1090- 1020 865 800	8.0 9.2 10.0 11.6 12.5	Strong Doublet,	*	20

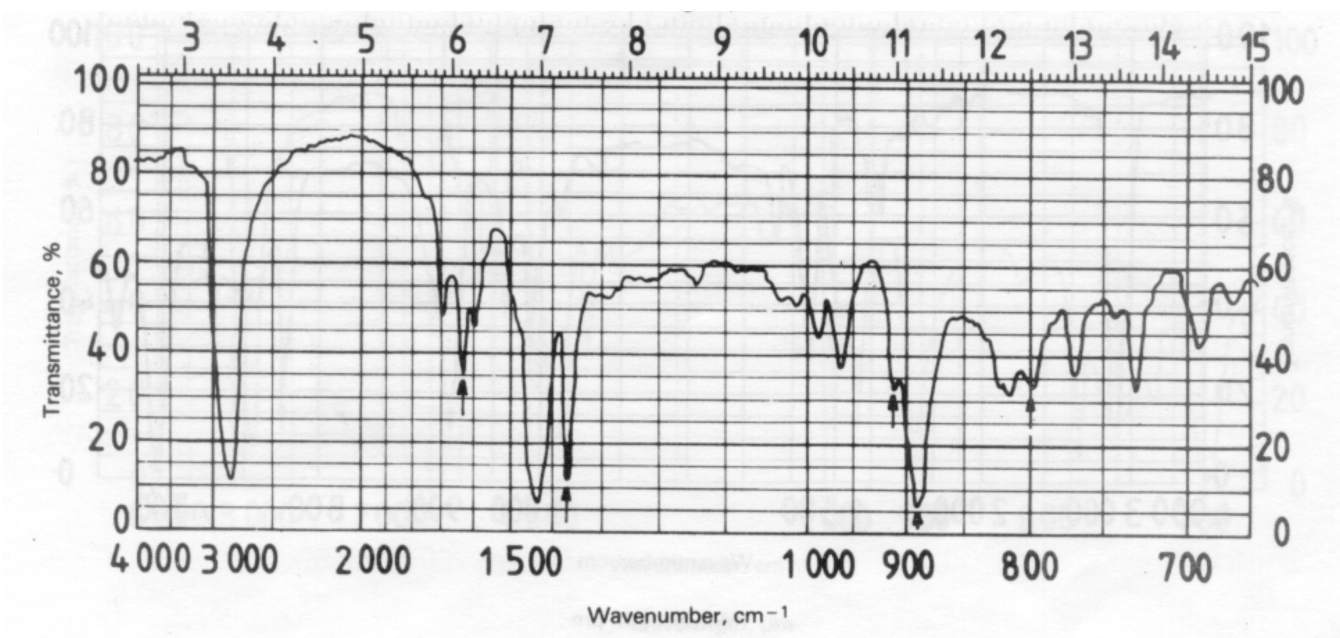
Rubber Polymer	Abb.	Wave number, cm^{-1}	Wave length, µm	Intensity	Ref. Spectra	
					Raw Rubber	Vulcanizate
Fluorosilicone elastomer	FVMQ	*	*	*	*	21
Polyurethanes	TPU	1730 1412 1220 1070 770	5.8 7.1 8.2 9.4 13.0	*	*	22
Ethylene Vinyl Acetate	EVA	1745 1375 1240 725 610	5.7 7.3 8.1 13.8 16.4	*	*	23
Following absorptions for Pyrolyzates, when they occur, are of no diagnostic value and should not be used for rubber identification						
-----	-----	**3300 2860 1700 1450**	**3.0 3.5 5.9 6.9**	------	----	

* Note : The required information is not available

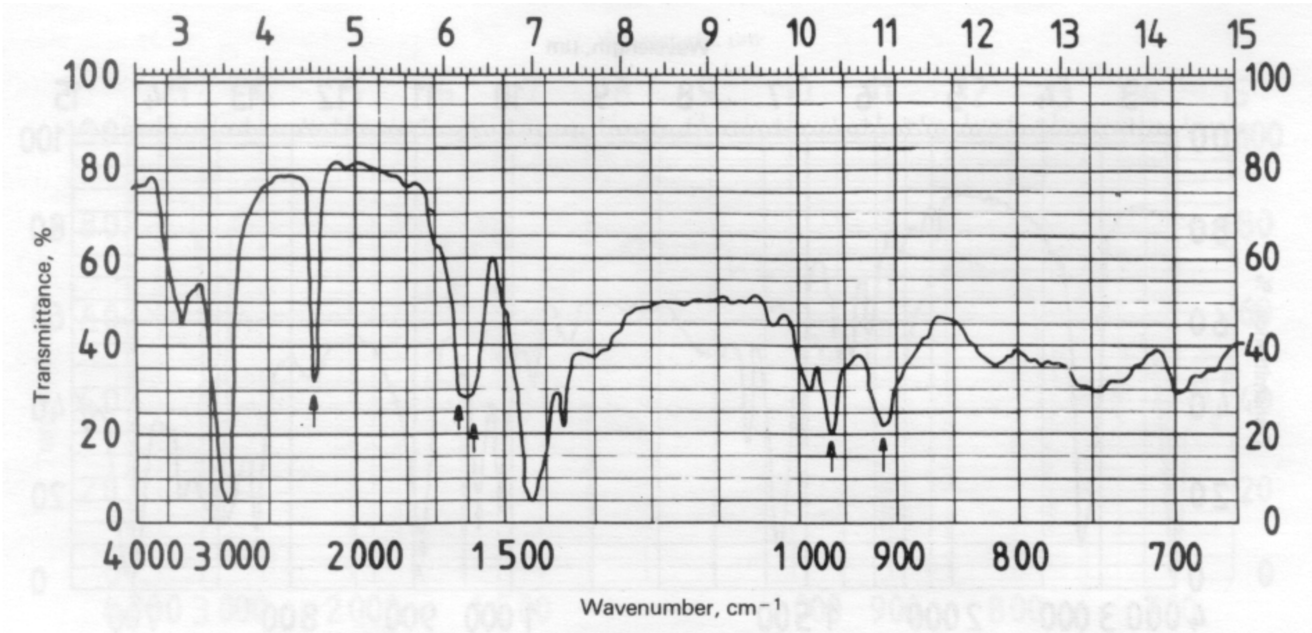
Reference FTIR Spectra of the Automotive Rubbers



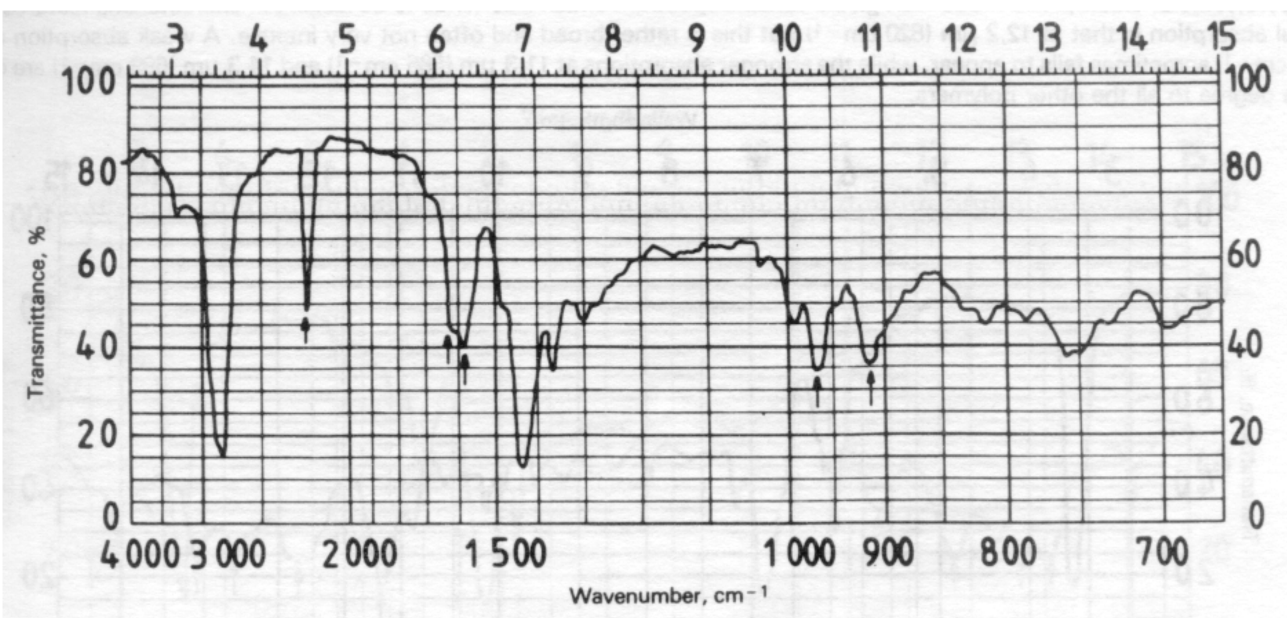
Spectra 1 For Isoprene Raw Rubber



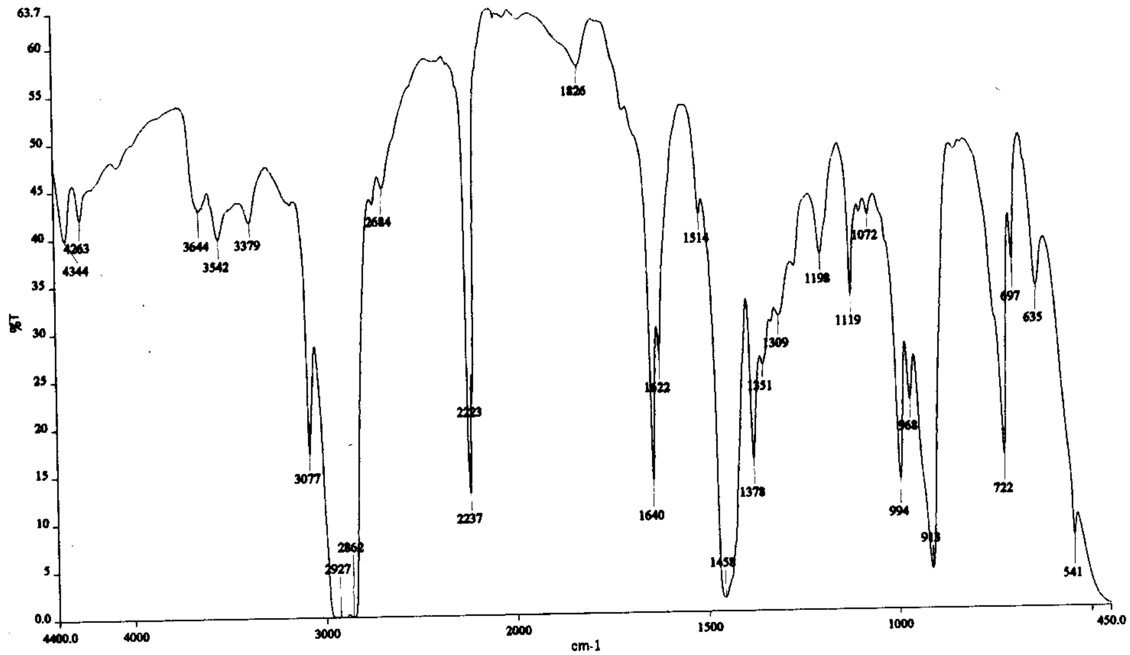
Spectra 2 For Isoprene Vulcanized Rubber



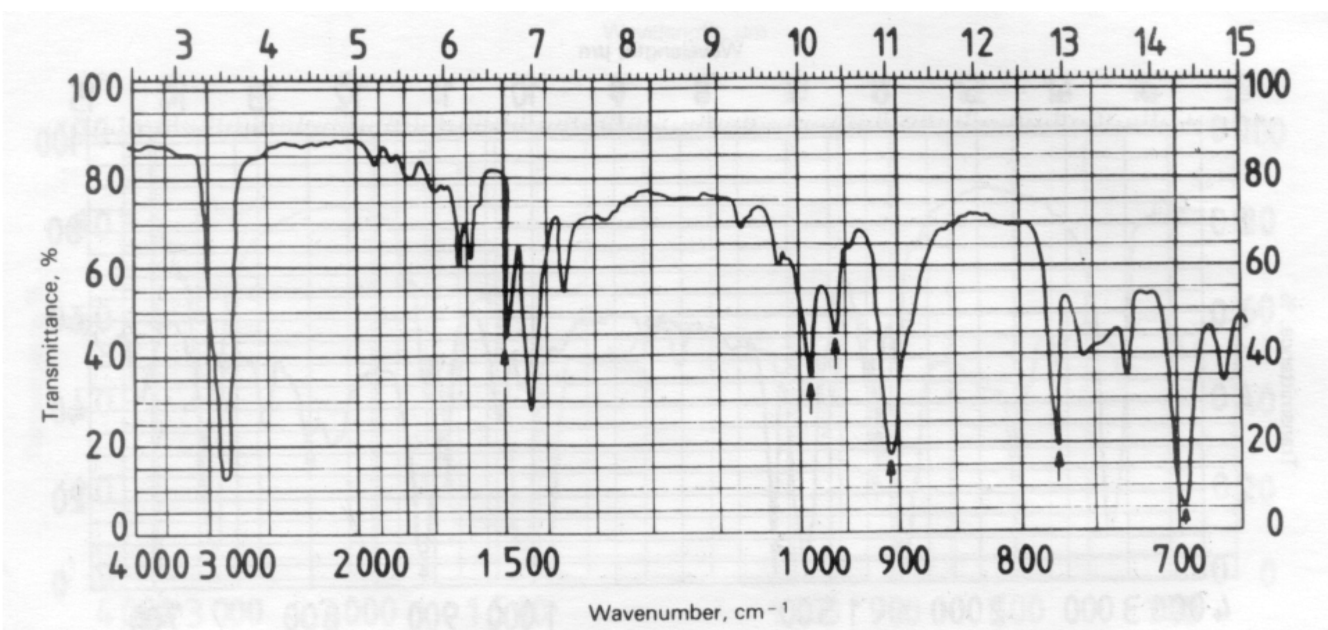
Spectra-3 For Butadiene-acrylonitrile Raw Rubber



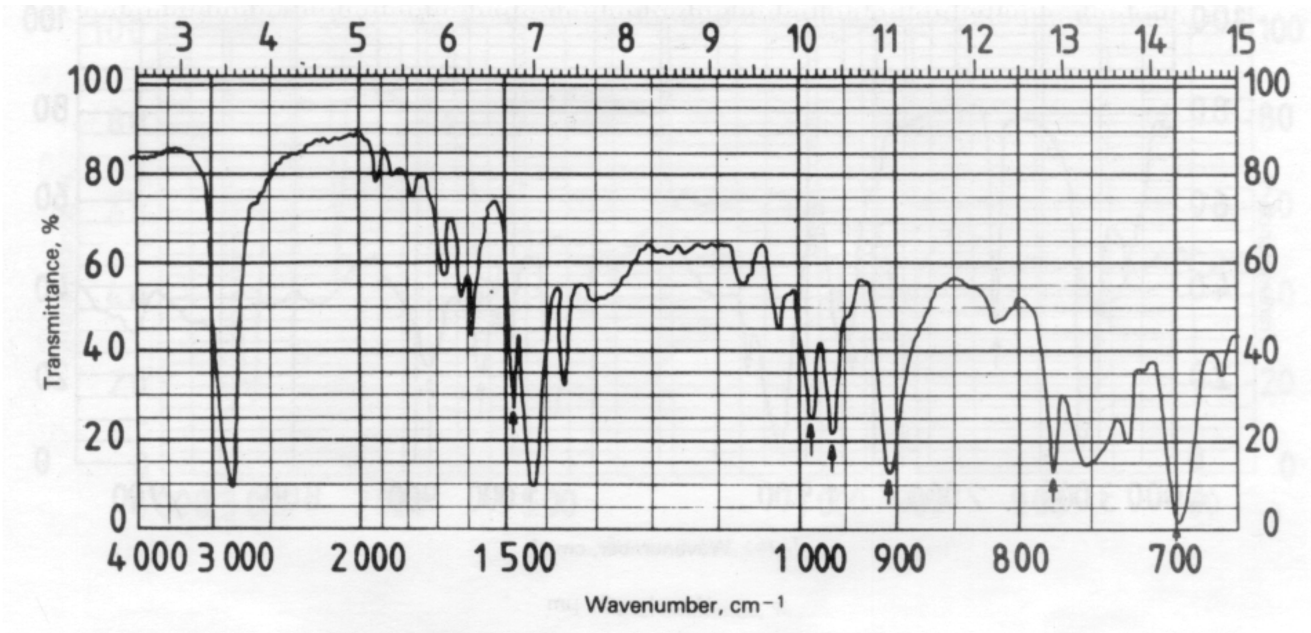
Spectra-4 For Butadiene-acrylonitrile Vulcanized Rubber



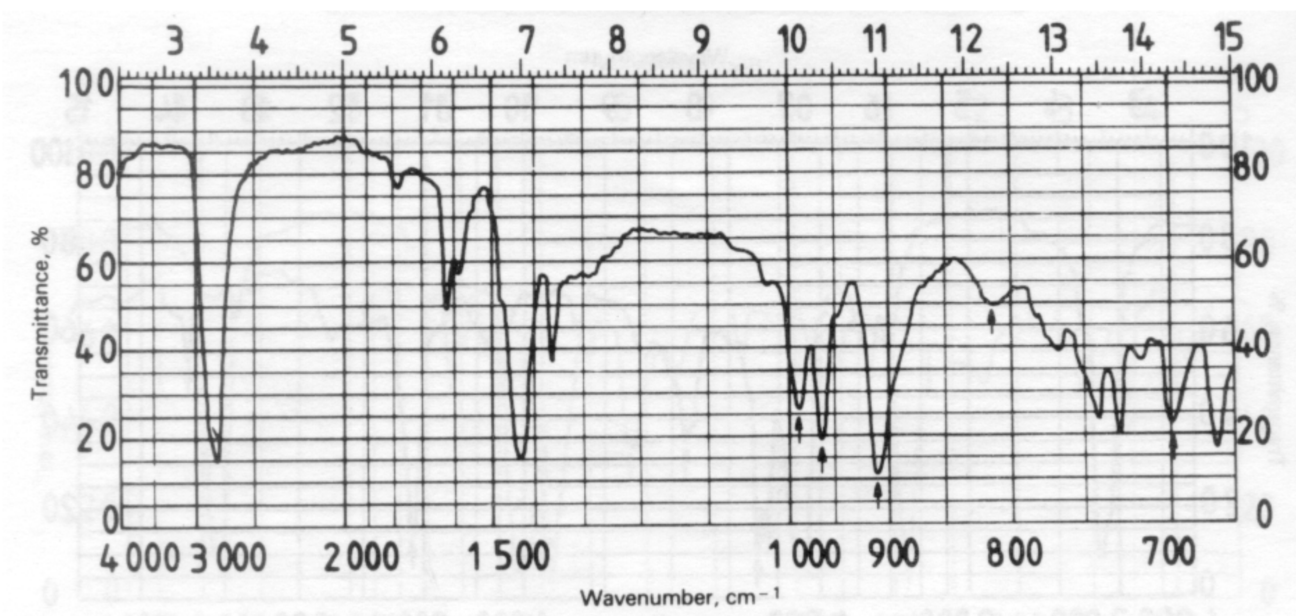
Spectra-5 For Hydrogenated Nitrile Butadiene Rubber



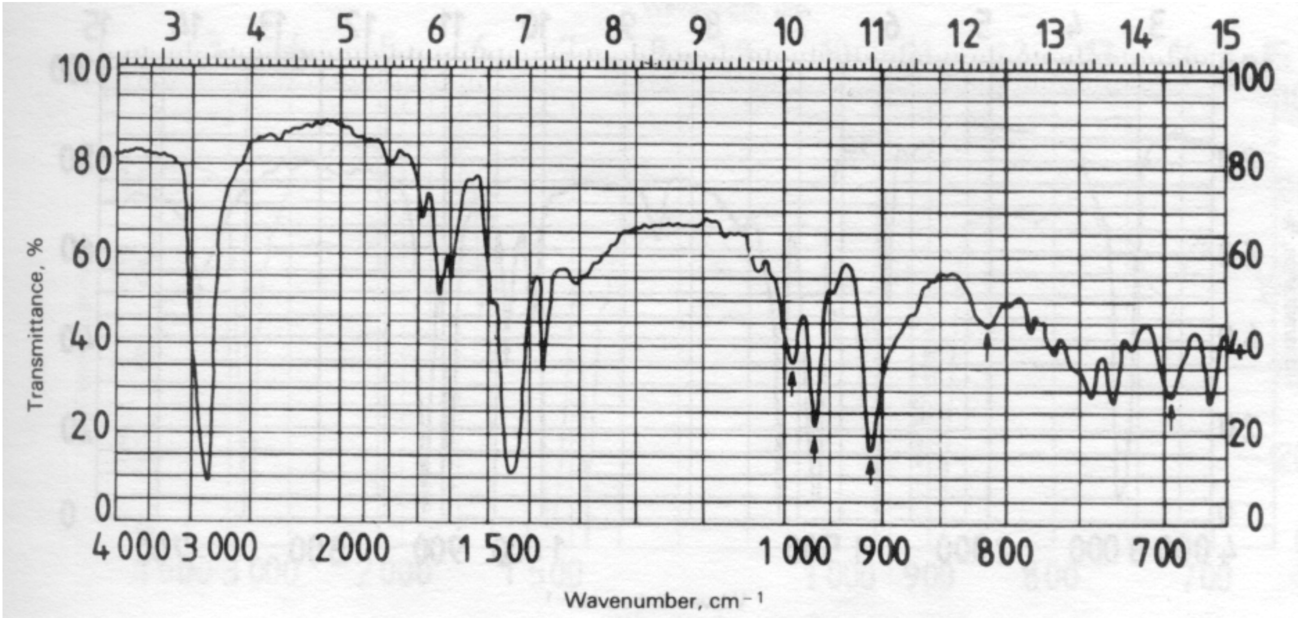
Spectra-6 For Styrene-butadiene Raw Rubber



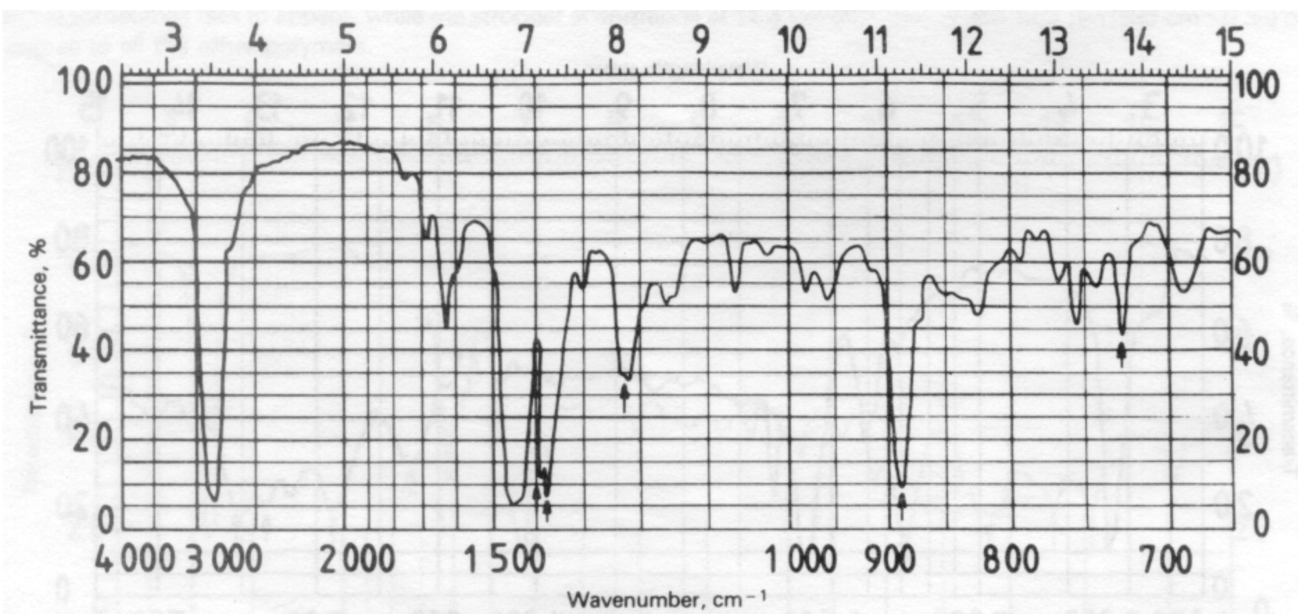
Spectra-7 For Styrene-butadiene Vulcanized Rubber



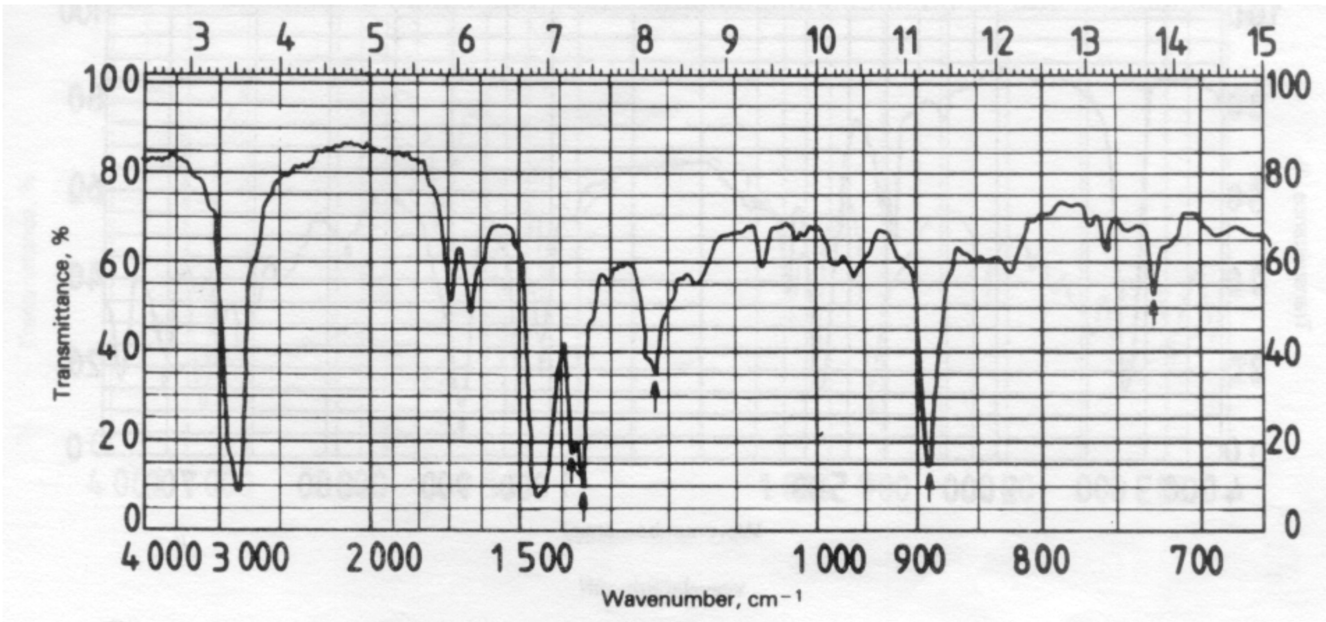
Spectra-8 For Polybutadiene Raw Rubber



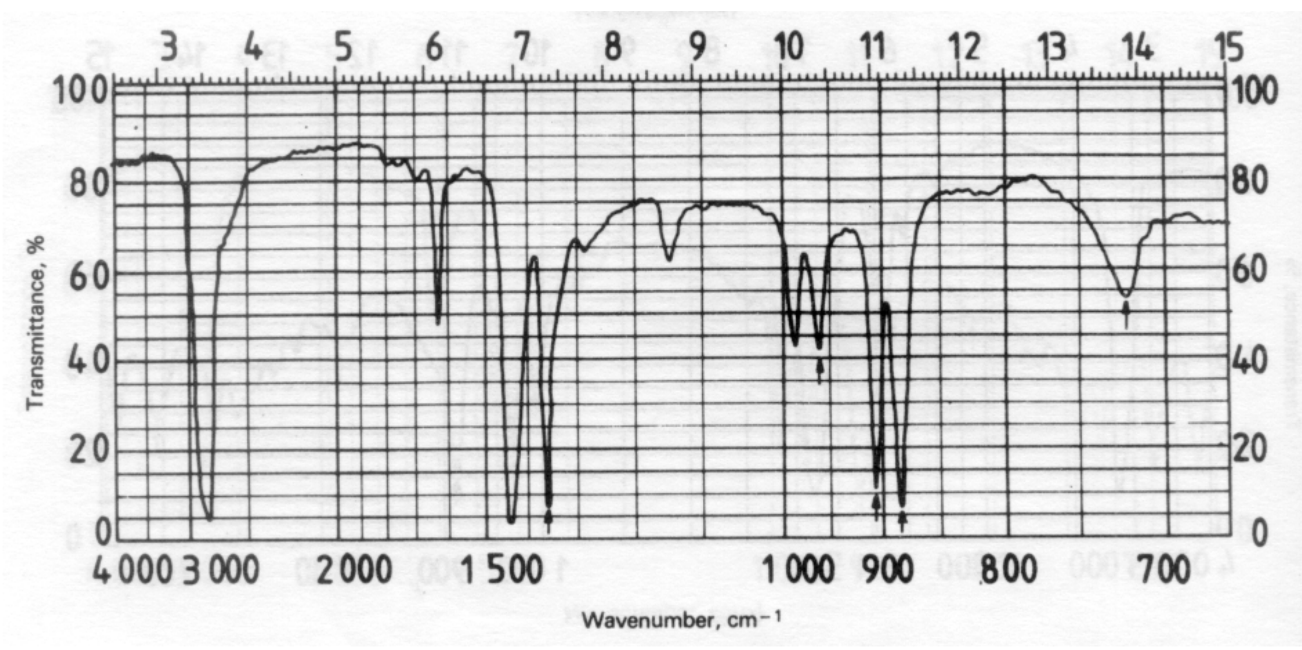
Spectra-9 For Polybutadiene Vulcanized Rubber



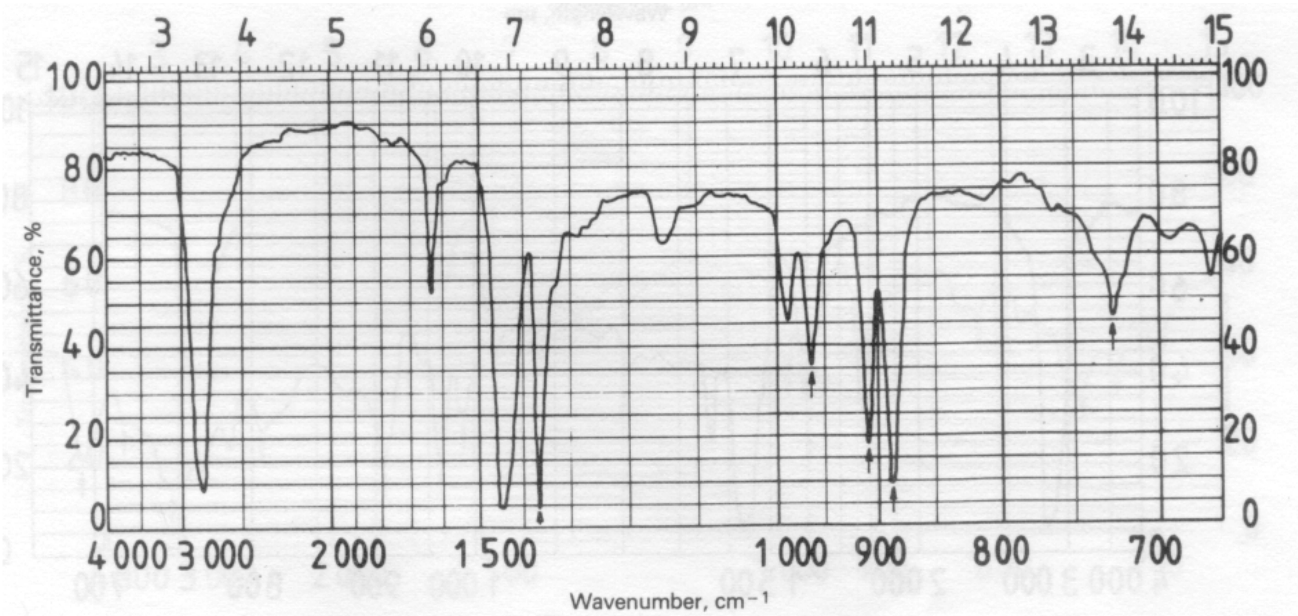
Spectra-10 For Isobutene-isoprene Raw Rubber



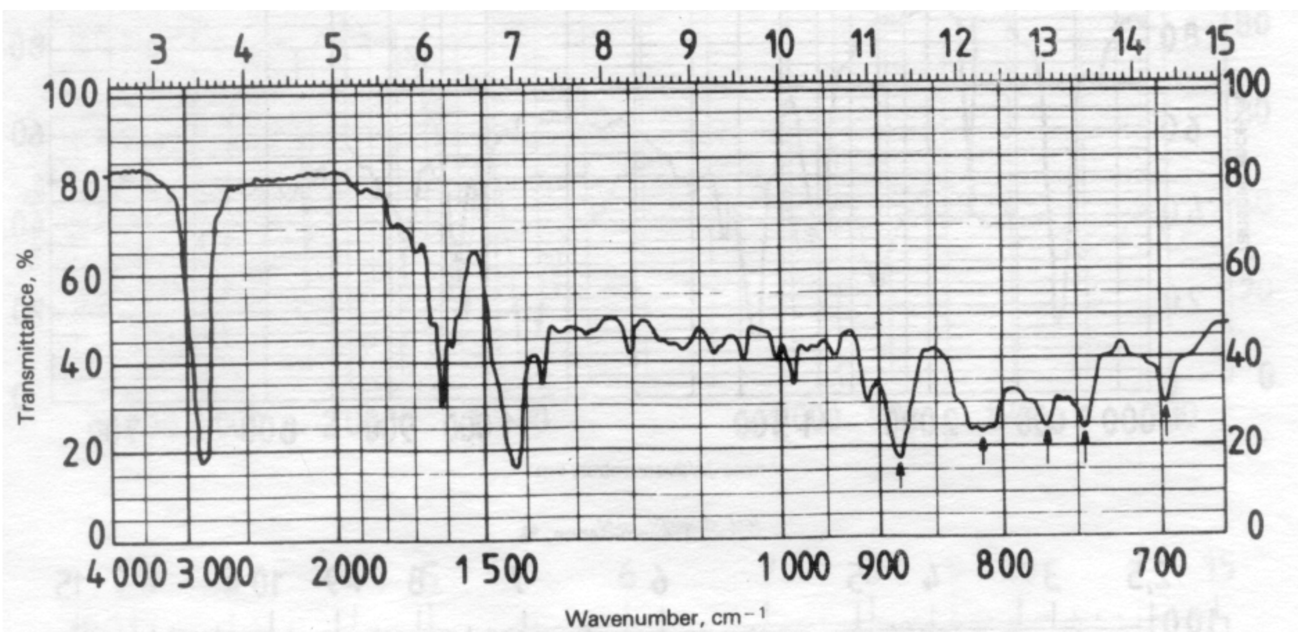
Spectra-11 For Isobutene-isoprene Vulcanized Rubber



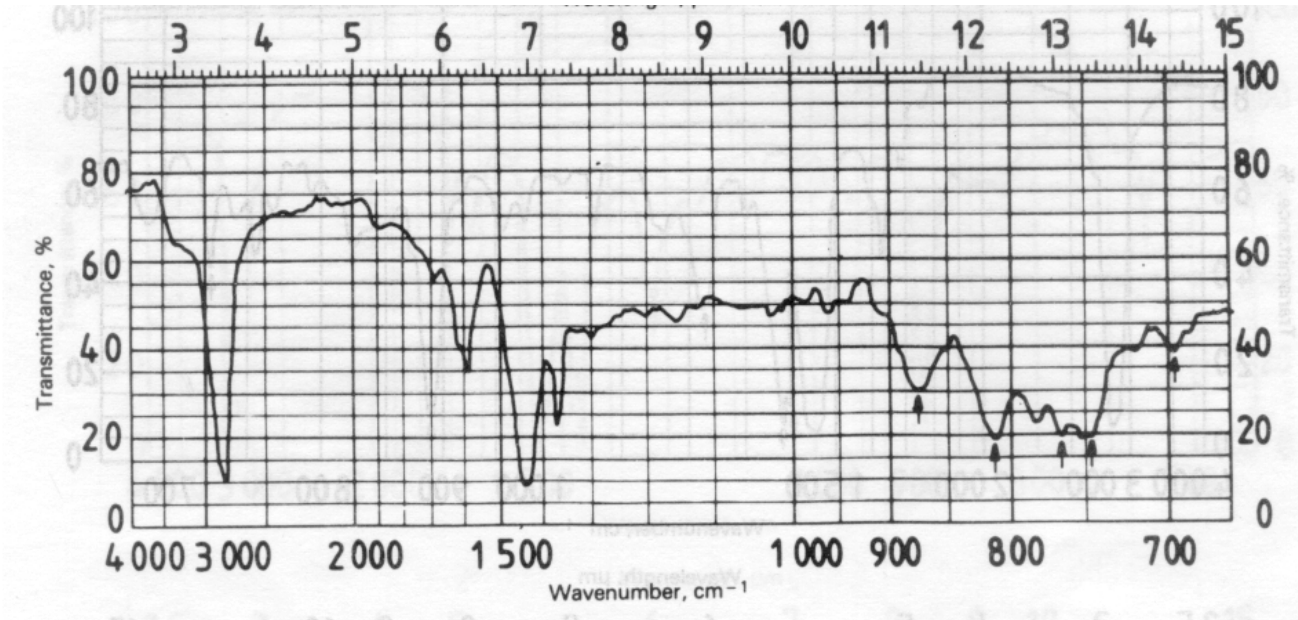
Spectra-12 For Ethylene-Propylene Raw Rubber



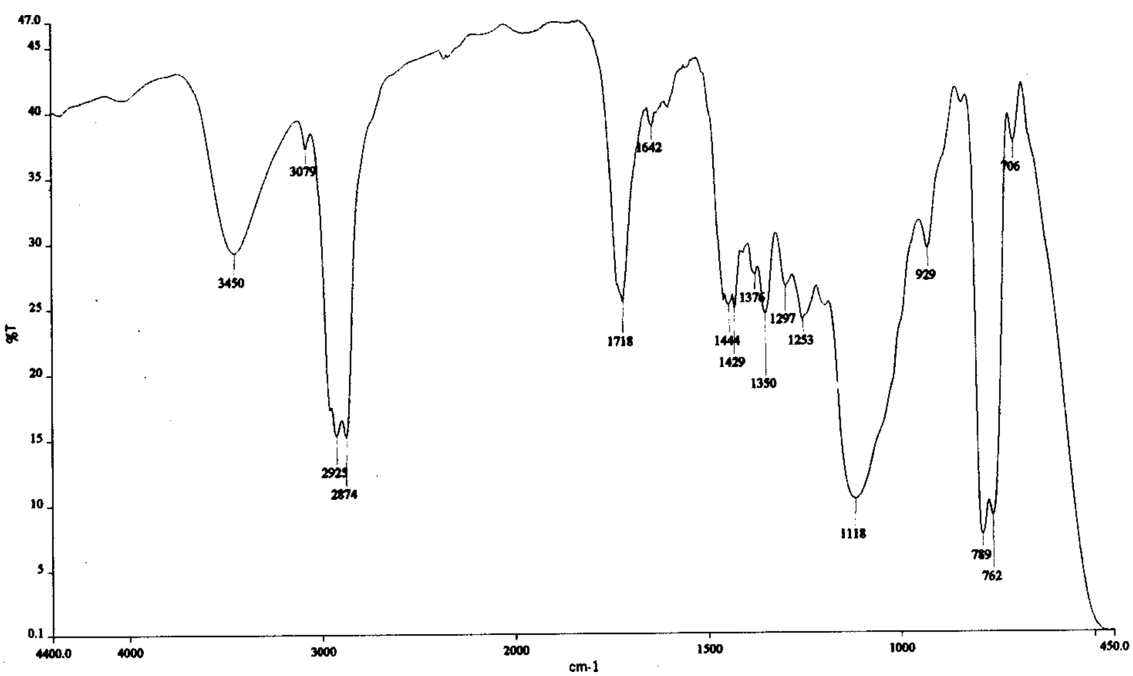
Spectra-13 For Ethylene -Propylene Vulcanized Rubber



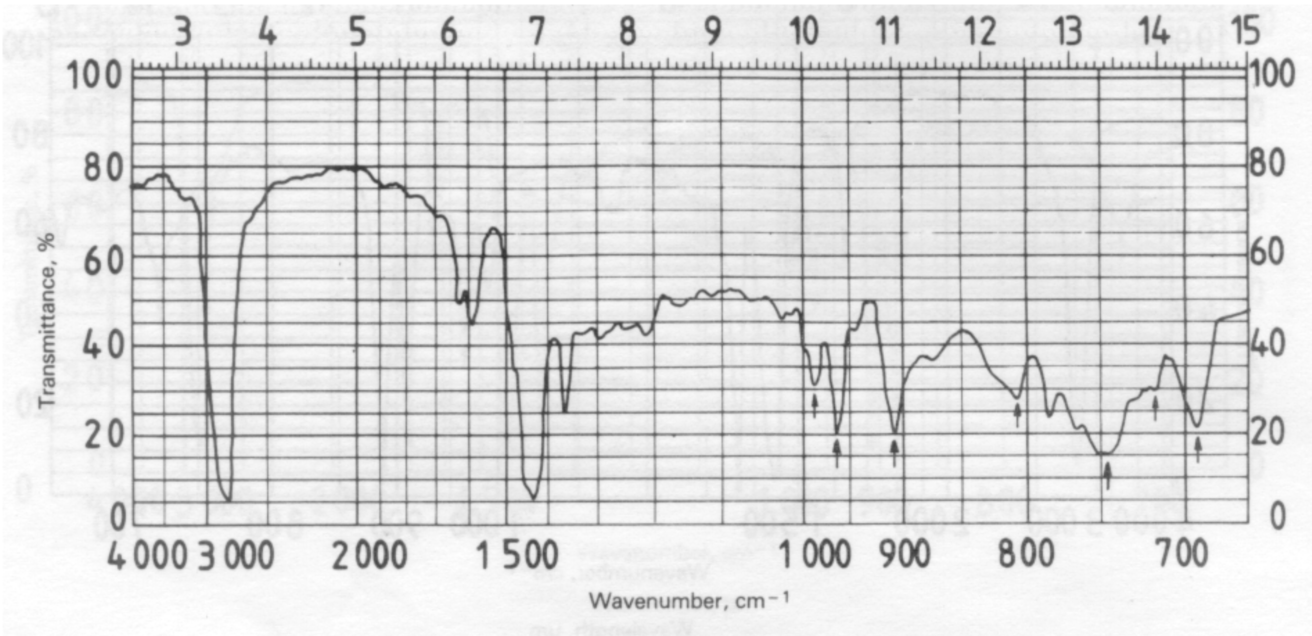
Spectra-14 For Chloroprene Raw Rubber



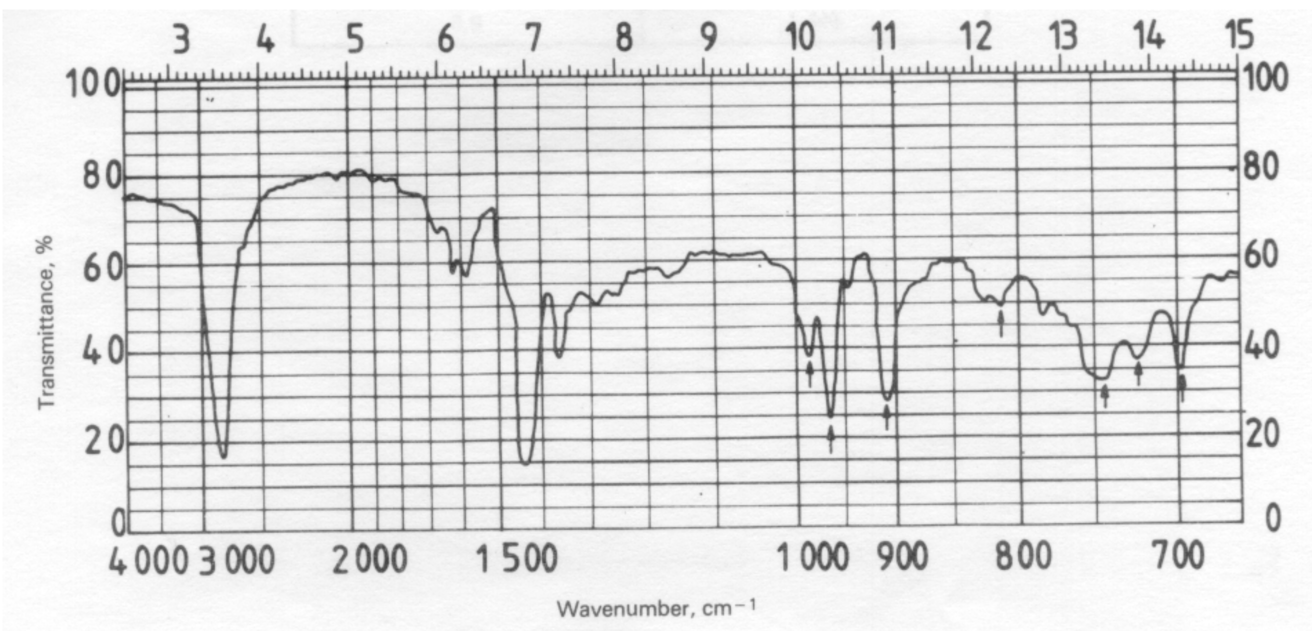
Spectra-15 For Chloroprene Vulcanized Rubber



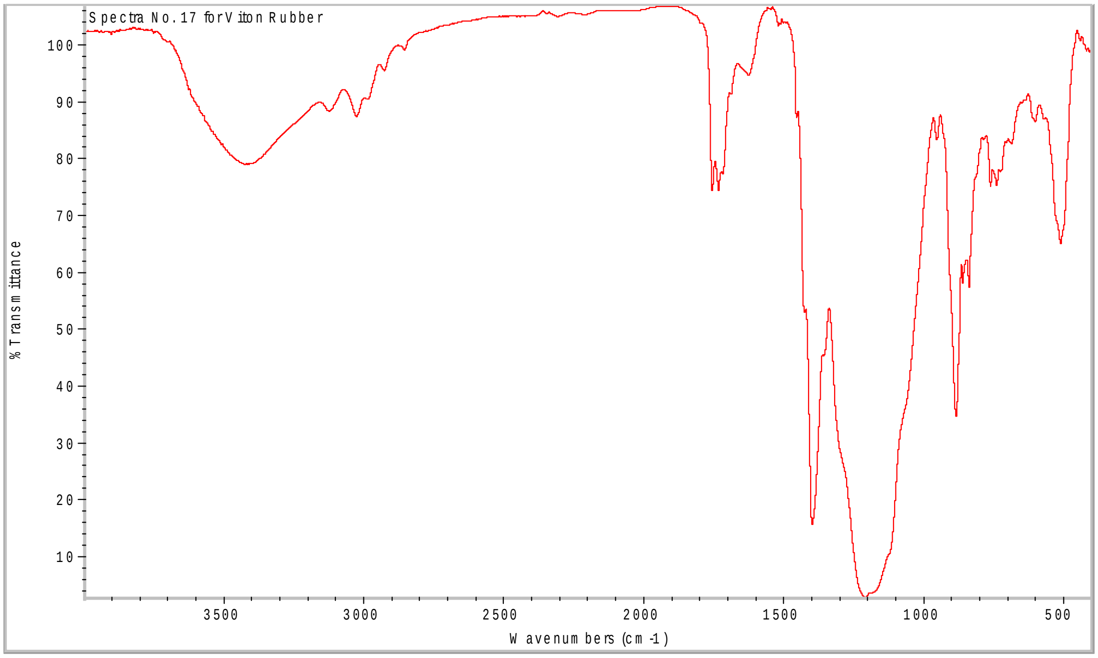
Spectra-16 For Epichlorohydrene Vulcanized Rubber



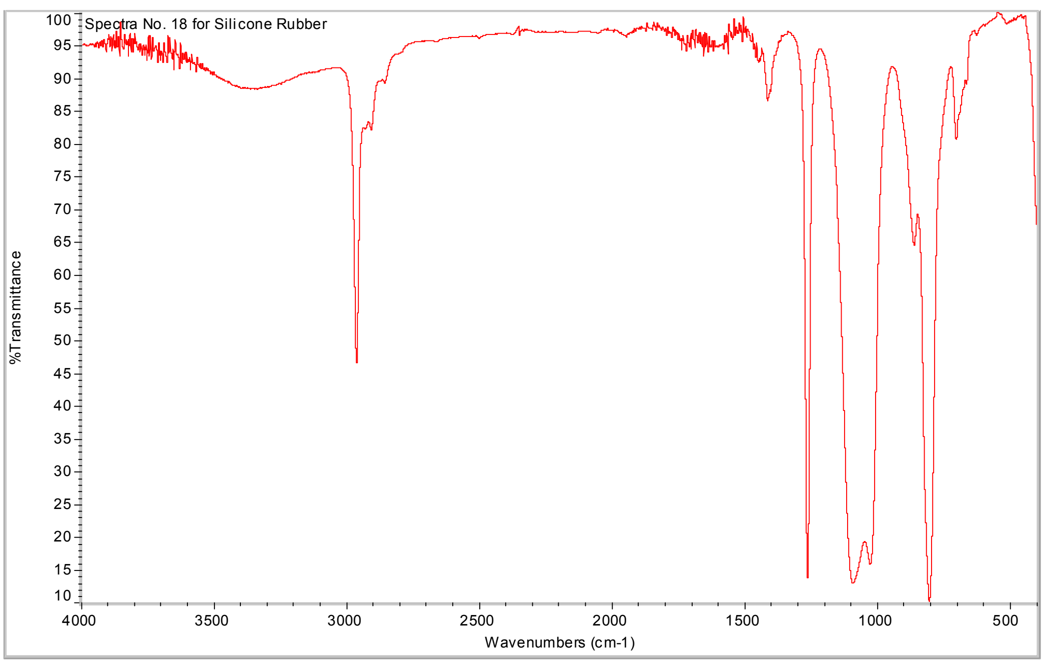
Spectra-17 For Chlorosulfonated polyethylene Raw Rubber



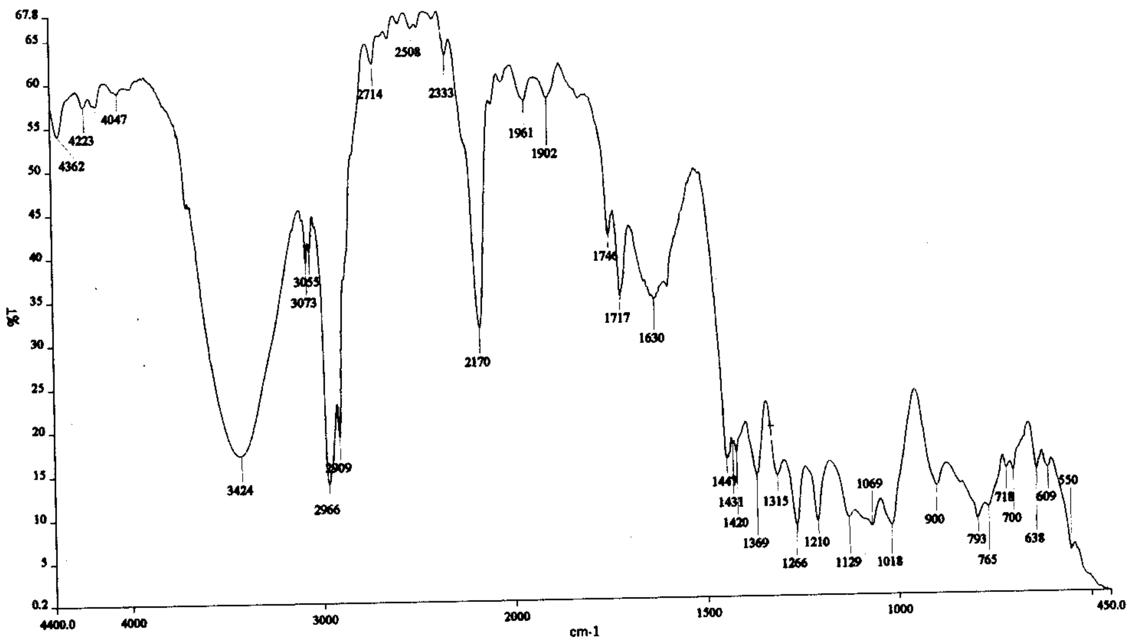
Spectra-18 For Chlorosulfonated polyethylene Vulcanized Rubber



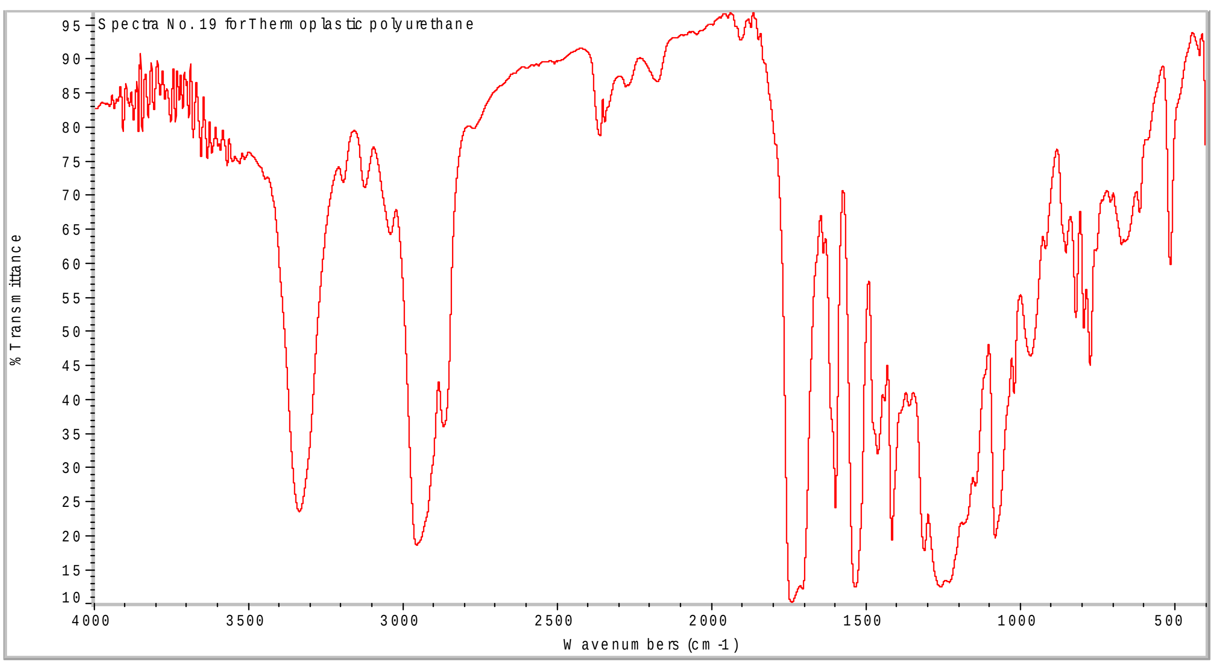
Spectra-19 For Viton Rubber



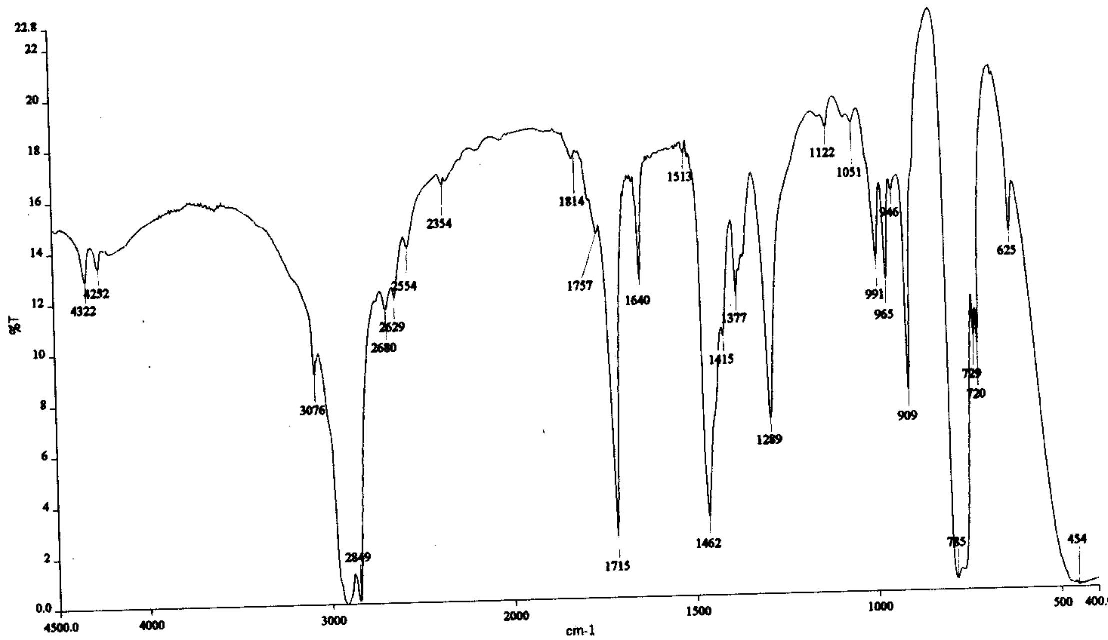
Spectra-20 For Silicone Rubber



Spectra-21 For Fluorosilicone Elastomer



Spectra-22 For Thermoplastic Polyurethane



Spectra-23 For Ethylene Vinyl Acetate

Annexure : II
(See Introduction)
COMMITTEE COMPOSITION
Automotive Industry Standards Committee

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Shri. Chandan Saha	Office of the Development Commissioner Small Scale Industries, Ministry of Small Scale Industries, New Delhi
Shri. Balwant Rai Shri K.K. Vashistha (Alternate)	Bureau of Indian Standards, New Delhi
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