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October 1990
An Investigation Conducted by:
Texas Research Institute Austin, Inc.
Austin, Texas 78733-6201

DEVELOPMENT OF A METHOD TO FINGERPRINT RUBBER FUEL HOSE MATERIALS

ABSTRACT Elastomeric fingerprinting is a quality control procedure designed to provide a reproducible graphical trace of a unique rubber compound. Comparative analysis between the first and subsequent production runs of the rubber compound is made possible and to some extent, quantifiable. This procedure, coupled with industry standard physical tests, will enable rigorous configuration control of the production of rubber goods. This report documents the work done to develop an elastomeric fingerprinting procedure based on acetone extraction, Fourier Transform Infra-Red (FTIR) spectroscopy, and thermogravimetry using Navy rubber fuel hoses as test samples. The elastomeric fingerprinting procedure is intended for use in Government/commercial procurements where the purchaser does not own the rubber compound formulations, yet requires production consistent with the first, approved rubber product. This report includes both the method development and the refinement of the method, including a draft specification. Additional work is required in the definition of FTIR spectroscopy acceptance criteria and in interlaboratory testing precision before the procedure is fully reliable.

NAVAL CIVIL ENGINEERING LABORATORY PORT HUENEME CALIFORNIA 93043

METRIC CONVERSION FACTORS

Approximate Conversions to Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
in	inches	*2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
		AREA		
in^2	square inches	6.5	square centimeters	cm^2
ft^2	square feet	0.09	square meters	m^2
yd^2	square yards	0.8	square meters	m^2
mi^2	square miles	2.6	square kilometers	km^2
	acres	0.4	hectares	ha
		MASS (weight)		
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2,000 lb)	0.9	tonnes	t
		VOLUME		
tsp	teaspoons	5	milliliters	ml
Tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft^3	cubic feet	0.03	cubic meters	m^3
yd^3	cubic yards	0.76	cubic meters	m^3
		TEMPERATURE (exact)		
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

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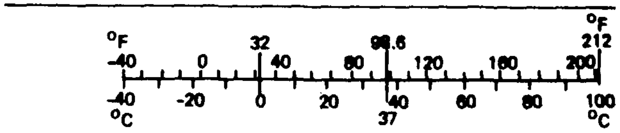
*1 in = 2.54 (exactly). For other exact conversions and more detailed tables, see NBS Misc. Publ. 286, Units of Weights and Measures, Price $2.25, SD Catalog No. C13.10:286.

Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
		AREA		
cm^2	square centimeters	0.16	square inches	in^2
m^2	square meters	1.2	square yards	yd^2
km^2	square kilometers	0.4	square miles	mi^2
ha	hectares (10,000 m^2)	2.5	acres	
		MASS (weight)		
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1,000 kg)	1.1	short tons	
		VOLUME		
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m^3	cubic meters	35	cubic feet	ft^3
m^3	cubic meters	1.3	cubic yards	yd^3
		TEMPERATURE (exact)		
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F



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13. ABSTRACT *(Maximum 200 words)*

Elastomeric fingerprinting is a quality control procedure designed to provide a reproducible graphical trace of a unique rubber compound. Comparative analysis between the first and subsequent production runs of the rubber compound is made possible and to some extent, quantifiable. This procedure, coupled with industry standard physical tests, will enable rigorous configuration control of the production of rubber goods. This report documents the work done to develop an elastomeric fingerprinting procedure based on acetone extraction, Fourier Transform Infra-Red (FTIR) spectroscopy, and thermogravimetry using Navy rubber fuel hoses as test samples. The elastomeric fingerprinting procedure is intended for use in Government/commercial procurements where the purchaser does not own the rubber compound formulations, yet requires production consistent with the first, approved rubber product. This report includes both the method development and the refinement of the method, including a draft specification. Additional work is required in the definition of FTIR spectroscopy acceptance criteria and in interlaboratory testing precision before the procedure is fully reliable.

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TABLE OF CONTENTS

PART 1—METHOD DEVELOPMENT

PART 2—REFINEMENT OF THE METHOD

ABSTRACT

This report covers the development of a method for ensuring that production rubber hoses are identical in composition to the first article. The method is based on thermogravimetry and FTIR spectroscopy and should be applicable to any compounded rubber formulation.

The report is presented in two parts. Part 1 is the initial development of the method under Contract N62583-88-P-1688. It describes the method and raises a number of concerns associated with the method.

Part 2 (Contract No. N47408-89-D-1004) is an attempt to resolve the issues raised in part 1. Each issue is handled as a separate task, with the results of each task presented. Finally, at the end of Part 2, conclusions with recommendations are presented concerning the entire study and what further work needs to be done.

PART 1—METHOD DEVELOPMENT

SUMMARY

One of the difficulties associated with the procurement of large quantities of manufactured goods is the ability to assess the quality of the materials over extended periods of time. The normal practice for the U.S. Navy is to thoroughly test a first article, then test the production lots on the basis of a more limited specification. This procedure is usually acceptable but there is a possibility that critical materials may be changed during production and those changes not be detected. This study was designed to address this possibility.

This report covers an investigation which developed and evaluated a method for characterizing rubber fuel hose materials which may be used to ensure that the materials used in production are identical to those used in the first article.

The types of hoses encountered varied widely in their construction. There were from three to seven different layers; reinforced with fibers or steel or both. In this study, six different hoses were evaluated and conclusions about their materials of construction were drawn.

The developed method was based on acetone extraction, thermogravimetry and IR spectroscopy. The amount of material removed by acetone extraction is a characteristic of the rubber compound and can help determine if a formulation is constant between different lots of rubber. Thermogravimetry produces information concerning the composition of the formulation by determining the percentage composition of organics, carbon black, and inorganic fillers. It also gives some information on the quality of the rubber. IR spectroscopy produces a chemical fingerprint of the materials of construction. This method was designed to determine the following characteristics:

- % acetone extractables
- % organics
- % carbon black
- % inorganic fillers
- elastomer thermal stability
- elastomer IR fingerprint
- acetone extract IR fingerprint
- inorganic filler IR fingerprint

The results of this study strongly suggest that this method is a viable candidate for ensuring the quality of rubber fuel hoses. However, a number of considerations and concerns are presented that must be addressed before the results generated by this method can be considered reliable.

NTRODUCTION

Over the years the U.S. Government has had a continual problem with the quality of production materials procured in large quantities. Normally, a first article has been thoroughly tested to qualify for a buy and then the production lots are evaluated on the basis of a more limited specification. One problem with this approach is that it is possible that critical materials could be changed from the first article to production. Even if the production material met the requirements of the production specification, it would not be identical to the first article.

The Naval Civil Engineering Laboratory (NCEL) has a specific need to qualify production lots of rubber fuel hoses to ensure that they are identical in chemistry and composition to the first articles. For this to be achieved one needs to determine the composition of the compounded elastomer, be able to identify or fingerprint the elastomer, soluble additives, and inorganic fillers, and be able to tell something about the quality of the elastomer.

One of the ways to determine the composition of an elastomer is by thermogravimetry (TG) (1,2). TG is a thermal analytical technique that continually measures the mass of a sample as it is heated at a constant rate in a controlled atmosphere. As a compounded elastomer is heated in an inert atmosphere like nitrogen it decomposes in an orderly manner. The first materials to decompose are the organic additives such as antioxidants, processing oils and waxes, and residual catalysts. Next, the polymers decompose leaving the carbon black and the inorganic fillers. If the atmosphere is switched from nitrogen to air after the polymers decompose, the carbon black will burn, leaving just the inorganic fillers or ash. Therefore, all of this information can be generated in one experiment by switching the atmosphere after the polymers decompose.

Another characteristic of a compounded elastomer is the amount of material that can be extracted from the rubber with an organic solvent. For example, acetone removes rubber resins, free sulfur, plasticizers, processing aids, mineral oils or waxes, some antioxidants, some organic accelerators, and fatty acids (3). Although the resulting solution contains a mixture of substances, the amount of material extracted during a specific length of time should be constant and a characteristic of the rubber compound.

Compounded rubbers can also be characterized by Fourier transform infrared spectroscopy (FTIR). This qualitative technique is useful for identifying the type of material a sample is made from, or simply generating a fingerprint of an unknown material. FTIR could be used to identify the type of rubber in a hose and give a fingerprint of the major component in an acetone extract. In general, rubbers containing carbon black are difficult to analyze by FTIR because the black strongly absorbs the IR radiation. However, there is a method which describes special ways to analyze compounded rubbers (4). The simplest way is to quickly pyrolyze a rubber sample to produce lower molecular weight decomposition products which can then be analyzed by conventional IR techniques. Even though the rubber is partially decomposed, its IR spectrum is still unique to the rubber, and therefore a fingerprint of the rubber.

The objective of this study was to evaluate a proposed method to characterize rubber hose compounds and to produce specification language which details the procedure required to perform the method.

A flow diagram of the method is shown in Figure 1-1 (Appendix A). Samples from the inner tube and the outer jacket of the hose are collected and ground to a fine powder with a liquid nitrogen grinder. The ground powder is then extracted with acetone to produce an extract and a residue. The solvent is evaporated, the extract dried and then analyzed by FTIR. Meanwhile, the residue is analyzed by TG, pyrolyzed for FTIR analysis and the organics burned off in a furnace to isolate the inorganic ash for FTIR.

EXPERIMENTAL

Hoses Tested

The NCEL supplied hoses tested in this study were all rubber fuel hoses and two were constructed according to MIL-H-2240E.

Hose A (New)

This hose appeared to be made in three layers. There was an outer jacket, a middle layer with two plies of fiber reinforcement, and an inner tube. All layers were black and it was difficult to distinguish between the layers.

Hose A (Used)

This hose was identical to the one above except that it had obviously been in service and appeared to be punctured at one end.

Hose B (New)

This hose was more complex in construction. Five different layers were identified. The outer jacket was black rubber. Inside of the outer jacket was a layer of green rubber. Next to that was a steel cord reinforcement layer which had 4 plys of cords and was much thicker than the others. Inside of that was a single ply of fiber reinforced rubber, followed by the black inner tube.

Hose C (New)

This hose was the most complex of all. It was composed of 7 distinct layers. There was a black outer jacket, a 3 ply fiber reinforcement, a thin black layer, a green rubber layer, another thin black layer, a 4 ply fiber reinforcement and a black inner tube.

Hose D (New)

This hose was similar to the hose A. It had three layers: a black outer jacket, a 2 ply fabric reinforcement, and a black inner tube.

Hose E (New)

This hose was distinctly different from all the others. It was a three layer construction in which a woven fabric was sandwiched between the black inner and outer layers of elastomer. The hose was very lightweight and had a shiny surface. It also appeared to be constructed from a different kind of material.

Sampling Procedures

Since the hoses varied in composition and construction, no single method for obtaining a sample was possible. In general, three, 10 g samples of inner and outer rubber were collected from both ends and the center of the length of hose. More specific methods are described below.

Samples of hoses A and D were obtained by first cutting three cylindrical strips, three inches wide, from the hose with a band saw. Strips were cut from both ends and the center. Next, three, 1" x 6" pieces were cut from each strip with a stainless steel die. About 10 g of inner and outer rubber was then collected by slicing off thin pieces with a scalpel. Care was taken to avoid the center layer of rubber because it was difficult to see the interface between the layers.

Samples of hose C were also obtained by cutting three cylindrical strips. However, the thickness of the hose prohibited the use of the die. Therefore, another way to sample this hose was sought. It was finally discovered that the thin inner and outer layers could be peeled off with pliers. The outer layer peeled cleanly but the inner retained a thin layer of the tan rubber adjacent to it. This was then removed by lightly sanding the sample on a belt sander. The 10 g of sample for analysis was taken from the center of the strip to avoid any effects from the edges that had been cut.

Hose B was the most difficult to sample because it contained several layers of steel cords and could not be cut with a band saw. Instead, a two inch disc was removed with a hole saw from the center of the hose length. Then the inner and outer samples were obtained with the use of a scalpel. The ends of the hose were sampled directly with a scalpel from the length of hose.

Samples were obtained from hose E by cutting 1" x 6" samples directly from the hose with the die. Then one layer was isolated by peeling the sample apart with pliers. This left one clean side and the other elastomer layer still bonded to the woven cloth. The cloth was easily stripped after it was soaked in warm water for about one hour.

Grinding Procedure

The rubber samples were ground with the use of a Spex Industries Model 6700 liquid nitrogen grinder. The rubber was cut into small pieces then ground at full power for 3 minutes, removed from the grinder and shaken, then ground for 2 more minutes.

Extraction Procedure

The extractions were performed with the use of a Soxhlet continuous extraction apparatus with acetone as the solvent. The samples ranged in weight from 3-10 g with 80% of them between 5 and 8g. The samples were weighed into tared 45x123mm thimbles and extracted with 400 ml of HPLC grade acetone for 24 hours. The color of the extract varied from yellow to black. After the extraction was completed, the thimbles were removed and dried in a vacuum oven overnight and weighed to determine the percent extractables. The solvent was removed from the extracted material by evaporation under reduced pressure and the sticky residue was collected for infrared analysis.

Thermogravimetry (TG)

The TG analysis was performed on a DuPont model 9900 thermal analysis system equipped with a model 951 TGA. The initial weight of all samples was between 12 and 14 mg with 88% of them between 13 and 14 mg. A sample was placed in the TGA and and allowed to stabilize under a flowing nitrogen blanket (100 ml/min) for 5 minutes. The sample was then heated at 25°C/min to 1000°C. At 600°C, the atmosphere was switched from nitrogen to air at the same flow rate.

Ashing

The inorganic filler (ash) was obtained by heating a rubber sample in a furnace at 1000 or 750°C in air for several hours until a homogeneous residue was obtained.

Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR analyses were performed on a Nicolet model 20SX spectrophotometer. The analysis method was different for each type of sample (rubber, extraction residue, ash).

The rubber was analyzed by the pyrolysis method described in ASTM method D3677. The samples were placed in a test tube and quickly heated with a propane torch for 15 seconds. As the rubber decomposed, the off-gas condensed onto the side of the tube as an oil. The oil was collected on a swab and smeared onto a KBr window for IR analysis.

The dried extraction residue was analyzed by adding a small amount of dry acetone to the residue, swirling it for a minute and placing the resulting solution onto a KBr window. After the acetone evaporated, the resulting film was analyzed.

The IR spectra on the ash samples were generated by making a KBr pellet from the ash.

RESULTS AND DISCUSSION

Sampling

One of the difficulties associated with this method is that it must be applicable to a wide variety of hoses. A review of the description of the hose types in the Experimental Section will attest to this fact. To simplify the procedure, only the inner tube layer and the outer jacket were analyzed. These were chosen because they are the layers exposed to the fuel and to the atmosphere.

The methods of sampling varied depending on the construction of the hose. In general, three, 10 g samples were taken from both ends and the middle of the 3-4 ft. lengths. The hoses that had only fiber reinforcement had 3" wide strips cut from them on a band saw. Then a 1"x6" die was used to cut samples from which the inner and outer layers were trimmed off with a scalpel. Hose C was too thick for the die so the inner and outer layers were simply pulled off with pliers. This procedure left residue from adjacent layers which was removed by carefully sanding the sample on a belt sander. At this point, the 10 g of sample could be cut out with scissors.

In all cases, the cut edges were avoided because of the heat generated during the cutting process. Hose B was more difficult to sample because it contained steel cords and could not be cut with a band saw. Instead, discs were cut from the middle of the hose with a 2 inch diameter hole saw. Samples were taken from the ends by cutting off pieces with a scalpel. Hose E was thin but flexible enough that strips could be cut with the die directly from the length of hose. Then, with the use of pliers, one of the layers could be stripped off leaving the other attached to the woven cloth reinforcement. The cloth could be easily removed after soaking in warm water for about one hour.

Extractions

The method used in this study was the Environmental Protection Agency (EPA) Method SW870. It is similar to the acetone extraction procedure in ASTM Method D297. The EPA method was chosen because it is commonly performed in these laboratories and is of a larger scale than the ASTM method. Although the ASTM method would work equally well, the results may not correlate because of different solvent-to-rubber ratios and different extraction times.

The important parameters that need to be controlled during this procedure are the sample mass, the amount of solvent, and the extraction time. Acetone will remove rubber resins, free sulfur, plasticizers, processing aids, oils and waxes, antioxidants and organic accelerators. Therefore, if one considers that the extraction process is controlled by distributive functions, it is easy to see why control of the solvent-to-rubber ratio, the boiling rate and the extraction time is important.

The results from the extraction of the rubber fuel hoses are shown in Table 1-1 (Appendix A). Hose A was selected as the baseline hose so 10 samples of it were extracted. Notice that for all the new hoses, the percent extracted varies less than 2%. The old hose A outer jacket had the largest variance.

These values represent the amount of material lost during a 24 hour extraction with acetone. The values may not have significance as a performance index. However, it does appear that percent extractables are a true characteristic of the material since the new and used hose A show statistically identical values for the inner tubes and similar values for the outer jacket. This value could therefore be used as a check when comparing first article materials with production hoses.

Thermogravimetry

TG is the thermal analytical technique that continuously weighs a sample while it is subjected to a controlled temperature program in a specific atmosphere. Typical thermal curves for each of the hoses are shown in Figures 1-2 through 1-13. The samples were heated at a rate of 25°C/min and at 600°C the atmosphere was switched from nitrogen to air. This allows the determination of percent carbon black because the polymer will decompose in nitrogen, then the black will burn in air. However, many polymers form a carbonaceous char when they decompose, so the value stated as percent black actually is the sum of black and polymer char. Therefore, percent black values will be in error to the high side and the magnitude of the error depends on how much char the particular polymer creates.

Except for hose E, all of the inner samples have a similar decomposition profile. Initially, there is a small amount of non-extractable, volatile material which appears as a slow weight loss from room temperature to about 350°C. The significance of this value is questionable because it is close to the minimum detection limit of the apparatus. The sensitivity of the thermobalance is about ±1% for a 10 mg sample. Therefore, if the percent volatiles are near this value they must be reported with caution. The sharp drop in weight starting around 350°C is the thermal decomposition of the polymers in the sample. The maximum value of the derivative is indicative of the thermal stability of the polymer. The next weight loss, which occurs after air is added, is the burning of the carbon black and the polymeric char. The residue is the inorganic fillers and additives that do not burn.

The outside samples all show another region of weight loss which occurs before the main decomposition of the polymer. Initially, it was believed that this represented residual non-extractable organic compounds. However, a more likely possibility is that this weight loss can be attributed to a step-wise decomposition of the polymer. In any case, this weight loss is reproducible and appears to be a characteristic of the hose.

Hose E shows a different decomposition profile as seen in Figures 1-7 and 1-13. This material is different from the others, shows one main weight loss, a relatively small amount of carbon black, and very little, if any, ash.

The TG results for all of the hoses are shown in Table 1-2. As with the extractions, ten baseline (hose A) samples were analyzed to determine the sensitivity of the technique. Overall, the precision of the method is good. The percent volatiles for all samples and the percent ash for the hose E were questionable because they are close to the minimum detection limit of the instrument. The percent polymers and black can be determined within about ±5%, based on two standard deviations. The peak derivative temperatures were similar for the inner tube samples and were around 475°C. The outer samples were not as similar. The first major weight loss peak temperature varied from 270°C (old hose A) to 372°C (hose C). Additionally, the magnitude of this weight loss also varied dramatically. In terms of temperature and weight loss there appears to be three groups (excluding hose E). The two hose A's and hose D showed a 5-7% loss at around 275°C. Hose B lost 25% at around 350°C and hose C lost about 20% at around 370°C. Therefore, it can be assumed that the polymers used in the outer jacket of hoses A and D are very similar. Hoses B and C contain similar polymers from a chemical point of view but are obviously different in composition.

Compositional Analysis

If the results from the extraction analysis and the thermogravimetry are combined, it is possible to calculate the relative amounts of organics, carbon black and ash for each hose. This was done and the results are shown in Tables 1-3 and 1-4. Notice that there is good agreement between the results for the new and old A hoses. The standard deviations presented in the table for the percent organics were found by taking the square root of the sum of the squares of the percent extractables, the percent volatiles, and the percent polymers. These data are represented graphically in Figures 1-14 and 1-15. Notice that generally the compositions were similar, except for the hose B inner tube which had a high ash content.

As mentioned previously, the percent carbon black will be in error depending upon the amount of char produced during the thermal decomposition of the polymer. Previous experience in this laboratory has shown substantial differences between the analyzed value and the actual value. For example, a specific Navy neoprene formulation is made with about 20% carbon black. When 13 samples were subjected to TG, the average value for percent carbon black was 45%. On the other hand, a nitrile rubber sample with 27% black was found to have 30% by TG. It must be emphasized that this technique will not accurately measure % black, but the results are precise and characteristic for the particular sample.

Fourier Transform Infrared Spectroscopy

FTIR Spectroscopy was performed on the rubber, the extract, and the ash for inner and outer samples for each hose. Since a different technique was used for each type of sample, they will be discussed separately.

Polymers

The polymers were analyzed by the gas flame pyrolysis method described in ASTM Method D3677. A small amount of extracted rubber is placed in a test tube and quickly heated in the hottest portion of a gas flame until the pyrolyzed product condenses in the cool part of the tube. A sample is then transferred to a KBr window with a cotton swab and an IR spectrum collected. It was discovered that the length of time between burning and analyzing is very important. This is demonstrated in Figure 1-16. Apparently, a volatile product is formed during pyrolysis and evaporates. Therefore, it is important to control the time after pyrolysis and to rescan the sample to determine if the spectrum is changing. Additionally, if too much time passes, the condensate becomes hard and difficult to remove from the tube. It is also important to control the mass of sample and the burning time during this procedure. In general, about 0.25 g were burned in the hottest portion of the flame for 15 seconds. The spectra for all of the hoses are shown in Figures 1-17 through 1-28.

The inside rubber for all the hoses except hose E are shown in Figures 1-17 through 1-21. Notice that these spectra are identical. The presence of a nitrile stretch at about 2225 cm^{-1} strongly suggests that all of the inside rubber is nitrile. This assumption is reasonable because nitrile rubber has excellent fuel resistance.

Figures 1-22 through 1-26 show the outside rubber for all hoses except E. Hoses A and D appear to contain identical rubber. Hoses B and C are similar to each other and the other three, but not identical. It is believed that all of the outside layers are made of neoprene. Even though they are not identical, the differences seen by IR and TG could be due to the presence of different co-resins.

The IR spectra for the inner and outer layers of the hose E are shown in Figures 1-27 and 1-28. These are identical compounds and a computer search identified them as polyurethanes. From all the data gathered, it is clear that both layers of this hose are identical in terms of composition and materials.

Extracts

The extracts were first isolated by evaporating the extraction solvent, then dried under a fume hood for at least a few days. The oily residues were analyzed by IR by first adding a small amount of dry acetone to the residue. After swirling, the resulting acetone solution was transferred to a KBr window and the solvent allowed to dry. The resulting film was then analyzed. It is possible that this method produces a spectrum not totally representative of the extract. If a particular compound is much less soluble in acetone than others, the use of a small amount of acetone may exclude less soluble components. This was not investigated, but the possibility of it occurring could be reduced by analyzing the solution formed during the extraction.

The IR spectra for all of the hoses are shown in Figures 1-29 through 1-40. Since all of these are mixtures, it is difficult to identify the components by a computer search. Therefore, even though some matches were obtained, they will not be presented because they are considered questionable. These spectra can, however, be considered fingerprints of the extractable material. One point of interest seen in these plots concerns the new and old hose A extracts from the inner tubes. Notice that the old hose shows a stronger nitrile absorption. This may indicate that the polymer has broken down which would allow more to be extracted.

The extracts from hose E could be reliably identified. They gave an excellent match with a polyether based polyurethane. This is not surprising because linear urethane molecules are easily extracted with acetone. In fact, there is an extraction method for the determination of crosslink density in polyurethanes.

Ash

The ash samples were the most difficult to analyze. They were done by making a KBr pellet out of the ash. The IR spectra for all of the samples except the hose E are shown in Figures 1-41 through 1-50. Hose E did not have any ash in it. Notice that the new and old hose A do not appear to have the same spectra. It is not known if this difference is significant or not. Sometime during this study, one of the heating elements failed in the furnace and the samples were ashed at 750°C instead of 1000°C. It is not known if this could have affected the chemical composition of the ash or not. Operator technique was eliminated by repeating the new hose A samples after all of the others were completed. They still appeared to be different. These results suggest that the old hose A outer jacket, the hose B inner tube and the hose D outer jacket all have an identical inorganic filler. The hose D inner tube is similar. The hose with the most different fillers is the hose C. Since the effect of heating temperature is not known, it is difficult to know if the new and old hose A really contain different fillers, as suggested by the results.

CONCLUSIONS AND RECOMMENDATIONS

The results from this study suggest that a method for characterizing rubber fuel hoses could easily be added to the current material specification. A proposed test method specification is provided as Appendix B. However, a number of unanswered questions and considerations about the method need to be addressed.

General concerns about the method are:

- Is it clear and comprehensive?
- Can it be performed by other laboratories?
- Is it reproducible in other laboratories and between laboratories?
- What defines acceptable results?

It is strongly recommended that this method be treated as a draft and be subjected to critical review by other laboratories that may perform the method.

There are also more specific considerations about the method that will be discussed in reference to the flow diagram in Figure 1-1. Ways to sample a variety of hoses have been successfully developed. However, only the inner tube and outer jacket of the hoses were considered in this study. Is it appropriate to consider sampling all layers in a complex hose? If so, more work is needed to develop methods to sample an entire hose.

The samples were ground to a powder to maximize the effectiveness of the extraction. It is not known if this is necessary or not, or whether the results would be different on samples not ground. Other similar methods involve simply cutting the samples into small pieces.

The concerns about the extraction process are the effects of variations in sample weight, solvent volume, extraction cup size, boiling rate, and time. Additionally, there are two generally used apparatuses for performing extractions and it is not known if the results are the same for both.

During this study, the compositional analysis was calculated by combining the extraction results with the TG results. This probably introduces errors that could be avoided by performing TG on a rubber sample that has not been extracted. In fact, if TG were performed before and after extraction, it may be possible to tell how much rubber was extracted. If this were true, then information could be obtained about the quality of the rubber used. This technique might provide a tool for production quality control because the amount of rubber extracted should relate to the cure process.

Each of the IR methods also have questions associated with them. It was discovered that the amount of time between pyrolysis and IR analysis was an important factor. Other possible variables that were not investigated include burning time and sample mass. The IR analysis of the extract raised questions because the dried residue was washed with a small amount of acetone and the resulting solution analyzed. It is possible that this procedure did not produce a sample that entirely represented the extract. This could be addressed by analyzing the acetone extract before the solvent is removed and comparing it to the analysis of the residue. The main difficulty with the ash analysis was that samples were unavoidably ashed at two different temperatures, 1000 and 750 °C. It is possible that subtle changes could have occurred in the ash between these temperatures. This should definitely be investigated because the old and new hose A samples contained inorganic ash that appeared different by IR. It is important to know if this apparent difference is real.

Finally, acceptance criteria for the IR results have not been developed. Preliminary results suggest that computer aided spectral subtraction is a viable approach. This technique eliminates common peaks leaving a spectrum of the differences between two spectra. This should be investigated to set precise criteria for determining if two spectra are identical. This will, however, limit this technique to FTIR instruments and eliminate dispersive ones.

In summary, this study is an excellent beginning for the development of a reliable method for the quality control of rubber fuel hoses. However, there are a number of unanswered questions that need to be addressed before results generated by this method can be considered reliable.

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2. Thompson, C.M. and Quinn, M.E., "Compositional Analysis Procedures for Selected Elastomers Used in Sonar Transducers," Naval Research Laboratory Memorandum Report Number 5746, March, 1987.

3 Method for Rubber Products - Chemical Analysis, Annual Book of ASTM Standards, ASTM D297-81, v. 09.01, 1984.

4 Method for Rubber - Identification by Infrared Spectrophotometry, Annual Book of ASTM Standards, ASTM D3677-83, v. 09.01, 1984.

PART 2—REFINEMENT OF THE METHOD

INTRODUCTION

The results of part 1 showed that the developed method may be a valuable tool for quality control of rubber hose materials. However, there were a number of unanswered questions and concerns presented. Part 2 has been designed to investigate some of these issues.

The objectives for part 2 can be presented as a series of tasks:

Task 1— Define FTIR acceptance criteria based on spectral subtraction.

Task 2— Compare IR spectra of extraction residues with new spectra generated from the extraction solutions.

Task 3— Study the effects of pyrolysis time, temperature and heating rate on the resulting IR spectrum. Compare the results when three different people prepare samples with a common set of instructions.

Task 4— Study the effect of ashing temperature on the IR of the ash.

Task 5— Since a liquid nitrogen grinder is not commonly available, compare ground vs. cut samples and how they affect extraction and TGA results.

Task 6— Compare the results of TGA on nonextracted rubber to the percent composition calculated from TGA on extracted rubber and percentage extract.

Task 7— Compare samples of new and old hoses A and D.

RESULTS AND DISCUSSION

Task 1—Define FTIR Acceptance Criteria

Since FTIR results are part of the analytical method it would be beneficial if one could determine if two spectra were identical or not based on some kind of objective evaluation.

The approach to this task was to use computer generated spectral subtraction. On most FTIR instruments there is available software that can subtract one spectrum from another. This technique is very useful in situations when the path length or concentration of material as seen by the IR beam is relatively constant. Unfortunately, the techniques used in this project make it difficult to control the effective concentration. The pyrolyzed rubbers are smeared onto a KBr window and the extraction solutions are evaporated onto a window to form a film. In either case, the thickness is difficult to control. The result of this is that each sample has a different total absorbance and the variation is large.

The instrument used in this study allows one to adjust the relative concentrations of the two spectra manually. This technique works well when the absorbances are close together but becomes less effective as the difference in absorbance increases.

The full scale absorbances for the pyrolysis products and the extraction solutions for hose D are shown in Tables 2-1 and 2-2. The full scale absorbance is found by subtracting the minimum value of the baseline from the maximum value of the largest absorbance band. The values are from a co-added spectrum which is the sum of three separate samples. There are two important factors seen in these two tables. The first is the low absorbancies seen in Table 2-1. This relates to how much IR was absorbed by the specimen and these values are low. This was caused by the small amount of pyrolysis oil formed during heating. It can be alleviated by pyrolyzing more rubber, resulting in more sample to analyze.

The second factor to notice is the large variance in full scale absorbance. As mentioned before, large differences in effective concentration make subtraction more difficult. A way to resolve this issue is to require that the full scale absorbances fall within a pre-determined range.

Tables 2-3 and 2-4 show the results of a series of computer generated subtractions. Table 2-3 shows the results of doing the subtractions on the same files two different times. The difference between the two trials demonstrates the effect of the operator adjusting the relative concentration of the individual spectra. The second letter of the files show whether the sample was from the outer jacket or the inner tube (O or I). Notice that in Table 2-3, in all cases except one (00G-N0G), the subtraction of outer from inner gives a relatively high subtraction value. The results in Table 2-4 are not as definitive but, in general, samples that are known to be different produce large differences.

These results have not led to a defined acceptance criteria for FTIR results. However, it does appear that this could be achieved by a requirement that all spectra have a defined absorbance.

Task 2—FTIR of Extraction Residue vs. Solution

During the first part of this study, the IR's of the extracts were generated by adding a small volume of dry acetone to the residue from the evaporated extraction solution. This procedure may exclude components of the extract because a small amount of acetone was added to a large amount of residue. To resolve this issue, the extraction solution was analyzed by placing 2-3 drops of the solution onto a KBr window and allowing the solvent to evaporate. This procedure ensured that everything in solution was analyzed.

The results are shown in Figures 2-1 and 2-2. There are small differences between the spectra, especially in the outside samples. The significance of this effect is dependent on how closely the IR results are scrutinized. It is possible that the difference would be large if spectral subtraction were performed. However, until the issue of spectral subtraction is resolved, it is not possible to determine the significance of these differences.

Task 3—Evaluate Pyrolysis FTIR

The purpose of this task was to determine if the pyrolysis procedure is reproducible when different people perform the pyrolysis. This was determined by comparing the spectra generated when three different people prepared the samples. Each person had identical instructions. The instructions were:

1. Add enough rubber to fill the round area in the bottom of the tube.
2. Hold the tube at 45° from horizontal.
3. Heat the tube in the hottest part of the flame for 20 seconds.

The results of this exercise are shown in Figure 2-3 through 2-5. Each figure shows the spectra from three different samples. Notice that there is a lot of differences between individual samples. It was initially thought that the differences seen related to the amount of time between pyrolysis and analysis, like reported in part 1. However, this time the spectra did not change with time. After interviews with the operators, it appears that the cleanest, most reproducible spectra are generated by high heat. Operator 1 was vigorous with heating during the pyrolysis procedure.

These results seem to suggest that the pyrolysis procedure is not straightforward and that a more reliable procedure needs to be identified. Possible alternatives may be found in ASTM D3677-83. These include the temperature controlled pyrolysis (Sec. 9.1), the dissolution method (Sec. 10.1) and the mild thermal degradation (Sec. 10.2).

Task 4—Repeat Ashing of New and Old Hose A

During part 1, a heating element failed in the muffle furnace and made it impossible to ash samples reproducibly. Additionally, the results indicated that the ash in hose A was different for new and old samples. Therefore, samples of new and old hose A were ashed side-by-side and then analyzed by IR.

The procedure for ashing was similar to that used before. About 1 g of rubber was placed in a crucible and pre-burned with a torch until most of the thick black smoke was evolved. The crucibles were then placed in a muffle furnace at 650°C and held there overnight.

The results are shown in Figures 2-6 and 2-7. Notice that the spectra are identical for new and old. It is now believed that the ashing temperature is a variable, but perhaps not the most important one. When preparing the KBr pellets for ash analysis, it was observed that it is very important to grind the ash thoroughly before the KBr is added. Therefore, the differences found in the previous results may be due to sample preparation technique.

These results raise the question of the validity of the IR results on the ashes from Part 1. However, this issue can be resolved by a requirement for preparing ashes at identical temperatures and for grinding the ash well during preparation of the KBr pellet.

Task 5—Evaluate the Effect of Grinding the Samples

Since a liquid nitrogen grinder may not be readily available, it was desirable to see how grinding affects the results. Samples that were cut into 1 cm^2 cubes were compared with ground samples by extraction and TGA. The results are shown in Table 2-5 and 2-6 for hose D inner tube and outer jacket samples respectively. Note that the TGA results are the actual values of extracted samples and not the calculated percentage composition.

There are two areas most affected by grinding. The first is the amount of material extracted. This is not surprising but does indicate that the unground samples are not totally extracted. This would either be a function of extraction time or extractables could be trapped in the center of the pieces. In either case, if the time and rate of boiling are controlled, the results seem to be precise and representative of the sample. The other area affected is the peak temperature of decomposition. This also is not surprising since decomposition occurs from the outside in and is dependent on surface area. Although the percentage difference in temperature is not high, the temperature differences are significant considering the precision of the measurement.

These results suggest that grinding does not affect the precision of the method but different results will be obtained. Therefore, it is important to know if the samples were ground or not and that all samples (first article and production) are treated the same way.

Task 6—Thermogravimetry

The purpose of this task was to compare two ways of determining the composition of the rubber formulations. The first way was used in part 1. This involves calculating the percent of composition from the TG results on extracted rubber and the percentage extracted. The second way uses the TG results from both extracted rubber and nonextracted rubber.

The samples studied include new and old, inner and outer, ground and not ground, and two levels of sample mass. The results are presented in Table 2-7. These results generally show that sample mass and surface area affect the results, but not always in a consistent manner. Therefore, it appears as if different masses and surface areas can be used as long as they remain relatively constant from sample to sample.

If the results before and after extraction are compared, a compositional analysis can be obtained. The two components that should remain constant after extraction are the percentages of carbon black and inorganic ash. Since the percentage ash is a relatively small number, the minimum detection limit is more important, so the percentage carbon black is probably a more reliable number. So, the ratio of carbon black before and after extraction can yield the percentage extracted and give percentages of the other components.

In part 1 of this study, the compositional analysis were based on the percentage extracted and the TGA results of the extracted rubber. A comparison of the two methods is shown in Tables 2-8 and 2-9. Notice the good agreement between the two methods.

In part 1, the compositional analysis was combined to give three components, namely organics, black and ash. It is now believed that a more detailed composition can be reliably determined. The necessary data was produced by TGA. What was called organics in part 1 can be divided into extractables, and organics step 1 and step 2. The organics are divided based on the temperatures at which decomposition occurs. Step 1 involves decomposition temperatures below 400°C while step 2 are those above 400°C. With the use of data from part 1 and the results of part 2 a detailed compositional analysis was produced for all the hoses except E. This hose was omitted because it is distinctly different from the others. The results of the analysis are shown in Tables 2-10 and 2-11.

These results show that both ways to calculate percent composition give comparable results and therefore validate each other. And, finally, this study has produced data that indicate that a more detailed compositional analysis can be reliably performed. This means that hoses can be compared in more detail than was done in part 1.

Task 7—Compare New and Old Samples of Hoses A and D

The complete method was performed on new and old hose A in part 1 and on new and old hose D in part 2. This section will evaluate the results in an attempt to demonstrate whether or not the hoses are identical. The properties used to evaluate the hoses are the compositional analysis and the FTIR fingerprints. It should be noted here that the old hose D was obtained along with all the other hoses, but it was not tested during part 1.

The detailed compositional analysis for hose A is shown in Table 2-12 and 2-13. The greatest difference seen in the inner tube is the % ash but notice that the difference is equal to the standard deviation. In the outer jacket, the old hose has slightly more extractables than the new.

The IR fingerprints of the various components of new and old hose A are shown in Figure 2-8 through 2-13. Notice that the inside and outside rubber samples are nearly indistinguishable. The extracts show some small differences. The inner extract of the old hose has a stronger nitrile stretch at about 2225 cm^{-1}. This probably is due to degradation of the rubber, which makes it more soluble. The outer jacket extracts also appear slightly different but without an objective criterion for evaluation, the significance of the difference is not known. However, it is clear that the extracts are very similar, if not identical. The ashes appear in the next two figures and are identical.

The results of this comparison show that there is a small difference in the percent extractables in the outer jacket, a small difference in the fingerprint of the inner tube extract and a small difference in the outer jacket extract. However, it is not believed that these differences are great enough to indicate that these hoses are of different composition.

The comparison of new and old hose D produces more definitive results. The compositional analyses are shown in Tables 2-14 and 2-15. Notice the relatively large differences seen in the inner tube % extractables, the inner tube % ash, and the outer jacket % ash.

The IR spectra (Figure 2-14 through 2-19) all appear identical except for the inner and outer ash. Notice that they are completely different. These results were verified by ashing a second set of samples.

Therefore, based on the differences seen in the compositional analysis and the IR results, it appears as if new and old hose D are definitely not identical.

CONCLUSIONS AND RECOMMENDATIONS

The effort in part 2 has resulted in more progress toward obtaining a working method for analyzing rubber fuel hoses. However, there are still a number of issues to resolve.

There still is no quantitative acceptance criteria for FTIR spectroscopy. Spectral subtraction appears to be a viable approach, but new requirements for controlling sample thickness need to be developed. This may be achieved by setting limits of total absorbance values that each specimen must fall within.

This work has demonstrated that grinding the samples before extraction produces slightly different results but the precision of measurement does not suffer. Therefore, it should be acceptable to not grind the samples as long as it is noted in the report and all comparable samples be treated the same.

The TG work in part 2 validated the calculated percent composition from part 1. It also showed that a more detailed analysis can be reliably determined. This is important because now we know that the method for calculating percent composition works and that more information can be extracted from the results.

The work on rubber pyrolysis showed that different operators will likely get different results. Although this is somewhat disturbing, it is important to know the limits of this method. ASTM method D3677-83 details three other alternatives for preparing samples for IR spectroscopy. These include temperature controlled pyrolysis in the presence of nitrogen, dissolution of a portion of the rubber in 1,2-dichorobenzene, and mild thermal degradation followed by dissolution. The third method is probably most appropriate for this application and should be evaluated.

Valuable information was also obtained concerning the analysis of the ash. It has become obvious that the results of this test are dependent on the furnace temperature during ashing, and the ashing time. Therefore, details of how the ashes were produced should be noted in the report and kept consistent. Additionally, it was discovered that the technique in preparing KBr pellets is also important.

Finally, the method was performed on two hoses (A and D) of which new and old samples were available. The results showed that new and old hose A were very similar. The results were quite different for hose D. The differences seen were in the amount of ash and the identity of the ash by IR. These results are promising because it seems that the method can pick up different formulations of compounded rubbers.

In conclusion, there are two main issues that need to be focused on to improve this method. The first is to identify IR techniques that will provide better spectra, and which will allow a detailed acceptance criteria.

The second area involves the interlaboratory precision of the method. This should be addressed by a round-robin experiment on well characterized rubber samples and involving several laboratories. The value of this method will only be determined when it is actually used.

APPENDIX A

FIGURES AND TABLES
TO PART 1

LIST OF FIGURES TO PART 1

LIST OF TABLES TO PART I

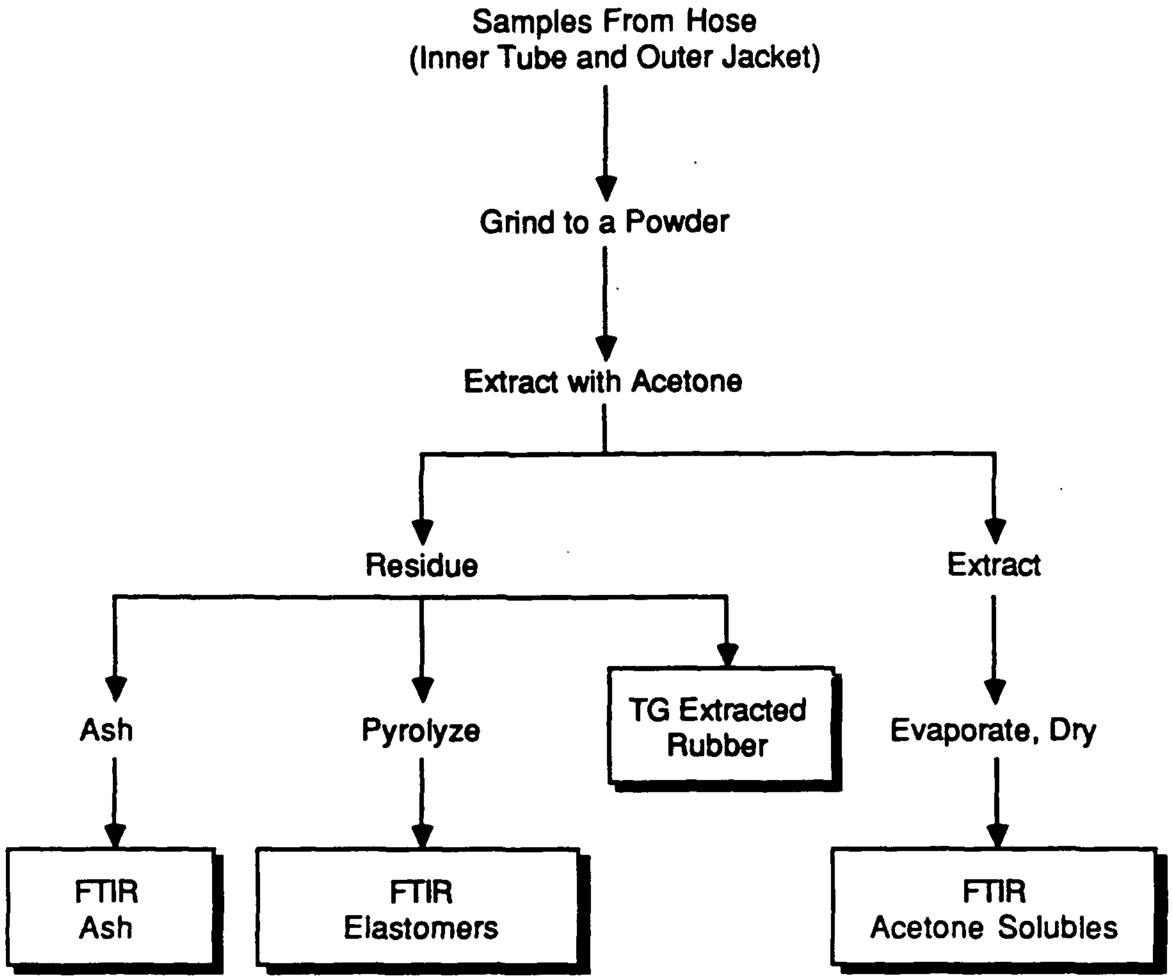

Figure 1-1 - Flow Diagram for Characterization of Rubber Hose Materials

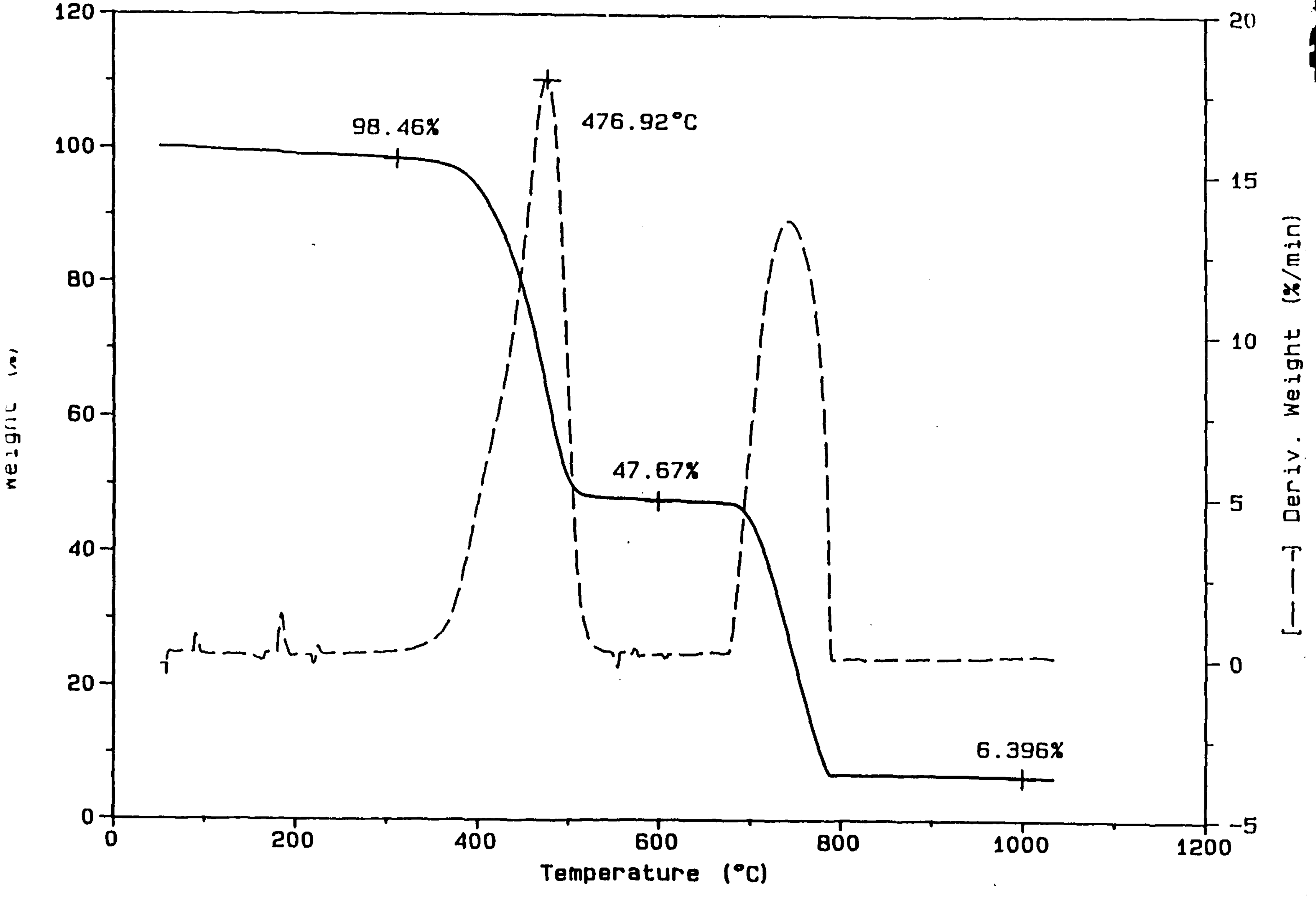

Figure 1-2 - TG Thermal Curve of the Inner Tube of the New Hose A

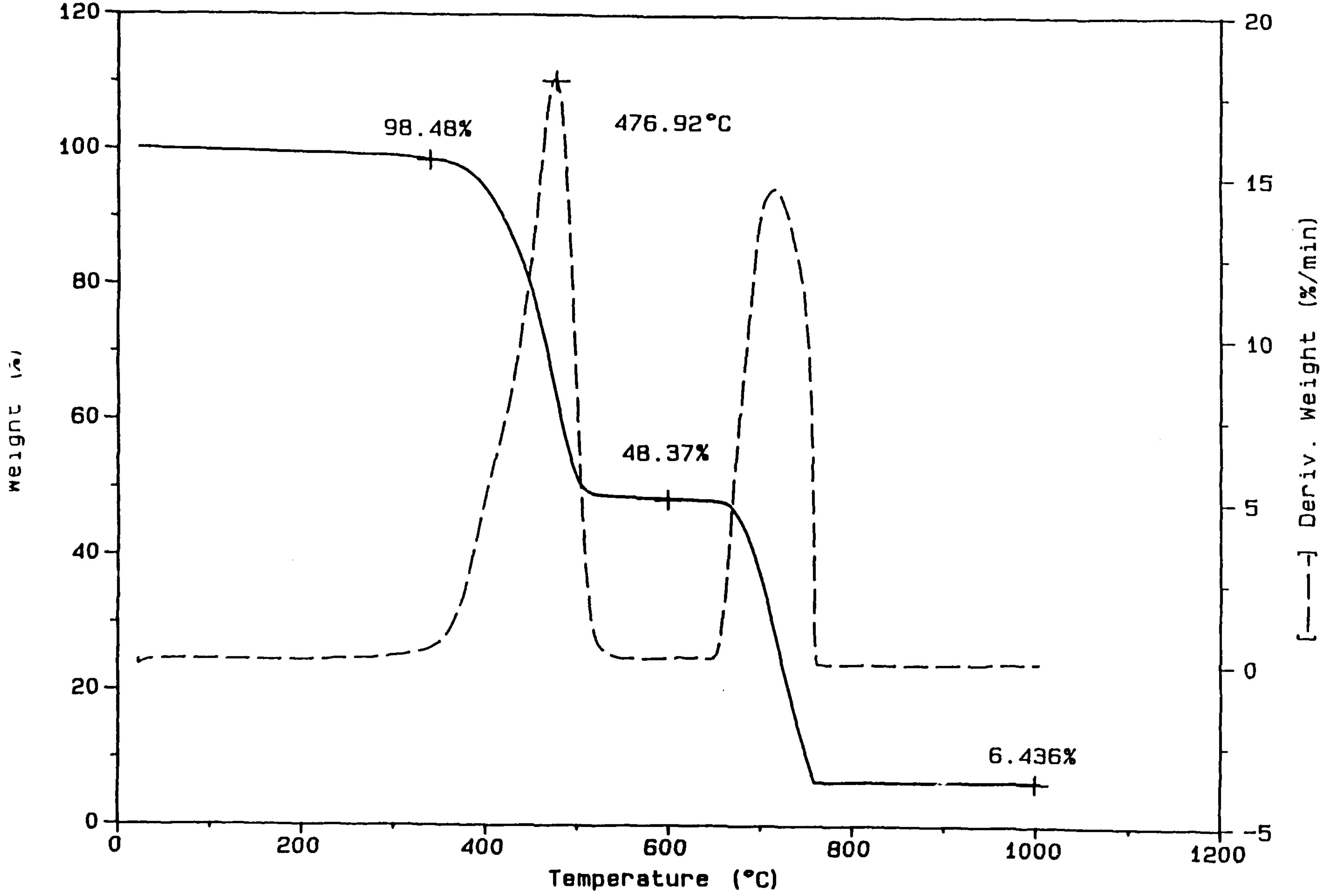

Figure 1-3 - TG Thermal Curve of the Inner Tube of the Old Hose A

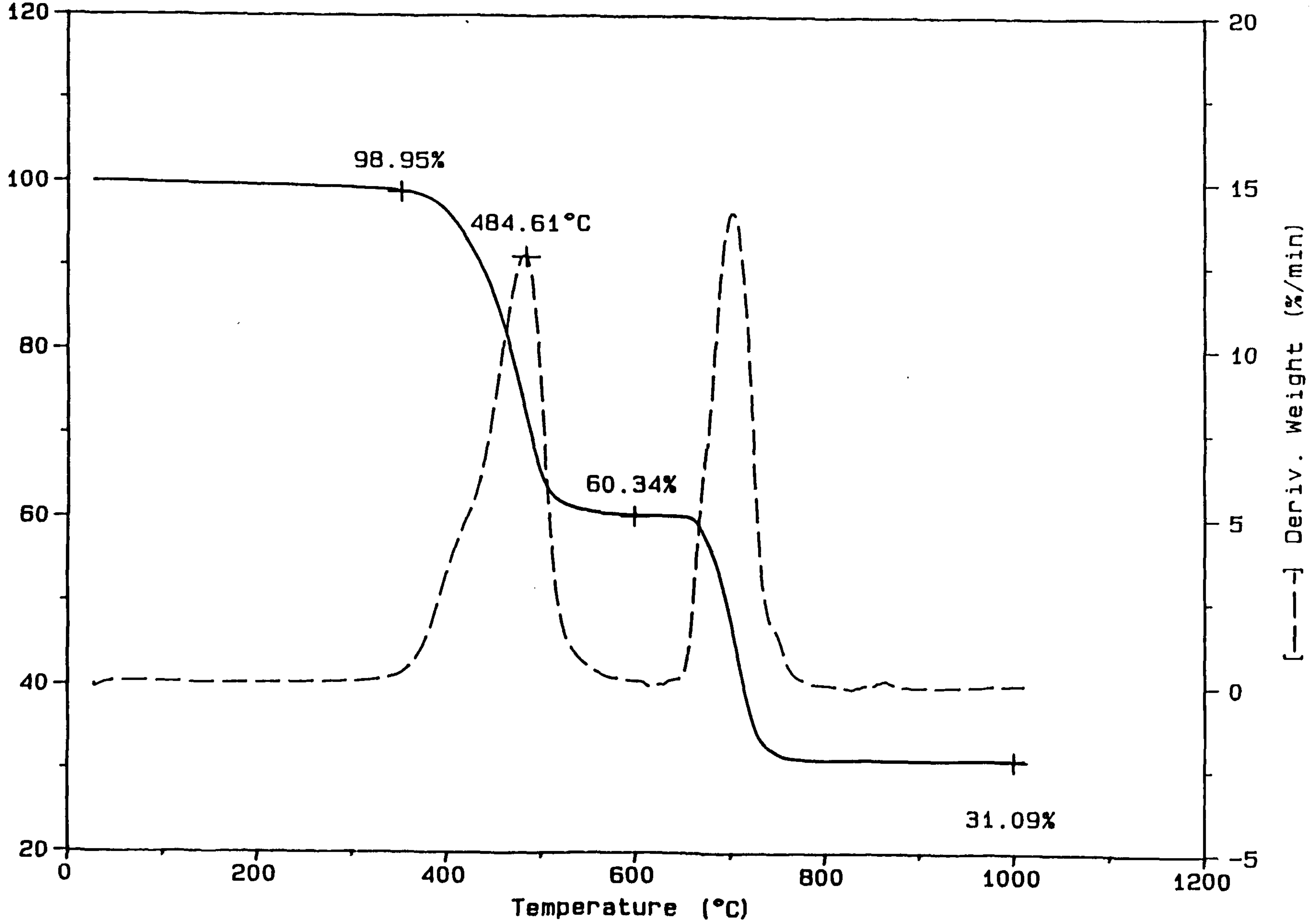

Figure 1-4 - TG Thermal Curve of the Inner Tube of Hose B

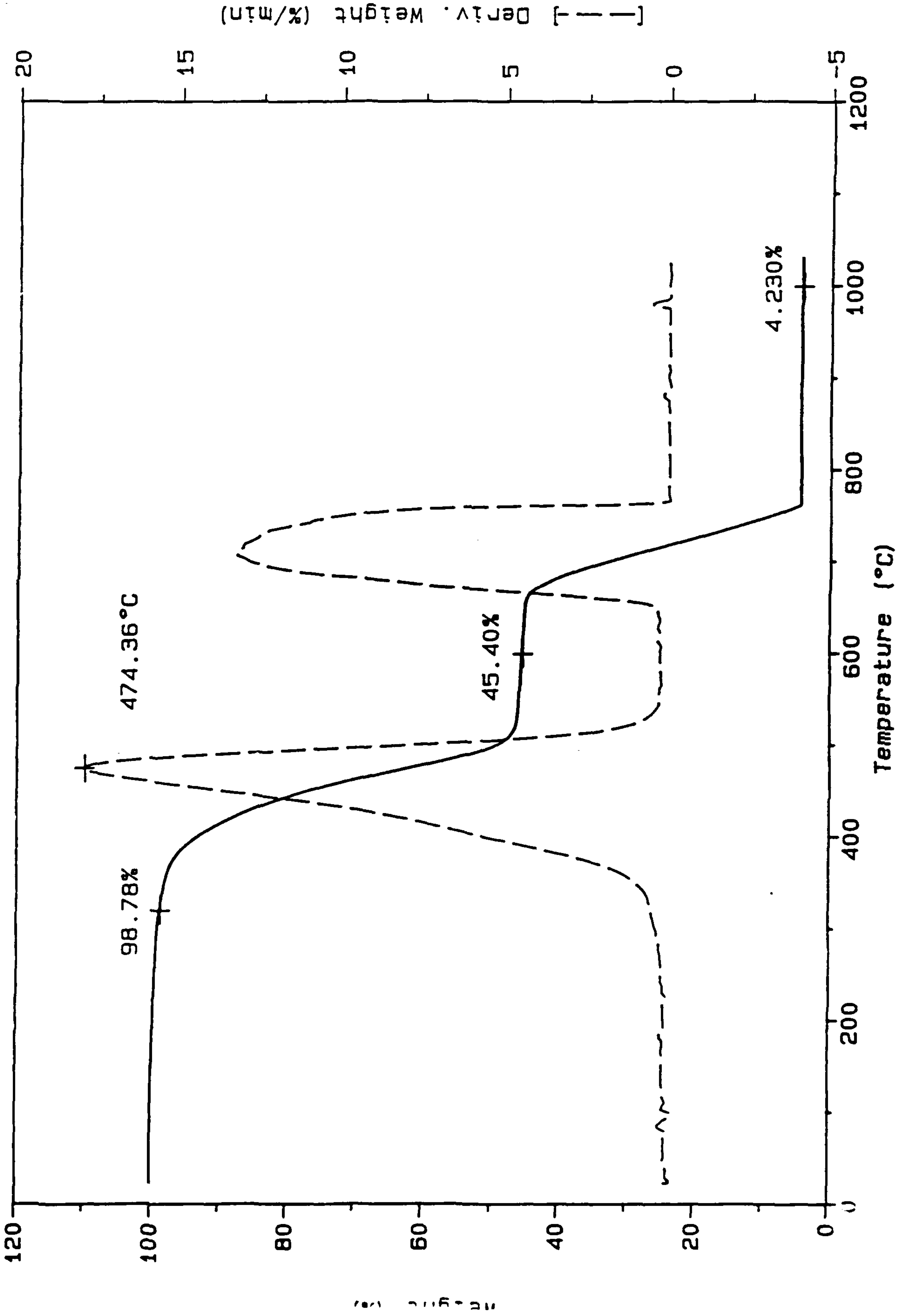

Figure 1-5 - TG Thermal Curve of the Inner Tube of Hose C

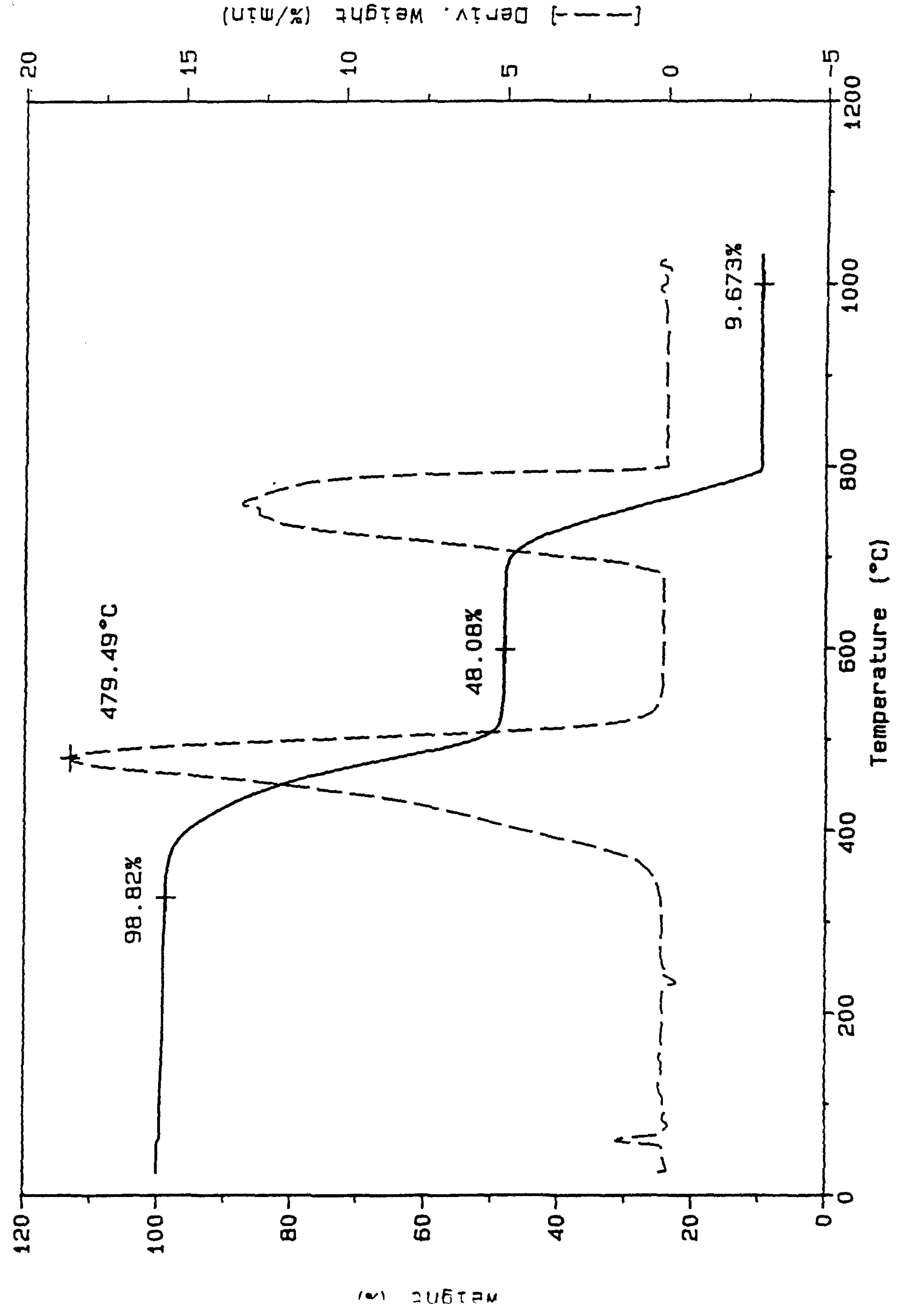

Figure 1-6 - TG Thermal Curve of the Inner Tube of Hose D

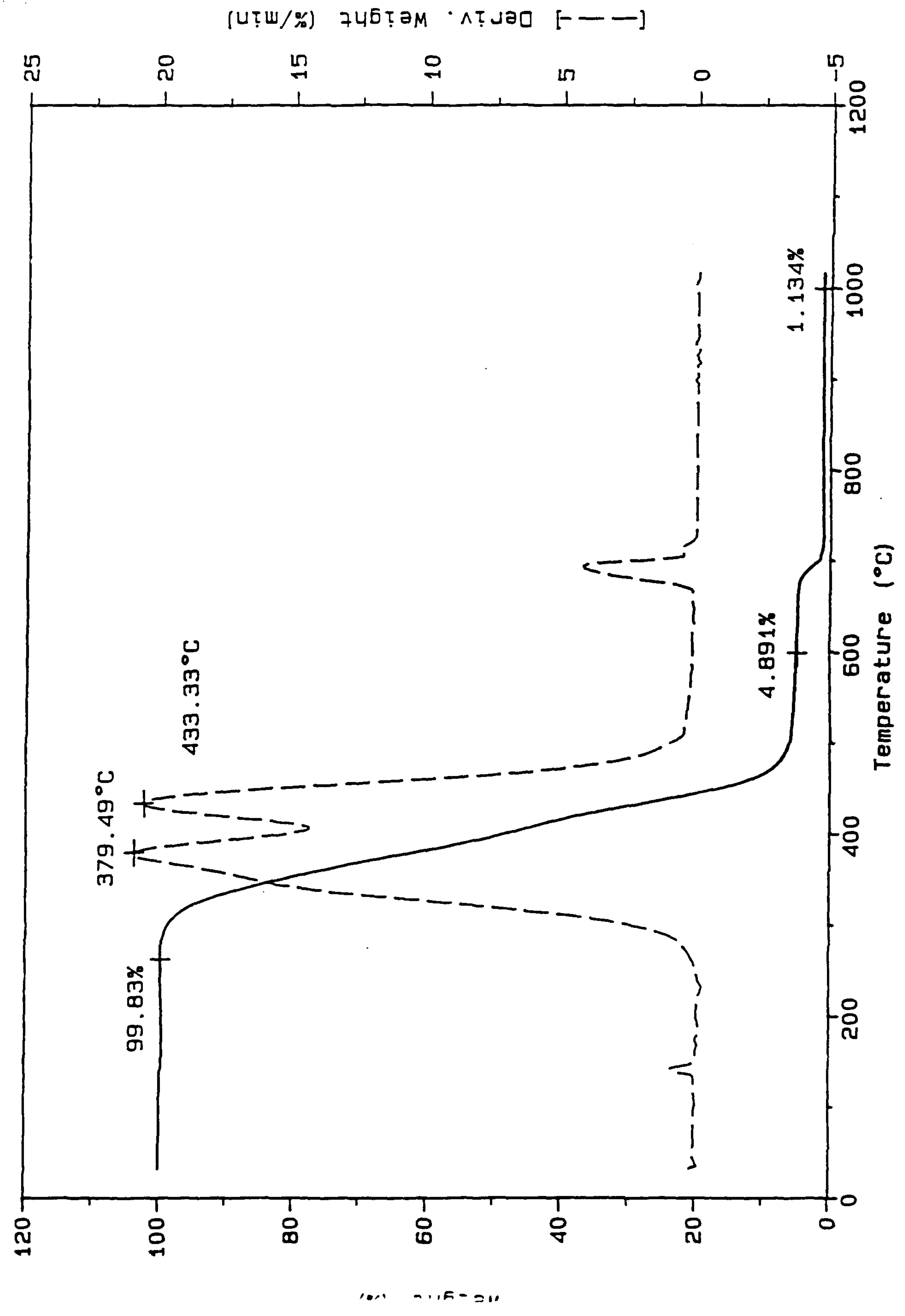

Figure 1-7 - TG Thermal Curve of the Inner Tube of Hose E

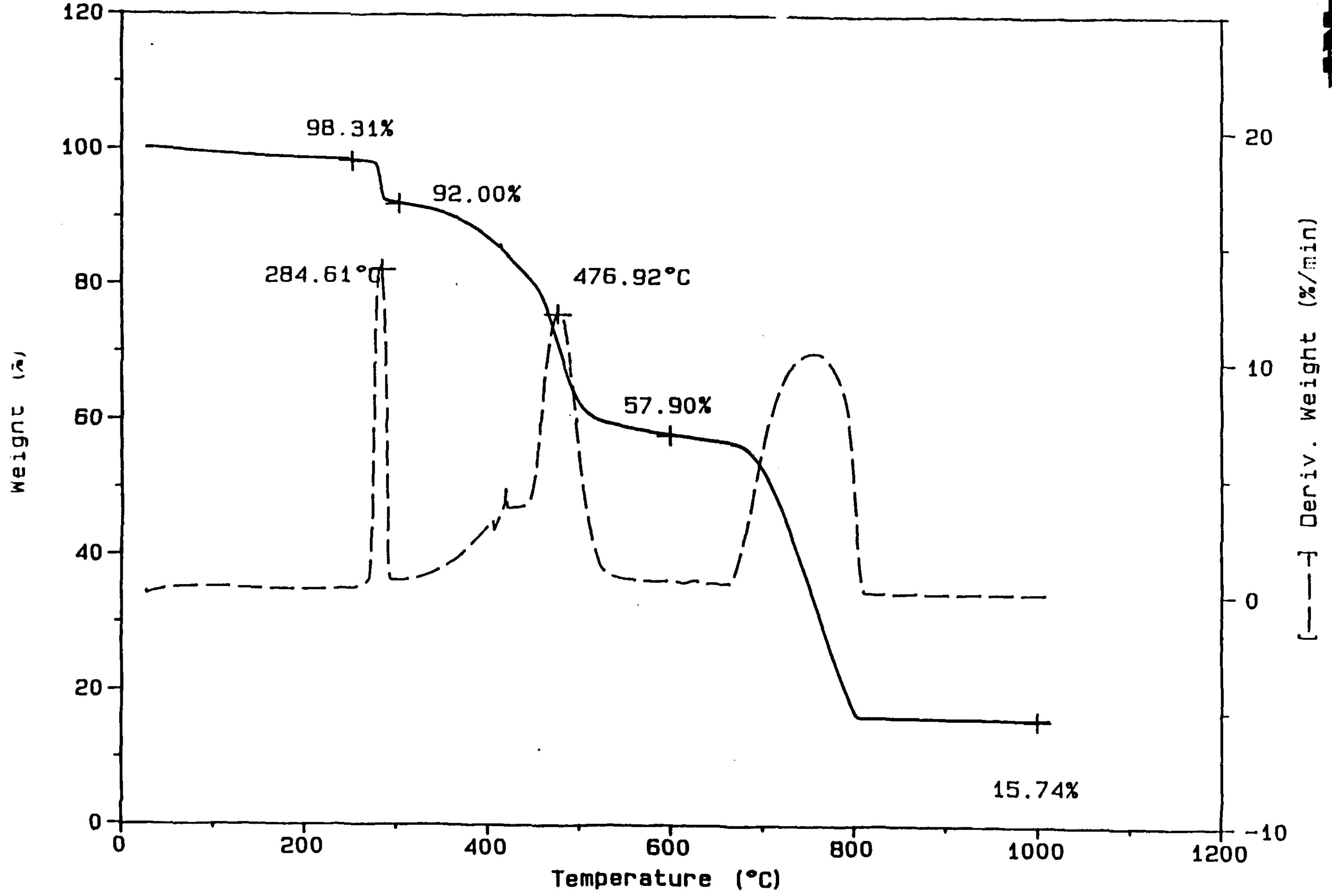

Figure 1-8 - TG Thermal Curve of the Outer Jacket of the New Hose A

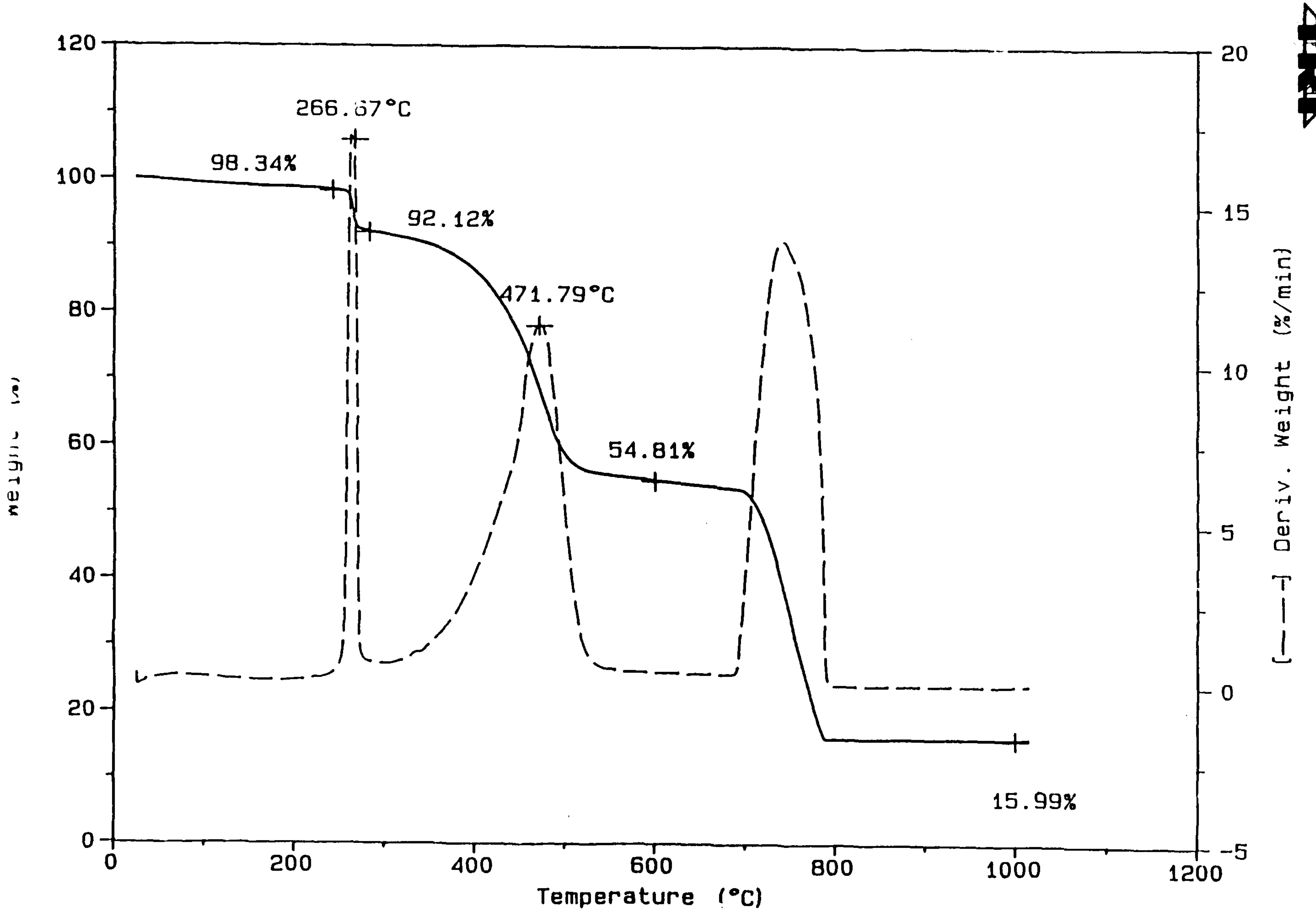

Figure 1-9 - TG Thermal Curve of the Outer Jacket of the Old Hose A

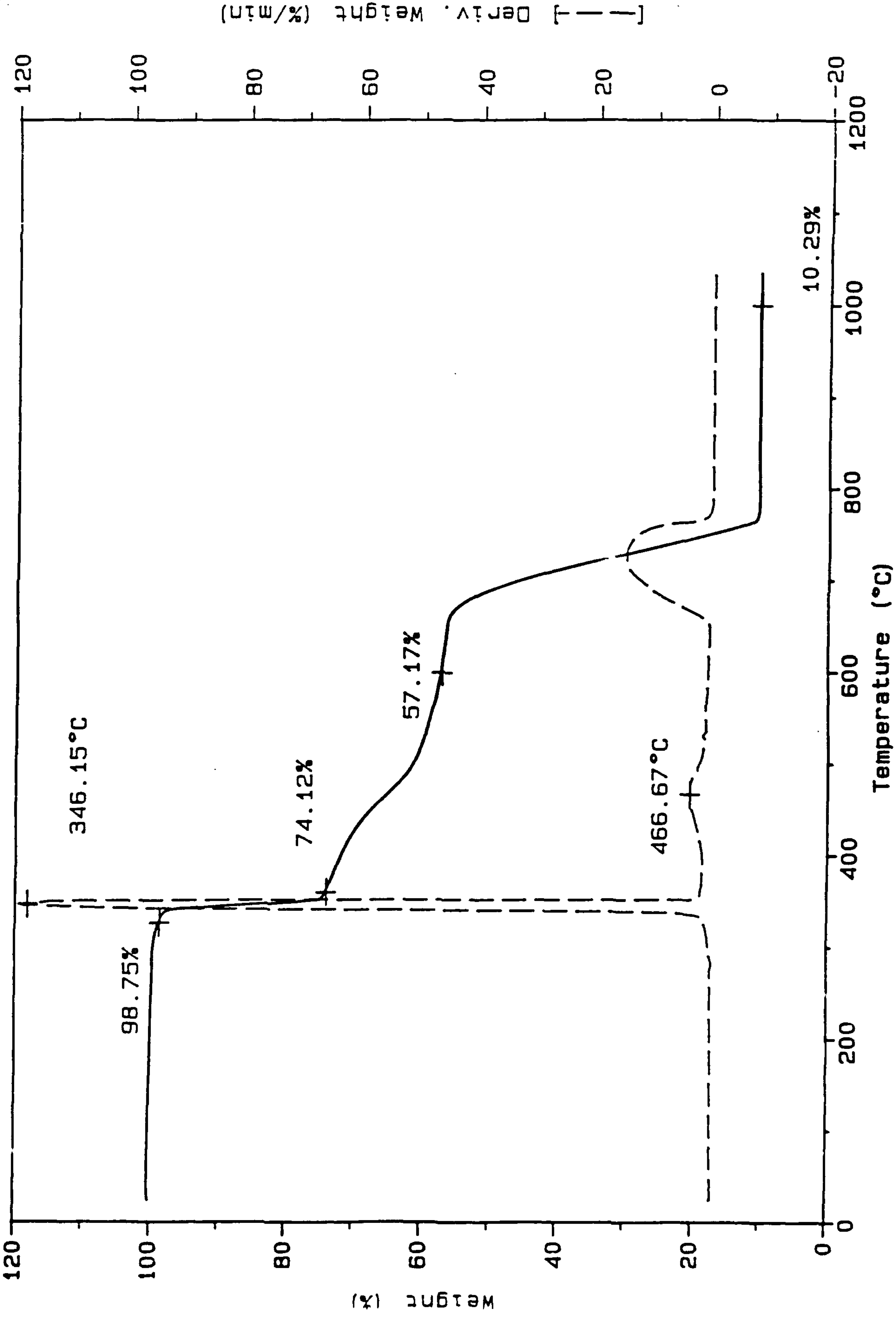

Figure 1-10 - TG Thermal Curve of the Outer Jacket of Hose B

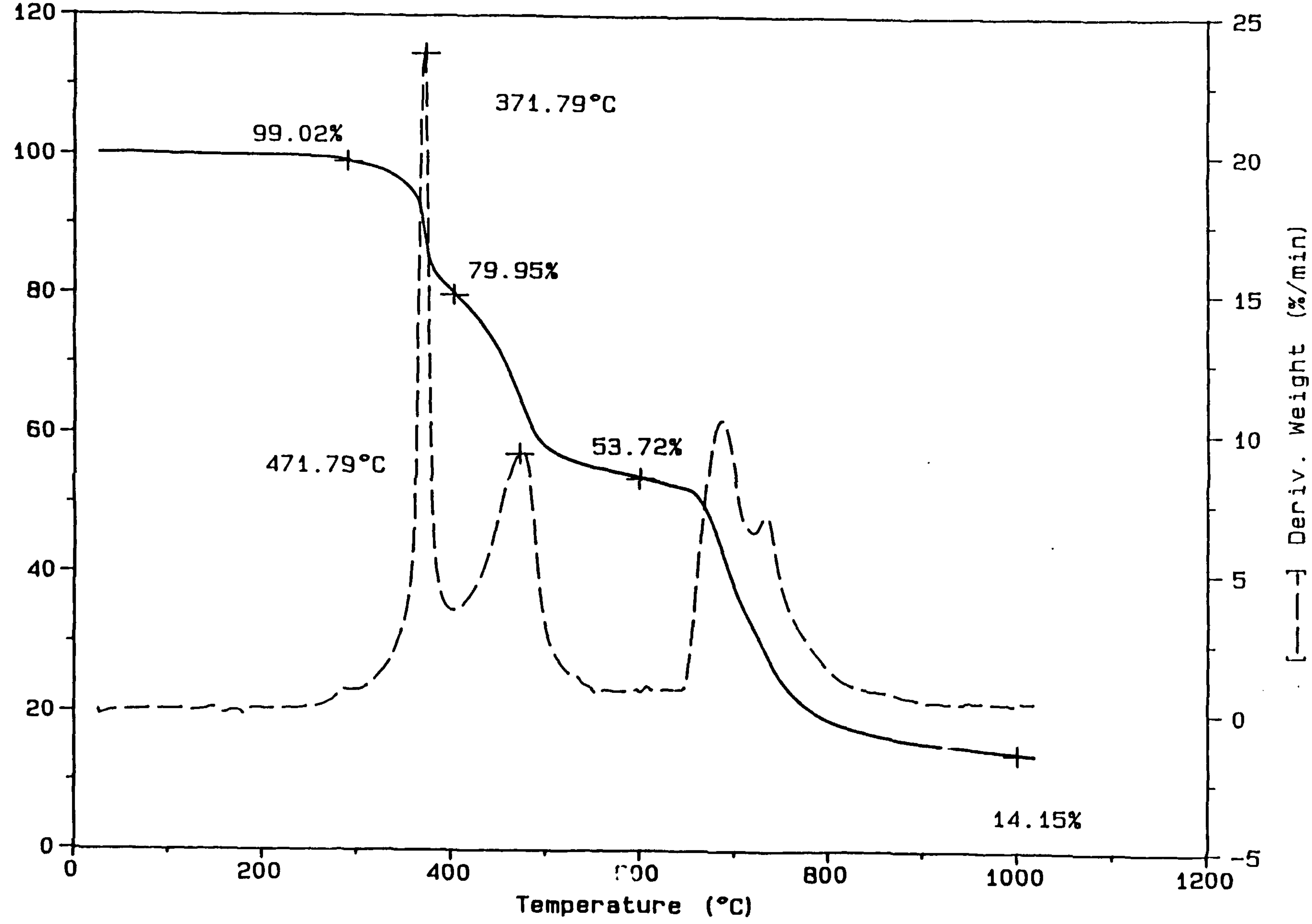

Figure 1-11 - TG Thermal Curve of the Outer Jacket of Hose C

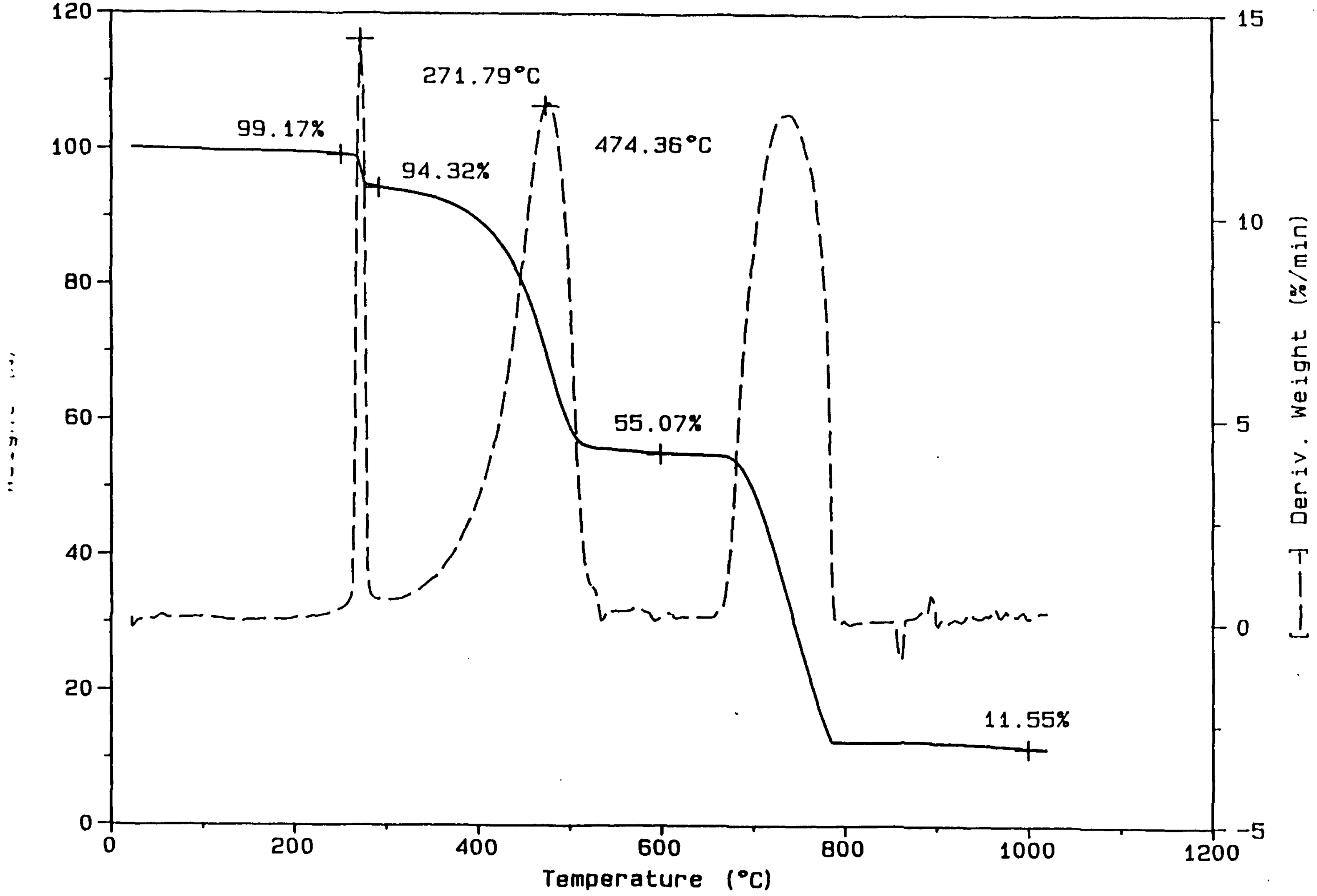

Figure 1-12 - TG Thermal Curve of the Outer Jacket of Hose D

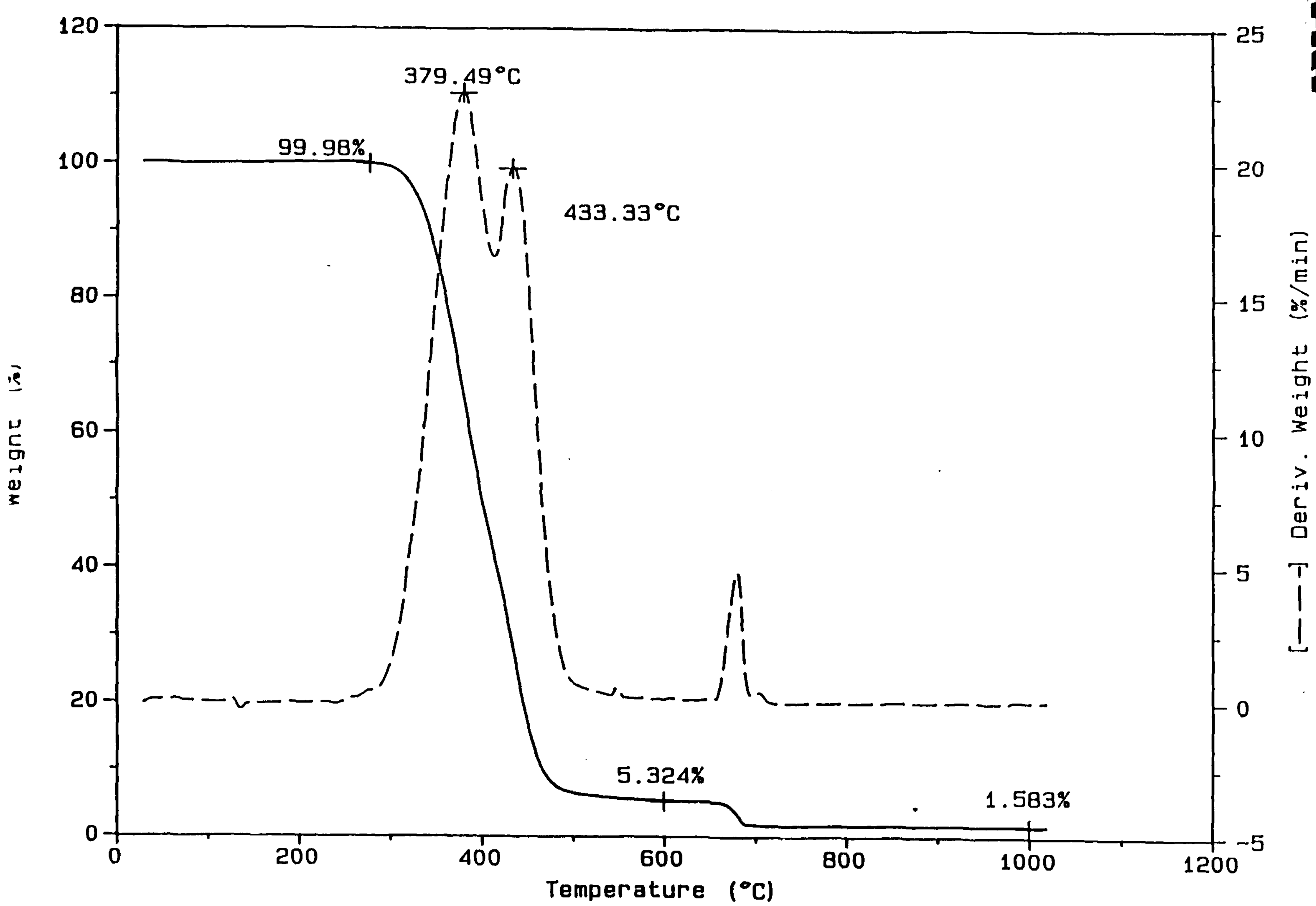

Figure 1-13 - TG Thermal Curve of the Outer Jacket of Hose E

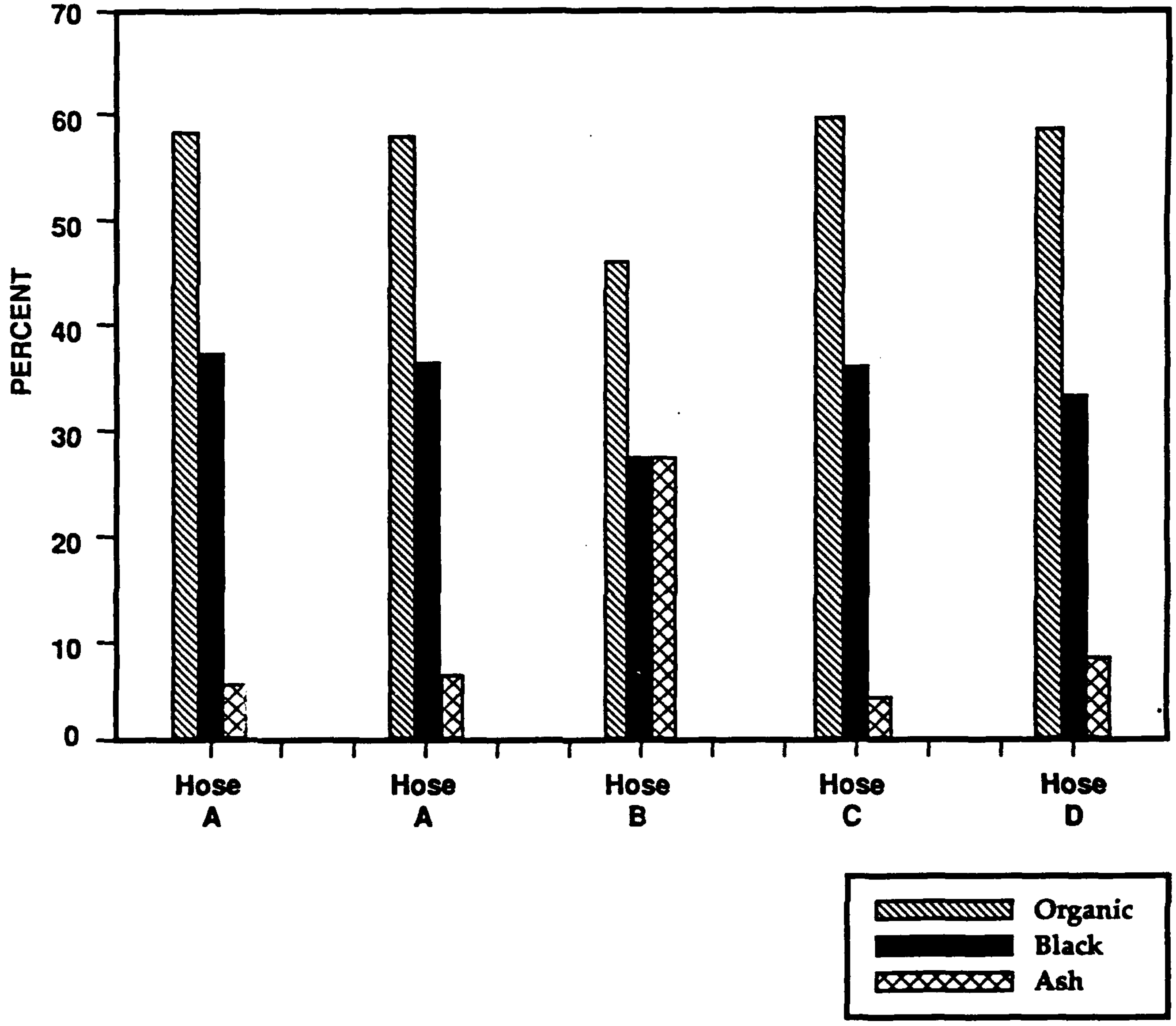

Figure 1-14 - Compositional Analysis of the Inner Tube of Five Hoses

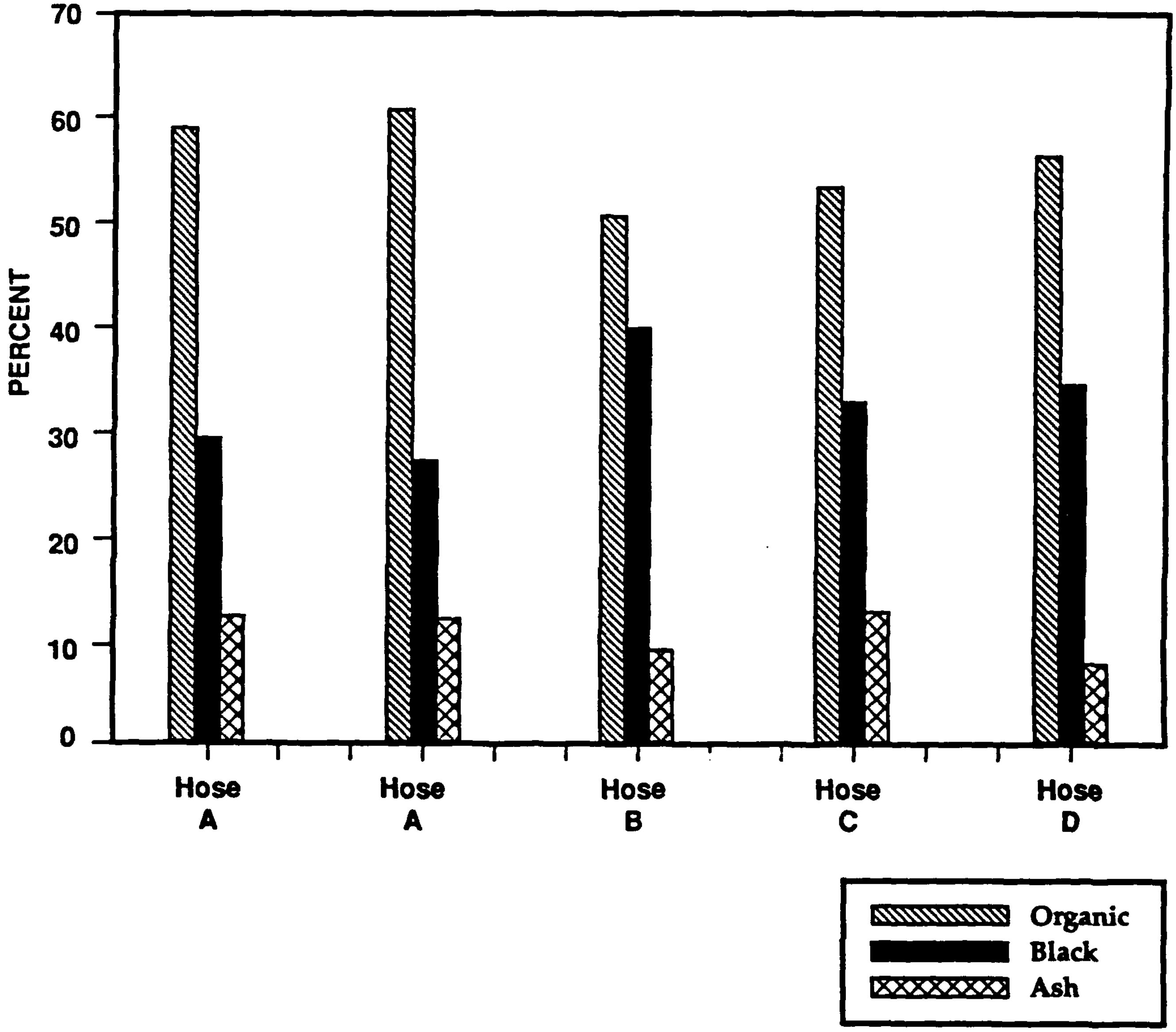

Figure 1-15 - Compositional Analysis of the Outer Jacket of Five Hoses

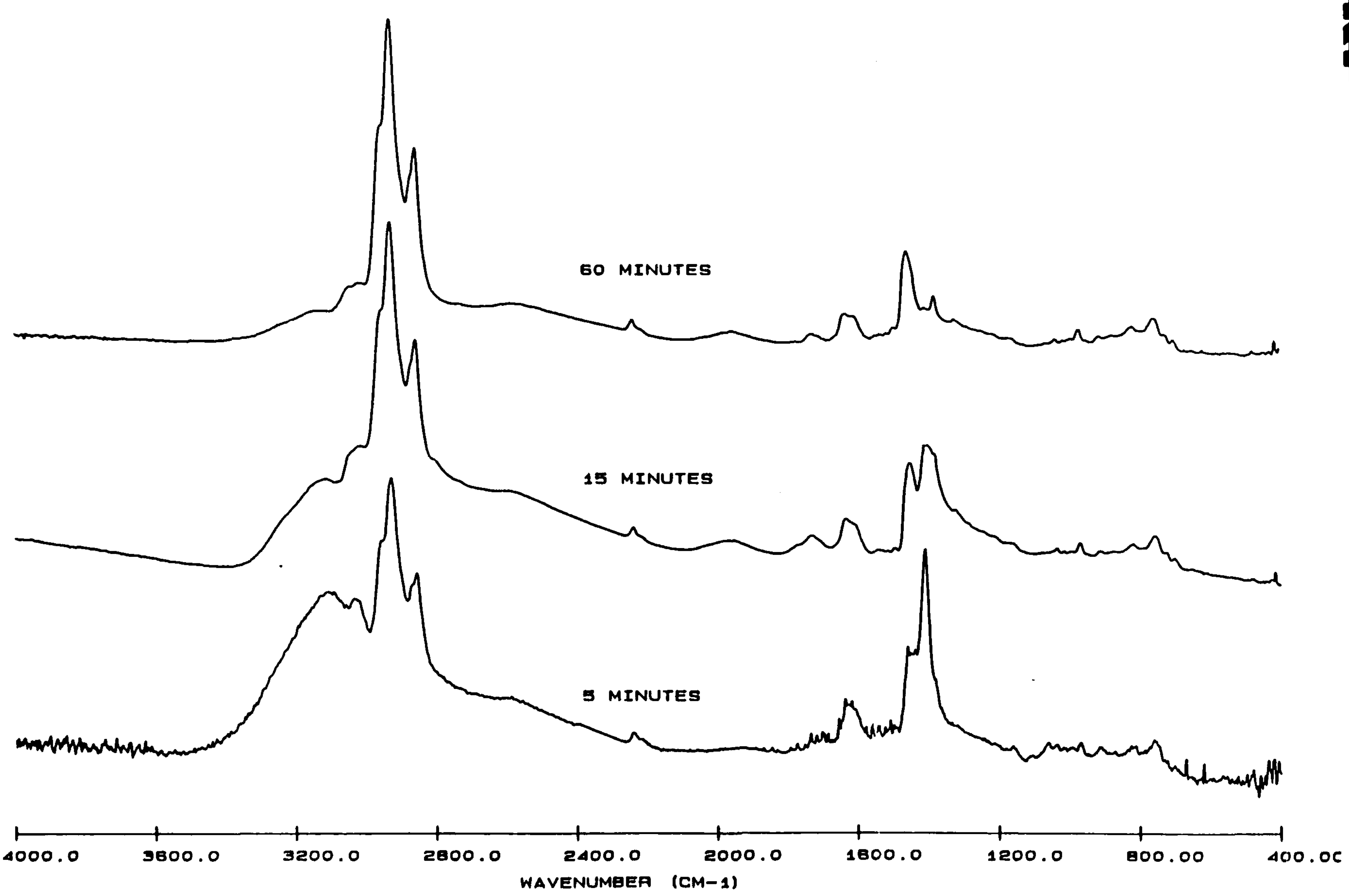

Figure 1-16 - The Effect of Delay Time Between Pyrolysis and FTIR Analysis

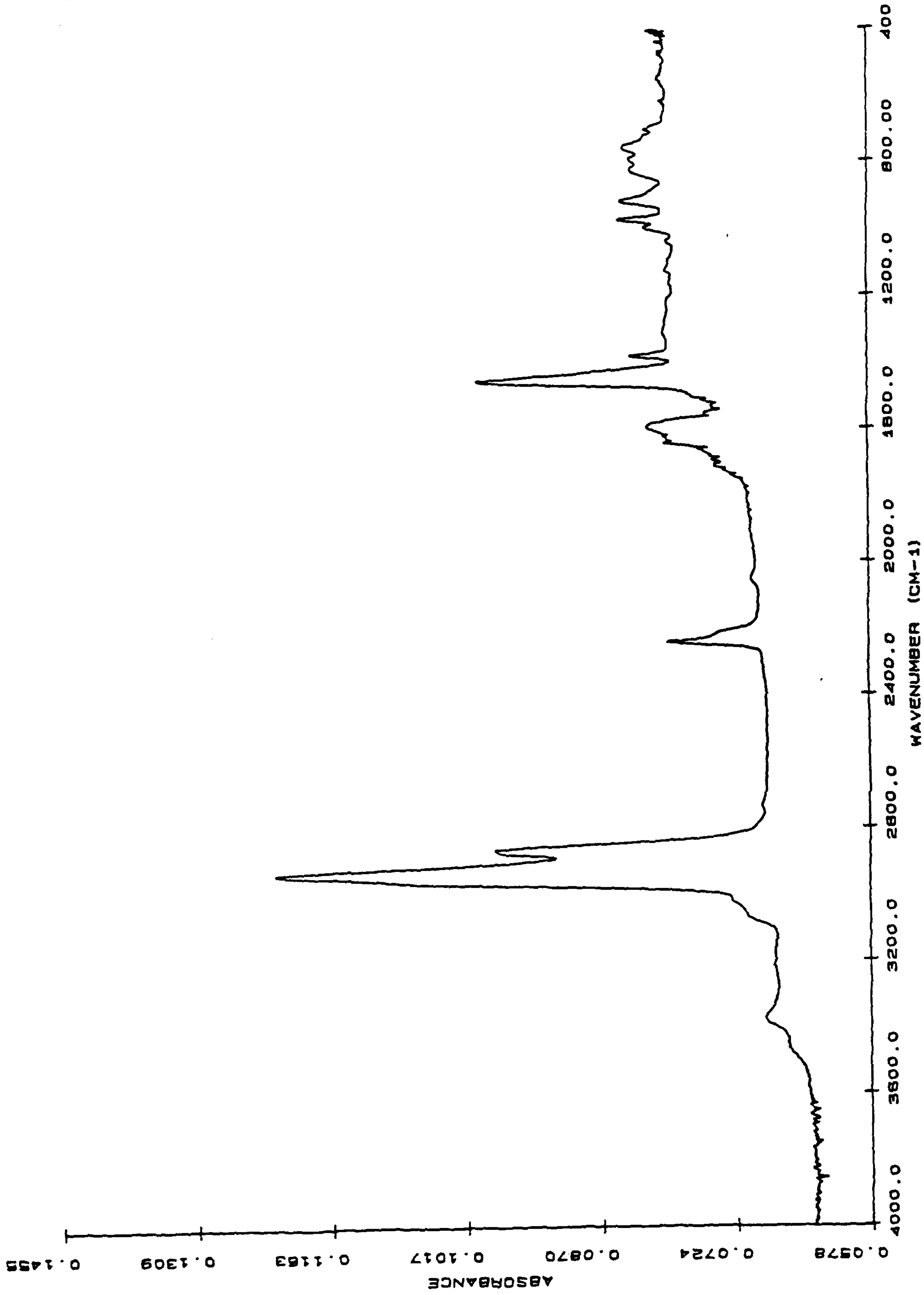

Figure 1-17 - FTIR Spectrum of the Inner Tube Rubber from the New Hose A

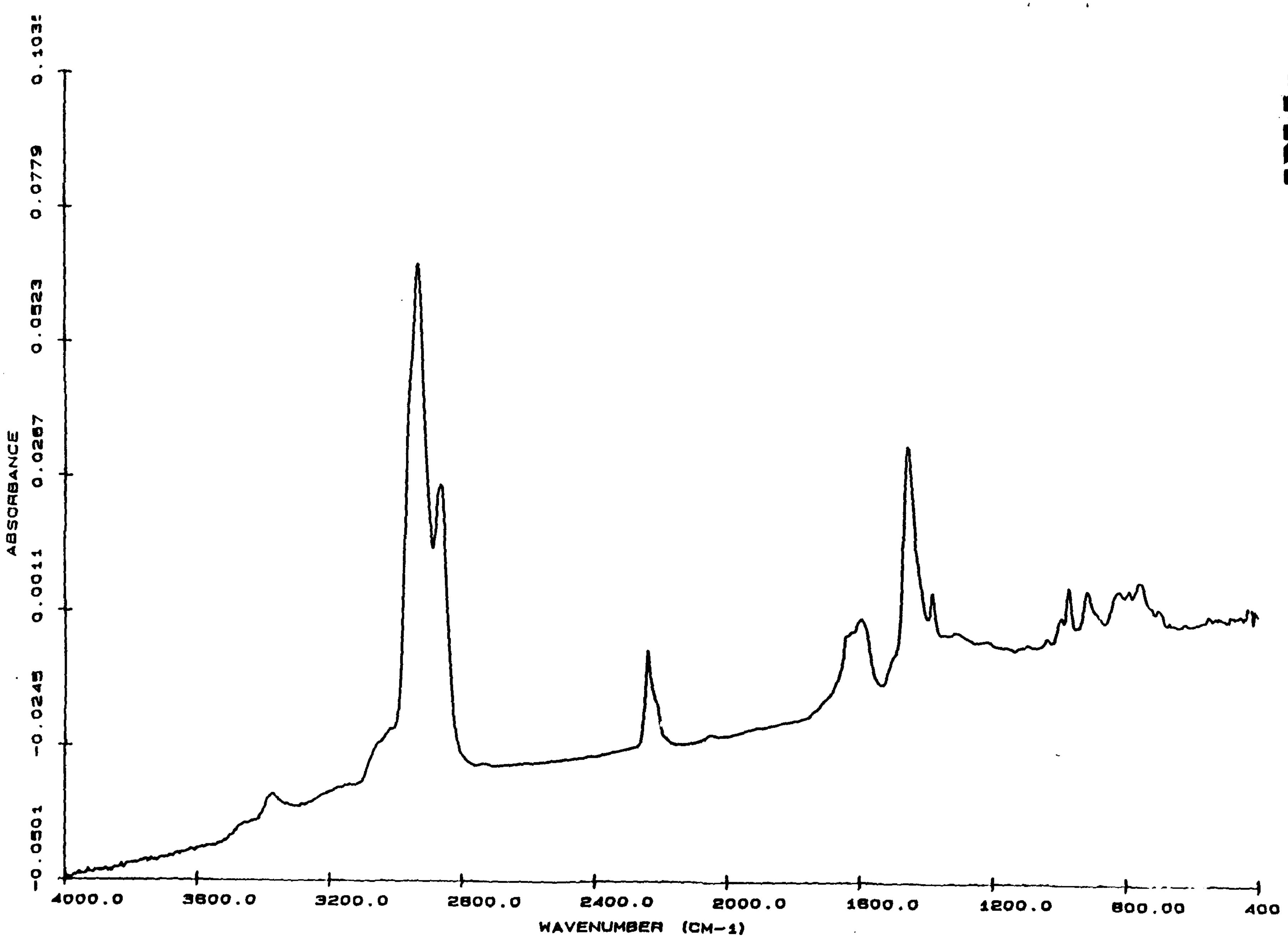

Figure 1-18 - FTIR Spectrum of the Inner Tube Rubber from the Old Hose A

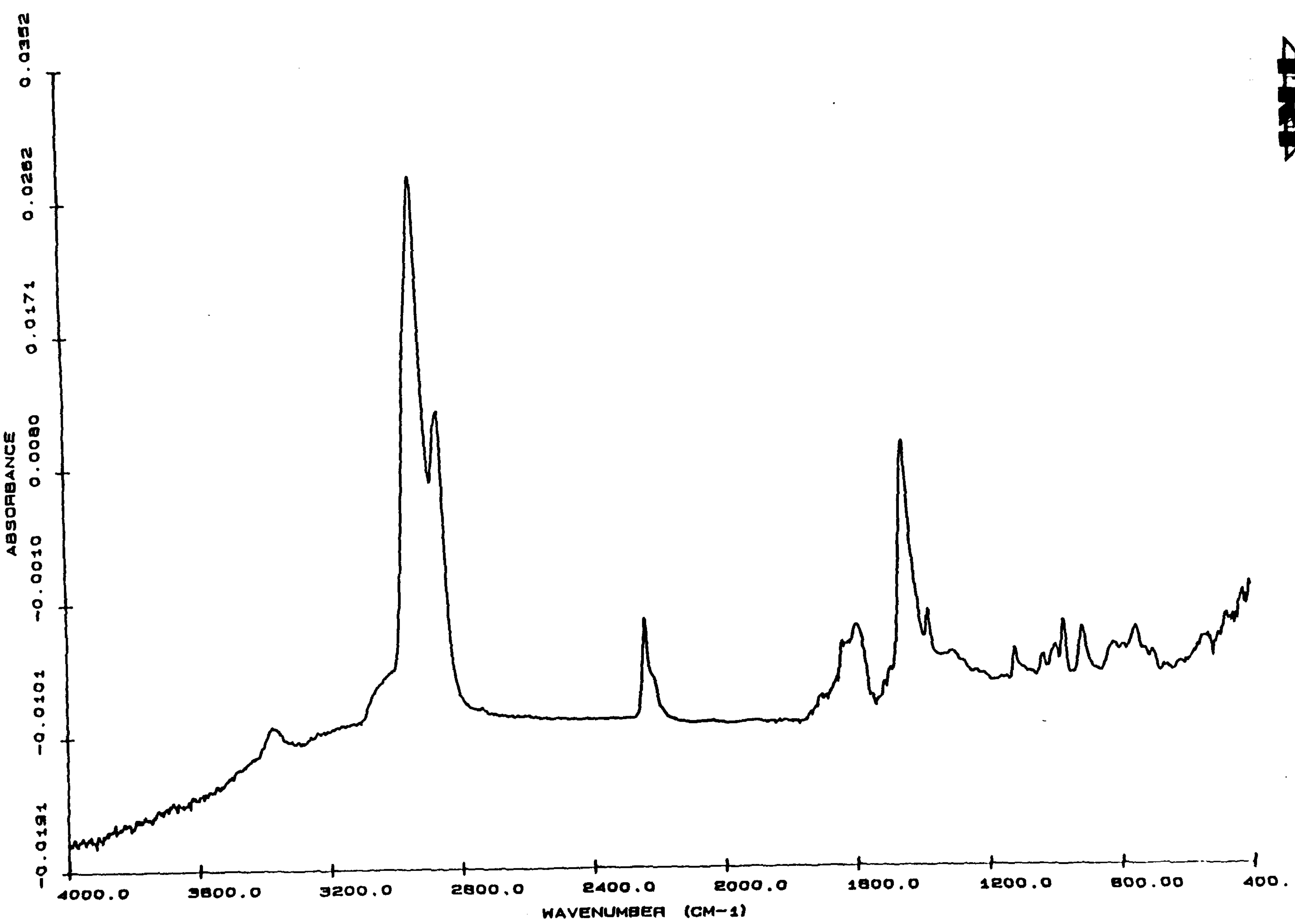

Figure 1-19 - FTIR Spectrum of the Inner Tube Rubber from Hose B

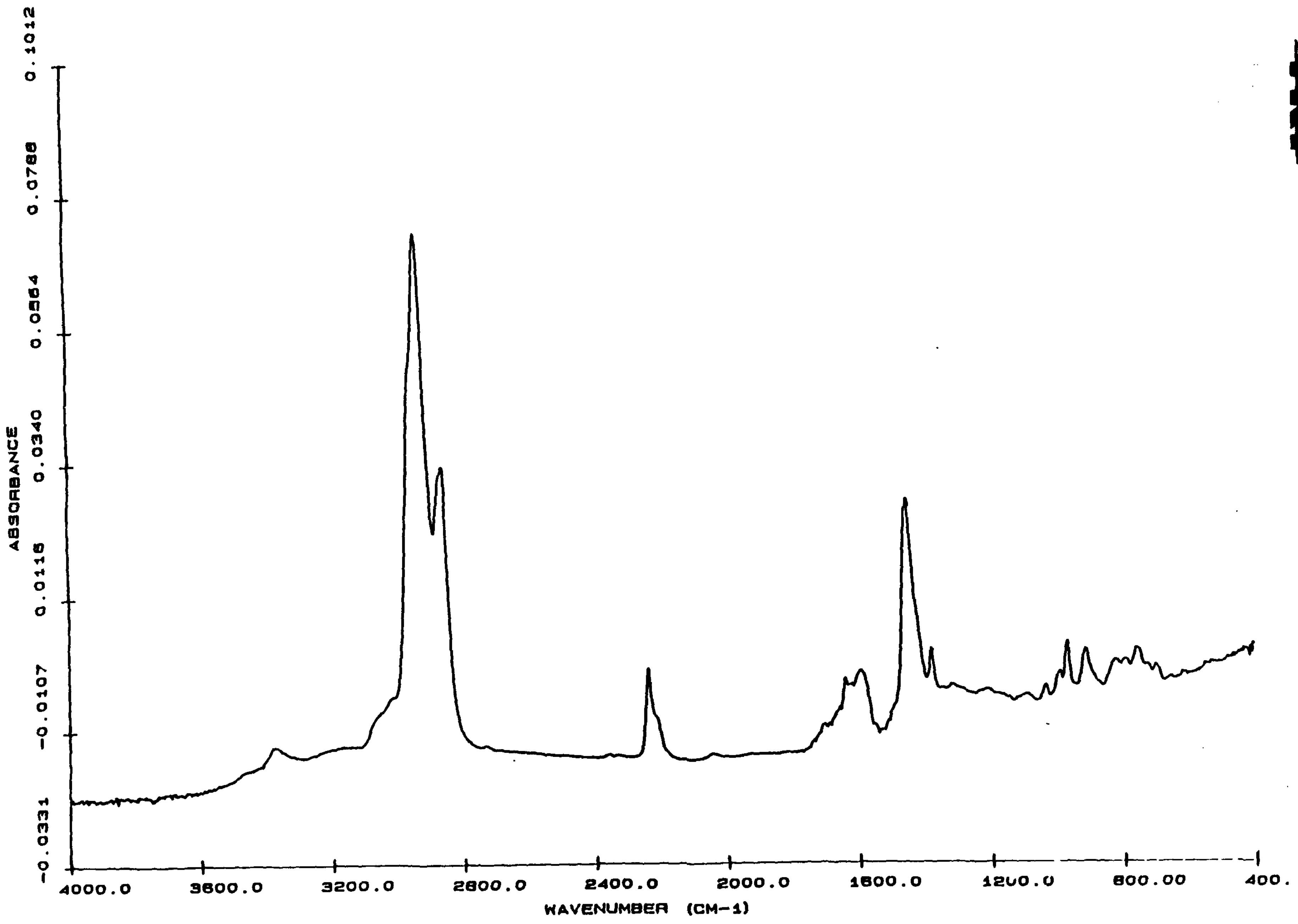

Figure 1-20 - FTIR Spectrum of the Inner Tube Rubber from Hose C

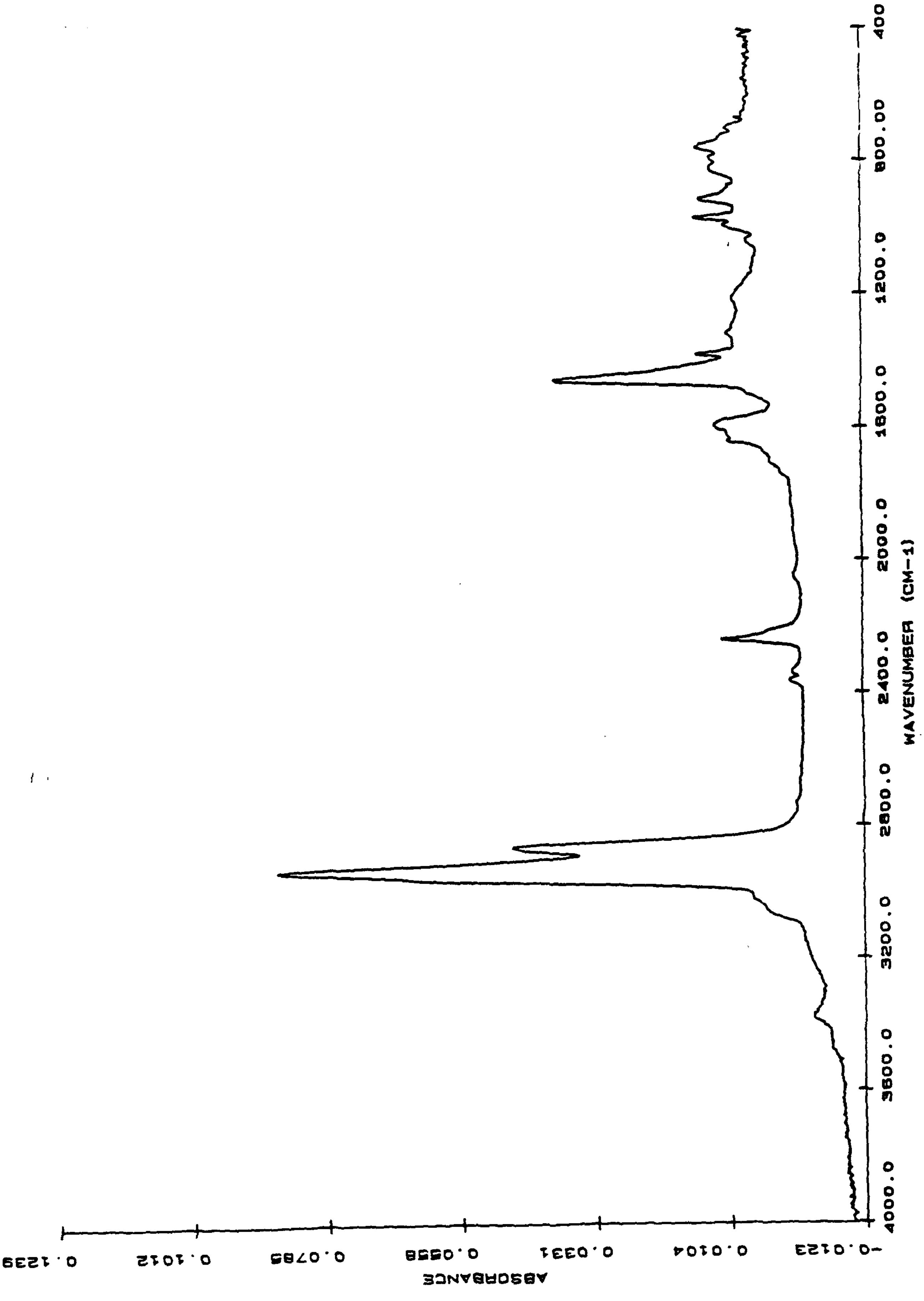

Figure 1-21 - FTIR Spectrum of the Inner Tube Rubber from Hose D

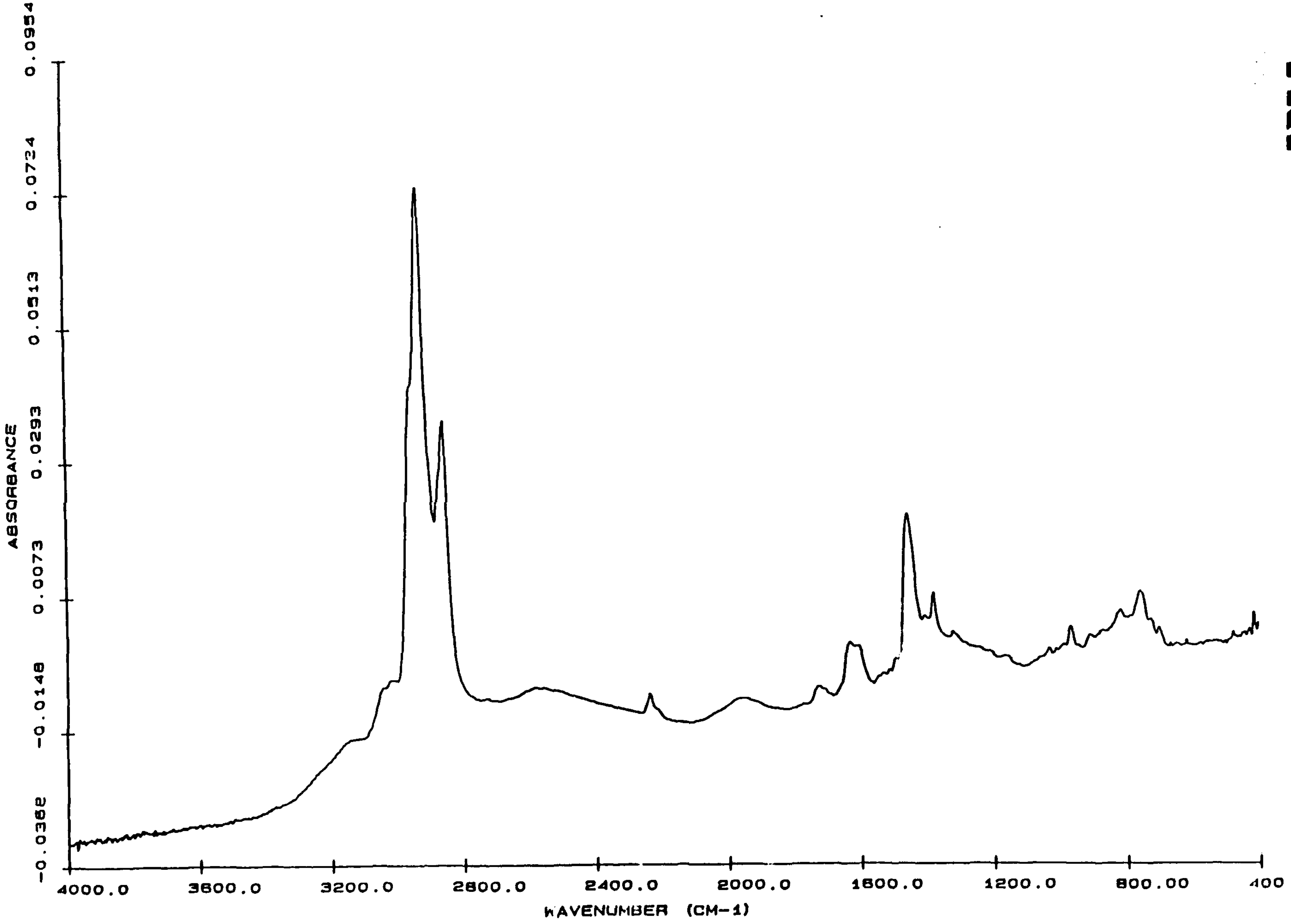

Figure 1-22 - FTIR Spectrum of the Outer Jacket Rubber from the New Hose A

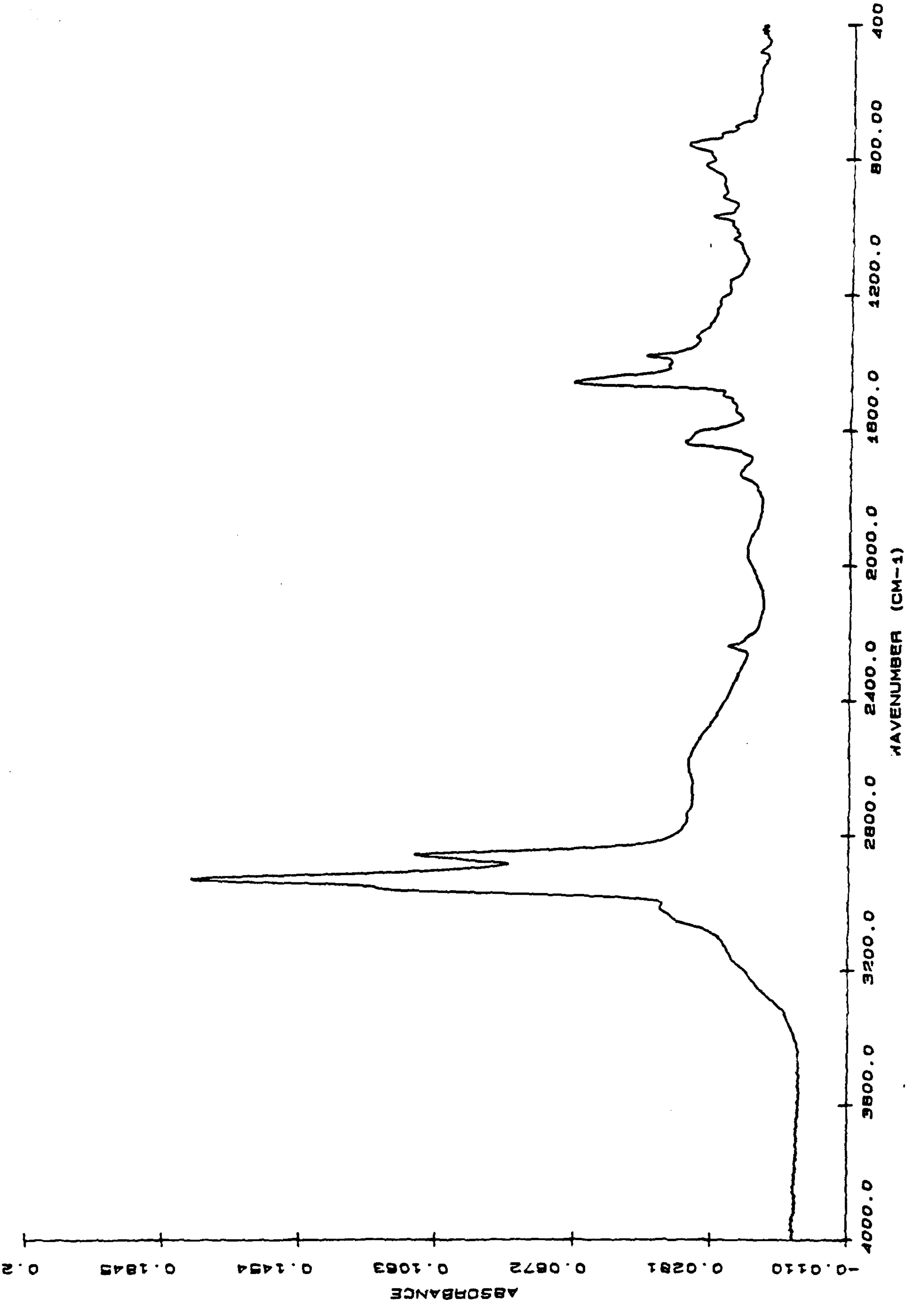

Figure 1-23 - FTIR Spectrum of the Outer Jacket Rubber from the Old Hose A

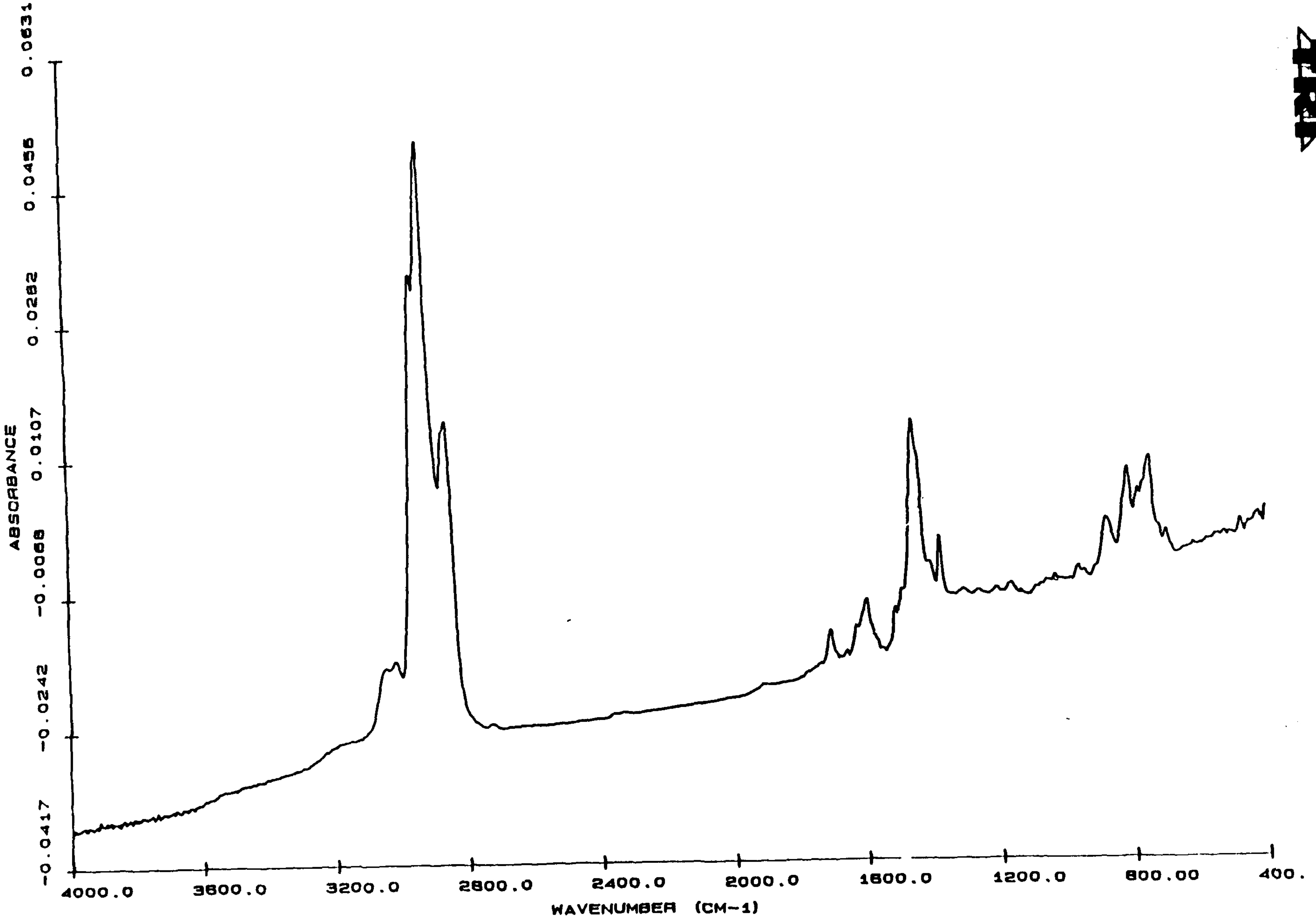

Figure 1-24 - FTIR Spectrum of the Outer Jacket Rubber from Hose B

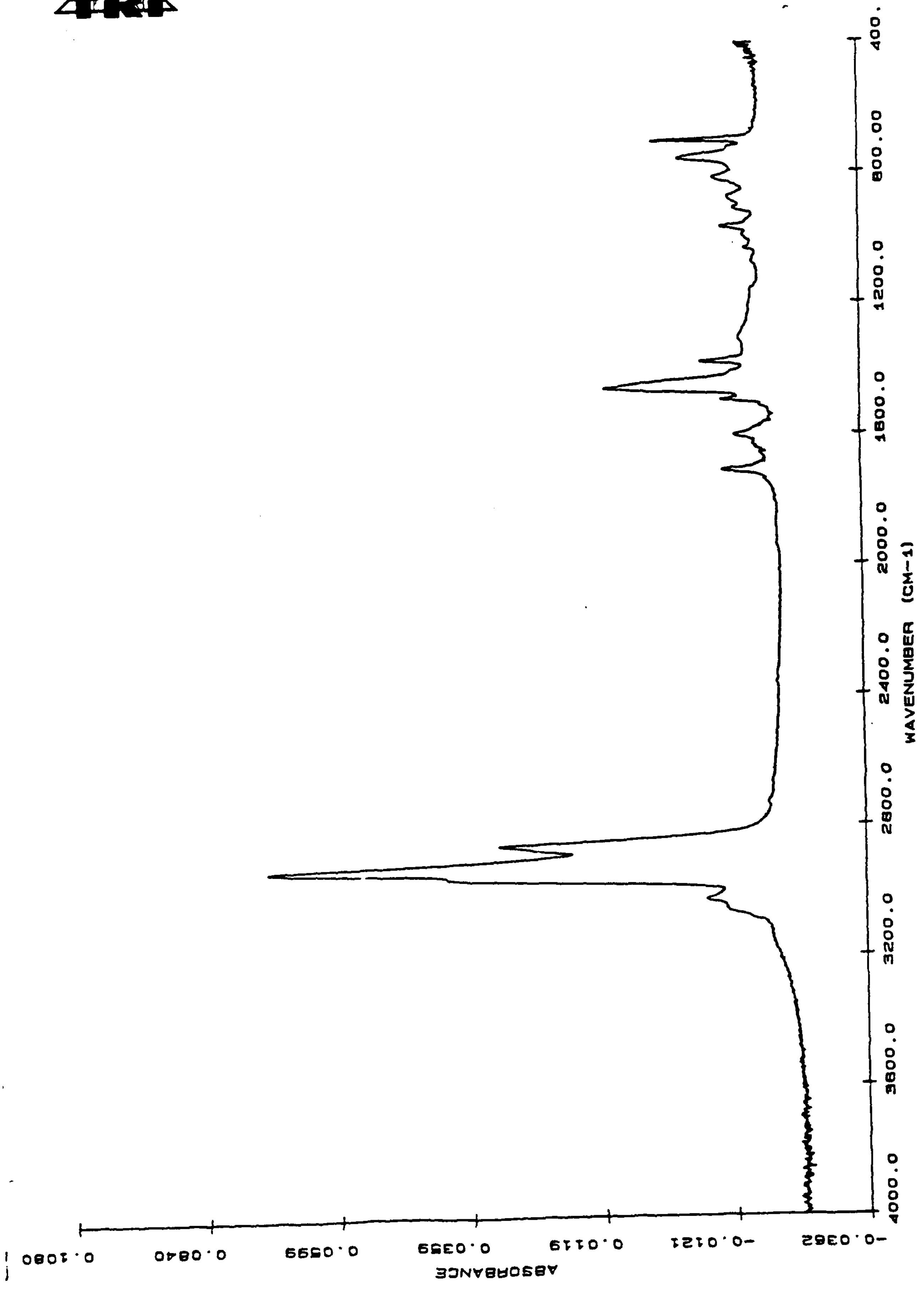

Figure 1-25 - FTIR Spectrum of the Outer Jacket Rubber from Hose C

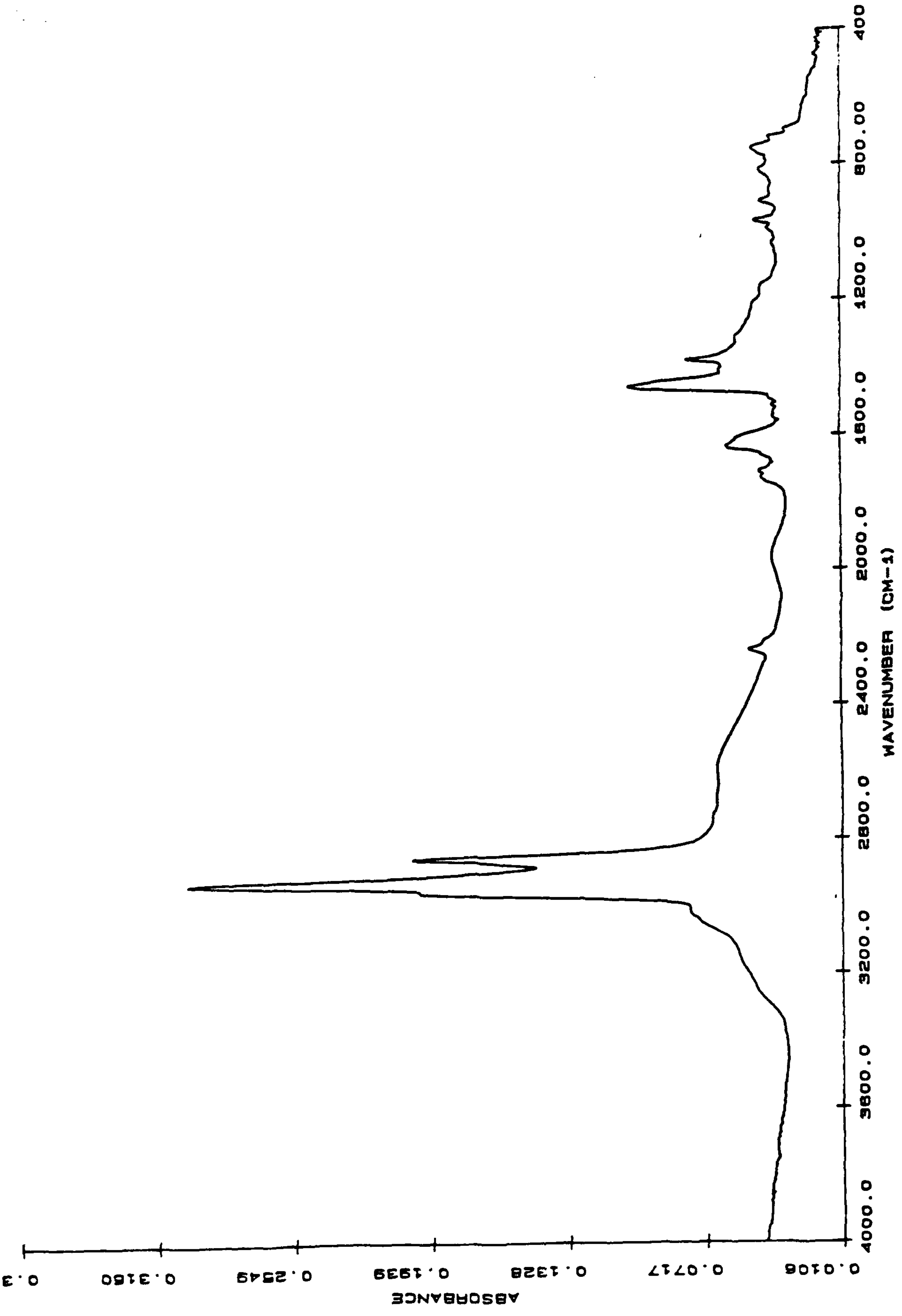

Figure 1-26 - FTIR Spectrum of the Outer Jacket Rubber from Hose D

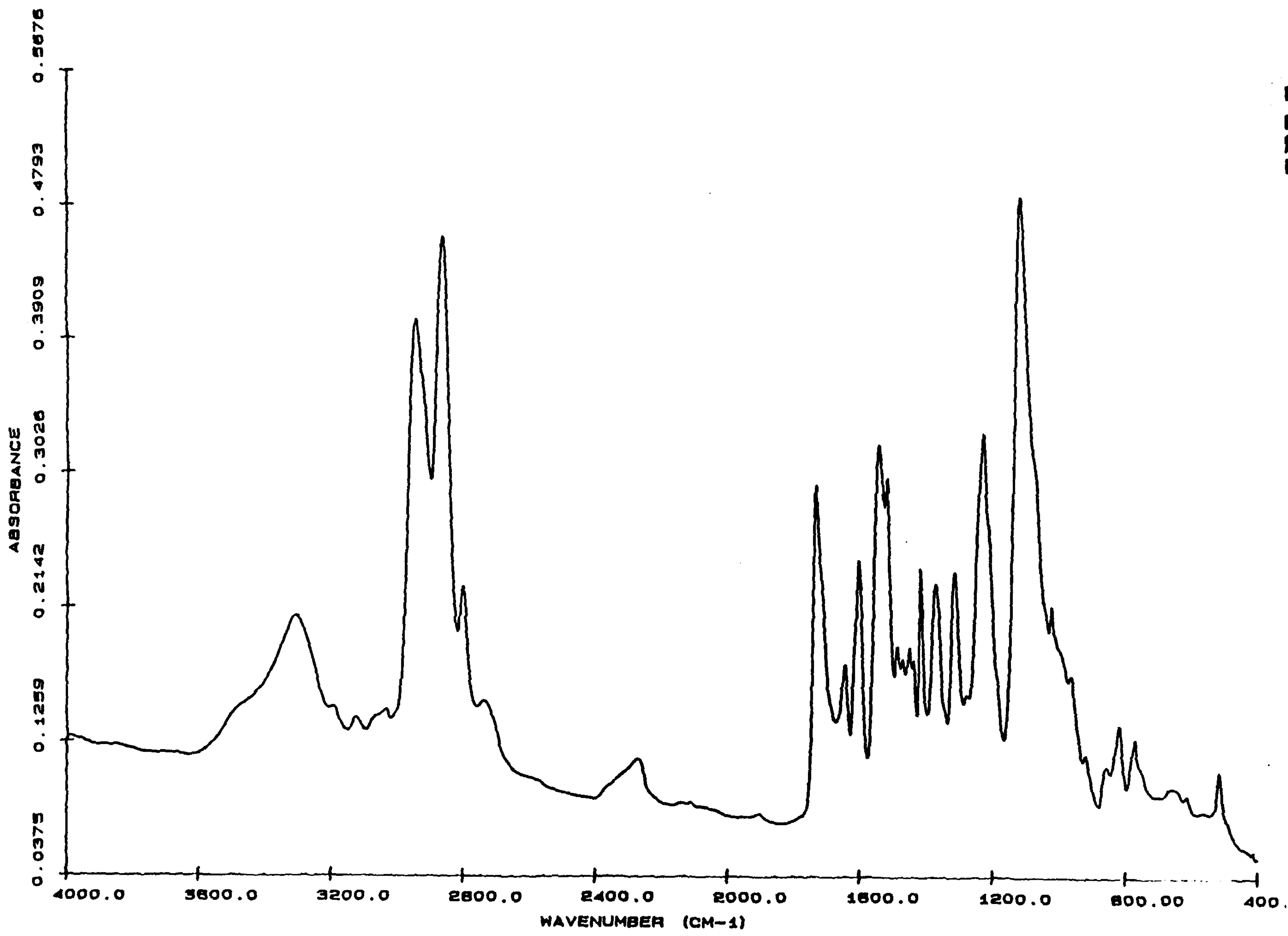

Figure 1-27 - FTIR Spectrum of the Inner Elastomer from Hose E

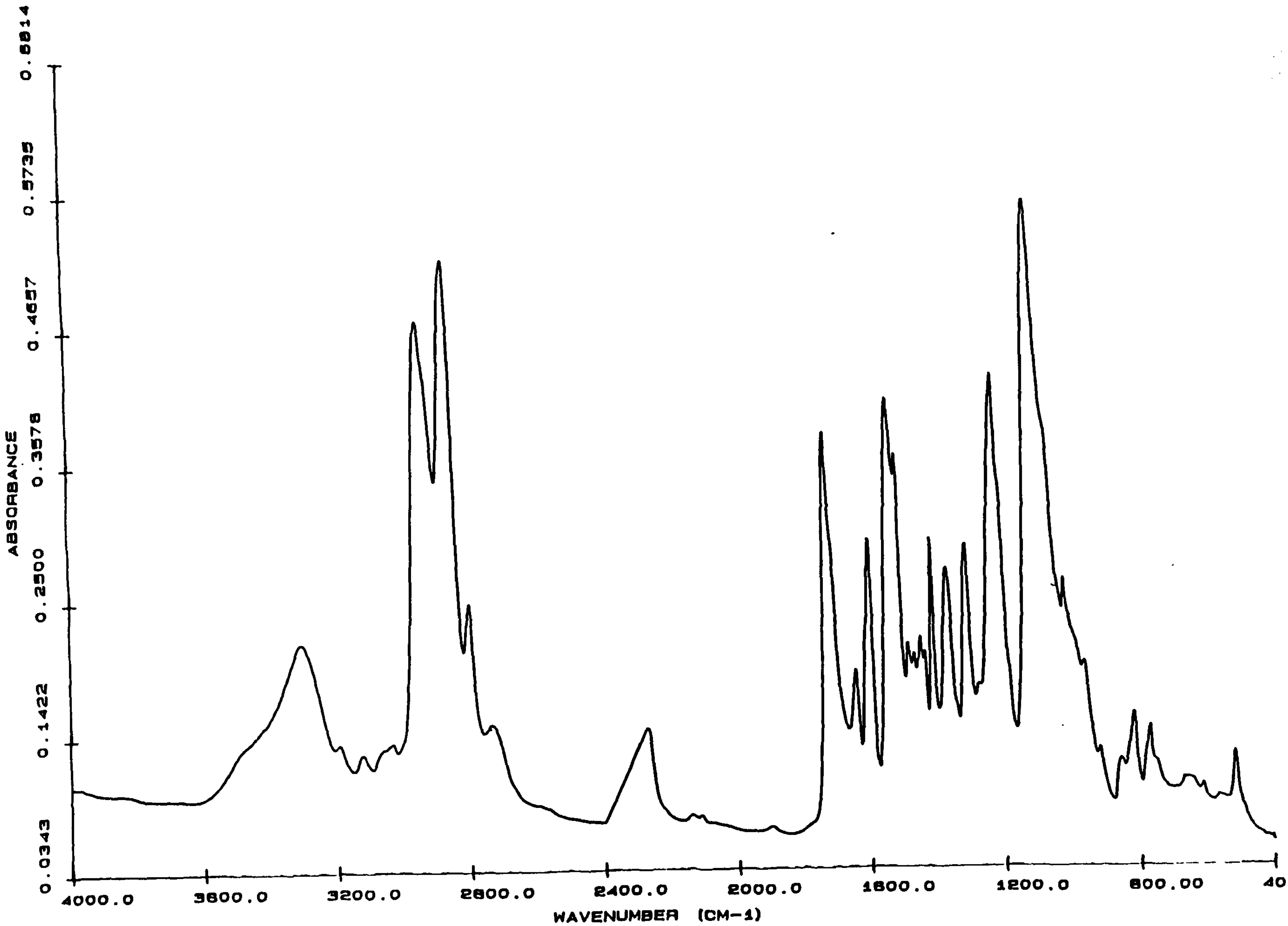

Figure 1-28 - FTIR Spectrum of the Outer Elastomer from Hose E

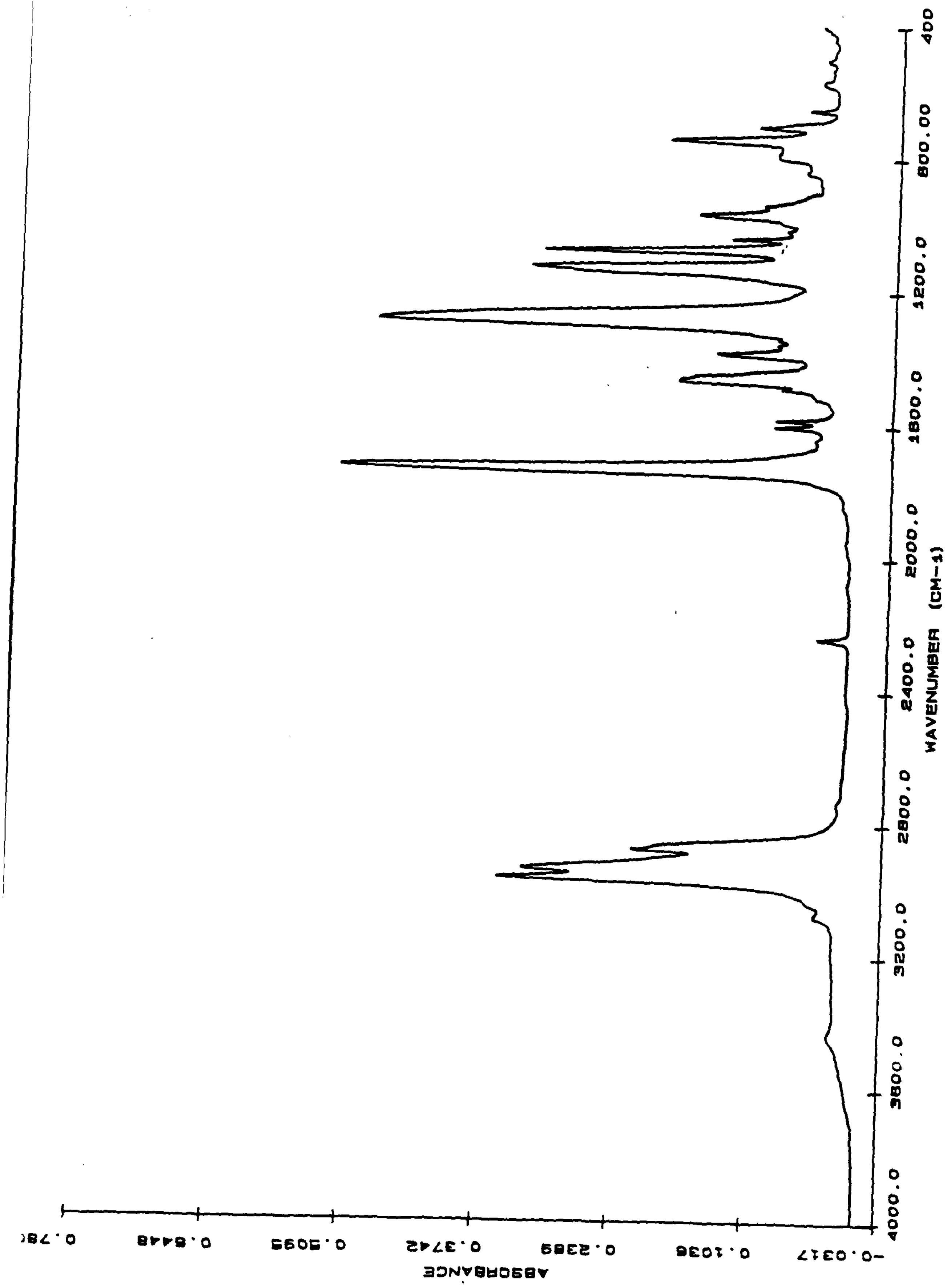

Figure 1-29 - FTIR Spectrum of the Inner Tube Extract from the New Hose A

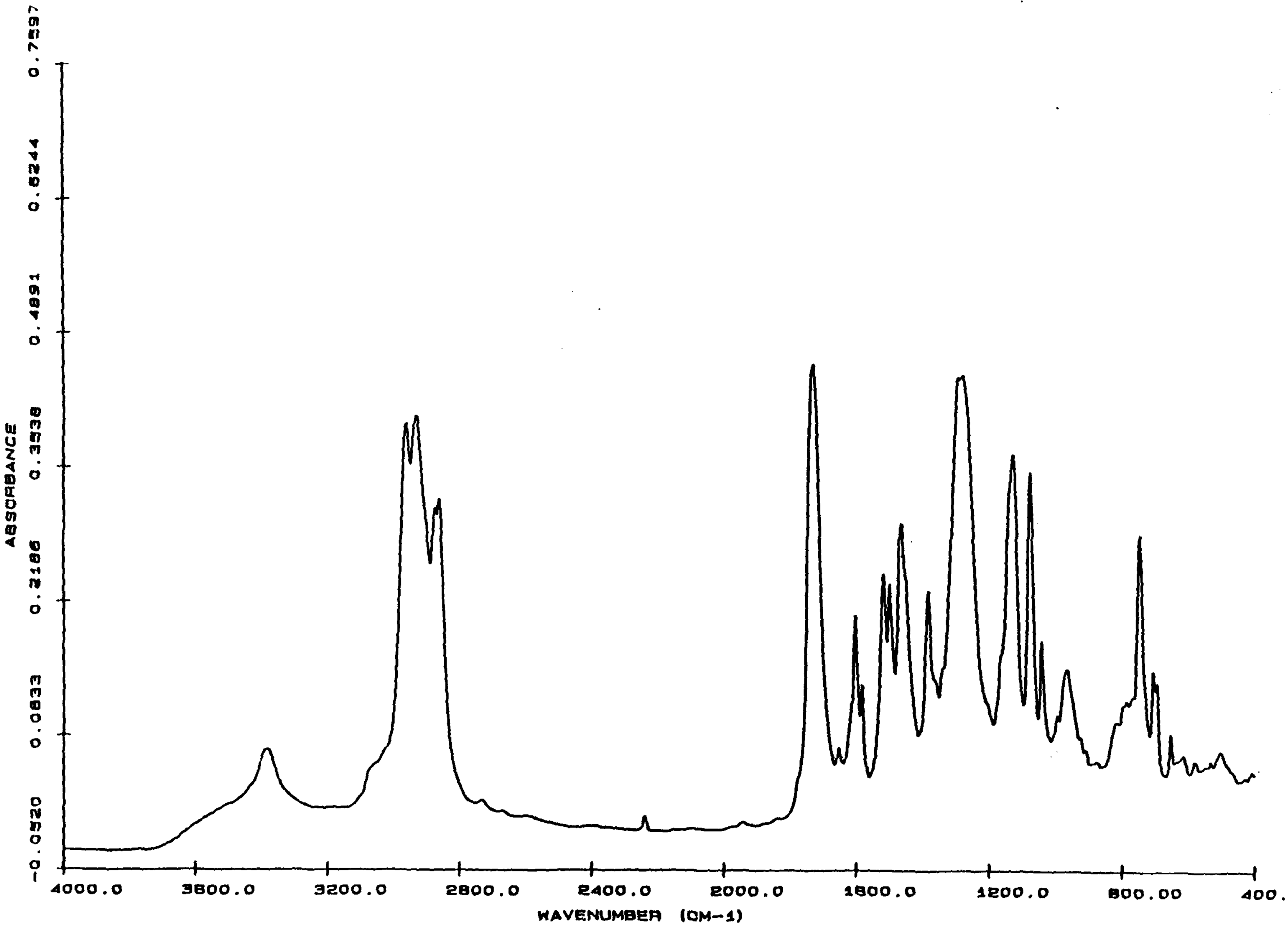

Figure 1-30 - FTIR Spectrum of the Outer Jacket Extract from the New Hose A

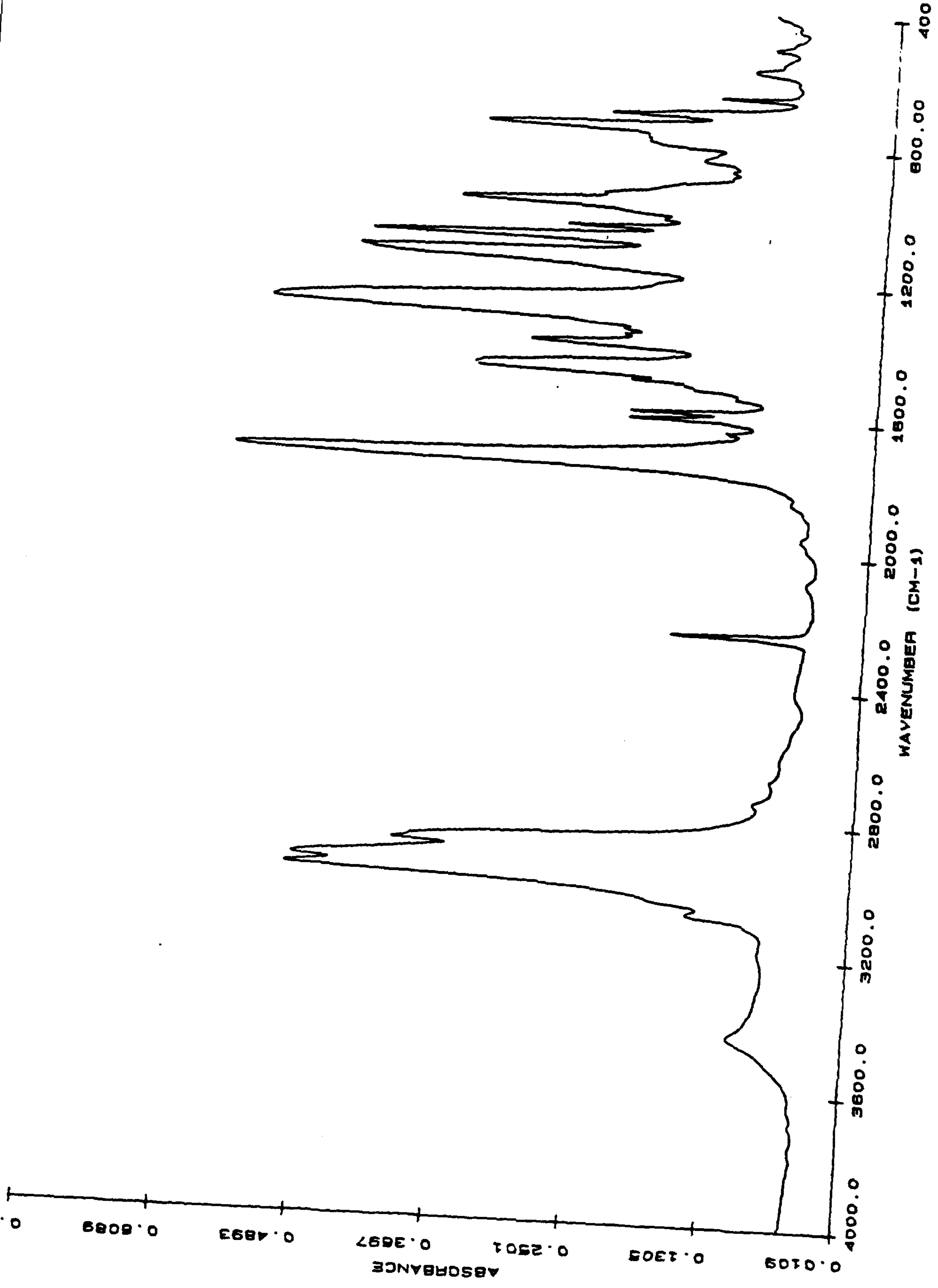

Figure 1-31 - FTIR Spectrum of the Inner Tube Extract from the Old Hose A

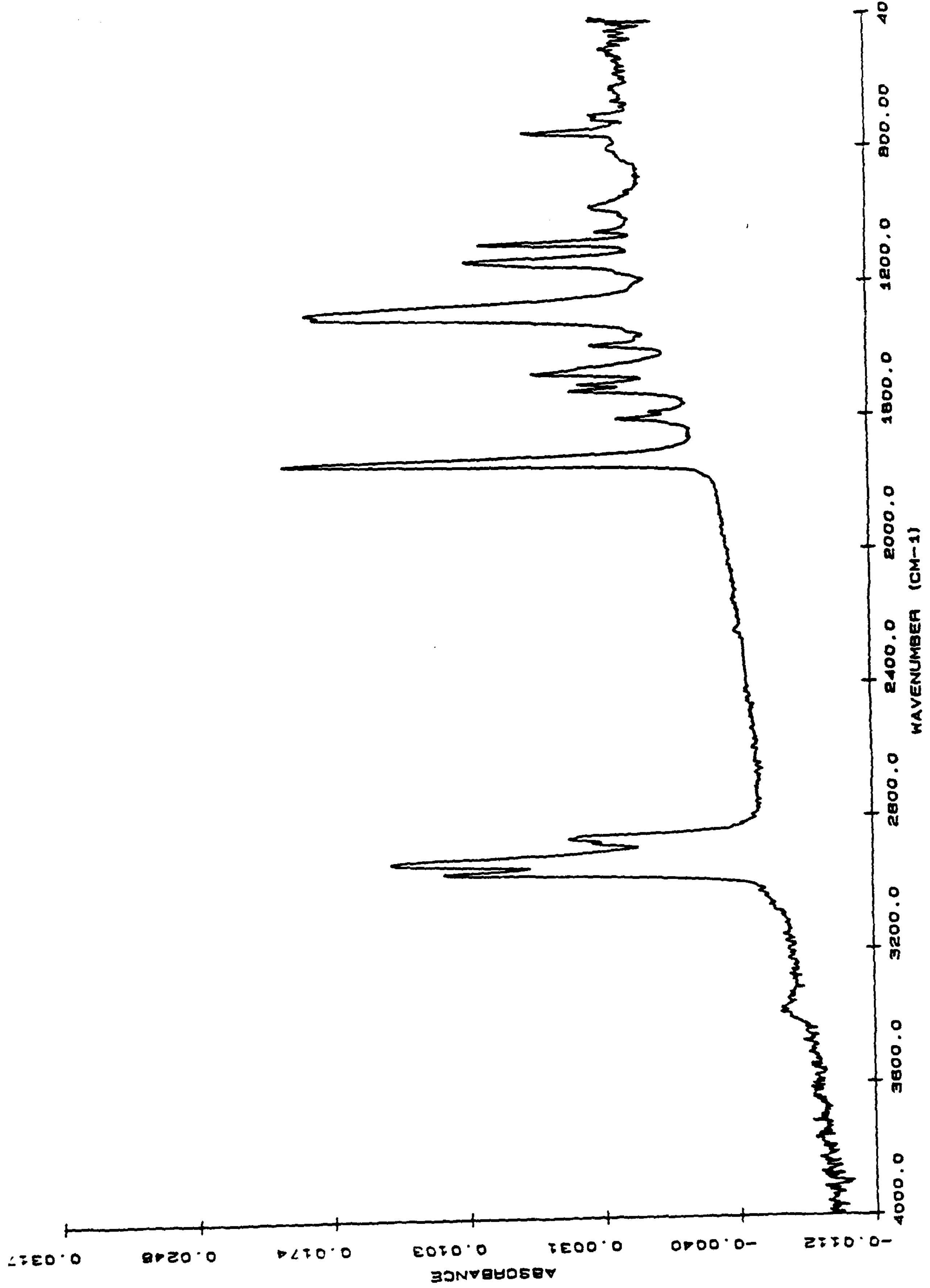

Figure 1-32 - FTIR Spectrum of the Outer Jacket Extract from the Old Hose A

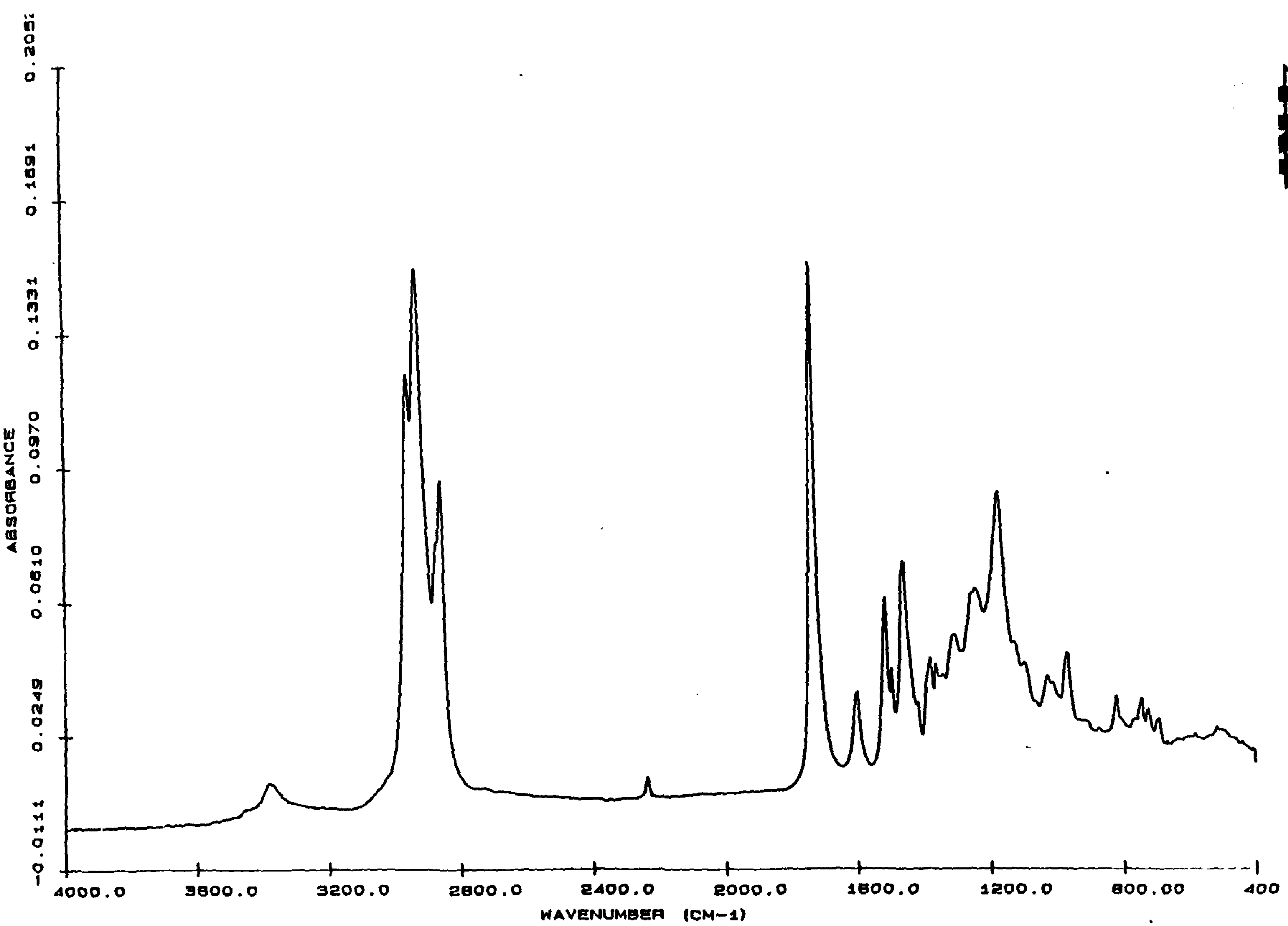

Figure 1-33 - FTIR Spectrum of the Inner Tube Extract from Hose B

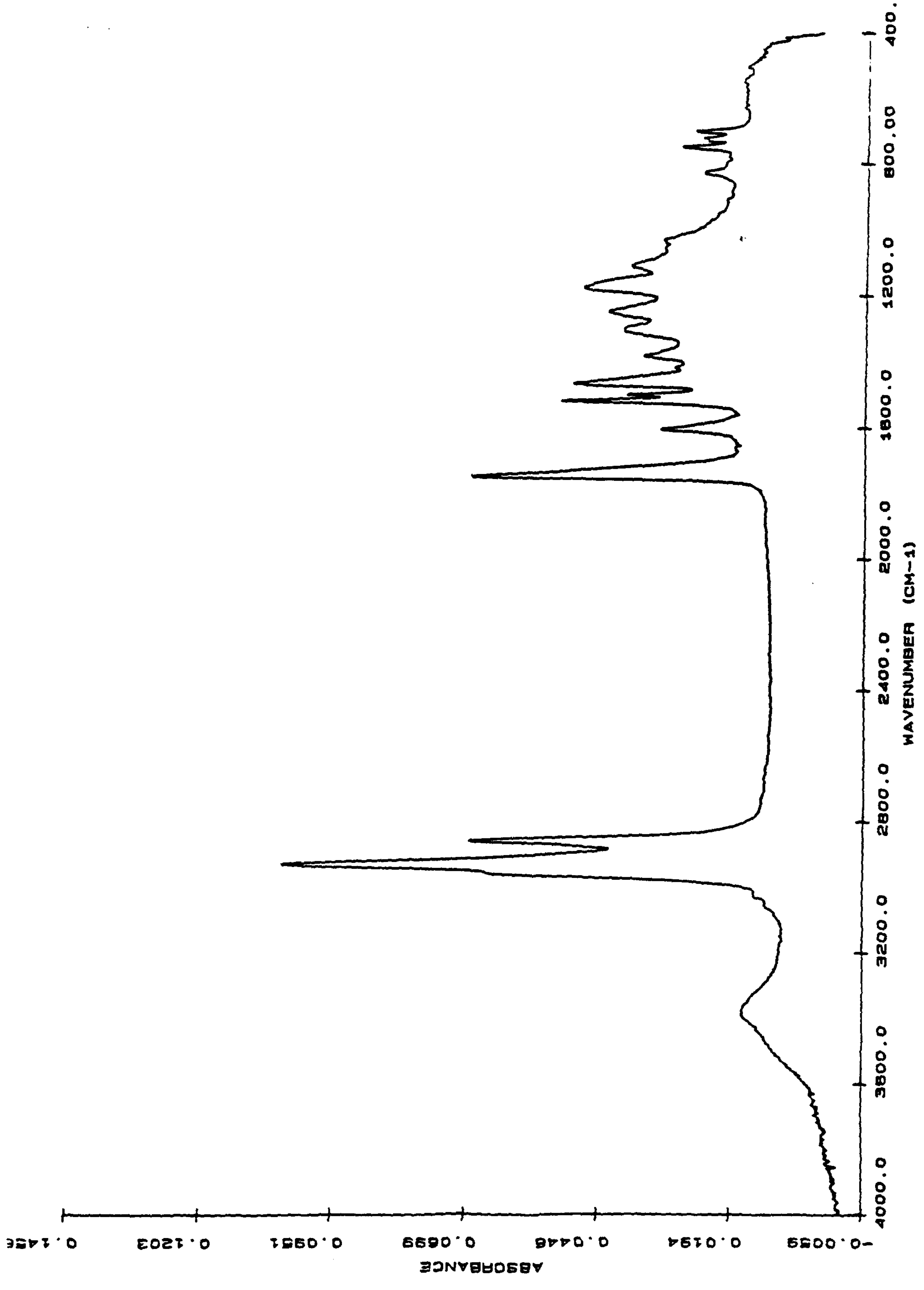

Figure 1-34 - FTIR Spectrum of the Outer Jacket Extract from Hose B

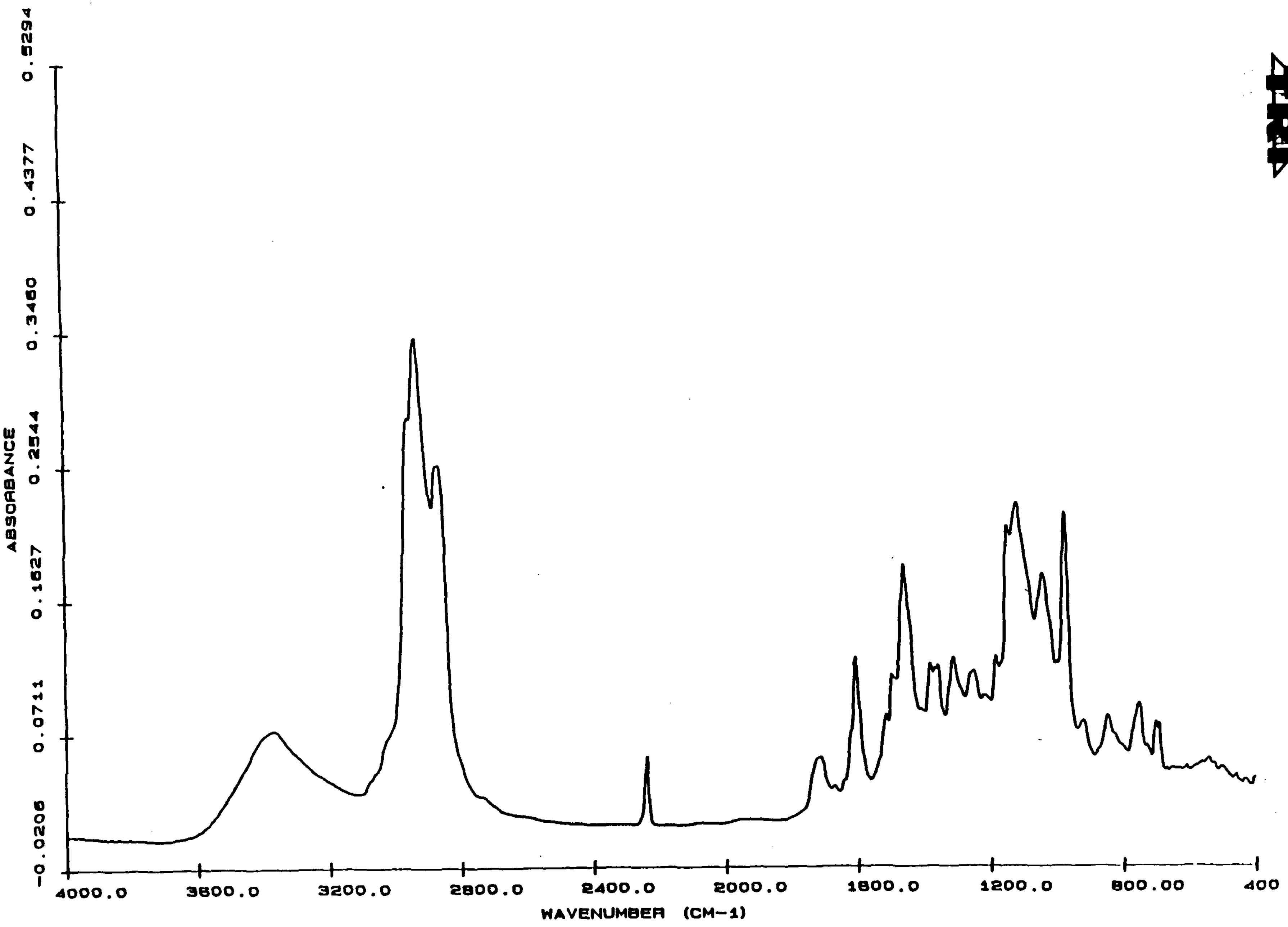

Figure 1-35 - FTIR Spectrum of the Inner Tube Extract from Hose C

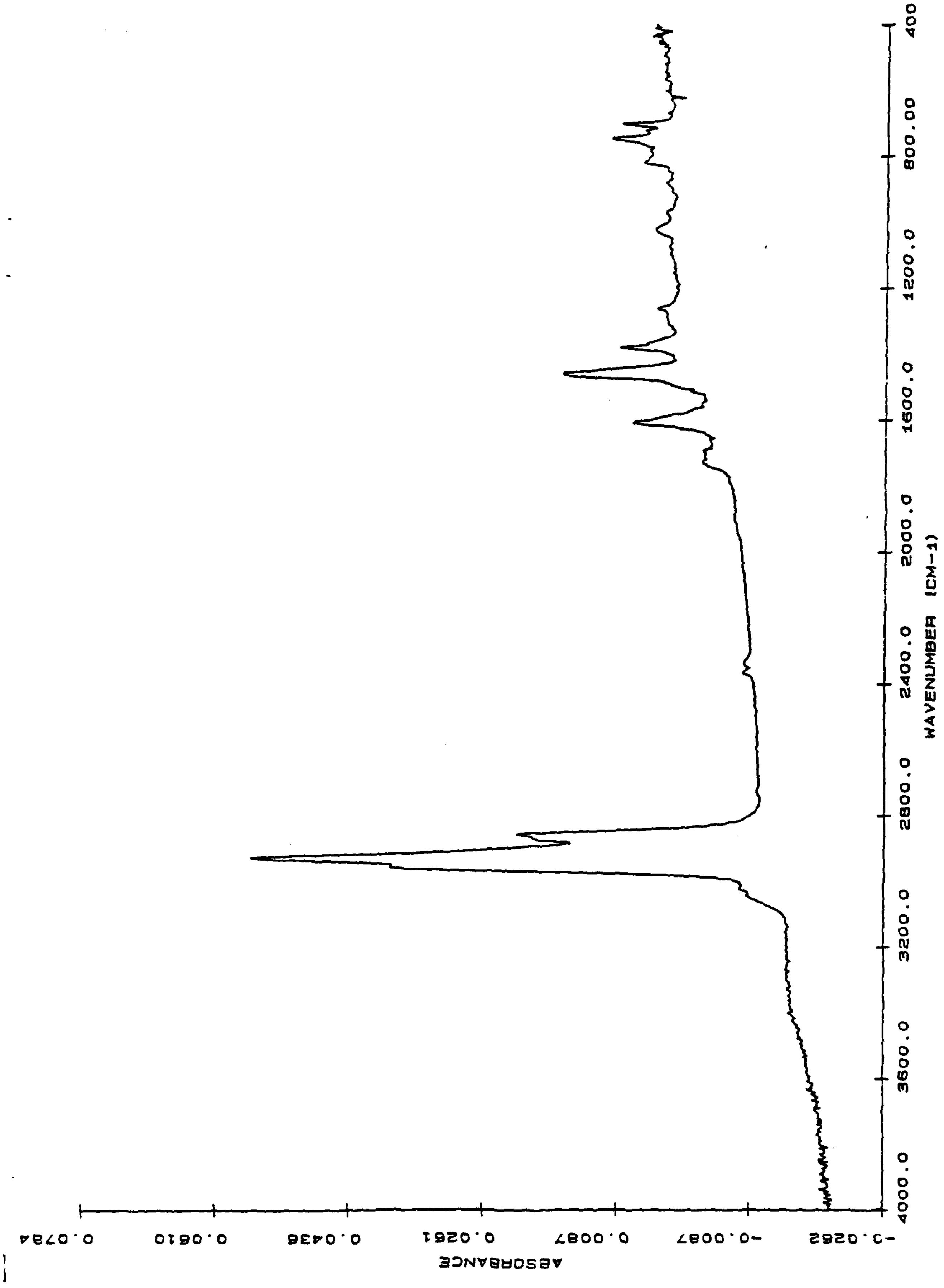

Figure 1-36 - FTIR Spectrum of the Outer Jacket Extract from Hose C

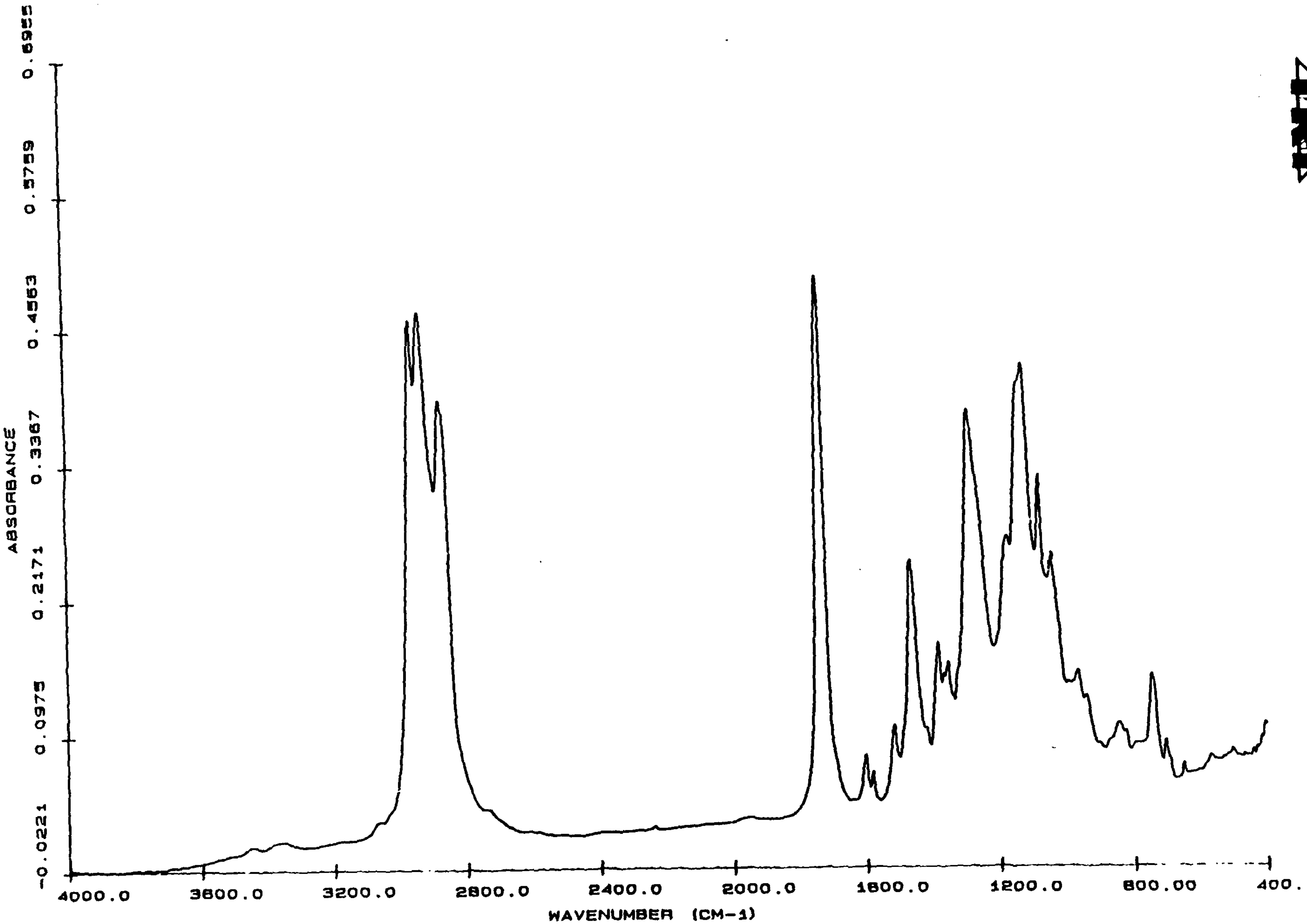

Figure 1-37 - FTIR Spectrum of the Inner Tube Extract from Hose D

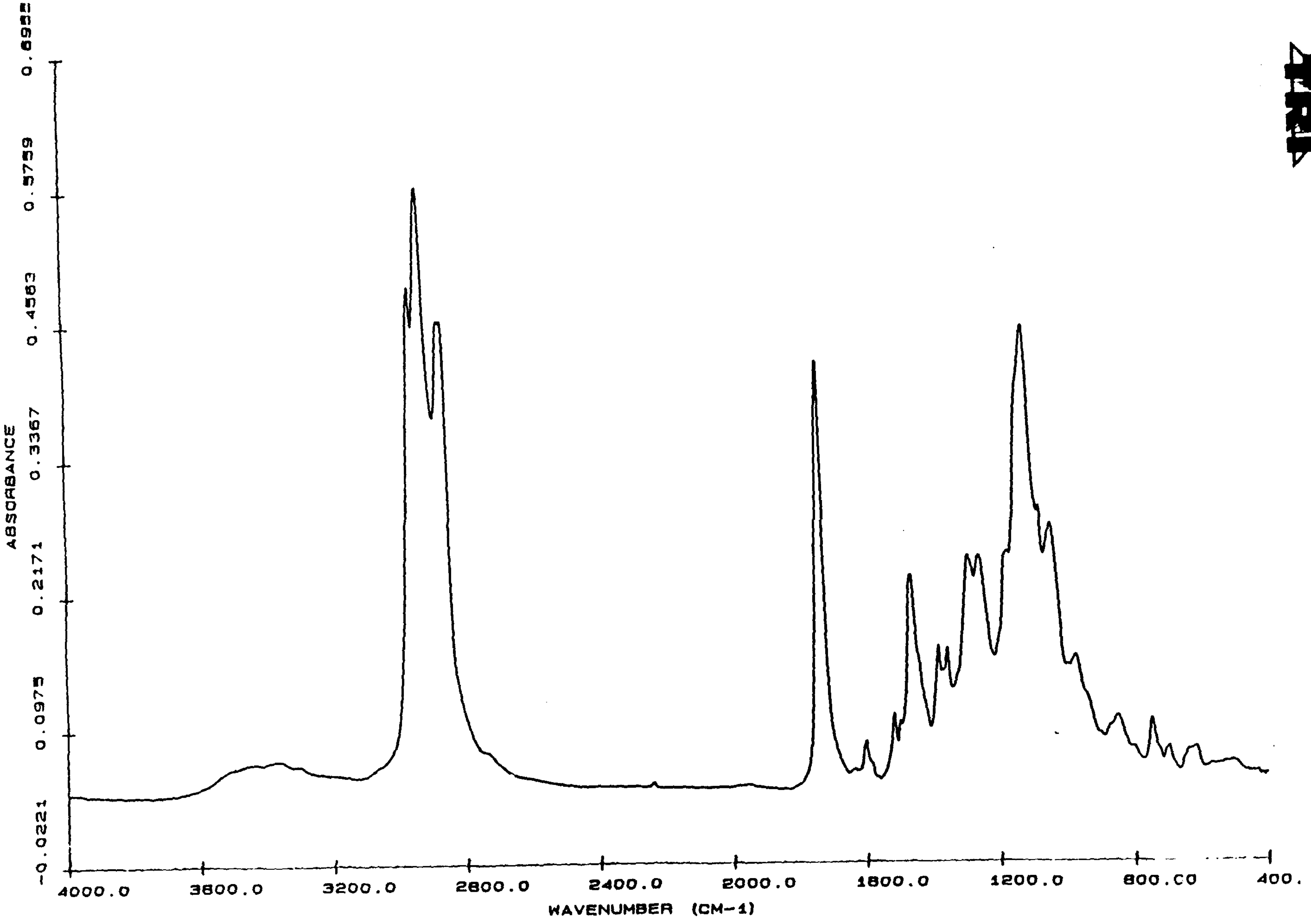

Figure 1-38 - FTIR Spectrum of the Outer Jacket Extract from Hose D

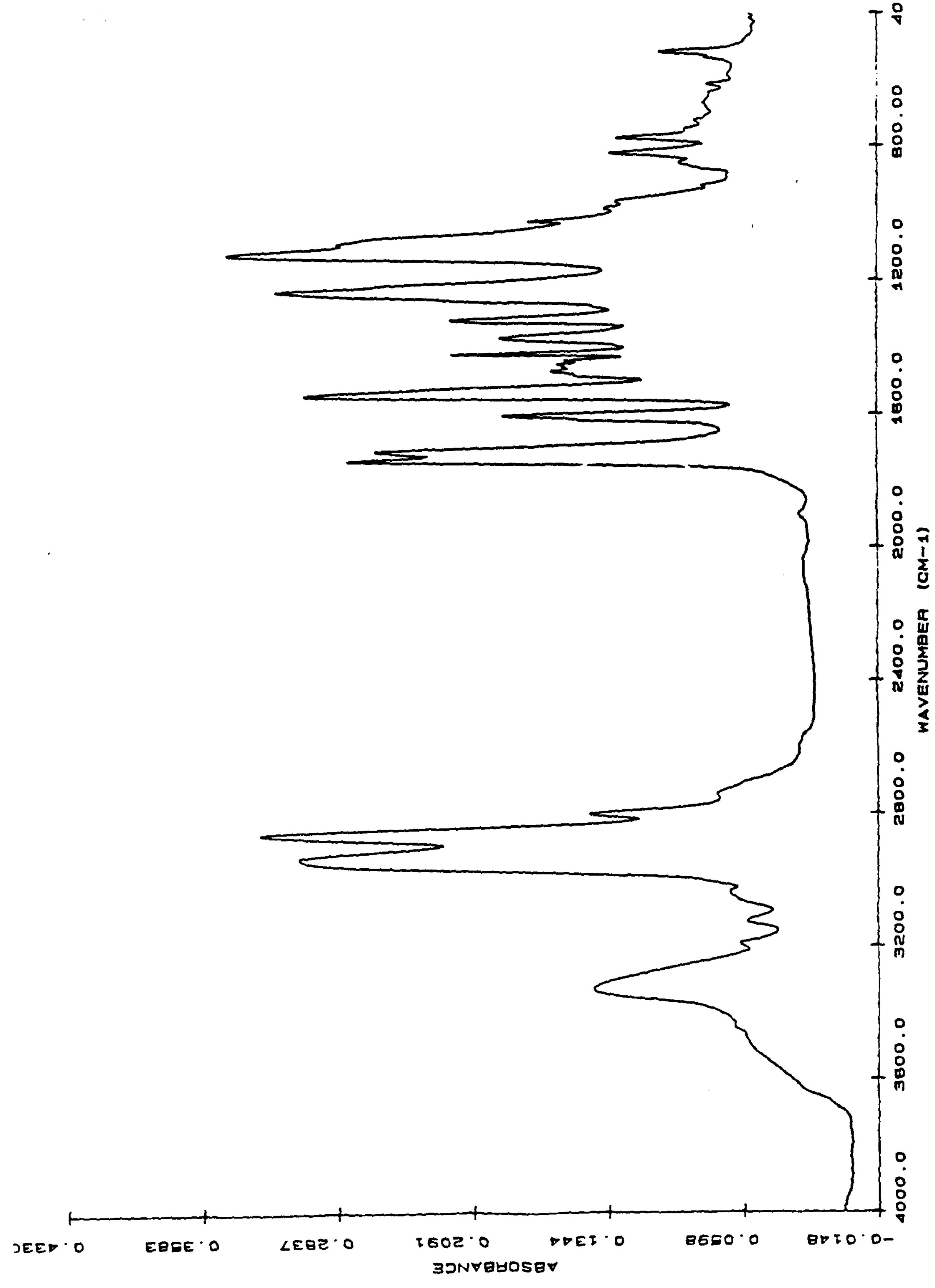

Figure 1-39 - FTIR Spectrum of the Inner Tube Extract from Hose E

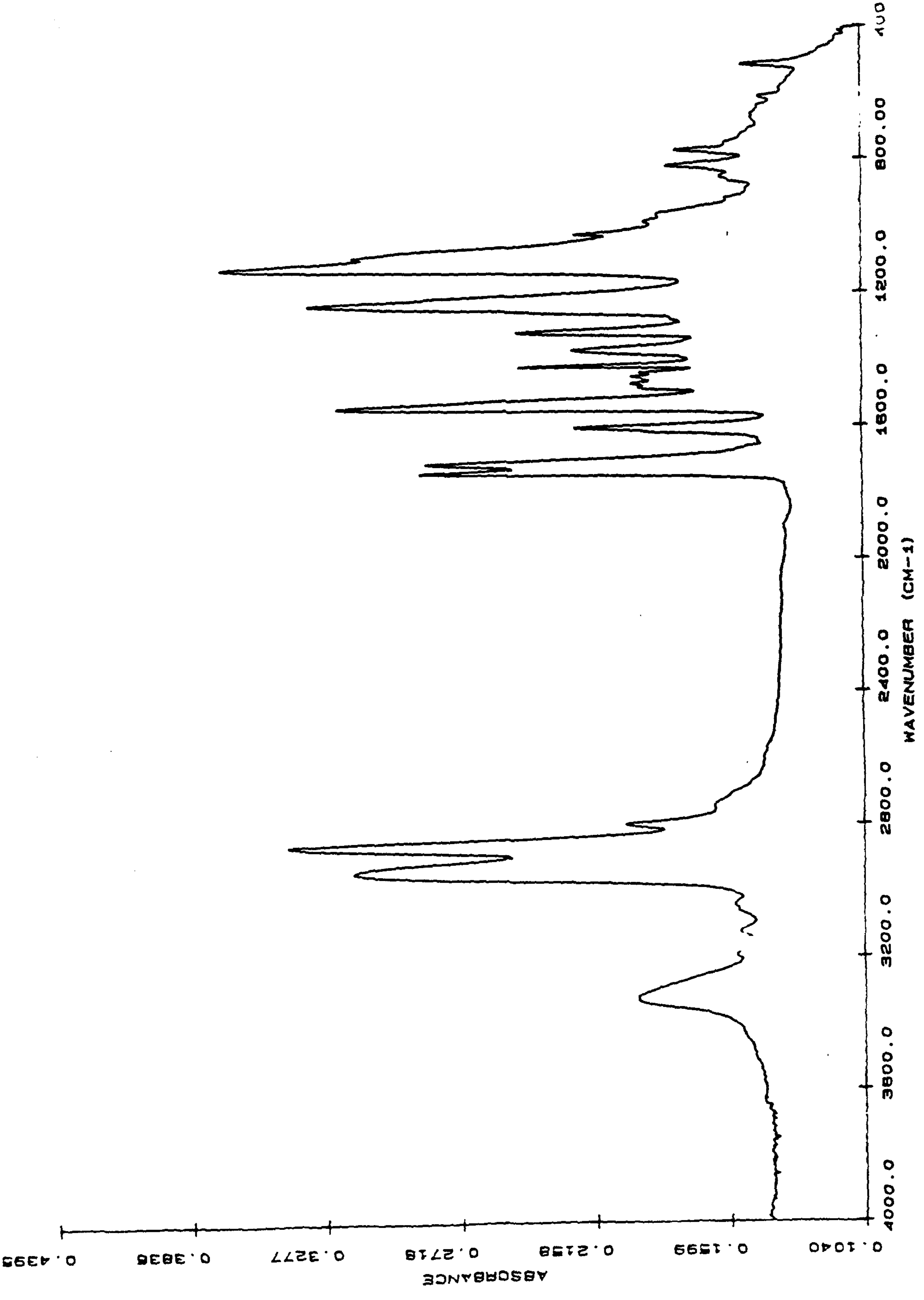

Figure 1-40 - FTIR Spectrum of the Outer Jacket Extract from Hose E

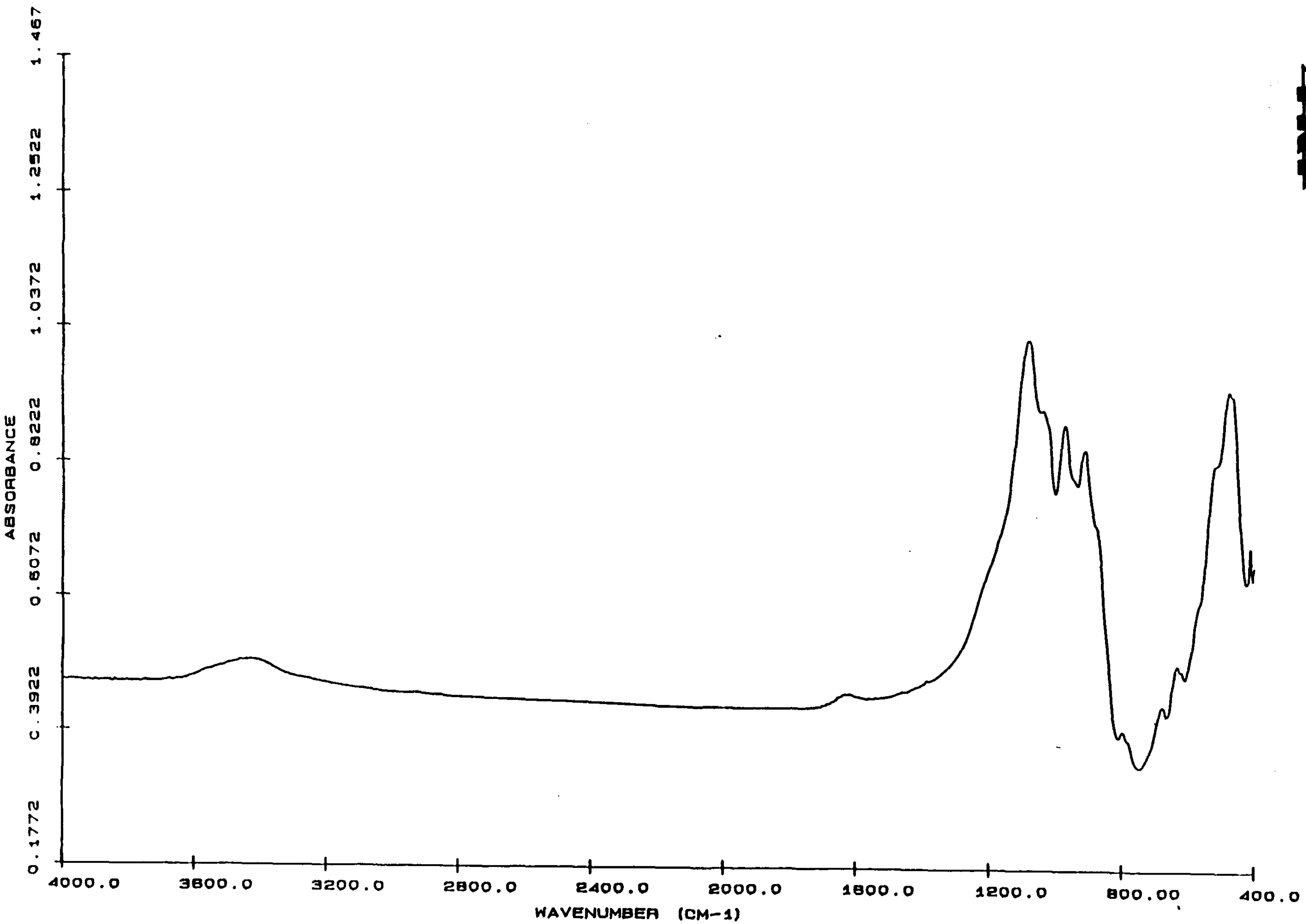

Figure 1-41 - FTIR Spectrum of e Inner Tube Ash from the New Hose A

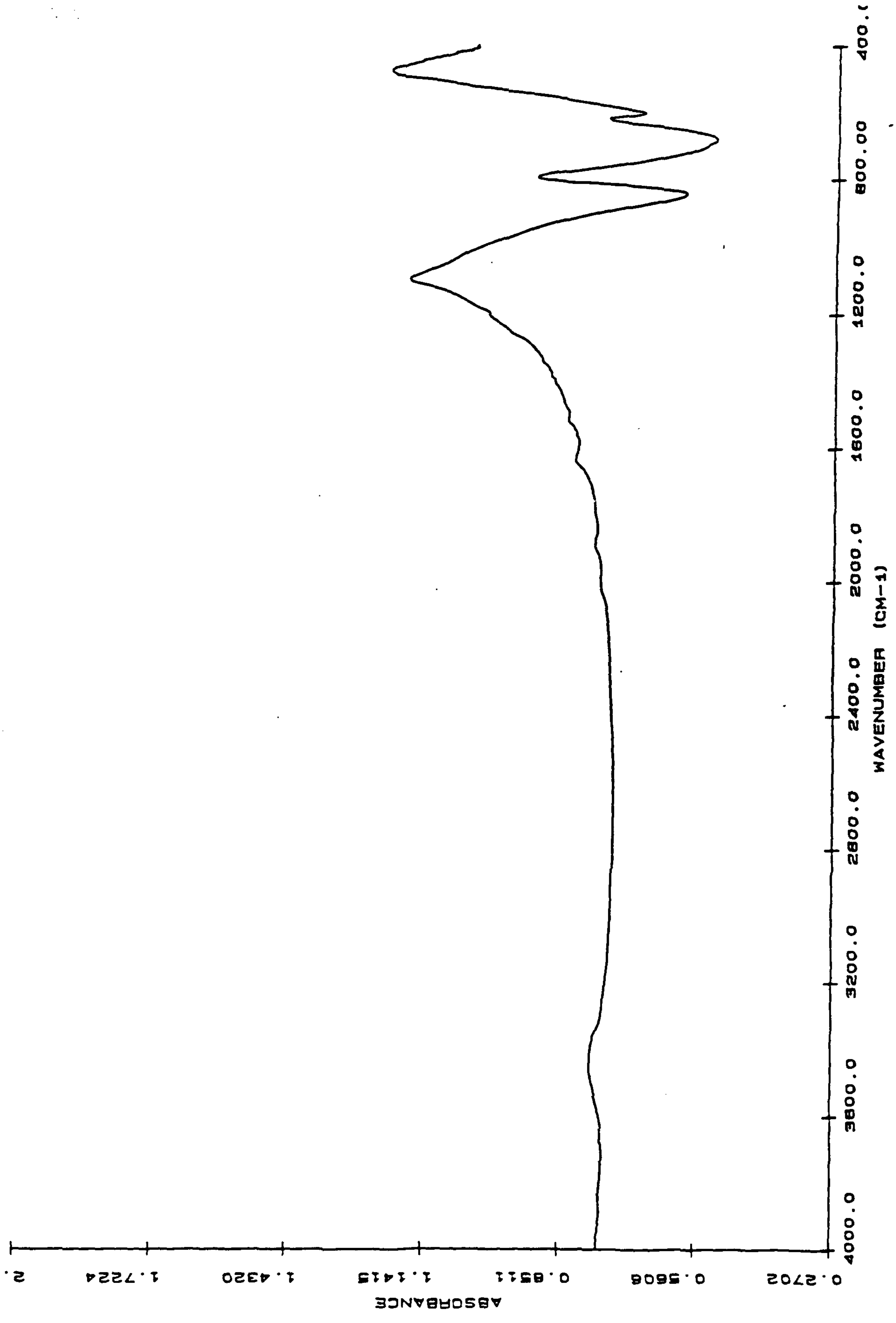

Figure 1-42 - FTIR Spectrum of the Outer Jacket Ash from the New Hose A

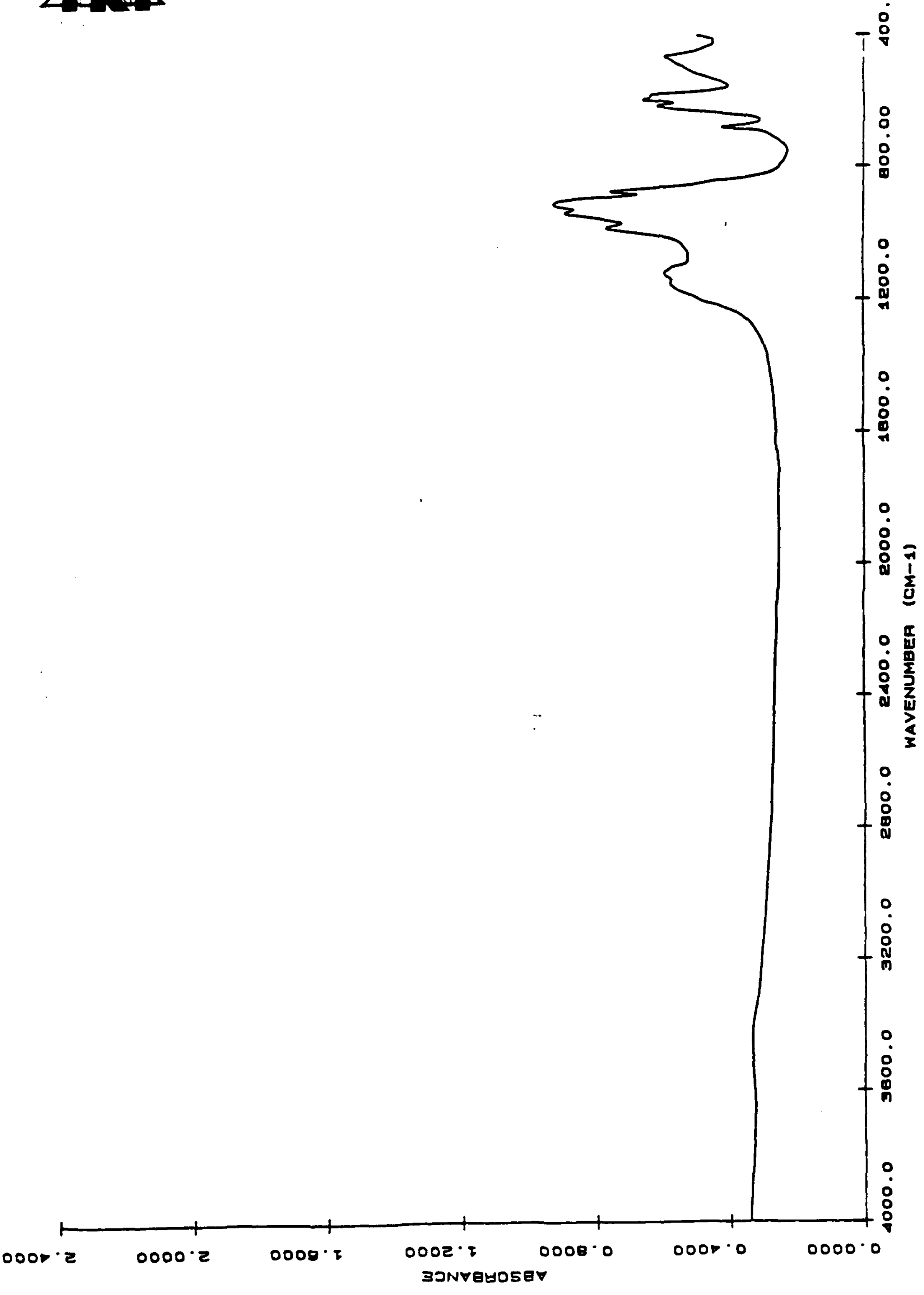

Figure 1-43 - FTIR Spectrum of the Inner Tube Ash from the Old Hose A

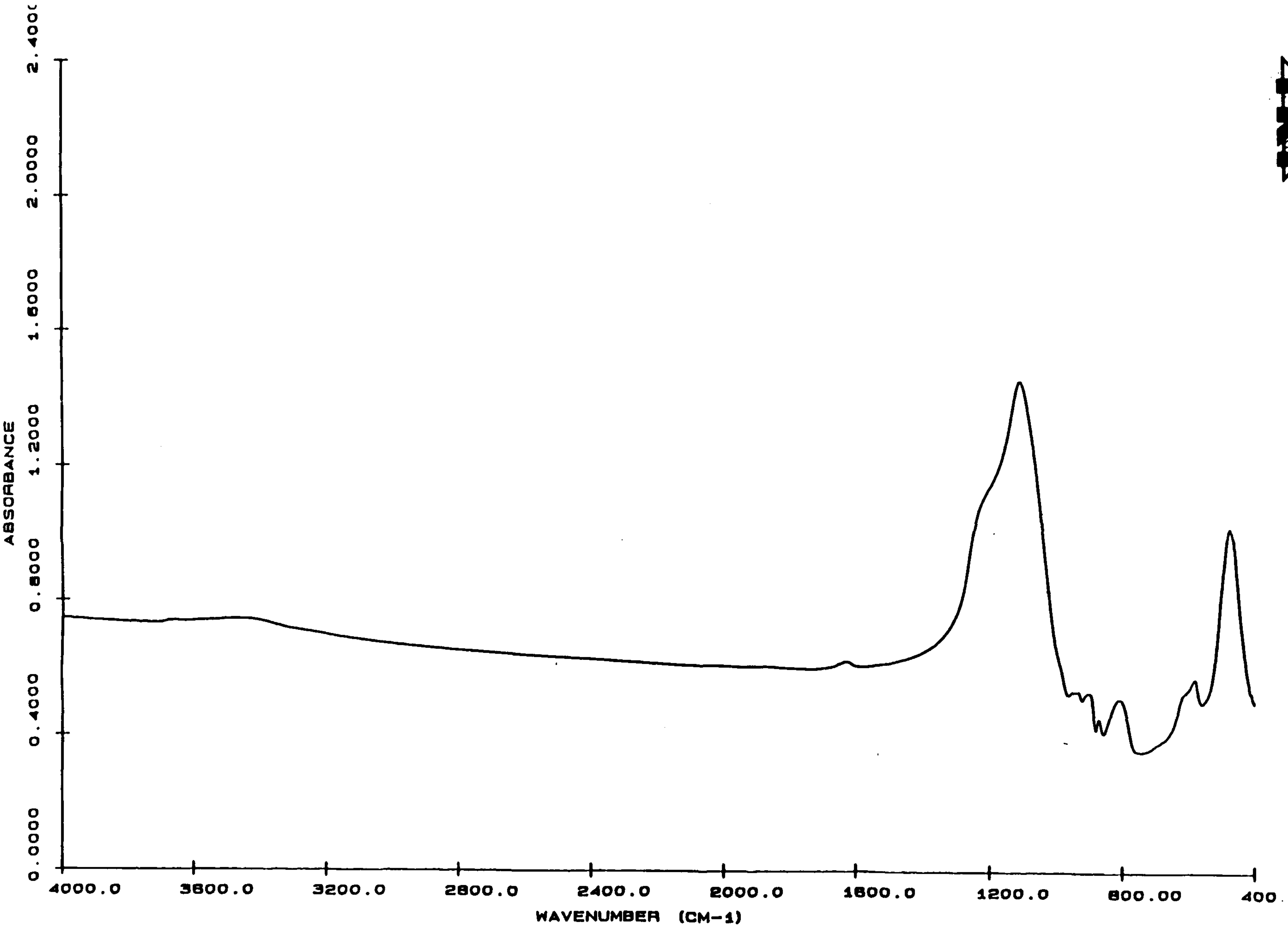

Figure 1-44 - FTIR Spectrum of the Outer Jacket Ash from the Old Hose A

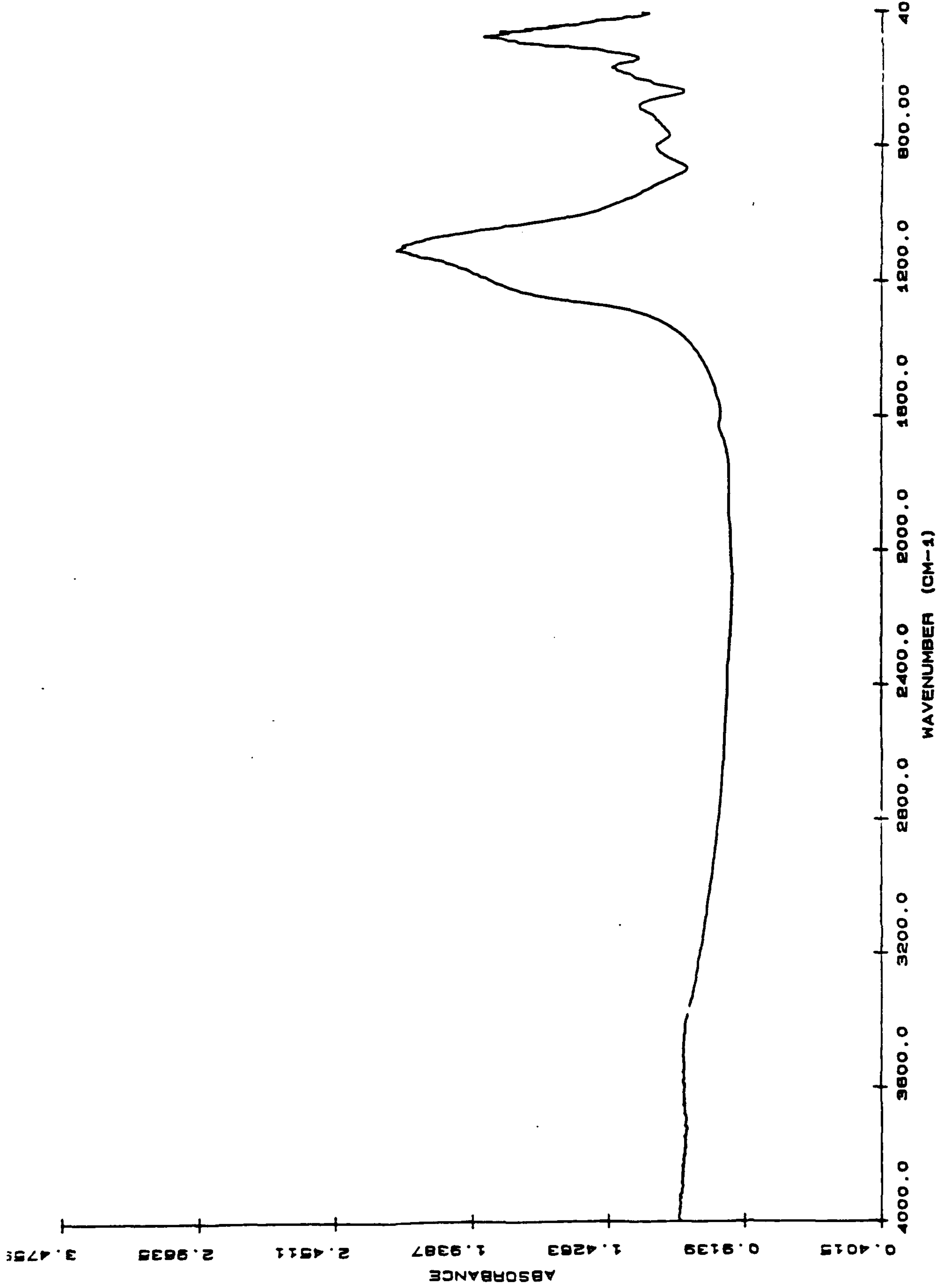

Figure 1-45 - FTIR Spectrum of the Inner Tube Ash from Hose B

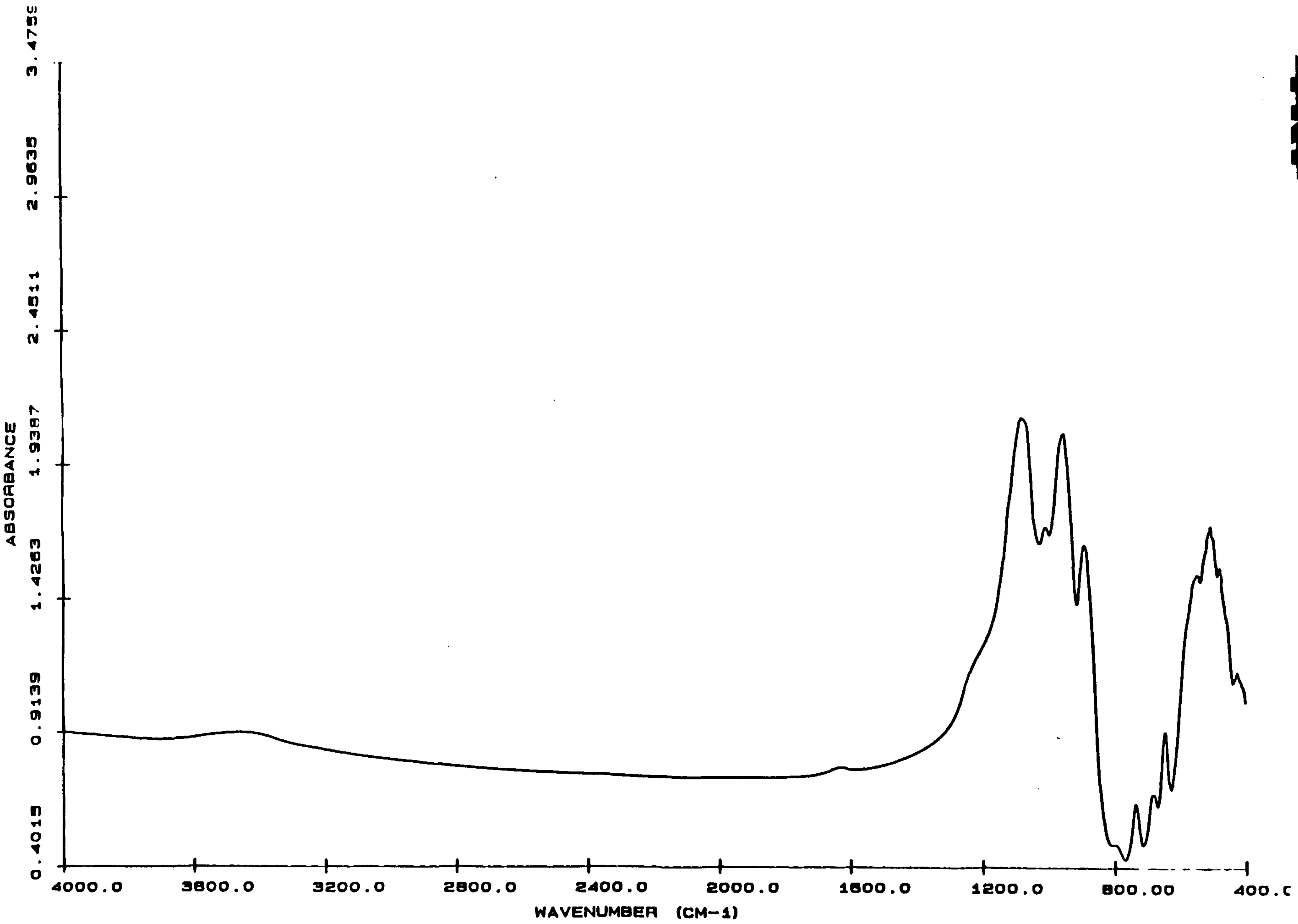

Figure 1-46 - FTIR Spectrum of the Outer Jacket Ash from Hose B

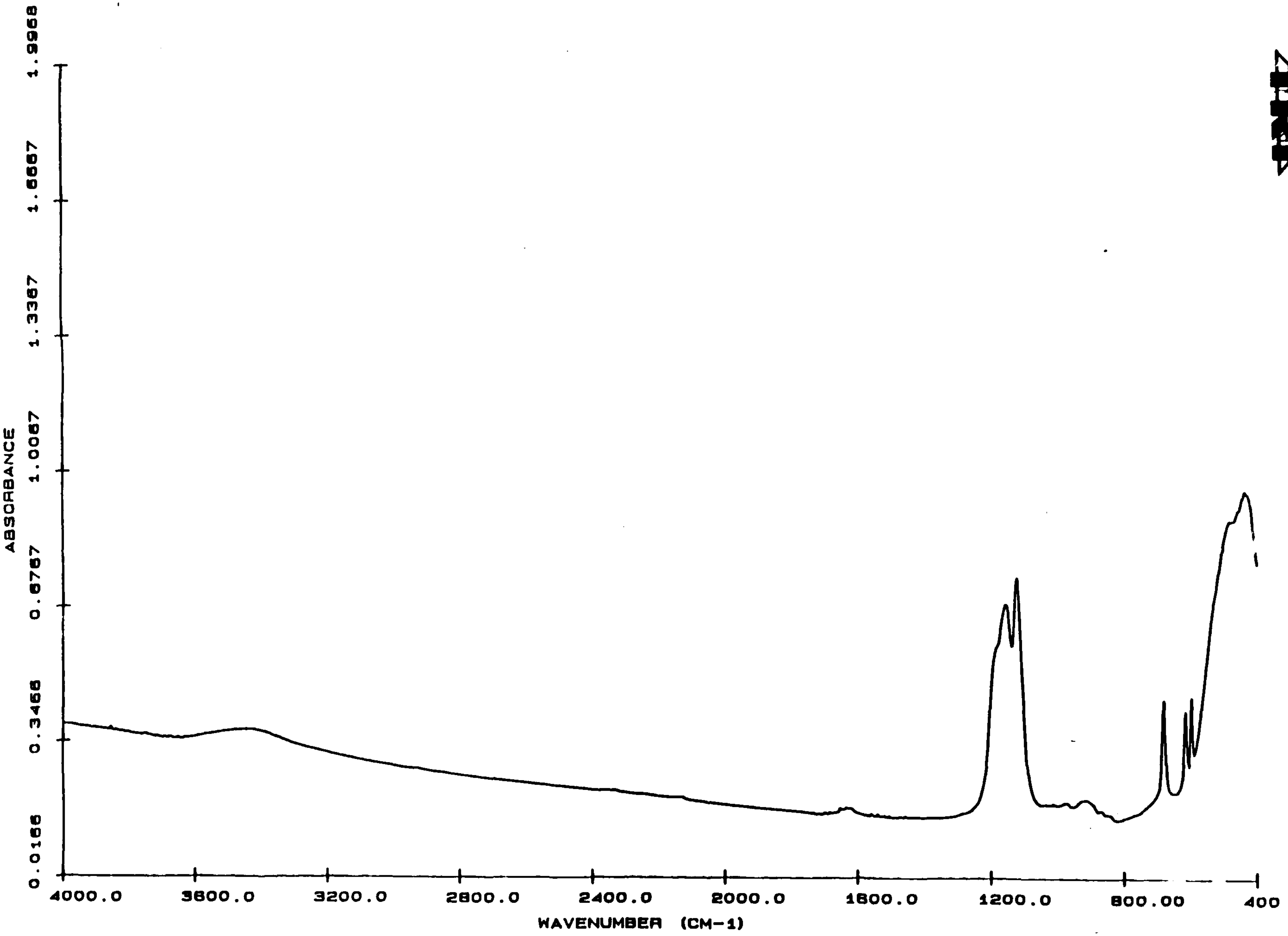

Figure 1-47 - FTIR Spectrum of the Inner Tube Ash from Hose C

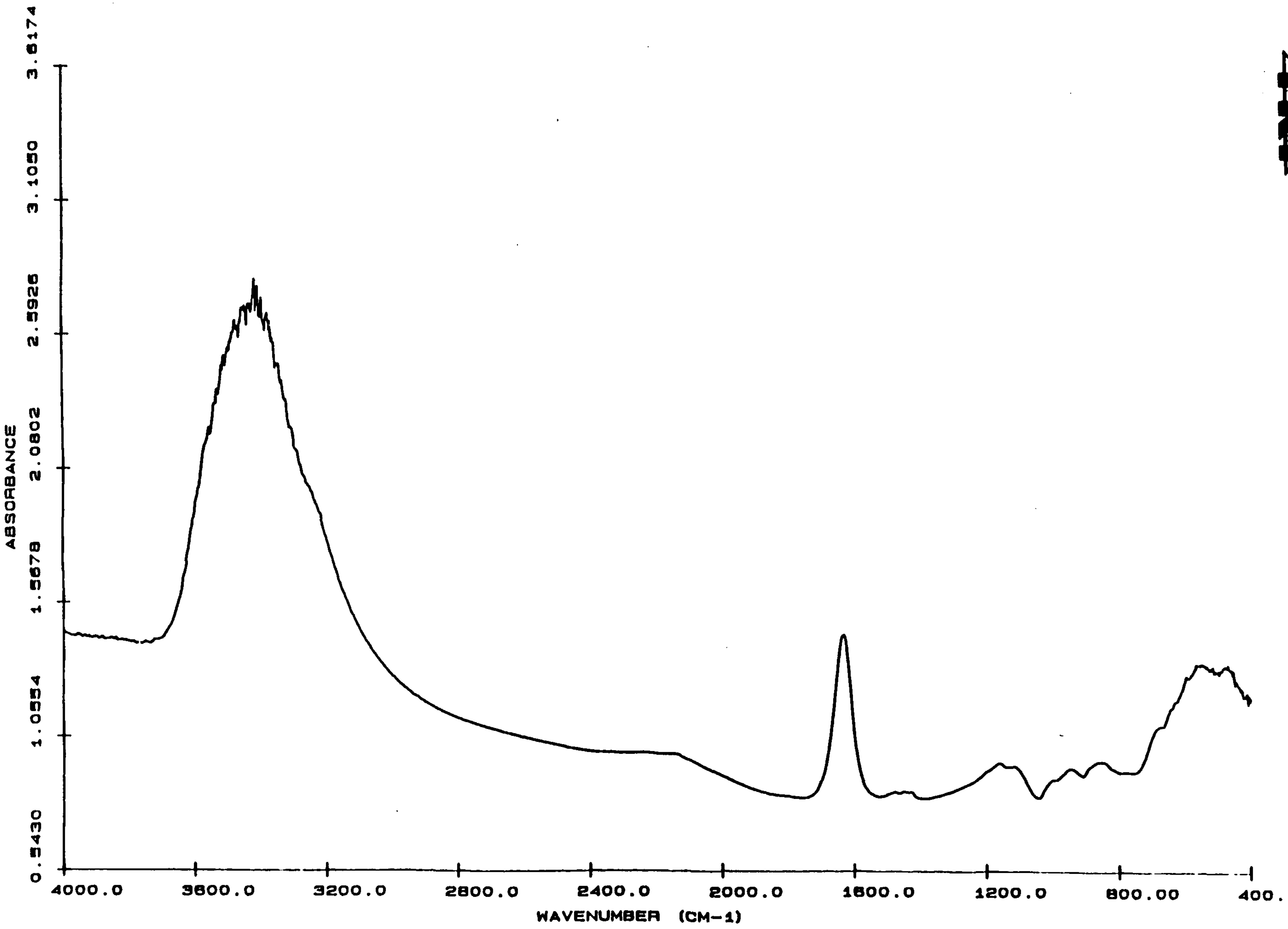

Figure 1-48 - FTIR Spectrum of the Outer Jacket Ash from Hose C

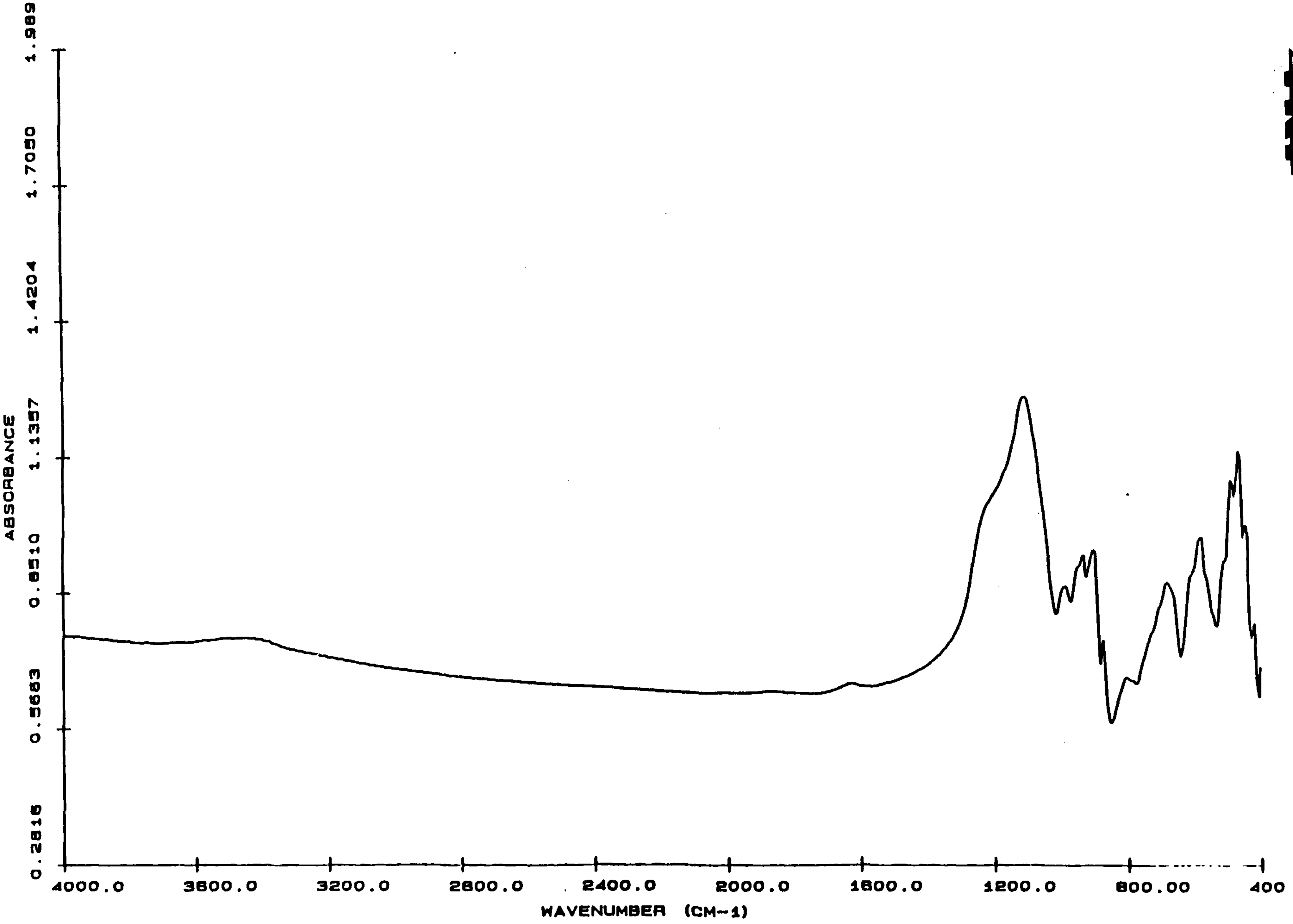

Figure 1-49 - FTIR Spectrum of the Inner Tube Ash from Hose D

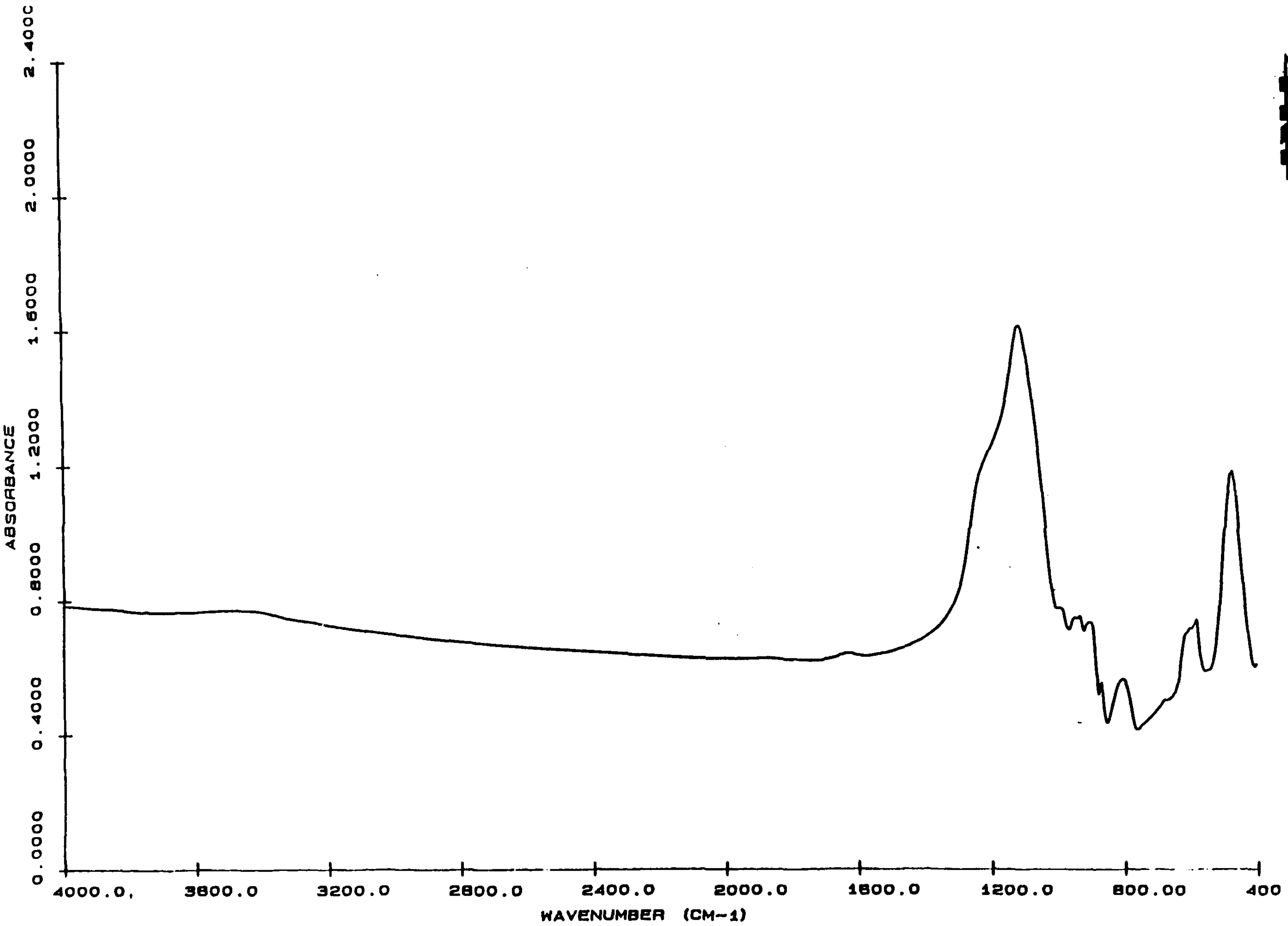

Figure 1-50 - FTIR Spectrum of the Outer Tube Ash from Hose D

Table 1-1
The Results of the Acetone Extraction of Rubber Hose Materials

Sample		% Extract Inner Tube	% Extract Outer Jacket
New Hose A	1	20.0	26.4
	2	14.4	26.4
	3	17.3	27.4
	4	15.2	27.3
	5	15.3	27.1
	6	15.5	29.1
	7	16.2	29.1
	8	15.7	26.5
	9	14.8	26.4
	10	14.0	26.9
Mean		15.8	27.3
Standard Deviation		1.7	1.0
Old Hose A	1	15.2	34.4
	2	16.1	28.1
	3	17.3	30.2
Mean		16.2	30.9
Standard Deviation		1.0	3.2
Hose B	1	13.5	13.2
	2	12.4	12.9
	3	11.6	11.6
Mean		12.5	12.6
Standard Deviation		1.0	0.9
Hose C	1	9.8	11.3
	2	10.5	12.6
	3	8.8	10.0
Mean		9.7	11.5
Standard Deviation		0.9	1.3

Table 1-1 (Continued)

Sample		% Extract Inner Tube	% Extract Outer Jacket
Hose D	1	15.7	25.7
	2	16.6	22.3
	3	14.2	22.2
Mean		15.5	23.2
Standard Deviation		1.2	1.6
Hose E	1	18.1	17.5
	2	17.3	16.6
	3	15.5	16.7
Mean		17.0	16.7
Standard Deviation		1.3	0.7

Table 1-2
Thermogravimetry Results

Sample		%Volatiles	%Polymers Step 1	%Polymers Step 2	%Black	%Residue	Polymer Peak Derivative Temp (°C)	
New Hose A	1	1.1		50.9	41.3	6.4		477
Inner	2	1.3		47.9	43.2	7.6		475
	3	1.3		48.9	43.7	6.1		472
	4	1.2		49.8	44.5	4.6		473
	5	0.9		48.6	44.4	6.0		473
	6	1.0		53.4	39.6	6.0		481
	7	1.1		50.5	42.5	5.9		475
	8	1.0		49.9	43.7	5.4		476
	9	1.2		45.4	46.2	7.3		488
	10	1.1		47.2	45.7	6.0		465
Mean		1.1		49.2	43.5	6.1		476
Standard Deviation		0.2		2.2	2.0	0.9		6.0
New Hose A	1	1.9	6.0	34.2	42.1	18.7	284	478
Outer	2	1.8	6.0	37.7	38.8	15.8	284	476
	3	1.6	6.2	33.8	42.9	15.4	280	480
	4	1.5	6.0	35.1	41.3	16.1	286	479
	5	1.7	5.9	35.0	40.8	16.5	299	480
	6	1.3	8.2	36.9	37.7	15.8	267	484
	7	1.8	8.3	40.5	34.6	14.8	266	482
	8	1.7	5.9	35.9	34.7	16.7	284	478
	9	1.6	6.5	34.2	42.4	15.3	281	474
	10	1.5	6.3	34.2	42.1	15.8	280	482
Mean		1.6	6.5	35.7	40.2	15.8	281	479
Standard Deviation		0.2	0.9	2.6	0.6	0.6	9.4	3.0

Table 1-2 (Continued)

Sample		%Volatiles	%Polymers Step 1	%Polymers Step 2	%Black	%Residue	Polymer Peak Derivative Temp (°C)	
Old Hose A	1	1.5		50.1	41.9	6.4		474
Inner	2	0.8		49.1	43.7	6.4		477
	3	0.4		48.5	43.2	7.8		477
Mean		0.9		49.2	43.0	6.9		476
Standard Deviation		0.6		0.8	1.0	0.8		1.7
Old Hose A	1	1.7	6.2	37.3	38.8	16.0	263	471
Outer	2	1.5	6.4	34.4	39.2	18.4	271	476
	3	1.6	6.6	35.3	40.6	15.9	276	482
Mean		1.6	6.4	35.7	39.5	16.8	270	476
Standard Deviation		0.1	0.2	1.5	0.9	1.4	6.5	5.5
Hose B	1	0.9		35.2	33.8	30.2		467
Inner	2	0.8		38.6	29.2	31.2		484
	3	0.4		38.0	30.5	30.5		474
Mean		0.9		37.3	31.2	30.6		475
Standard Deviation		0.1		1.8	2.4	0.4		8.5
Hose B	1	1.2	24.6	17.0	46.9	10.3	347	468
Outer	2	1.5	25.9	16.9	45.2	10.4	347	468
	3	1.7	26.4	17.4	44.3	10.2	344	461
Mean		1.5	25.6	17.1	45.5	10.3	346	466
Standard Deviation		0.3	0.9	0.3	1.3	0.1	1.7	4.0

Table 1-2 (Continued)

Sample		%Volatiles	%Polymers		%Black	%Residue	Polymer Peak Derivative Temp (°C)	
			Step 1	Step 2				
Hose C	1	1.2		53.4	41.1	4.3		471
Inner	2	1.4		52.1	42.3	4.2		467
	3	1.5		55.9	37.9	4.6		475
Mean		1.4		53.8	40.4	4.4		471
Standard Deviation		0.2		1.9	2.3	0.2		4.0
Hose C	1	1.0	19.0	26.3	38.1	15.6	371	471
Outer	2	1.4	18.6	29.5	37.8	12.7	373	475
	3	1.0	22.4	24.9	36.1	15.5	373	475
Mean		1.1	20.0	26.9	37.3	14.6	372	475
Standard Deviation		1.0	2.1	2.3	1.1	1.6	1.1	0.6
Hose D	1	1.2		50.7	38.4	9.7		481
Inner	2	0.0		49.9	39.1	11.2		479
	3	2.0		48.7	40.7	8.6		478
Mean		1.1		49.8	39.4	9.8		479
Standard Deviation		1.0		1.0	1.2	1.3		1.5
Hose D	1	0.8	4.8	39.2	43.5	11.5	272	474
Outer	2	1.2	4.8	40.1	44.1	9.7	270	475
	3	1.1	5.8	36.4	48.0	8.7	277	467
Mean		1.0	5.1	38.6	45.2	10.0	273	472
Standard Deviation		0.2	0.6	1.9	2.4	1.4	1.4	4.3

Table 1-2 (Continued)

Sample		%Volatiles	%Polymers Step 1	%Polymers Step 2	%Black	%Residue	Polymer Peak Derivative Temp (°C)	
Hose E	1	1.2		94.9	3.9	1.0	378	435
Inner	2	0.2		95.3	3.6	0.8	381	435
	3	0.0		95.3	3.6	0.8	387	438
Mean		0.5		95.3	3.7	0.9	382	436
Standard Deviation		0.6		0.3	0.2	0.1	4.6	1.7
Hose E	1	0.0		94.7	3.7	1.6	380	434
Outer	2	0.2		95.5	3.0	1.3	383	434
	3	0.2		94.0	4.2	1.6	379	433
Mean		0.1		94.7	3.6	1.5	381	434
Standard Deviation		0.1		0.7	0.6	0.1	2.1	0.6

Table 1-3
Compositional Analysis of the Inner Tube of the Rubber Hoses

Sample	%Organics	%Black	%Ash
New Hose A	58±2.8	37±2.0	5±0.9
Old Hose A	58±1.4	36±1.0	6±0.8
Hose B	46±2.1	27±2.4	27±0.4
Hose C	60±2.1	36±2.3	4±0.4
Hose D	59±1.9	33±1.2	8±1.3
Hose E	97±1.5	3±0.2	0

Table 1-4
Compositional Analysis of the Outer Jacket of the Rubber Hoses

Sample	%Organics	%Black	%Ash
New Hose A	59±2.5	29±2.6	12±0.6
Old Hose A	61±3.5	27±0.9	12±1.4
Hose B	51±1.3	40±1.3	9±0.1
Hose C	54±3.8	33±1.1	13±1.6
Hose D	57±2.6	35±2.6	8±1.4
Hose E	96±1.0	3±0.6	1±0.1

APPENDIX B

FIGURES AND TABLES TO PART 2

LIST OF FIGURES TO PART 2

LIST OF TABLES TO PART 2

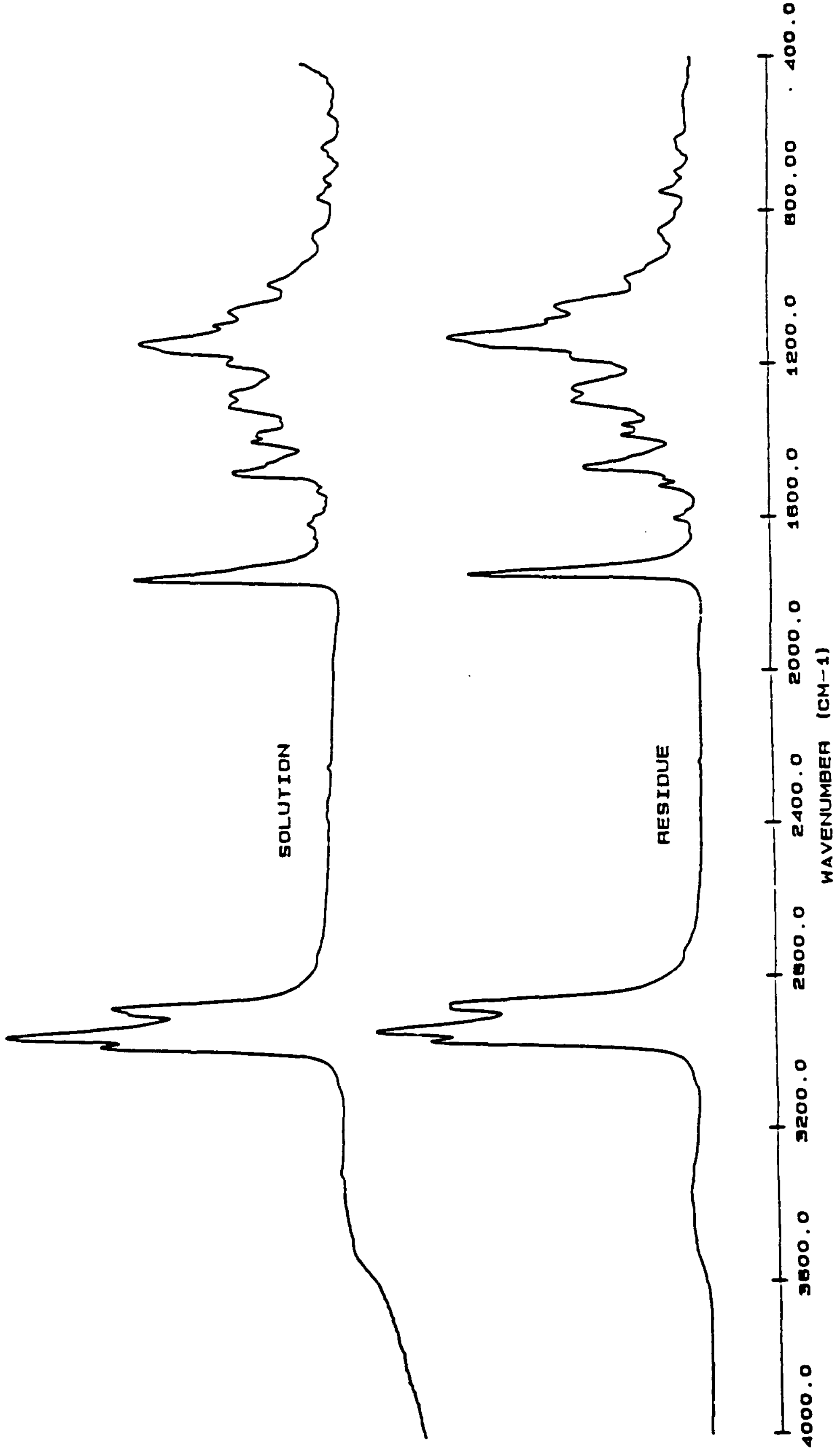

Figure 2-1 - Comparison of Solution vs. Residue for New Outside Hose D Extract

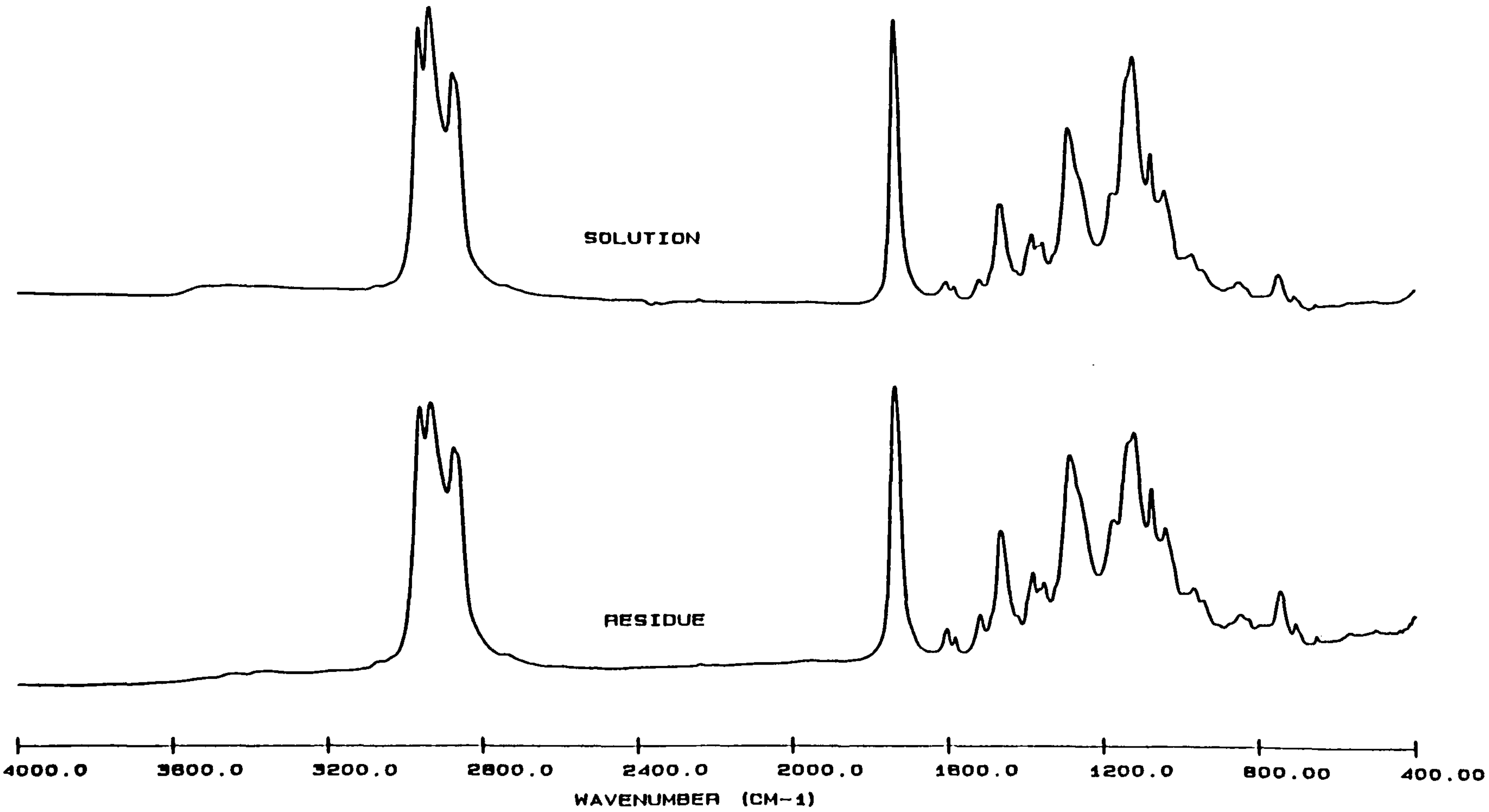

Figure 2-2 - Comparison of Solution vs. Residue for New Inside Hose D Extract

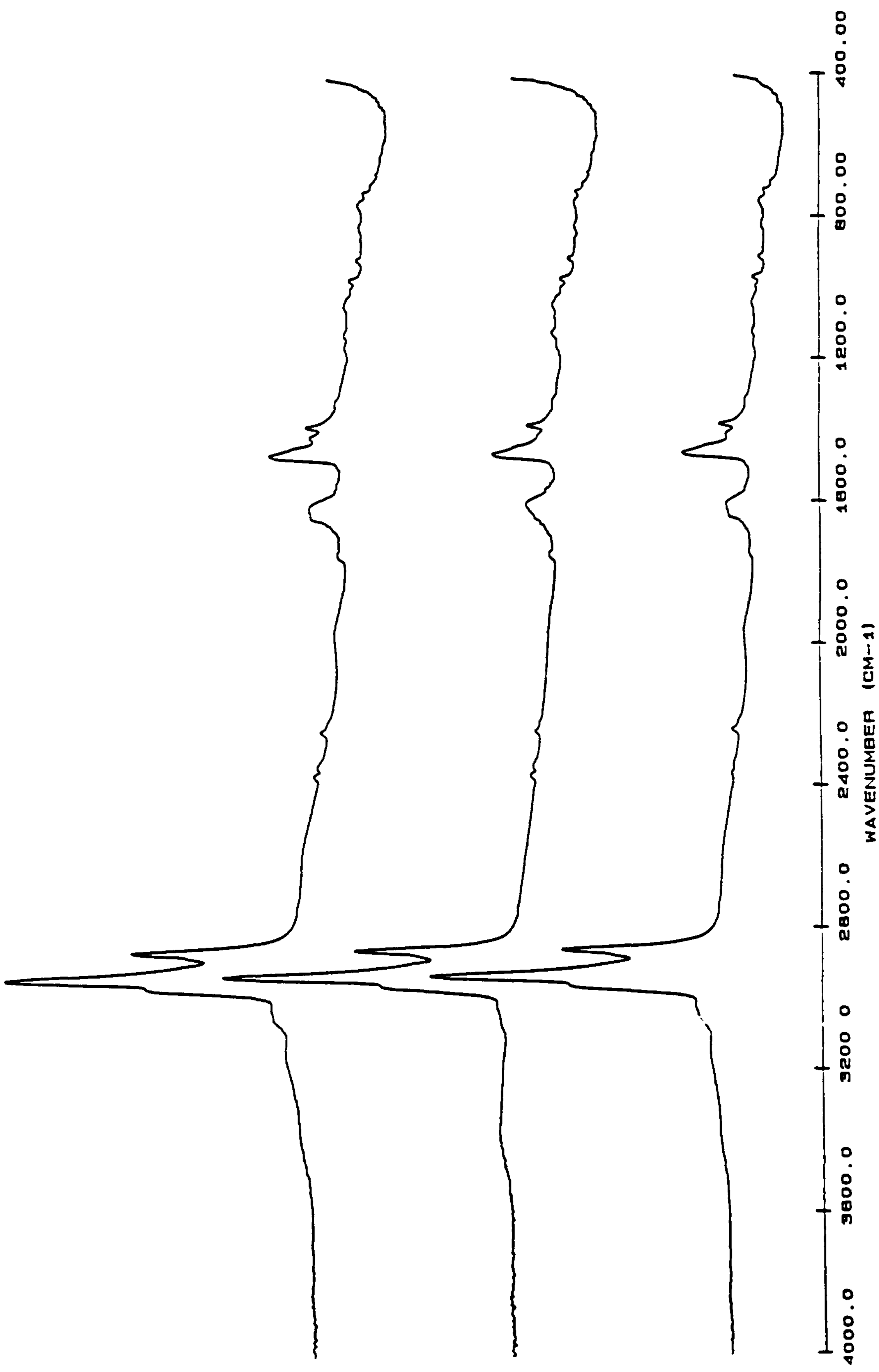

Figure 2-3 - Operator 1 Pyrolysis Samples

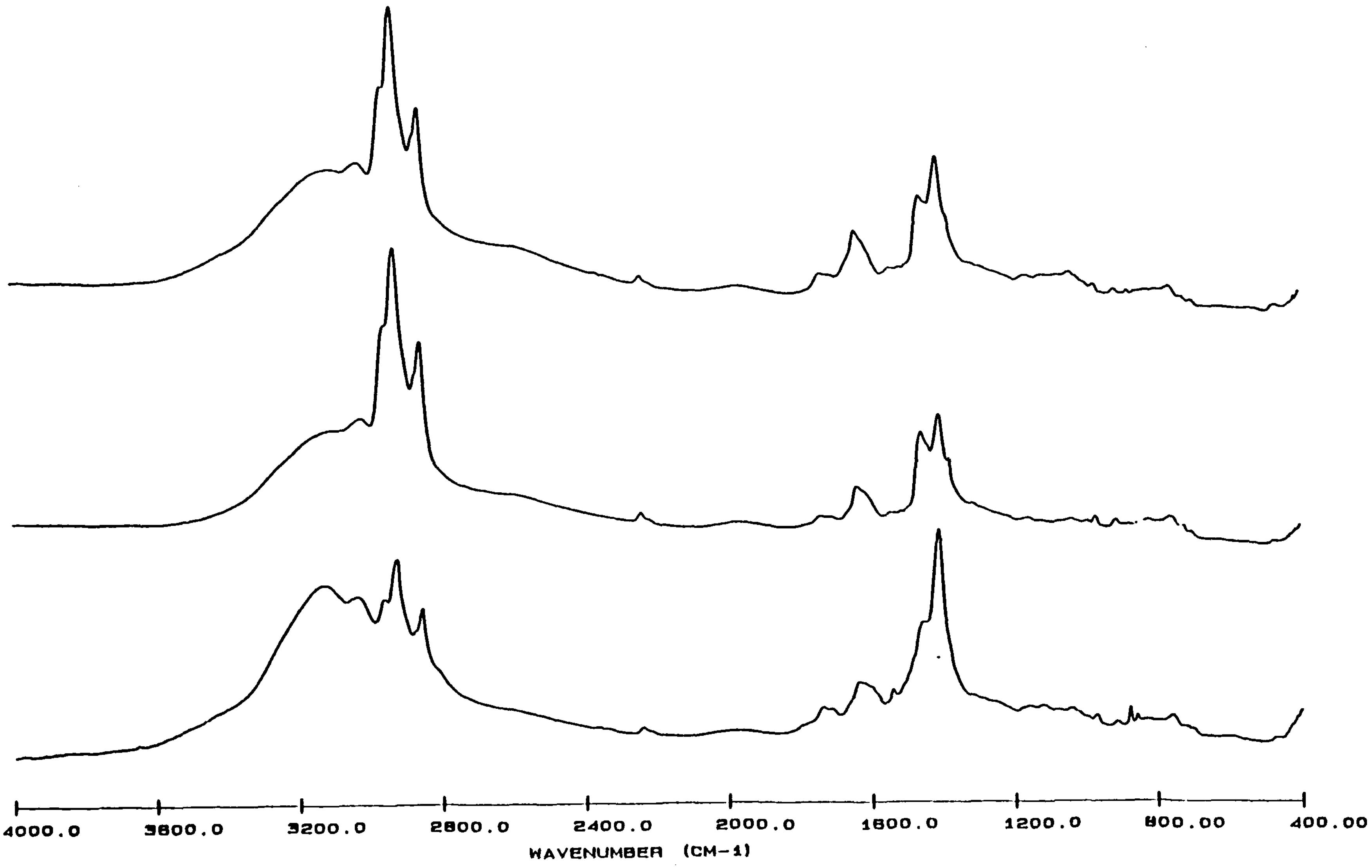

Figure 2-4 - Operator 2 Pyrolysis Samples

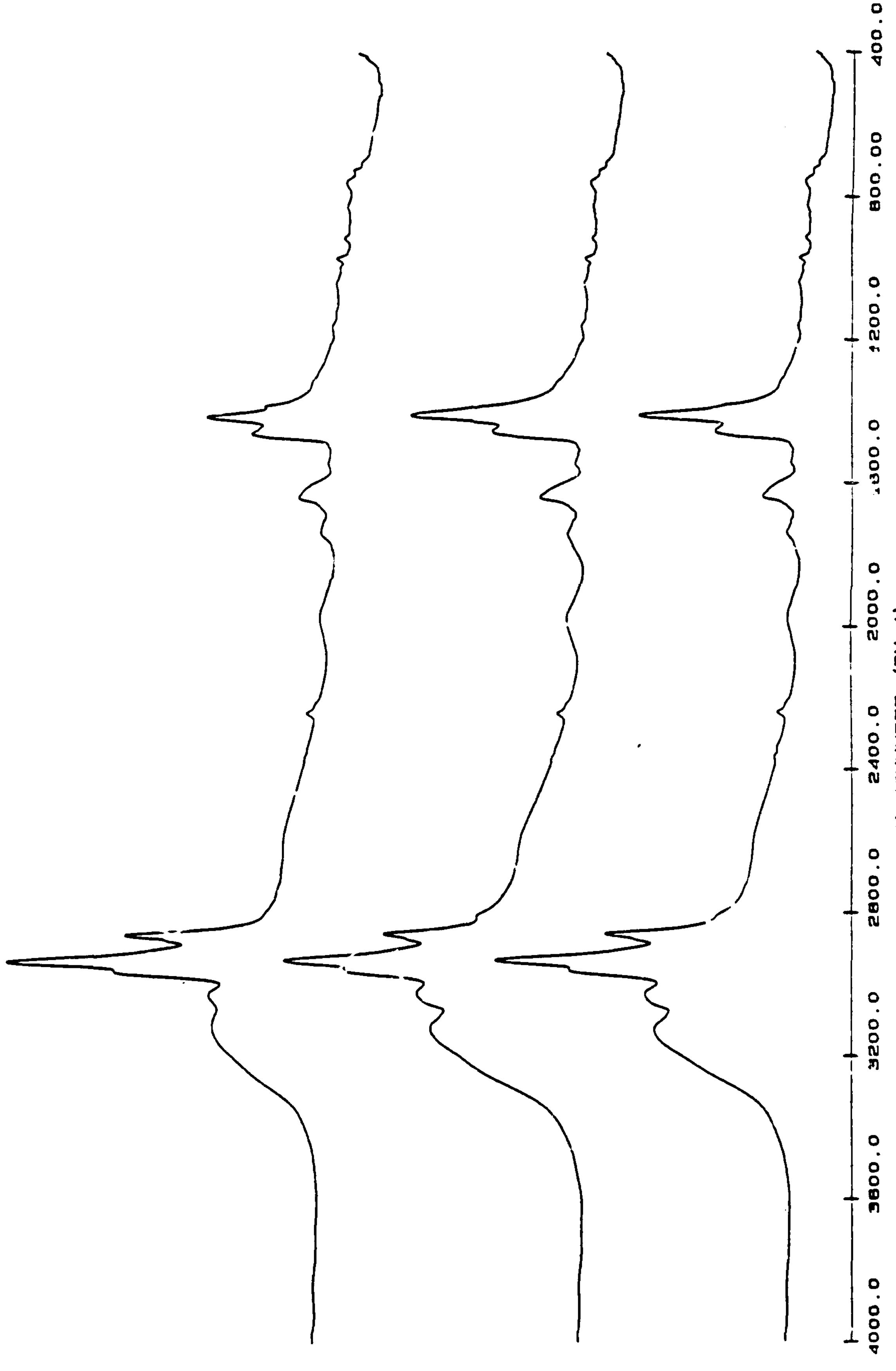

Figure 2-5 - Operator 3 Pyrolysis Samples

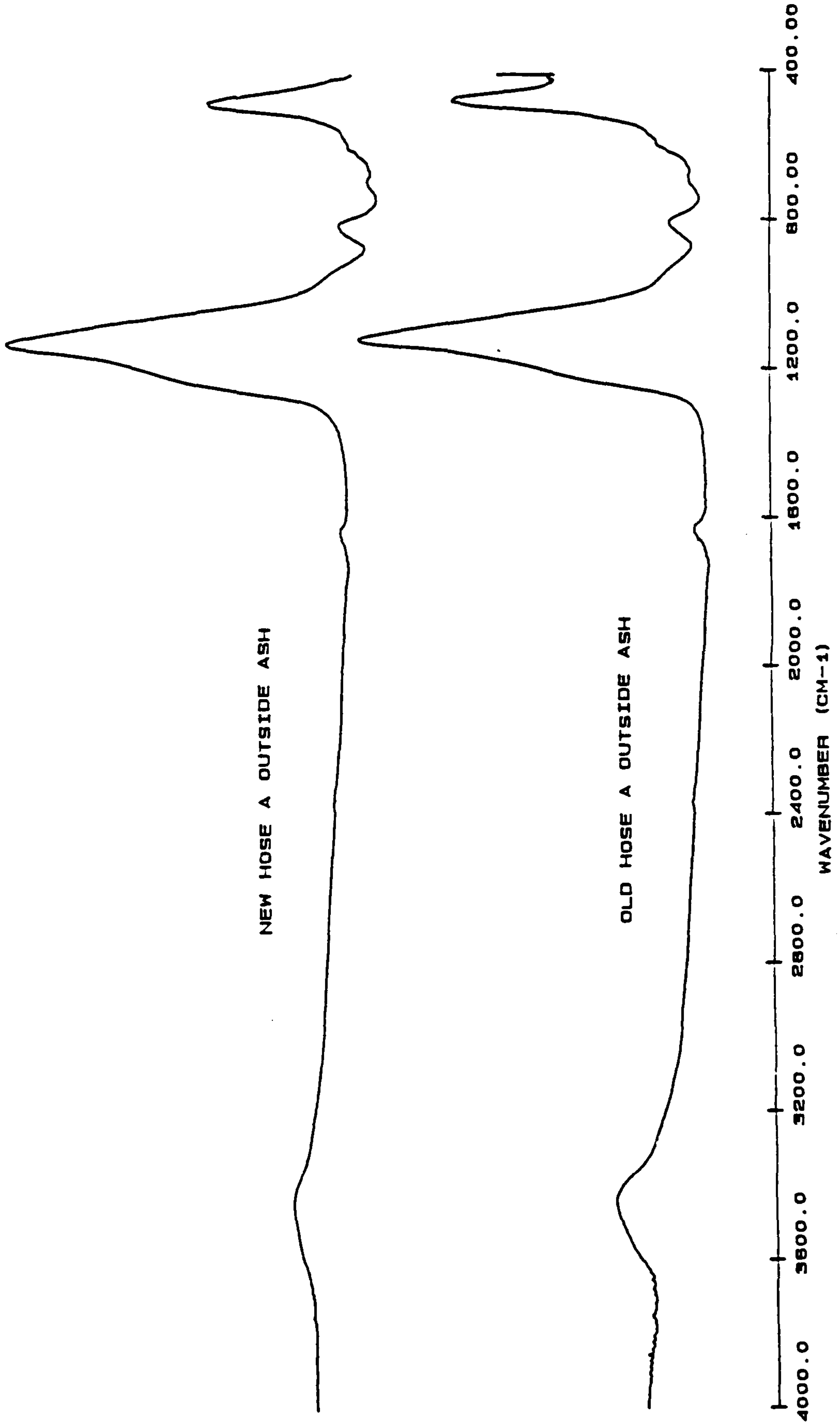

Figure 2-6 - Comparison of New and Old Hose A Outside Ash

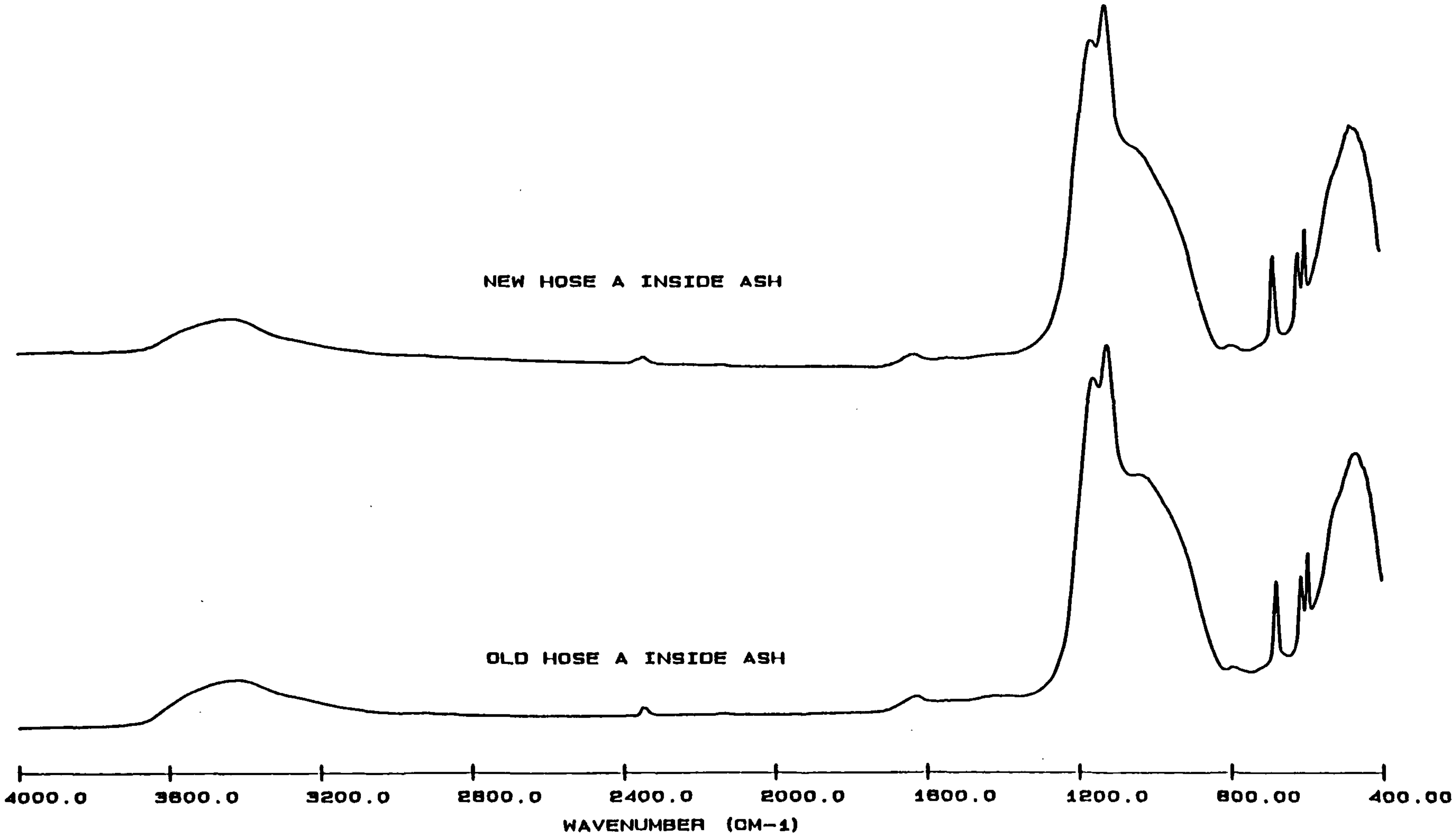

Figure 2-7 - Comparison of New and Old Hose A Inside Ash

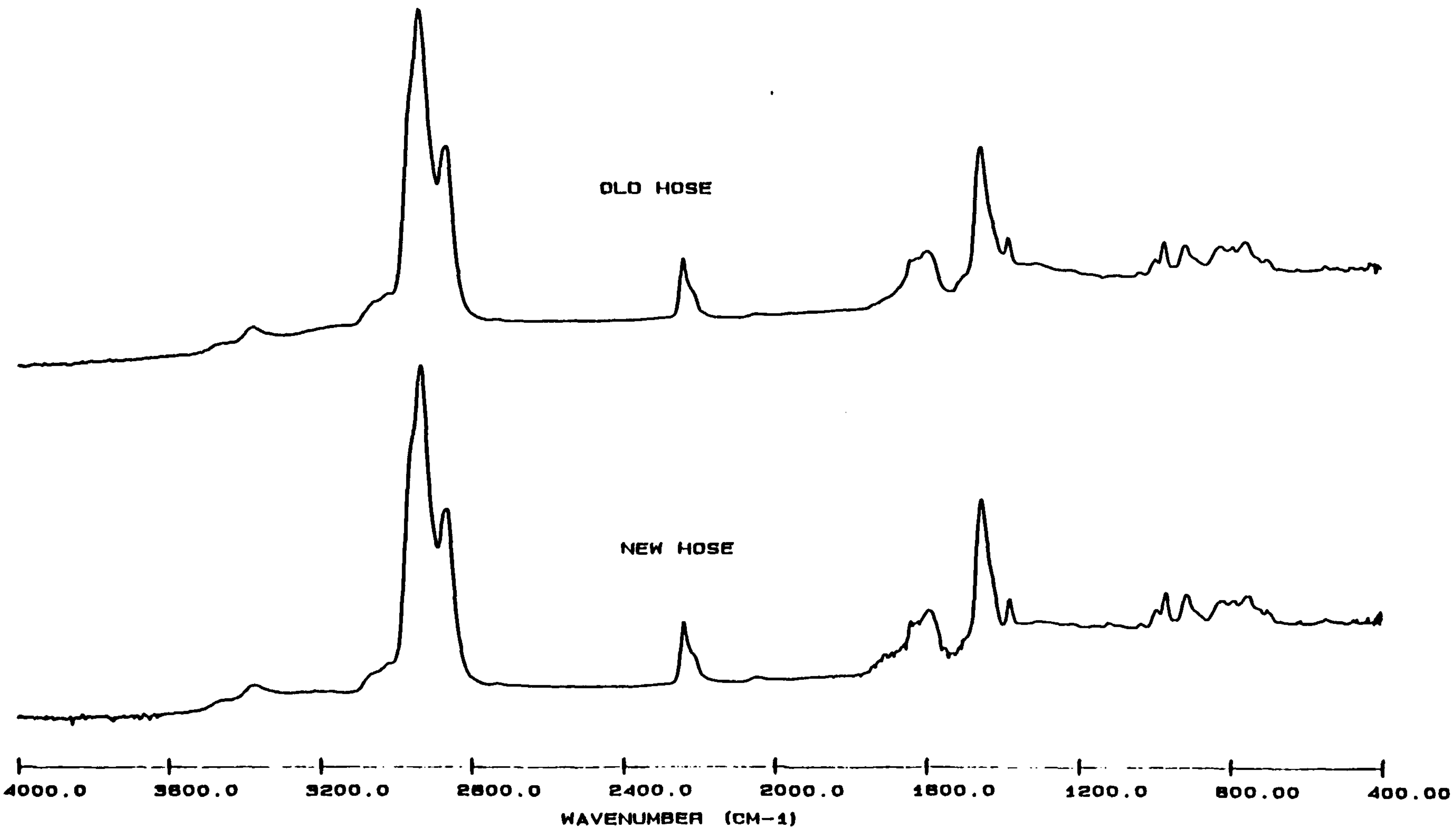

Figure 2-8 - Comparison of New and Old Hose A Inside Rubber

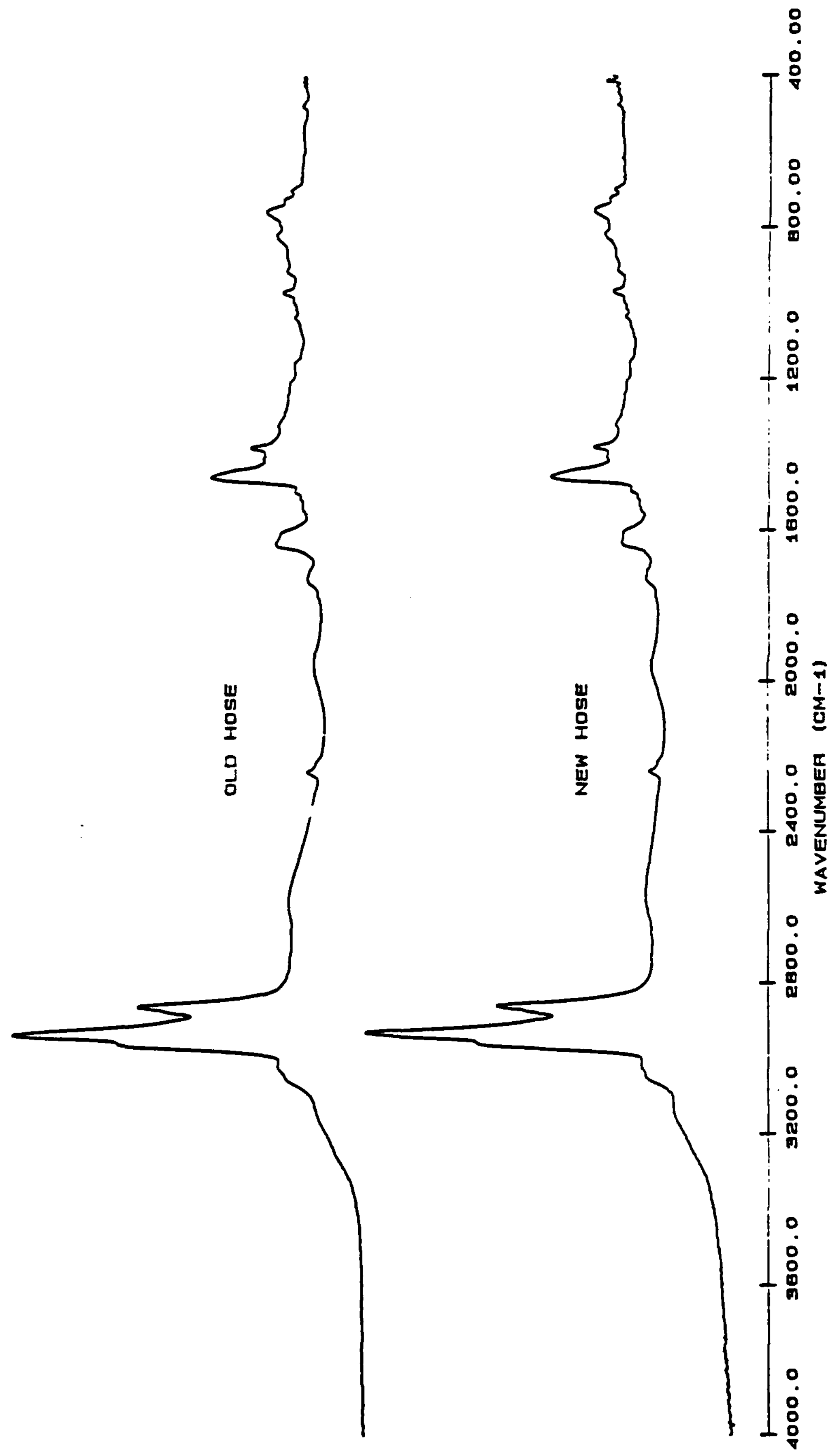

Figure 2-9 - Comparison of New and Old Hose A Outside Rubber

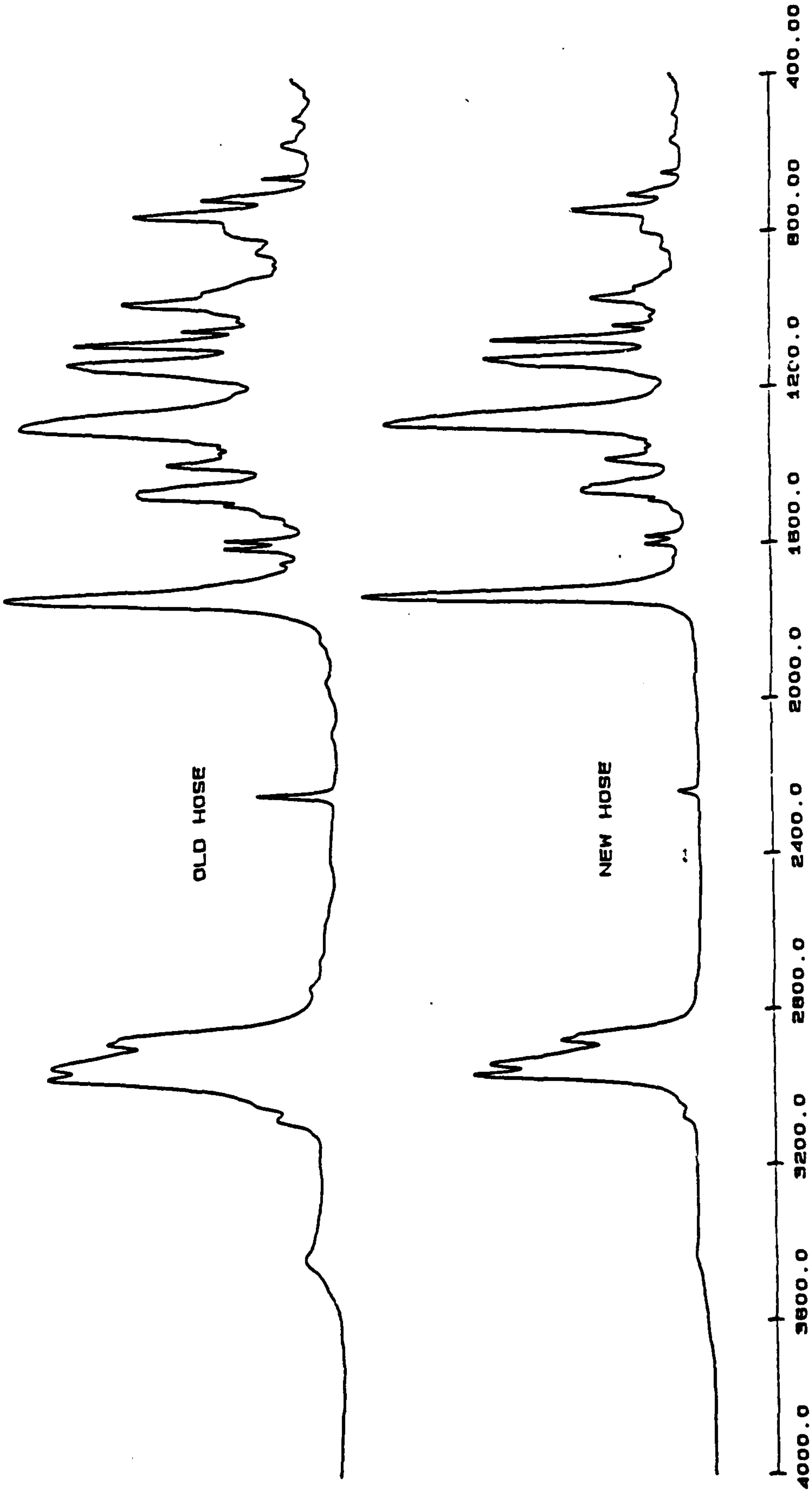

Figure 2-10 - Comparison of New and Old Hose A Inside Extract

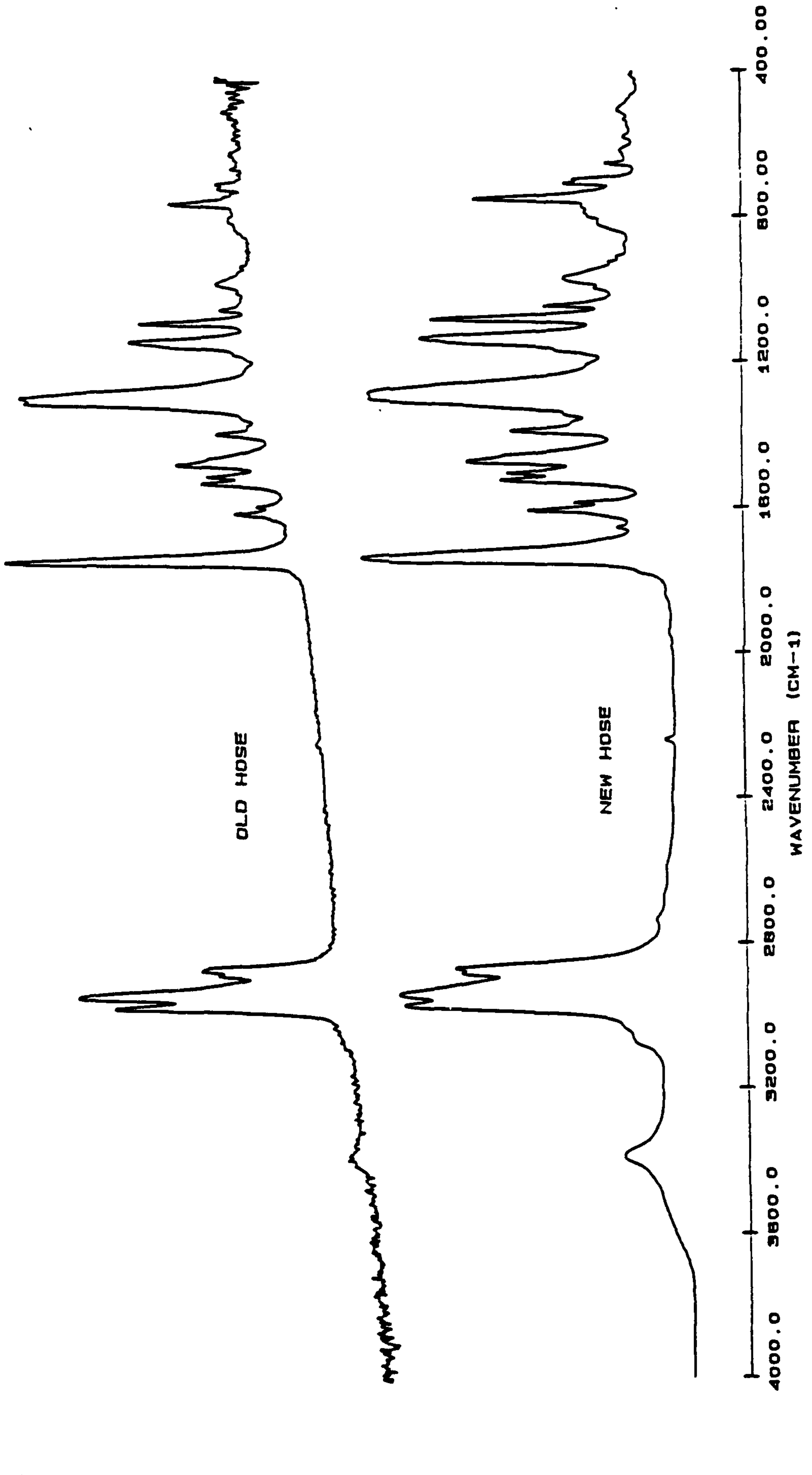

Figure 2-11 - Comparison of New and Old Hose A Outside Extract

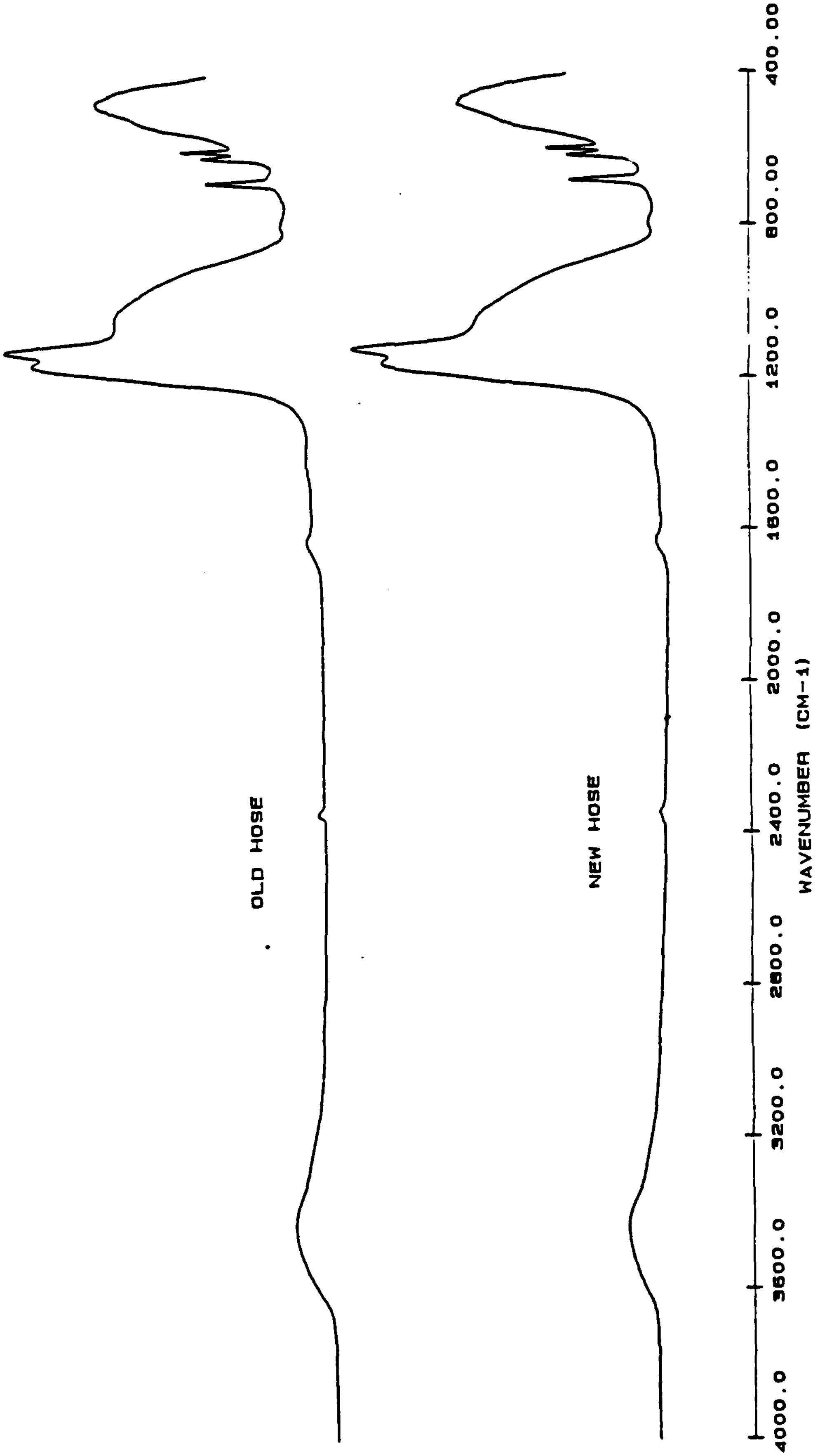

Figure 2-12 - Comparison of New and Old Hose A Inside Ash

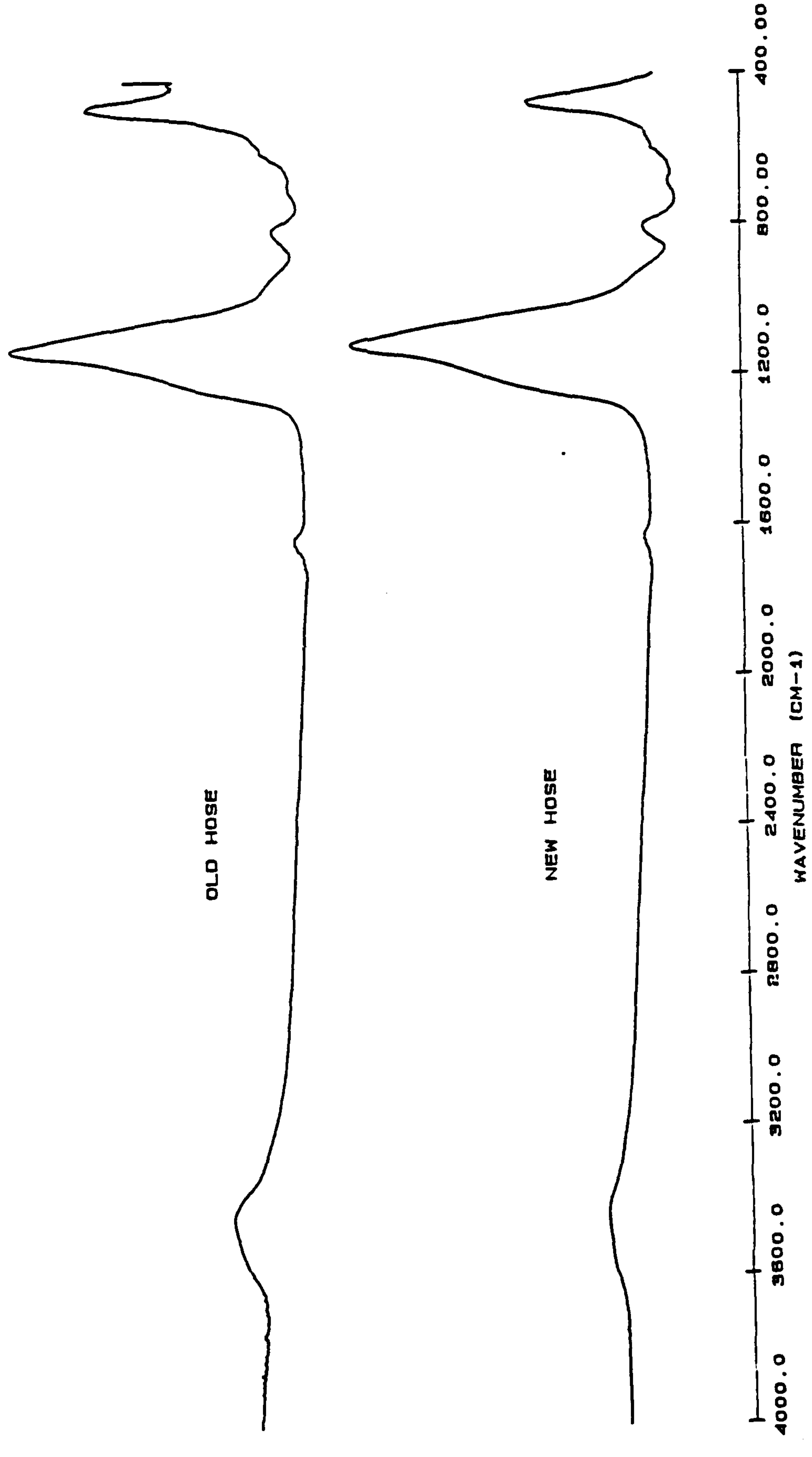

Figure 2-13 - Comparison of New and Old Hose A Outside Ash

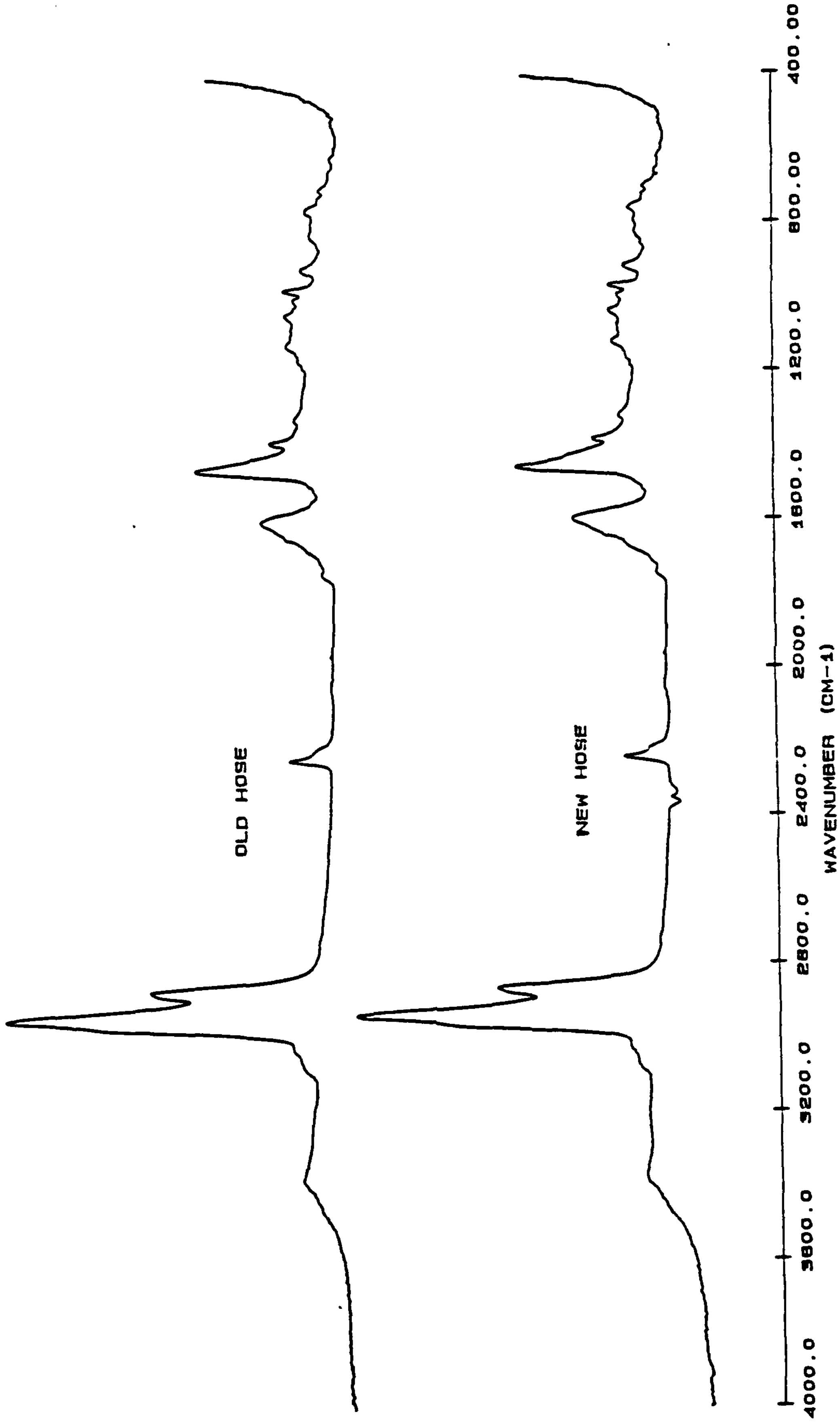

Figure 2-14 - Comparison of New and Old Hose D Inside Rubber

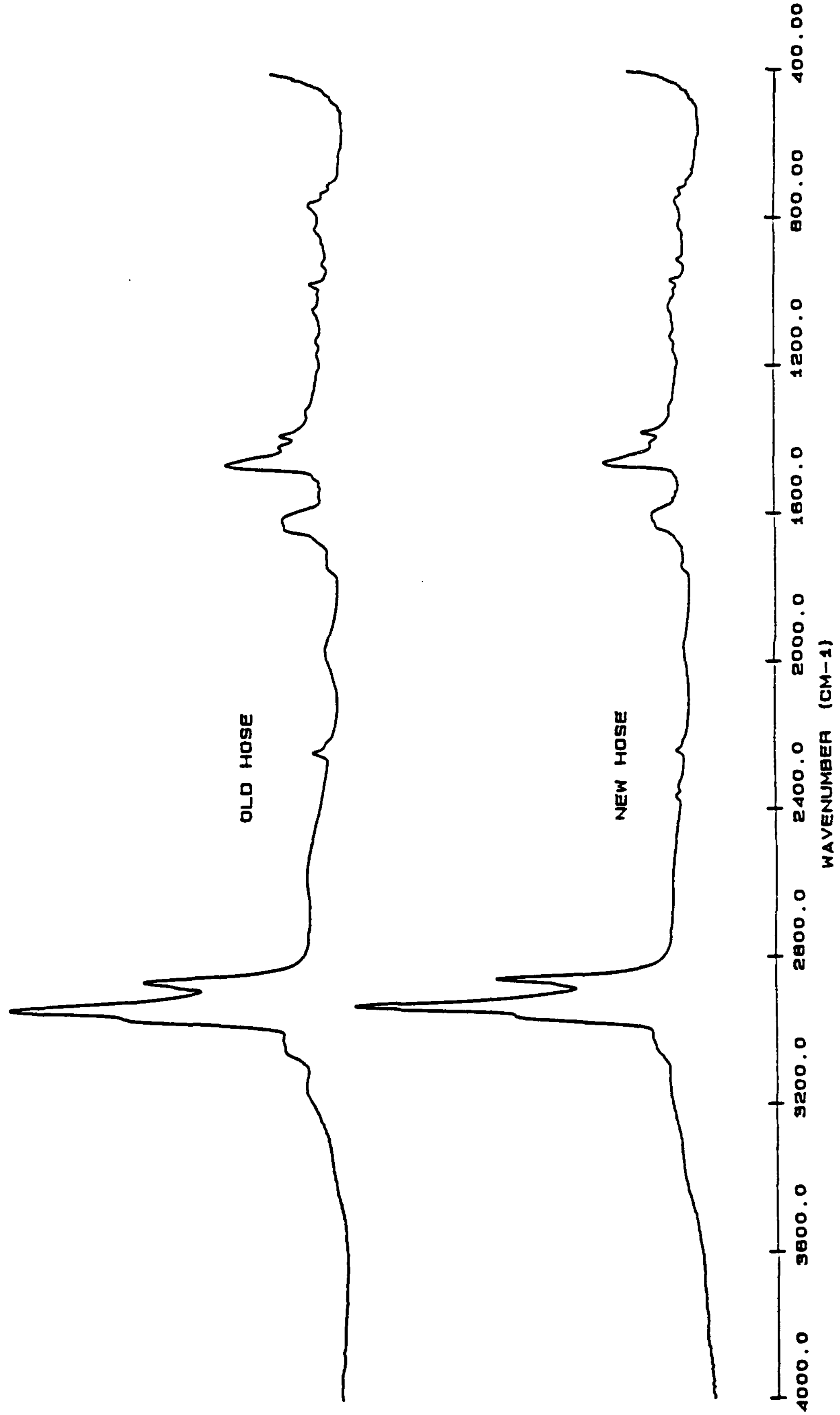

Figure 2-15 - Comparison of New and Old Hose D Outside Rubber

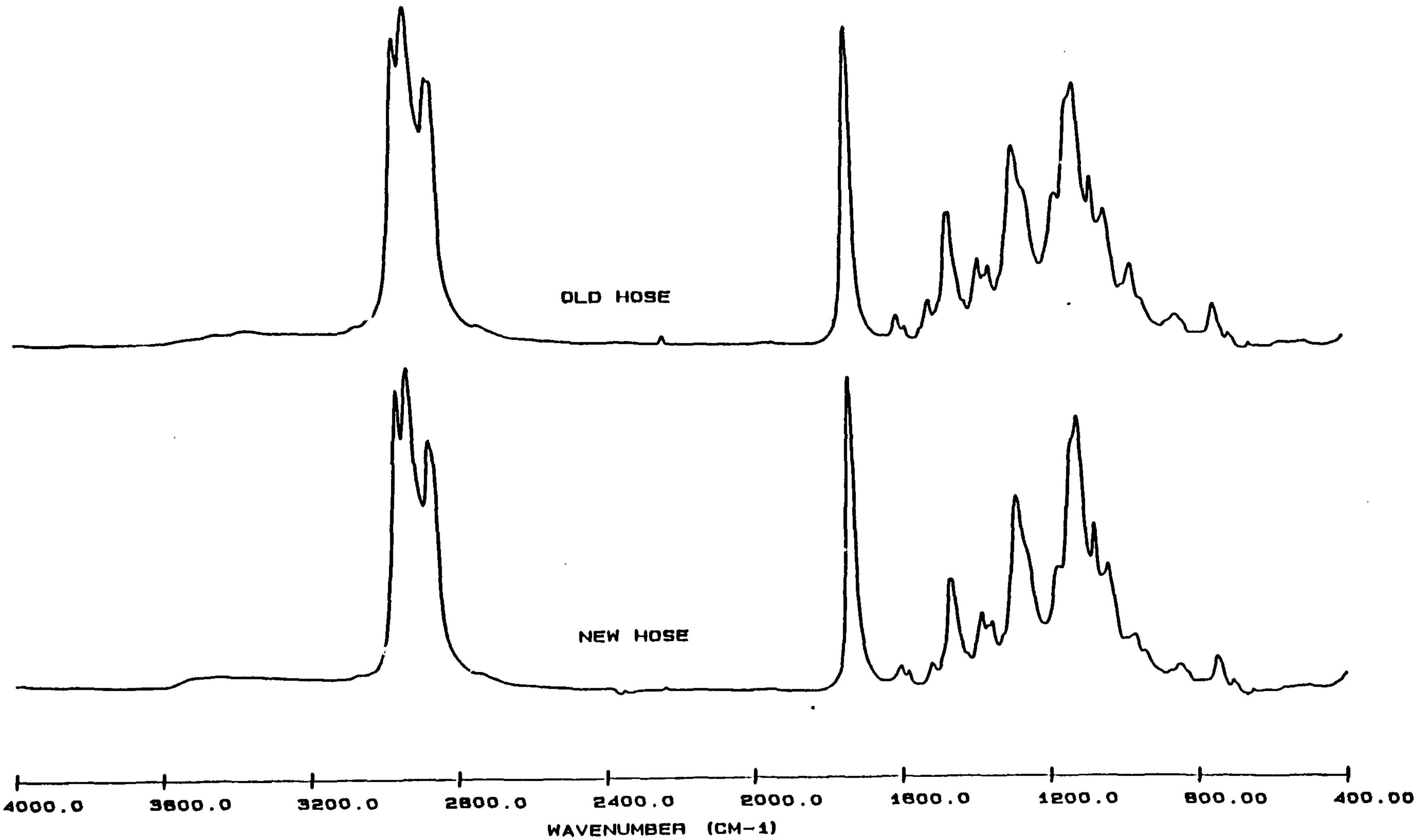

Figure 2-16 - Comparison of New and Old Hose D Inside Extract

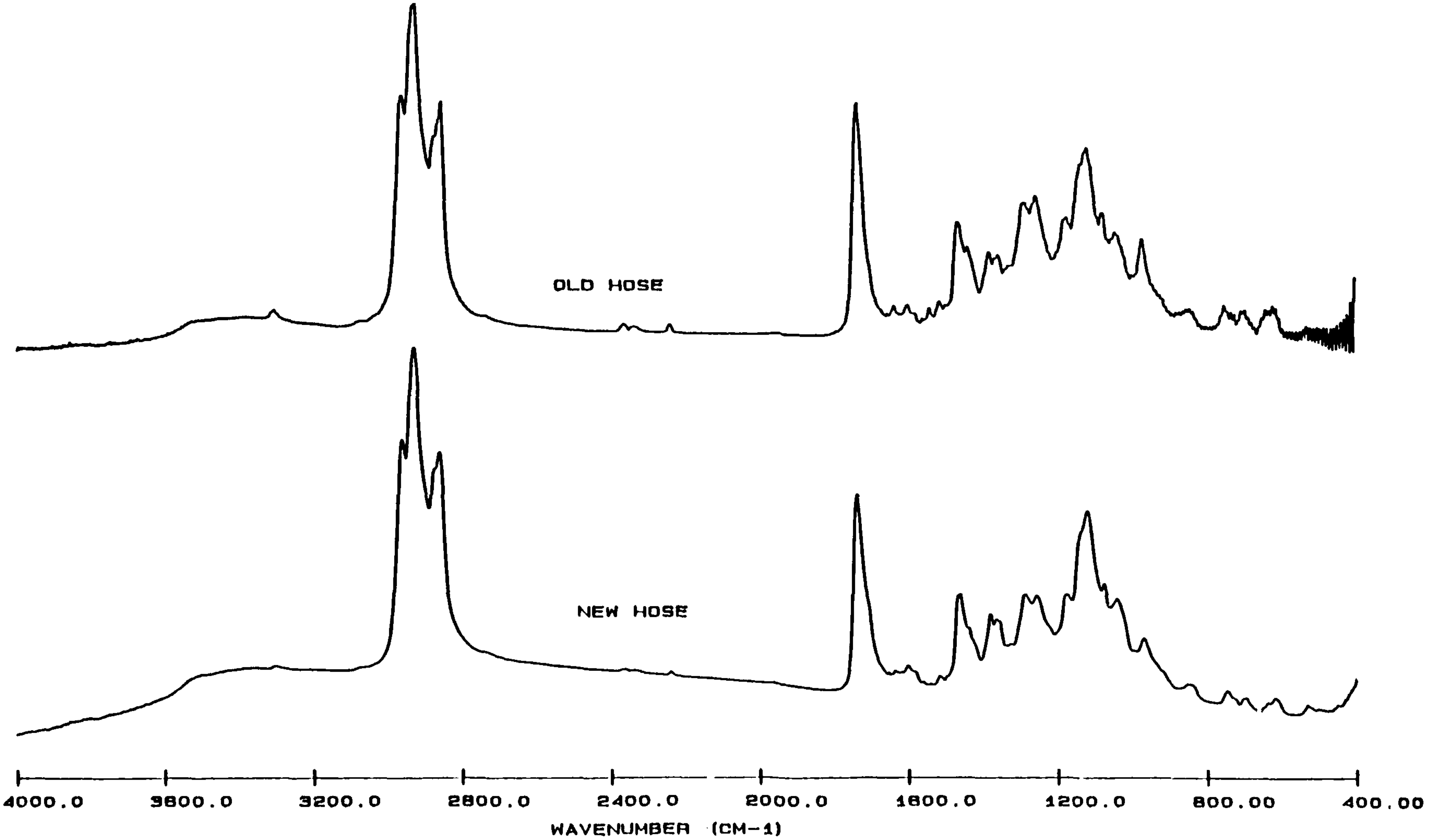

Figure 2-17 - Comparison of New and Old Hose D Outside Extract

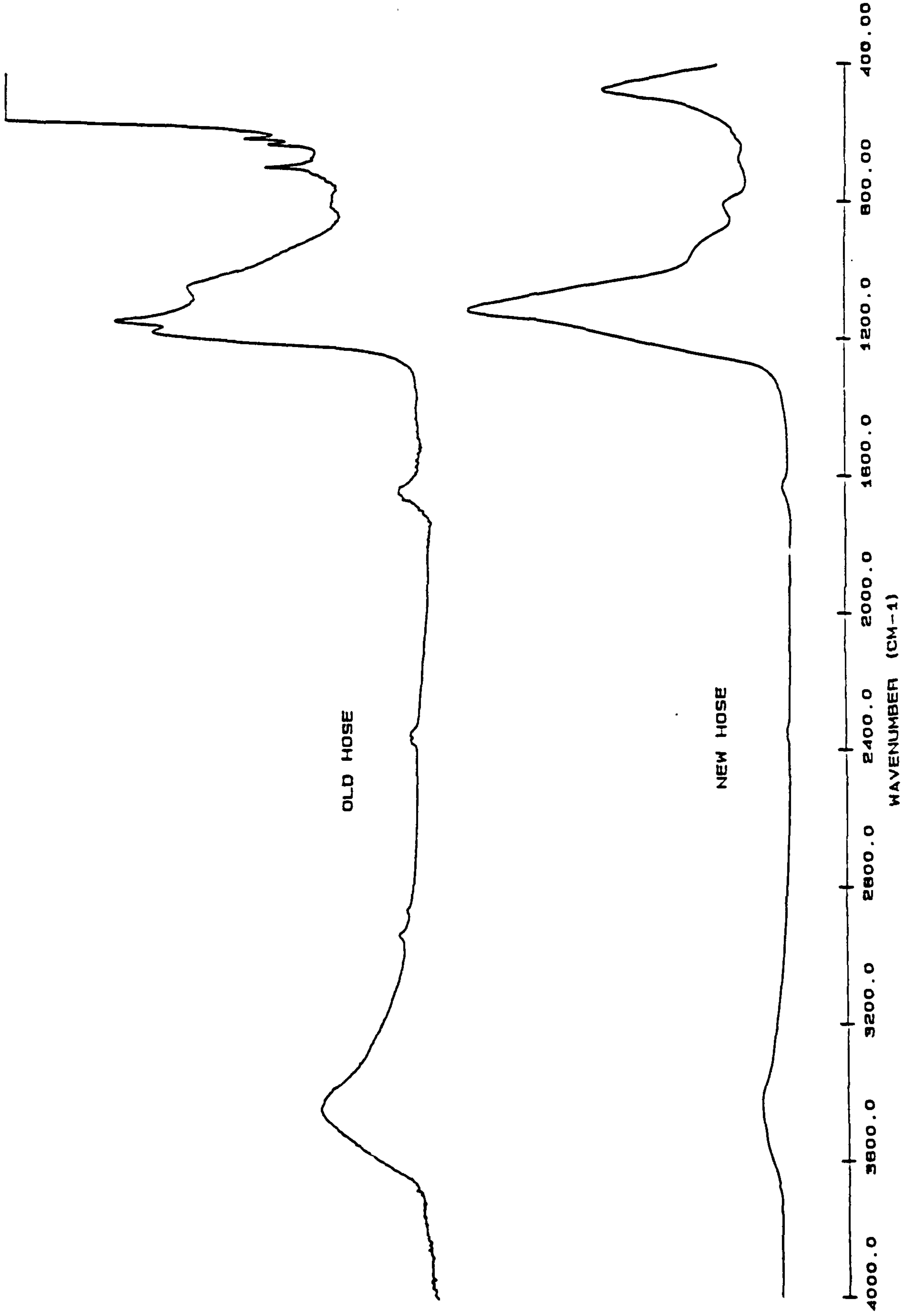

Figure 2-18 - Comparison of New and Old Hose D Inside Ash

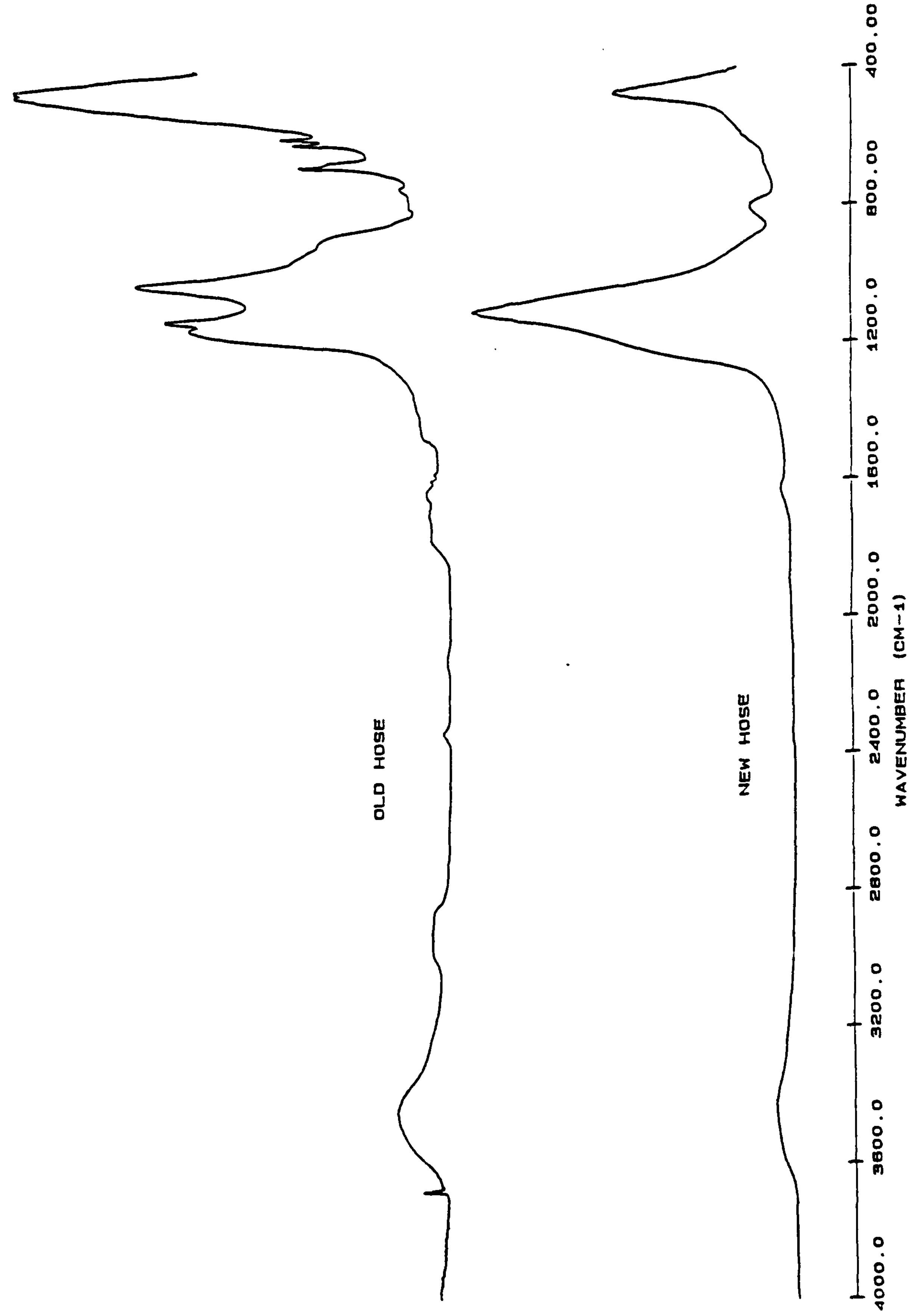

Figure 2-19 - Comparison of New and Old Hose D Outside Ash

Table 2-1
The Full Scale Absorbances of Hose D Pyrolysis Samples

Sample	Full Scale Absorbance Value
Old, Inside, Ground	0.11
Old, Outside, Ground	0.20
New, Inside, Ground	0.10
New, Outside, Ground	0.22
New, Inside, Unground	0.11
New, Outside, Unground	0.23

Table 2-2
The Full Scale Absorbances of Hose D Extraction Samples

Sample	Full Scale Absorbance Value
Old, Inside, Ground	1.22
Old, Outside, Ground	0.62
New, Inside, Ground	0.71
New, Outside, Ground	0.32
New, Inside, Unground	0.62
New, Outside, Unground	1.53

Table 2-3
Peak Height Intensities of Subtracted Files for Hose D Pyrolysis Samples

Files Subtracted	Absorbance of Largest Peak		Percentage of Smallest Full Scale Value	
	Trial 1	Trial 2	Trial 1	Trial 2
0IG – 00G	0.017	0.014	15.4	12.7
NIG – N0G	0.035	0.029	35.0	29.0
NIU – N0U	0.031	0.026	28.2	23.6
0IG – NIG	0.007	0.007	7.0	7.0
0IG – NIU	0.007	0.009	6.4	8.2
00G – N0G	0.034	0.032	17.0	16.0
00G – N0U	0.019	0.028	9.5	14.0
N0G – N0U	0.004	0.011	2.0	5.0

Table 2-4
Peak Height Intensities of Subtracted Files for Hose D Extraction Samples

Files Subtracted	Absorbance of Largest Peak	Percentage of Smallest Full Scale Value
0IG – 00G	0.40	64.5
NIG – N0G	0.22	68.7
NIU – N0U	0.21	33.9
0IG – NIG	0.16	22.5
0IG – NIU	0.18	29.0
00G – N0G	0.09	28.1
00G – N0U	0.10	16.1
N0G – N0U	0.05	15.6

Table 2-5
The Effect of Grinding on % Extraction and TGA Results for the Hose D Inner Tube

Property	Ground	Unground	% Difference
% Extracted	14.5 ± 0.1	12.3 ± 0.2	15.2
% Organic 1			
% Organic 2	48.8 ± 3.7	52.8 ± 1.3	8.2
% Black	42.3 ± 3.7	39.2 ± 0.2	7.3
% Ash	8.9 ± 0.1	8.7 ± 0.3	2.2
Peak Der. Temp. 1 (°C)			
Peak Der. Temp 2 (°C)	481 ± 4	487 ± 3	1.2

Table 2-6
The Effect of Grinding on % Extraction and TGA Results for the Hose D Outer Jacket

Property	Ground	Unground	% Difference
% Extracted	23.9 ± 0.3	19.5 ± 0.5	18.4
% Organic 1	5.5 ± 0.4	7.2 ± 0.1	30.9
% Organic 2	36.7 ± 0.6	35.6 ± 0.4	3.0
% Black	49.0 ± 1.0	49.2 ± 0.6	0.4
% Ash	8.9 ± 0.2	8.0 ± 0.3	11.2
Peak Der. Temp. 1 (°C)	273 ± 1	278 ± 4	1.8
Peak Der. Temp 2 (°C)	467 ± 3	482 ± 0	3.2

Table 2-7
Thermogravimetry Results for Hose D

		% Organics				Polymer Peak Derivative Temp. (°C)	
Sample		Step 1	Step 2	% Black	% Residue	Step 1	Step 2
New, Inner	1	14.3	42.1	35.9	7.7	256.4	474.4
Ground, 13 mg	2	14.3	42.0	36.0	7.7	256.4	476.9
	3	14.1	42.2	35.7	7.8	256.4	474.4
Mean		14.2	42.2	35.9	7.7	256.4	475.2
Standard Deviation		0.1	0.2	0.2	0.1	0.0	1.4
New, Inner	1	13.1	42.0	36.9	8.0	267.3	477.6
Ground, 20 mg	2	13.7	43.9	34.4	8.0	266.7	482.0
	3	13.8	42.4	36.2	7.6	265.7	476.0
Mean		13.5	42.8	35.8	7.9	266.6	478.5
Standard Deviation		0.4	1.0	1.3	0.2	0.8	3.1
New, Inner	1	10.6	47.4	34.1	8.0	277.9	488.1
Unground, 13 mg	2	11.3	47.2	34.0	7.5	274.4	489.7
	3	11.2	46.2	35.0	7.6	284.6	492.3
Mean		11.0	46.9	34.4	7.7	279.0	490.0
Standard Deviation		0.4	0.6	0.6	0.3	5.2	2.1

Table 2-7 (Continued)

Sample		% Organics		% Black	% Residue	Polymer Peak Derivative Temp. (°C)	
		Step 1	Step 2			Step 1	Step 2
New, Inner	1		46.1	45.1	8.8		482.0
Ground, Extracted	2		53.0	38.1	8.9		484.6
13 mg	3		47.2	43.8	9.0		476.9
Mean			42.2	42.3	8.9		481.2
Standard Deviation			3.7	3.7	0.1		3.9
New, Inner	1		46.0	45.0	9.0		489.7
Ground, Extracted	2		50.0	41.2	8.8		474.8
20 mg	3		52.4	38.8	8.8		487.2
Mean			49.5	41.7	8.9		483.9
Standard Deviation			3.2	3.1	0.1		8.0
New, Inner	1		52.5	39.1	8.4		489.7
Unground, Extracted	2		54.2	39.0	8.8		487.2
13 mg	3		51.7	39.4	8.9		484.6
Mean			52.8	39.2	8.7		487.2
Standard Deviation			1.3	0.2	0.3		2.5

Table 2-7 (Continued)

Sample		% Organics		% Black	% Residue	Polymer Peak Derivative Temp. (°C)	
		Step 1	Step 2			Step 1	Step 2
New, Outer	1	19.8	33.0	40.1	7.1	276.6	474.4
Ground, 13 mg	2	19.2	33.9	39.4	7.5	273.5	471.8
	3	17.8	34.6	39.0	8.8	276.5	476.5
Mean		18.9	33.8	39.5	7.8	275.5	474.2
Standard Deviation		1.0	0.8	0.6	0.9	1.8	2.3
New, Outer	1	19.4	30.0	44.0	6.6	276.1	465.8
Ground, 20 mg	2	16.8	31.6	42.6	9.0	272.6	467.5
	3	19.0	33.9	40.2	6.4	269.2	469.2
Mean		18.4	31.8	42.3	7.5	272.6	467.5
Standard Deviation		1.4	2.0	1.9	1.3	3.4	1.7
New, Outer	1	17.4	36.5	39.6	6.5	275.2	480.3
Unground, 13 mg	2	17.2	36.1	40.3	6.4	273.5	476.1
	3	16.8	36.2	40.5	6.5	276.1	481.2
Mean		17.1	36.3	40.1	6.5	274.9	479.2
Standard Deviation		0.3	0.2	0.5	0.1	1.3	2.7

Table 2-7 (Continued)

Sample		% Organics Step 1	% Organics Step 2	% Black	% Residue	Polymer Peak Derivative Temp. (°C) Step 1	Polymer Peak Derivative Temp. (°C) Step 2
New, Outer	1	5.2	36.9	49.0	8.9	273.1	470.5
Ground, Extracted	2	5.3	36.0	50.0	8.7	273.1	465.4
13 mg	3	5.9	37.1	47.9	9.1	271.8	466.7
Mean		5.5	36.7	49.0	8.9	272.7	467.5
Standard Deviation		0.4	0.6	1.0	0.2	0.7	2.6
New, Outer	1	5.7	36.8	49.1	8.4	270.1	470.1
Ground, Extracted	2	5.7	35.3	50.5	8.5	280.3	475.2
20 mg	3	6.1	36.6	48.6	8.7	271.8	471.8
Mean		5.8	36.2	49.4	8.5	274.1	472.4
Standard Deviation		0.2	0.8	1.0	0.2	5.5	2.6
New, Outer	1	7.1	35.3	49.9	7.7	276.9	482.0
Unground, Extracted	2	7.2	35.4	49.1	8.3	274.8	482.0
13 mg	3	7.3	36.0	48.6	8.1	282.0	482.0
Mean		7.2	35.6	49.2	8.0	277.9	482.0
Standard Deviation		0.1	0.4	0.6	0.3	3.7	0.0

Table 2-7 (Continued)

Sample		% Organics Step 1	% Organics Step 2	% Black	% Residue	Polymer Peak Derivative Temp. (°C) Step 1	Polymer Peak Derivative Temp. (°C) Step 2
Old, Inner	1	10.6	46.1	38.9	4.4	255.5	476.0
Ground, 13 mg	2	10.5	46.8	38.9	3.8	266.7	487.2
	3	10.1	46.8	39.3	3.8	264.1	487.2
Mean		10.4	46.6	39.0	4.0	262.1	483.5
Standard Deviation		0.3	0.4	0.2	0.3	5.9	6.5
Old, Inner	1	9.7	43.2	43.5	3.6	261.5	476.9
Ground, 20 mg	2	9.5	45.1	41.8	3.6	259.0	474.4
	3	9.9	44.0	41.8	4.3	259.0	474.4
Mean		9.7	44.1	42.4	3.8	259.8	475.2
Standard Deviation		0.2	1.0	1.0	0.4	1.4	1.4

Table 2-7 (Continued)

Sample		% Organics		% Black	% Residue	Polymer Peak Derivative Temp. (°C)	
		Step 1	Step 2			Step 1	Step 2
Old, Inner	1		53.1	42.7	4.2		476.9
Ground, Extracted	2		52.2	42.8	4.9		479.5
13 mg	3		50.2	43.7	6.1		476.9
Mean			51.8	43.1	5.1		477.8
Standard Deviation			1.5	0.6	1.0		1.5
Old, Inner	1		51.5	44.6	3.9		476.9
Ground, Extracted	2		49.7	46.2	4.1		476.9
20 mg	3		51.0	44.3	4.7		482.0
Mean			50.7	45.0	4.2		478.6
Standard Deviation			0.9	1.0	0.4		2.9

Table 2-7 (Continued)

Sample		% Organics Step 1	% Organics Step 2	% Black	% Residue	Polymer Peak Derivative Temp. (°C) Step 1	Polymer Peak Derivative Temp. (°C) Step 2
Old, Outer Ground, 13 mg	1	19.3	33.3	44.6	2.8	271.8	481.4*
	2	19.6	31.9	45.2	3.3	274.4	478.1*
	3	20.5	31.3	46.3	1.9	270.1	482.0
Mean		19.8	32.2	45.4	2.7	272.1	480.5
Standard Deviation		0.6	1.0	0.9	0.7	2.2	2.1
Old, Outer Ground, 20 mg	1	19.7	30.9	47.1	2.3	271.8	482.0*
	2	19.2	31.0	47.1	2.7	268.0	478.2*
	3	19.3	30.4	47.7	2.6	269.2	477.6*
Mean		19.4	30.8	47.3	2.5	269.7	479.3
Standard Deviation		0.3	0.3	0.3	0.2	1.9	2.4

*Two Step 2 peaks

Table 2-7 (Continued)

Sample		% Organics				Polymer Peak Derivative Temp. (°C)	
		Step 1	Step 2	% Black	% Residue	Step 1	Step 2
Old, Outer	1	7.1	35.6	53.6	3.7	273.9	474.0*
Ground, Extracted	2	6.7	33.7	55.7	3.9	270.9	476.5*
13 mg	3	6.8	34.9	53.5	4.8	273.5	476.1*
Mean		6.9	34.7	54.3	4.1	272.8	475.5
Standard Deviation		0.2	1.0	1.2	0.6	1.6	1.3
Old, Outer	1	7.3	39.6	49.5	3.6	277.3	482.5
Ground, Extracted	2	6.9	34.3	55.4	3.4	278.2	481.0*
20 mg	3	7.6	34.4	54.3	3.7	275.2	481.0*
Mean		7.3	36.1	53.1	3.6	276.9	481.5
Standard Deviation		0.3	3.0	3.1	0.1	1.5	0.9

*Two Step 2 peaks

Table 2-8
Compositional Analysis of the Outer Jacket of New Hose D

Component	Percentage Based on Extraction	Percentage Based on TGA
Extractables	23.9	19.4
Non-Extractable Volatiles	4.4	4.4
Organics	29.6	29.6
Black	39.5	39.5
Ash	7.2	7.2

Table 2-9
Compositional Analysis of the Inner Tube of New Hose D

Component	Percentage Based on Extraction	Percentage Based on TGA
Extractables	14.5	15.1
Non-Extractable Volatiles	0.0	0.0
Organics	42.6	41.4
Black	36.9	35.9
Ash	7.8	7.6

Table 2-10
Detailed Compositional Analysis of the Inner Tube of the Rubber Hoses

Sample	% Extractables	Organics 1	Organics 2	% Black	% Ash
Hose A (new)	16 ± 1		43 ± 3	38 ± 2	5 ± 1
Hose A (old)	16 ± 1		43 ± 2	37 ± 1	6 ± 1
Hose B	13 ± 1		34 ± 2	28 ± 3	27 ± 1
Hose C	10 ± 1		50 ± 2	37 ± 3	4 ± 1
Hose D (new)[a]					
Trial 1	16 ± 2		44 ± 2	34 ± 2	8 ± 2
Trial 2	15 ± 1		43 ± 4	37 ± 4	8 ± 1
Hose D (old)	10 ± 1		47 ± 2	39 ± 1	5 ± 1

[a] Trial 1 is from part 1 results
Trial 2 is from part 2 results

Table 2-11
Detailed Compositional Analysis of the Outer Jacket of the Rubber Hoses

Sample	% Extractables	Organics 1	Organics 2	% Black	% Ash
Hose A (new)	27 ± 1	6 ± 1	28 ± 3	31 ± 1	12 ± 1
Hose A (old)	31 ± 3	6 ± 1	27 ± 2	30 ± 1	13 ± 2
Hose B	13 ± 1	24 ± 2	15 ± 1	40 ± 2	9 ± 1
Hose C	12 ± 2	19 ± 3	24 ± 3	33 ± 2	13 ± 2
Hose D (new)[a]					
Trial 1	23 ± 2	5 ± 1	31 ± 2	37 ± 3	8 ± 2
Trial 2	24 ± 1	4 ± 1	30 ± 1	40 ± 1	7 ± 1
Hose D (old)	21 ± 2	6 ± 1	29 ± 1	45 ± 2	3 ± 1

[a] Trial 1 is from part 1 results
Trial 2 is from part 2 results

Table 2-12
Compositional Analysis of the Inner Tube of New and Old Hose A

Component	New	Old	% Difference
% Extractables	16 ± 2	16 ± 1	0.0
% Organic 1			
% Organic 2	43 ± 3	43 ± 2	0.0
% Black	38 ± 2	37 ± 1	2.6
% Ash	5 ± 1	6 ± 1	20.0

Table 2-13
Compositional Analysis of the Outer Jacket of New and Old Hose A

Component	New	Old	% Difference
% Extractables	27 ± 1	31 ± 3	14.8
% Organic 1	6 ± 1	6 ± 1	0.0
% Organic 2	28 ± 3	27 ± 2	3.6
% Black	31 ± 1	30 ± 1	3.2
% Ash	12 ± 1	13 ± 2	8.3

Table 2-14
Compositional Analysis of the Inner Tube of New and Old Hose D

Component	New	Old	% Difference
% Extractables	15 ± 1	10 ± 1	33.3
% Organic 1			
% Organic 2	43 ± 4	47 ± 2	9.3
% Black	37 ± 4	39 ± 1	5.4
% Ash	8 ± 1	5 ± 1	37.5

Table 2-15
Compositional Analysis of the Outer Jacket of New and Old Hose D

Component	New	Old	% Difference
% Extractables	24 ± 1	21 ± 2	4.2
% Organic 1	4 ± 1	6 ± 1	50.0
% Organic 2	30 ± 1	29 ± 1	3.3
% Black	40 ± 1	45 ± 2	12.5
% Ash	7 ± 1	3 ± 1	57.1

APPENDIX C

TEST METHOD FOR CHARACTERIZATION OF RUBBER FUEL HOSES BY ACETONE EXTRACTION, THERMOGRAVIMETRY AND FOURIER TRANSFORM INFRARED SPECTROSCOPY

1. Scope

1.1 The method covers the characterization of rubber fuel hoses in terms of their composition and materials of construction.

2. Applicable Documents

2.1 ASTM Standards

D297 - Rubber Products - Chemical Analysis, Sec 16-18
D3421 - Extraction and Analysis of Plasticizer Mixtures from Vinyl Chloride Plastics
D3677 - Rubber-Identification by Infrared Spectrophotometry

2.2 EPA Standards

SW-870 - Test for the Extractable Content of Unexposed Lining Materials

3. Apparatus

3.1 Liquid Nitrogen Grinder - Optional

3.2 Extraction Apparatus - Either a Soxhlet extraction apparatus or a rubber extraction apparatus are acceptable.

3.3 Thermogravimetric Analyzer

3.4 Ashing Furnace

3.5 FTIR Spectrophotometer

4. Collection and Preparation of Test Specimens

4.1 Scope - This method covers the procedures for collecting test specimens from different types of hoses.

4.2 Method A

4.2.1 Scope - This method describes a procedure for obtaining test specimens from rubber fuel hoses that are relatively thick and contain fiber reinforcements.

4.2.2 Procedure

4.2.2.1 Cut three cylindrical strips, approximately three inches wide from both ends and the center of the hose length with a band saw or other appropriate tool.

4.2.2.2 Cut through the cylinders to produce three strips of hose.

4.2.2.3 Cut from each strip, three pieces, 1"x6" with a steel die and an appropriate press. Each set of three pieces will produce one test specimen. If the strip is too thick to be die cut, the specimens may be taken directly from the strip as long as no rubber is collected from the cut edges.

4.2.2.4 Remove about 10 g of the inner tube and outer jacket of the hose from each of the three sets of three pieces. A scalpel is useful for slicing thin strips. Care must be taken to avoid cutting into adjacent layers. This is especially important for hose with adjacent black layers because the interface between layers is difficult to see.

4.2.2.5 Place each 10 g specimen in six separate containers and label them. Be sure to label them as inner tube or outer jacket.

4.2.2.6 Cut each 10 g specimen into pieces about 1cm^2 with a scalpel.

4.2.2.7 Divide the specimen into two equal portions and grind them in a suitable liquid nitrogen grinder.[1] (This step can be omitted but should be noted in the report.)

4.3 Method B

4.3.1 Scope - This method describes a procedure for obtaining test specimens from rubber fuel hoses that contain steel cord reinforcement and cannot be cut on a band saw. This method can also be used for hoses covered in Method A (Section 3.2) if a band saw is not available.

4.3.2 Procedure

4.3.2.1 Cut three discs from the center of the tube length with a hole saw about two inches in diameter. Other sizes may also be used. These three discs will produce one inner test specimen and one outer test specimen.

4.3.2.2 Remove about 10 g of the inner tube and the outer jacket of the hose from the three disks with a scalpel. Care must be taken to avoid cutting into adjacent layers or including cut edges into the specimen.

4.3.2.3 The other two 10 g test specimens can be obtained directly from each end of the hose length by slicing off pieces with a scalpel.

4.3.2.4 Prepare for testing as described above (4.2.2.5 - 4.2.2.7)

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[1] Such as Spex Industries Model 6700 Freezer Mill

4.4 Method C

4.4.1 Scope - This method describes a procedure for obtaining test specimens from rubber fuel hoses that are very thin and have a woven fiber reinforcement sandwiched between the inner and outer layers of rubber.

4.4.2 Procedure

4.4.2.1 Cut out three sets of two 1" x 6" strips from the ends and the center of the hose length with a steel die and an appropriate press. Be sure to note inside and outside.

4.4.2.2 From one end of a strip, cut into the fabric layer about 1/2". Then, peel the two rubber layers apart with pliers. This should produce one clean layer and one layer still bonded to the woven fabric. Soak the fabric covered rubber layer in warm water for about one hour then pull off the fabric.

4.4.2.3 Collect three, 10 g specimens of the inner and outer layers and prepare for testing as described above (4.2.2.5 - 4.2.2.7).

5. Acetone Extraction

5.1 Scope - This method covers the removal of all constituents soluble in acetone from rubber samples found in fuel hoses.

5.2 Extraction Apparatus - A Soxhlet extraction apparatus or the rubber extraction apparatus are both acceptable. Adjustments in sample size and solvent volume should be made accordingly.

5.3 Solvent - Acetone, HPLC grade or equivalent.

5.4 Samples - The test specimen shall be a ground powder or pieces not more than 1 cm long on any side.

5.5 Procedure

5.5.1 This shall be done on each of the three samples obtained in Section 4.

5.5.2 Weigh 4-6 g of the rubber into a dried, tared extraction thimble (2-3 g for the rubber extraction apparatus). Small thimbles shall be plugged with a cotton ball to prevent loss of sample.

5.5.3 Add a volume of solvent to the flat bottom flask equal to two times the capacity of the extractor barrel. Add boiling chips to reduce bumping.

5.5.4 Assemble the apparatus and run the extraction for 24 hours.

5.5.5 Remove the thimble, allow it to drip dry and thoroughly dry it in a vacuum oven or desiccator until a constant weight is achieved.

5.5.6 Reweigh the thimble plus extracted rubber, label and store the sample for further analysis.

5.5.7 Evaporate the extract by any appropriate means, dry, label and save the sample for IR analysis.

5.6 Calculations - Calculate the percent extractables as follows:

$$\% = [(A - B) / A] \times 100$$

where A is the initial sample weight and B is the final sample weight.

5.7 Precision - These data are based on tests of 10 samples taken from one hose and performed on 5 different days by two operators.

5.7.1 Repeatability (Single Laboratory) - The repeatability has been estimated to be ±1.7%. Two results are significantly different if their difference exceeds 4.2% extractables.

5.7.2 Reproducibility (Multi-Laboratory) - No data have been obtained.

5.8 Acceptance - A production sample will be considered identical to the first article if the mean percentage extractables falls within plus or minus two standard deviations of the first article values.

6. Thermogravimetry

6.1 Scope - This method describes the determination of volatiles, organics, black and ash of an extracted rubber sample by thermogravimetry.

6.2 Apparatus - Any instrument that continuously monitors the mass of a sample as it is heated in a controlled manner in a specific atmosphere is acceptable.

6.3 Procedure

6.3.1 This shall be done on each of the three samples from Section 4.

6.3.2 Calibrate the balance according to the manufacturers recommendations.

6.3.3 Start nitrogen flow (100 ml/min) and let the balance stabilize. Zero balan

6.3.4 Place 10-20 mg of rubber into the sample pan and let the balance stabilize.

6.3.5 Ramp 25°C/min to 1000°C and switch from nitrogen to air at 600°C.

6.4 Thermal Curve - Prepare a plot of percent weight and the derivative of percent weight versus temperature. Record the percent weight loss for each peak in the derivative curve plus the percent volatiles and residue at 1000°C. Percent volatiles are determined by the weight loss from the start of the experiment to right before the first derivative peak.

6.5 Data Table - Prepare a table of the percent weight loss for each step on the thermal curve, the percent volatiles, and the residue. Include the mean and standard deviation.

6.6 Acceptance - A production sample will be considered equivalent to the first article if each weight loss falls within two standard deviations of the first article.

7. Infrared Spectroscopy

7.1 Scope - This method covers the procedures used to generate IR spectra of extracted rubber, extract residue, and ash.

7.2 Rubber Analysis by Pyrolysis

7.2.1 Procedure

7.2.1.1 This shall be performed on each of the three samples from Section 4.

7.2.1.2 Prepare extract, dry and place a small amount in the bottom of a glass test tube. The sample size is not critical but should remain relatively constant from sample to sample.

7.2.1.3 Hold the tube at about 45° from vertical and heat with the hottest part of a gas flame for 15 seconds or until the resulting smoke condenses on the cool part of the tube.

7.2.1.4 Allow the condensed oil to dry for at least one hour before IR analysis. Moisture and other volatiles can contaminate the sample.

7.2.1.5 Transfer the condensed oil from the test tube to a suitable IR window with a cotton swab. Smear the oil to a uniform thickness.

7.2.1.6 Collect an IR spectrum, wait 5 minutes and collect another. Repeat this until there is no change in the resulting spectrum. There are volatile components present after pyrolysis that interfere and therefore shall be allowed to evaporate completely.

7.2.2 IR Spectra - Produce a hard copy of the resulting spectra in a manner appropriate to the instrument. If data manipulation is available, the three files shall be coadded to produce a composite of the three samples.

7.2.3 Acceptance - No acceptance criteria for FTIR has been determined.

7.3 Extract Residue Analysis

7.3.1 Procedure

7.3.1.1 This shall be performed on each of the three samples from Section 4.

7.3.1.2 The residue from the extraction solvent shall be thoroughly dry.

7.3.1.3 Add a few milliliters of dry acetone to the extract residue and swirl the container to dissolve some residue.

7.3.1.4 Place two drops of the solution on an appropriate IR window and allow to dry into a thin film.

7.3.1.5 Collect an IR spectrum, wait 2 minutes and collect another. This will ensure that the solvent has dried completely.

7.3.2 IR Spectra - See Section 7.2.2

7.4 Ash Analysis

7.4.1 Procedure

7.4.1.1 This shall be performed on each of the three samples from Section 4.

7.4.1.2 Prepare an ash sample by heating a rubber sample in a furnace until a homogeneous powder remains. The ash time will be a function of furnace temperature. The temperature will be recorded.

7.4.1.3 Prepare a KBr pellet for IR analysis with any appropriate die and press designed for this purpose.

7.4.1.4 Collect an IR spectrum for each sample.

7.4.2 IR Spectra - See Section 7.2.2

8. Report

8.1 The report shall include, but not be limited to the following:

8.1.1 Any deviations from the method.

8.1.2 How the samples were prepared for extraction (ground or cut).

8.1.3 Type of extraction apparatus and approximate size of sample.

8.1.4 % Extractables for each sample, the mean, and the standard deviation.

8.1.5 Type of TGA used.

8.1.6 TG thermal curves for each sample clearly labeled with weight losses of each step and the residue.

8.1.7 Percent weight loss for each step in the thermal curve and the residue, the mean, and the standard deviation.

8.1.8 Furnace temperature for ash preparation.

8.1.9 Type of IR Spectrophotometer.

8.1.10 IR Spectra of pyrolyzed rubber, extract, and ash. One for each sample, or one computer generated composite spectrum shall be provided.

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