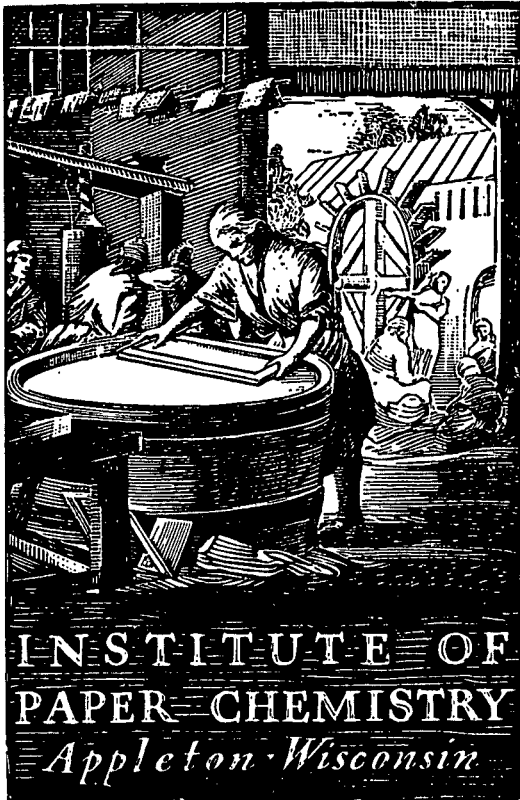


**TECHNICAL**



**DETERMINATION OF PULP YIELD  
AND COMPOSITION BY  
PYROLYSIS-GAS CHROMATOGRAPHY**

Project 2926-5

Report One

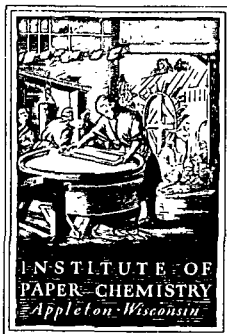
A Progress Report

to

**FOURDRINIER KRAFT BOARD INSTITUTE, INC.**

March 14, 1975

( FORM LETTER )



THE INSTITUTE OF PAPER CHEMISTRY  
Post Office Box 1048  
Appleton, Wisconsin 54911  
Phone: 414/734-9251

April 25, 1975

Project 2926-5

Dear Mr. Boren:

Enclosed is a copy of Report One, Project 2926-5, entitled Determination of Pulp Yield and Composition by Pyrolysis-Gas Chromatography, dated March 14, 1975. This study was initiated because of interest by various members of the Fourdrinier Kraft Board Institute, Inc., in an improved method for determining kraft pulp yields. The traditional method has been Kappa number, however, this may give misleading results when applied to high-yield pulps -- 55% and over.

A method has been developed for the characterization of S. W. high-yield kraft pulps by use of pyrolysis-gas chromatography. This involves the pyrolysis of the pulp sample and an analysis by gas chromatography of the products generated which in turn can be related to yield via correlation.

The possible applicability of the method to a mill laboratory is discussed. The need for reference pyrograms of pulps of known yield for the particular process and wood species involved is emphasized.

Yours very truly,

R. C. McKee, Chairman  
Container Section

Mr. A. R. Boren  
President  
Fourdrinier Kraft Board  
Institute, Inc.

RCM/mjm  
Enclosure

Same mailing to T. J. Gross

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THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

DETERMINATION OF PULP YIELD AND COMPOSITION BY  
PYROLYSIS-GAS CHROMATOGRAPHY

SUMMARY

A method is described for the characterization of high-yield kraft pulps by use of pyrolysis-gas chromatography. The method provides an alternative to the use of Kappa number for high-yield pulps. The pyrograms resulting from pulp pyrolyses contain certain peaks which are representative of the residual lignin and other peaks which reflect the carbohydrate content. The method relies on measurement of relative peak heights to provide an indication of the relative amounts of lignin and carbohydrates present. A parameter is obtained from the pyrogram which correlates well with lignin content and yield of kraft pulps in the range of 55-70% yield. The parameter (3L value) is dependent on three lignin-related peaks and two carbohydrate-related peaks. The average error for the 3L parameter based on three to five replicate pyrolyses of each pulp is within  $\pm 3\%$ .

The lignin peaks of primary value to the method were shown by mass spectrometry to be creosol, 4-vinylguaiacol and trans-isoeugenol. Guaiacol was also identified. The carbohydrate peaks have not been identified but appear to be derived from both cellulose and hemicelluloses in the pulp. Useful peaks distinctive only of hemicelluloses were not observed. Limited experiments showed that inorganic materials present in amounts over 2% based on the weight of pulp could interfere with the correlation by altering the 3L parameter.

The possible applicability of the method to a mill laboratory is discussed. Applicability will depend on reference pyrograms of pulps of known yield relating to the particular process and wood species used.

## INTRODUCTION

### BACKGROUND

This research was initiated because of an interest by various members of the F.K.I. Technical Division in an improved method for determining kraft pulp yields. The traditional method of choice has been Kappa number measurement, but misleading results are obtained when this method is applied to high-yield pulps (over 55%).

The determination of pulp yield is desirable from the standpoint of achieving better control of the pulping process. There are certain difficulties, however, associated with the analysis of a pulp to obtain a yield value. In kraft pulping, the major components of the wood are removed at different rates and these rates have different temperature dependences. In the early stages of the cook before the temperature has risen to 170°C, the major material loss is that of carbohydrate. When the temperature reaches 170°, the dissolution of lignin becomes much more important than loss of carbohydrate. Recent work (1) documents in detail the changes in lignin and carbohydrate composition of a series of kraft pulps at various yield levels from slash pine.

Since, in the yield ranges of primary interest, the major difference between kraft pulps of different yields is their lignin content, it is not surprising that correlations have been developed between lignin content and yield. Figure 1 illustrates that for kraft pulping the relationship between lignin content and yield is not simple and is dependent on the nature of the wood species (2). Lignin content is only a valid measure of pulp yield if a suitable correlation curve has been developed for the particular wood species.

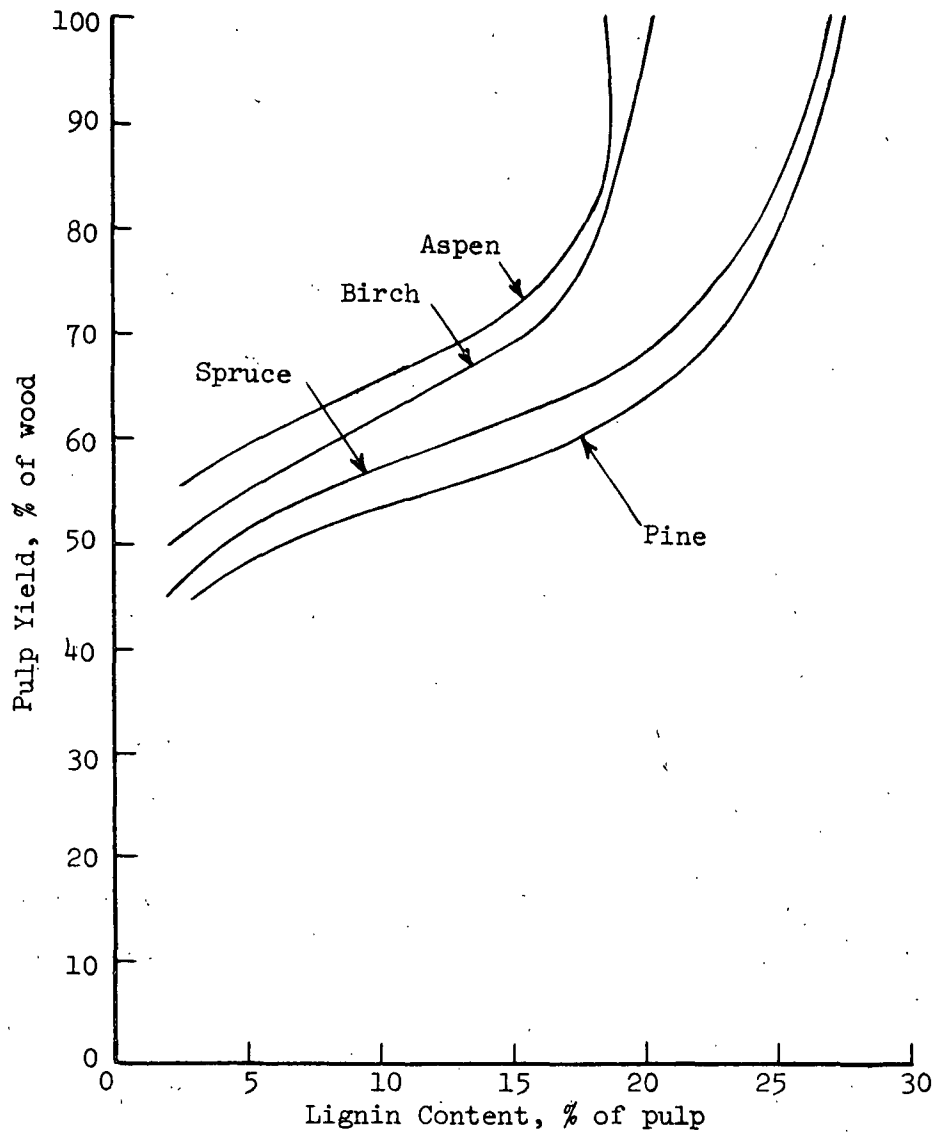


Figure 1. Relationship Between Pulp Yield and Lignin Content for Various Wood Species (2)

It is also reasonable to expect variables of the cooking process such as the temperature and cooking time profile, presence of additives, alkalinity and sulfidity to have an influence on the relationship between lignin content and yield of the pulp. For example, two pulps from the same wood might have the same lignin content but different yield levels because of the difference in the pulping conditions. Thus, it is important to know what the lignin

content-pulp yield relationship is for a particular pulping process before lignin content can be used as a reliable indicator of yield.

#### PYROLYSIS-GAS CHROMATOGRAPHY

Prior to the beginning of this research program exploratory studies were carried out which indicated that pyrolysis-gas chromatography held promise as a means of characterizing pulp samples in "fingerprint" fashion. That is, it appeared that high temperature pyrolysis followed by gas chromatographic separation of products could be done in a controlled, reproducible manner. Further, it seemed likely on the basis of ongoing thesis research (3) at the Institute that the resulting pyrograms contained peaks some of which would be related only to residual lignin and others would be related primarily to carbohydrates (cellulose and hemicelluloses).

Many applications of pyrolysis-gas chromatography to polymer identification are described in the literature. Frequently, degradation of a polymer or copolymer produces substantial amounts of the monomer units (4-7). Identification of the monomer units is achieved by retention times and/or spectral methods. Recent work covering applications of pyrolysis-gas chromatography to polymers has been reviewed (8).

A considerable amount of work has been published involving pyrolysis of wood and of the various individual components of wood including cellulose, certain hemicelluloses and lignin. In marked contrast, there is essentially nothing in the literature concerning the application of pyrolysis-gas chromatography as a means of characterizing pulps.

The literature pertinent to pyrolysis of wood and of lignin preparations has been reviewed by Fleck (3). Two extensive discussions of pyrolysis of cellulose have appeared recently with numerous references (9,10). The complexity of cellulose pyrolysis can be illustrated by Schwenker and Beck's (11) finding that 37 different products were detected after pyrolysis-gas chromatography of purified cotton heated to 370°. Previous work (10) has demonstrated that important variables which influence the relative amounts of pyrolysis products include rate of heating, pyrolysis temperature, and inorganic impurities. The mechanism of pyrolysis of cellulose has recently been discussed (12).

Few studies have focused on the pyrolysis of hemicelluloses. High-yield kraft pulps retain a portion of the hemicelluloses of the original wood. With softwood pulps these include glucuronoxylan and galactoglucomannan. The major volatile products resulting from pyrolysis of a 4-O-methylglucuronoxylan were reported to be 2-furaldehyde, water, methanol and carbon dioxide (13). Since 2-furaldehyde (a five-carbon system) has also been produced from hexose systems, including cellulose, its value as a possible indicator of hemicellulose content is uncertain. It has been noted (14,15) that xylan is less thermally stable than other wood components.

Recent thesis research (3) at the Institute involved the use of pyrolysis-gas chromatography to characterize the changes in the lignin (left in the wood) after loblolly pine had been treated with dilute peracetic acid for various durations. With the aid of mass spectrometry, the major lignin product peaks were shown to be guaiacol, creosol, 4-ethylguaiacol, 4-propylguaiacol, 4-vinylguaiacol, eugenol, trans-isoeugenol and vanillin. In general, these findings confirmed earlier reports concerning pyrolyses of a variety of

lignin preparations (16-19) where product identification had been based on chromatographic retention times.

Of particular interest in Fleck's work (3) was the observation of real and reproducible differences in pyrograms of partly delignified wood samples. Differences were detected in the relative amounts of lignin products when pyrolyses were run on, for example, samples at the 98 and 99% yield levels. In the earliest stage of delignification (first 1% yield loss), the amount of vanillin and homovanillin products was seen to increase in the pyrograms while the quantity of other products decreased. The fact that pyrolysis-gas chromatography was sensitive enough to detect such differences between very closely related materials encouraged us to press forward and try to apply the method to the characterization of pulps.

#### RESEARCH PROGRAM

The objective of this research was to follow up encouraging preliminary studies and explore thoroughly the feasibility of employing pyrolysis-gas chromatography as a method for characterizing high-yield pulps. The research was to focus on softwood kraft pulps with the main emphasis on pulps in the approximate yield range 55-70%. If promising results were obtained, later research could be directed toward broadening the scope to hardwood kraft pulps and to other pulping processes.

The approach was to include the study of major variables which would affect the appearance and reproducibility of pyrograms. These would include particularly pyrolysis conditions and operating conditions associated with the subsequent gas chromatographic separation of products. It was believed that certain peaks would be found that would be representative of lignin and that others would reflect the presence of carbohydrates. It was recognized that

hemicelluloses might well give rise to pyrolysis products similar and, in some cases, identical with those resulting from cellulose. If, however, a product uniquely derived from a hemicellulose were found, this could be of considerable value in determining pulp composition.

The research program was also to include use of mass spectrometry for identification of major peaks which would be important to the development of a quantitative method.

It was hoped that this research would lead to a method of characterizing the pulps in terms of composition and yield. If such a method was shown to be feasible, then a mill laboratory could utilize it with appropriate reference pyrograms from standard pulps prepared according to its own wood furnish and pulping conditions.

EXPERIMENTAL

KRAFT PULPS

Two series of kraft pulps were employed in the pyrolysis experiments. Most of the work was carried out using pulps from Series A having yields in the range 54.4-70.0%. Table I gives the results of lignin analysis of these pulps. Klason lignin was determined using TAPPI Standard Method T 222 os-74, and the acid-soluble lignin was measured by suitable dilution of the Klason lignin filtrate to 500 ml followed by measurement of absorbance at 208 nm where lignin absorptivity was taken as 105 liters  $g^{-1} cm^{-1}$ .

TABLE I

YIELDS AND LIGNIN CONTENTS OF KRAFT PULPS -  
SERIES A

Pulp No.	Yield, %	Klason Lignin, %	Acid-Soluble Lignin, %	Total Lignin, %
A-1	70.0	23.4	0.45	23.8
A-2	66.5	20.8	0.50	21.3
A-3	63.7	18.0	0.53	18.5
A-4	57.4	14.4	0.54	14.9
A-5	57.5	12.6	0.5 <sup>a</sup>	13.1
A-6	54.4	10.6	0.53	11.1

<sup>a</sup> Estimated value, not determined.

The Series A pulps were prepared in the pulp laboratory using southern pine chips which had been screened (4 mesh). The pulps were prepared simultaneously in bombs which were rotated three times per minute in a controlled temperature oil bath. Each bomb was charged with 75 g (ovendry basis) of chips and kraft

cooking liquor to provide 15% active alkali (as Na<sub>2</sub>O) and 25% sulfidity. The bombs were brought to a maximum temperature of 172° over 60 min and were removed and quenched at intervals to provide pulps of different yields. The pulps were fiberized in a Waring Blendor, and the fibers were washed thoroughly on a sintered glass funnel. Oven drying of the pulp allowed calculation of the yield. Pulp No. A-4 was found to be of lower yield than anticipated (57.4 vs. 60%) based on the cooking time.

Series B pulps were softwood kraft pulps (pine) obtained from St. Regis Paper Company. Kappa numbers were obtained for each of these pulps and Klason and acid-soluble lignin were either measured or estimated as indicated in Table II.

TABLE II

YIELDS AND LIGNIN CONTENTS OF KRAFT PULPS -  
SERIES B

Pulp No.	Yield, %	Kappa No.	Klason Lignin, %	Acid-Soluble Lignin, %	Total Lignin, %
B-1	61.2	115.8	17.4	0.47	17.9
B-2	57.9	104.8	(15.2) <sup>a</sup>	0.5 <sup>b</sup>	15.7
B-3	53.5	85.5	12.4	0.49	12.9
B-4	50.8	68.8	(10.0) <sup>a</sup>	0.5 <sup>b</sup>	10.5
B-5	49.7	53.2	7.5	0.47	8.0

<sup>a</sup>Estimated on basis of Kappa no. (0.145) = Klason lignin.

<sup>b</sup>Estimated on basis of other measured values.

In order to prepare the pulp samples for pyrolysis experiments, a 2-3 g wedge was cut out of the dried pulp disk. The wedge was pulled apart, and any shives present were discarded. The pulp was then fed into a Wiley mill fitted with a No. 40 screen. This yielded finely divided pulp fibers which could be conveniently loaded into a pyrolysis sample tube.

#### RELATED REFERENCE MATERIALS

Interpretation of pyrograms resulting from kraft pulps was aided by pyrolysis of reference materials such as hemicelluloses, an isolated lignin and pure cellulose. The cellulose used was a sample of cotton linters. Hemicellulose samples were obtained from N. S. Thompson and E. E. Dickey. As a representative xylan, a sample of glucuronoxylan isolated from yellow poplar heartwood was chosen. The mannan selected was a glucomannan isolated from Englemann spruce. A fir holopulp sample (chlorite delignification) was obtained from N. S. Thompson.

The isolated lignin sample used was a dioxane lignin from loblolly pine. The procedure for its preparation involved removal of extractives from wood meal by acetone followed by extraction with 0.2N HCl in dioxane-water (9:1) (3).

#### PYROLYSIS-GAS CHROMATOGRAPHY: EQUIPMENT AND METHOD

Pyrolyses were run using a Hamilton multipurpose sampling system, and the volatile products were swept into a Varian Model 1400 gas chromatograph. The equipment is shown in Fig. 2 along with the Du Pont 21-491 mass spectrometer (at the extreme right) which was used at one point in the work to identify four of the major pyrolysis products. A close-up view of the furnace and heated line assembly is provided in Fig. 3.

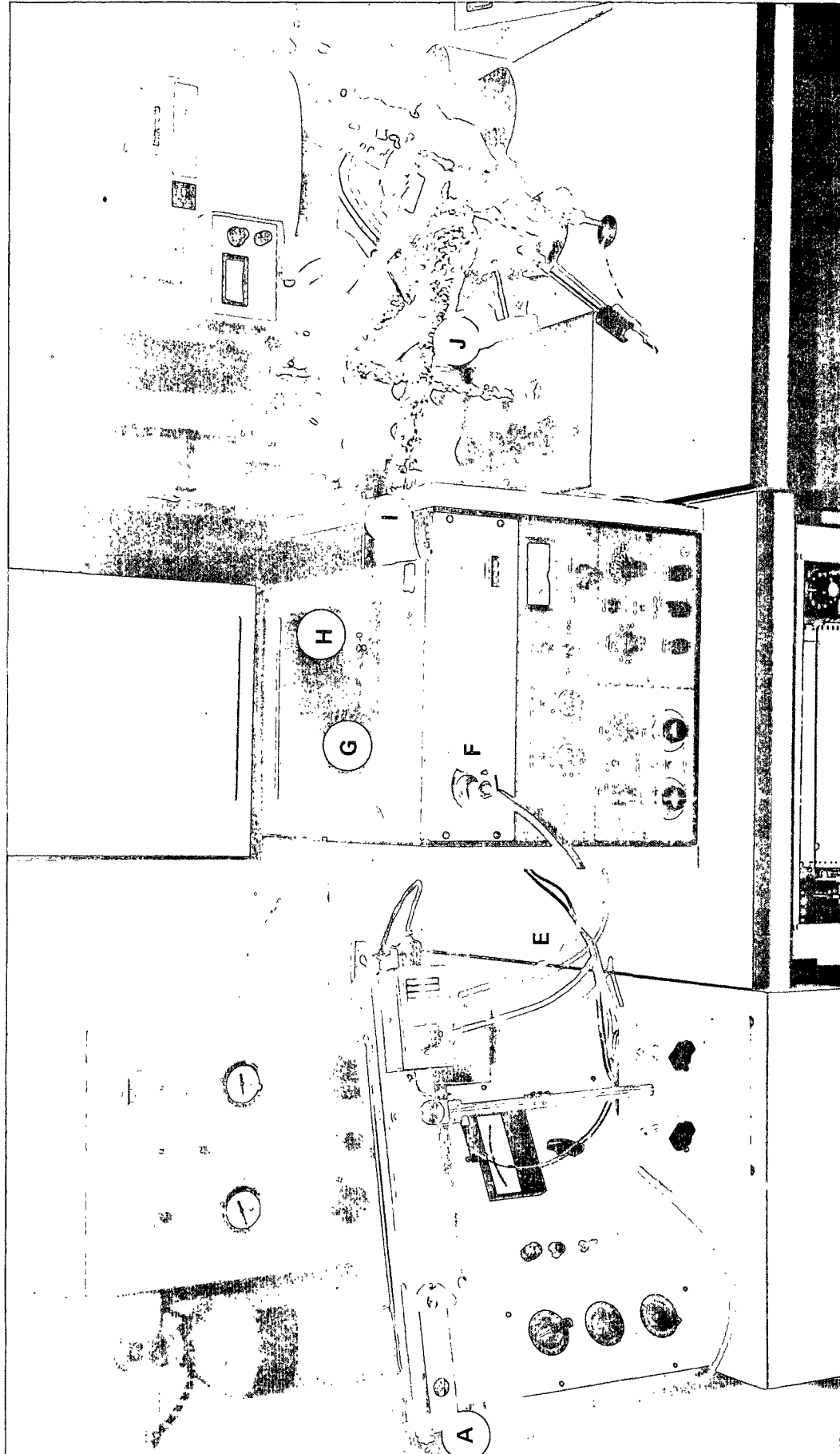


Figure 2. Pyrolysis-Gas Chromatography-Mass Spectrometry System

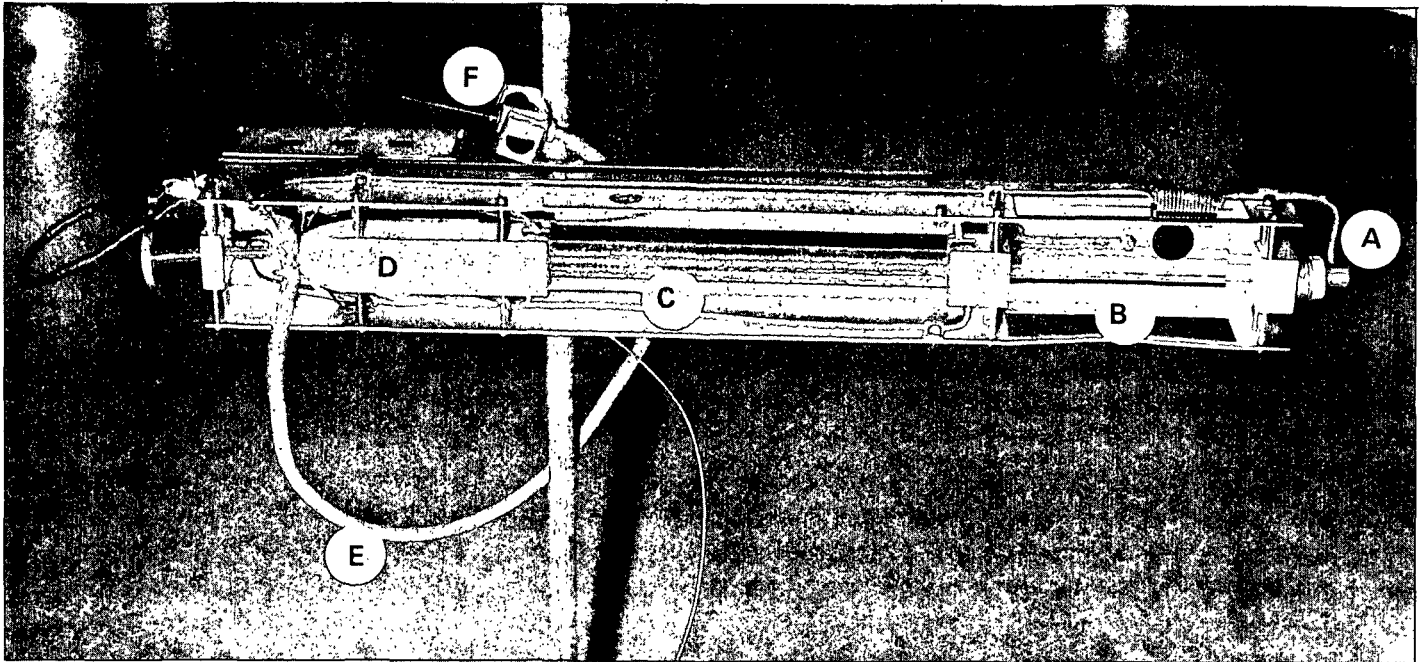


Figure 3. Furnace and Heated Line Assembly of Pyrolysis Unit

The GC column was stainless steel (1/8 inch by 5 feet) and was packed with 5% Dexil on 80/100-mesh Chromosorb W (acid washed, DMCS treated). The column was preconditioned overnight at 330° prior to its initial use.

The pulp sample to be pyrolyzed was weighed in a quartz sample tube (OD 1.7 mm, ID 1.2 mm, length 20 mm) so that the amount was in the range of 1.2-2.0 milligrams. Both ends of the sample tube were open but one end was tapered so that the opening was smaller. The pyrolysis method for pulp characterization is based on relative peak heights so that knowledge of the exact weight is unnecessary. However, samples larger than 2 mg contributed to changes in the carbohydrate-related peaks and should be avoided in quantitative work.

The sample tubes were cleaned in an oxygen-gas flame prior to use. They were always held and manipulated with a forceps to avoid contamination. After pyrolysis, the residue was pushed out with a wire, and the tubes could be heat-cleaned for reuse.

The Hamilton pyrolysis system was equipped with a temperature control unit which permitted temperatures to be independently controlled for the furnace and oven zones (C and D, Fig. 3) and the heated line (E). The temperatures were allowed to stabilize, and the sample tube was then inserted via the sample port access (A) into the room temperature zone (B). The system was sealed and the needle assembly (F) was interfaced with the gas chromatograph. The valve system was adjusted to flush helium (30 ml/min) through the pyrolysis system for three to five minutes prior to pyrolysis. The pyrolysis was then initiated by pivoting the sample port access end upward in one quick movement so that the tube slid into the furnace zone coming to rest against a porous quartz wool plug. The position of the plug was checked periodically with a rod to assure that the sample tube stopped at the same point in the furnace zone in each pyrolysis. Helium was allowed to continue to flow through the furnace, oven and heated line during the entire course of gas chromatographic separation. Zero time on the pyrogram was assigned as the moment the sample tube was tipped into the furnace zone.

Reproducibility was somewhat improved after an injector insert was added just in front of the gas chromatograph column. Separation of the peaks representing pyrolysis products was facilitated by use of temperature programming.

The conditions generally used for obtaining pyrograms were as follows:

Pyrolysis unit temperatures: furnace, 400°; oven, 260°; heated line, 280°.

Chromatograph temperatures: injector, 280°; detector, 300°; column, programmed from 75° → 175° at 4°/min then the temperature was increased at maximum rate to 330°.

Pyrograms were recorded on a Hewlett Packard strip chart recorder (Model 7128A) using a chart speed of 0.5 inch/min and a GC attenuation setting of  $128 \times 10^{-11}$ . The gas chromatograph was equipped with a flame ionization detector.

#### Cleanup Procedure

Sample tubes were heat-cleaned after pyrolyses as was previously mentioned. After about 20 pyrolyses (samples of 2 mg or less), it was necessary to clean the furnace tube, heated line, and injection port needle. The need for cleaning was apparent when the furnace tube had visibly darkened in the region of the oven zone. The furnace tube was cleaned by heating its full length in an oxygen-gas flame while air passed through it. The flow rate of the air was kept low enough to avoid dislodging the quartz wool plug. If the latter could not be completely cleaned (white), it was replaced and the new plug positioned carefully with the gage rod.

The heated line was cleaned by aspirating about 5 ml of each of the following solvents: dimethyl sulfoxide, distilled water, acetone, chloroform, or 1,2-dichloroethane, absolute ethanol, and petroleum ether (b.p. 60-110°). After cleaning, the line was heated with a helium gas flow to assure complete removal of solvent.

The injection needle was cleaned by aspiration in the reverse direction of normal gas flow using the same solvents cited above.

#### Mass Spectrometry

Identification of four of the major lignin-related peaks ( $L_1$ ,  $L_2$ ,  $L_3$ , and  $L_4$ ) was achieved by comparison of their mass spectra with the spectra of authentic samples. The mass spectrometer permitted rapid mass scanning of peaks

as they reached the detector. The GCMS splitter valve (H in Fig. 2) was opened by a knob on the outside of the chromatograph just after the peak of interest reached the GC detector. Part of the material was thus diverted into the mass spectrometer, and its mass spectrum was scanned over a 10 sec period. A block heater (I) and a heater tape (J) were each maintained at about 300° to minimize condensation of the sample. Continuous pumping kept the pressure in the mass spectrometer at about  $1 \times 10^{-6}$  Torr so that the GC "peak" was rapidly pumped out and, if desired, another peak in the same pyrogram could be introduced into the spectrometer.

The mass spectra for identification of pyrolysis products were run on peaks representing the products from kraft pulp No. A-3 (63.7% yield). Sample size was scaled up to about 5 milligrams to provide sufficient material in the individual peaks. Efforts to obtain useful mass spectra of the carbohydrate-related peaks, C-2 and C-3, have not been successful. It is apparently more difficult to attain an adequate concentration level in the ionizing beam of the spectrometer with these carbohydrate-related systems.

#### QUANTITATIVE ANALYSIS

The pyrograms obtained from pulps of various yields and from other related materials were studied to determine whether certain peaks were primarily carbohydrate- or lignin-related. It was found that the lignin-related peaks except for L<sub>1</sub> (guaiacol) dominated the pyrogram after 12-13 min retention time. The carbohydrate-related peaks in pulp pyrograms were confined to shorter retention times. The carbohydrate material contributed to a broad background detector response which decreased in importance at longer retention times. The effective base line thus had finite slope until after about 20 min. Therefore, it was

necessary to establish a procedure to deal with this base-line problem in a consistent manner. As shown in Fig. 4, the general approach was to extend a straight line through several minima on the pyrogram and use that as the base line on which to base peak height measurements.

Four lignin-related and two carbohydrate-related peaks were chosen to be the basis for determination of a parameter which would reflect the relative amounts of carbohydrate and lignin in the pulp sample.

The peak heights (in mm) were measured for the six main peaks using the adjusted base line. These peak heights were used in defining two parameters that would be useful in characterizing the pulps in terms of the amounts of carbohydrate and lignin present. These are defined as follows:

$$\text{1L parameter: } \frac{L_1}{L_1 + C_2 + C_3}$$

$$\text{3L parameter: } \frac{L_2 + L_3 + L_4}{L_2 + L_3 + L_4 + C_2 + C_3}$$

The quantities  $L_1$ ,  $C_2$ ,  $C_3$ , etc., are simply the peak heights measured directly from the pyrograms. They correspond to the peaks so identified in Fig. 4.

The 3L parameter gave somewhat better precision than the 1L parameter, especially for pulps of over 54% yield. This may reflect a significant contribution of carbohydrate material to the  $L_1$  peak. In general, the average error (in the 3L parameter) for replicate pyrolyses involving 3-5 separate runs was within  $\pm 4\%$ . As experience was gained with the method, the average error (Series A pulps) was found to be within  $\pm 3\%$ .

Theoretically, the areas of the peaks would seem to be more desirable quantities since peak heights are dependent on retention time with longer retention times producing broader peaks of diminished height. The liquid phase,

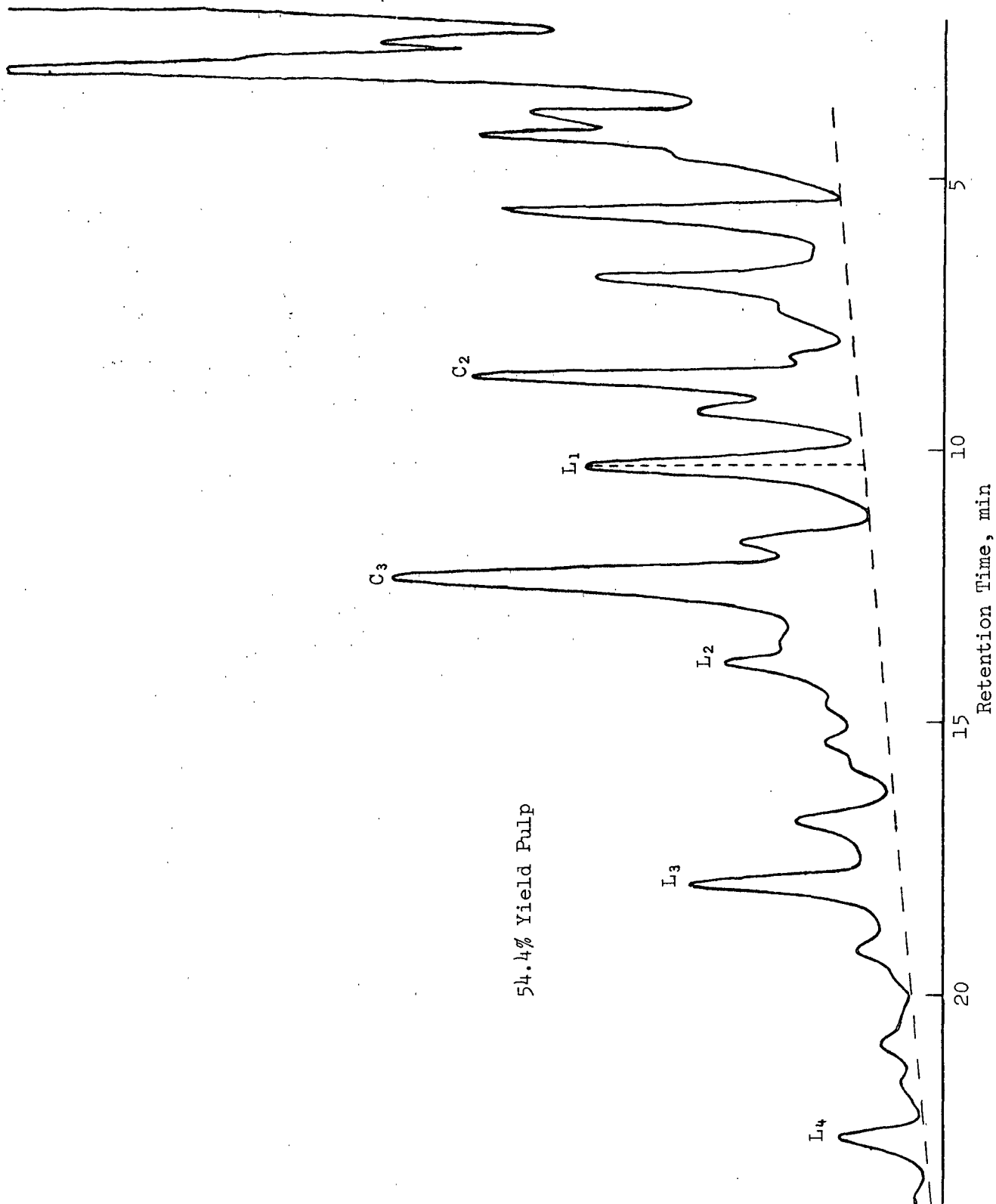


Figure 4. Sample Pyrogram of 54.4% Yield Kraft Pulp Sample Pyrogram Showing Basis of Peak Height Measurements

Dexil, used in the GC column was remarkably stable, and the retention times did not change markedly during the work which involved approximately 100 pyrograms. It was thought that peak areas should be investigated to see if improved precision could be attained.

Fourteen pyrograms were analyzed by determination of the areas of the six major peaks, and corresponding 3L and 1L parameters were calculated. No significant gain in precision was noted over the approach based on peak heights. Thus, the peak height method was used for the remaining work since it is simpler and less tedious.

## RESULTS AND DISCUSSION

### PYROLYSIS METHOD DEVELOPMENT

Previous work at the Institute (3) indicated that a pyrolysis temperature of 400°C would be sufficiently high to give useful and reproducible pyrograms. It was also likely that higher temperatures would promote rearrangement of initially formed phenolic products from the lignin. Thus, most of this work on pyrolysis of kraft pulps in the range 50-70% involved pyrolysis temperatures of 400°C. The pyrolysis is, in essence, a controlled thermal decomposition in the presence of an inert gas, helium. The pyrolysis products which give rise to peaks in the pyrogram are formed within the first five seconds (3) and swept onto the GC column. The residual char may undergo further, slow degradation but there is no evidence that this subsequent degradation contributes significantly to the pyrograms.

With such a flash pyrolysis, the amount of sample used is undoubtedly an important factor in obtaining reproducible results. We found that samples of 2.5 mg or more gave rise to problems with reproducibility. The difficulty seemed to lie mainly with the carbohydrate-related peaks. The preferred pulp sample size for this pyrolysis method is in the range of 1-2 mg.

Good separation of peaks was achieved by the use of temperature programming. Several rates of programming were tried, and the one chosen involved a 4° per minute rise from 75 to 175°; when the limit of 175° was reached all the peaks of interest had been eluted, and the temperature was then raised at maximum rate to 330° to remove less volatile material from the column.

We found it prudent to occasionally run a reference sample for comparison with earlier runs to be sure that the equipment was operating properly. Periodic cleaning of the high temperature regions is essential, and details for this are included in the Experimental section. A gas leak was encountered infrequently, but was apparent from the diminished peak heights in the pyrogram. Such pyrograms were rejected for quantitative analysis.

At the outset it was thought that certain distinct peaks in the pyrogram would reflect lignin degradation products and certain others would originate from carbohydrate systems in the pulp. Thus, there would be a reasonable chance of using these same peaks as a means of determining the relative amount of lignin and carbohydrates in the pulp.

The results of this study, as well as earlier thesis research (3), suggest that there are indeed several lignin-related peaks that are not appreciably contaminated with carbohydrate degradation products. The peak labeled L<sub>1</sub> in the pyrograms (for example, Fig. 4) is a possible exception to this because it has a retention time close to the major carbohydrate-related products. The peaks labeled L<sub>2</sub>, L<sub>3</sub>, and L<sub>4</sub> were of major interest in the development of a parameter from the pyrograms that would provide an indication of both yield and lignin content.

Mass spectra were obtained for each of the four major lignin-related peaks (degradation products). By reference to the spectra we had run on known samples, the lignin-related peaks were identified as follows: L<sub>1</sub>, guaiacol; L<sub>2</sub>, creosol; L<sub>3</sub>, 4-vinylguaiacol; L<sub>4</sub>, trans-isoeugenol.

Thus far, we have been unable to obtain useful mass spectra of the major carbohydrate degradation products,  $C_2$  and  $C_3$ . The spectra generated were not intense enough to permit distinction from background.

The heights of Peaks  $L_1$ ,  $C_2$ , and  $C_3$  were used initially to develop a 1L parameter,  $L_1/(L_1+C_2+C_3)$ , that provided reasonable correlations with the pulp yield level and with lignin content (as measured by Klason and acid-soluble lignin). Further work led to an alternative parameter (3L using 3 lignin peaks) which was defined as  $(L_2+L_3+L_4)/(L_2+L_3+L_4+C_2+C_3)$ . In other words, the parameter is the quotient of a quantity related only to the lignin in the sample and a quantity related to the amount of both lignin and carbohydrate. This latter 3L parameter was generally obtained with higher precision than the 1L parameter. This is probably because of the possible contribution of carbohydrate to the  $L_1$  peak which is ignored in the 3L method.

As can be seen in Appendix I, the average error for replicate determinations is within  $\pm 4\%$  for the 1L method and within  $\pm 3\%$  for the 3L method.

We also looked at peak areas to see whether they would provide improvement over peak heights, but no significant improvement was observed. Therefore, the simplicity of peak height measurements dictated that they be employed rather than areas.

#### PYROGRAMS OF KRAFT PULPS - SERIES A

A series of kraft pulps ranging in yield from 54.4 to 70.0% was prepared by cooking six batches of southern pine chips for different periods of time. After washing and drying of the resulting pulps, samples of each were Wiley-milled so that they could be conveniently loaded into the small pyrolysis tubes. Details are provided in the Experimental section.

Typical pyrograms for these pulps are shown in Fig. 5-8. The changes in the relative heights of the major lignin-related ( $L_1$ ,  $L_2$ ,  $L_3$ , and  $L_4$ ) and the major carbohydrate-related peaks ( $C_2$  and  $C_3$ ) as the pulp yield decreases are quite apparent from inspection of the curves. Although six peaks have been designated as major ones with respect to defining parameters characteristic of pulp composition, it is also apparent that the relative heights of several other peaks are changing as well.

In addition to kraft pulps, certain other samples were subjected to pyrolysis under the same conditions during the course of this research. These included available samples of hemicelluloses, cotton linters, levoglucosan, a fir holopulp, and an isolated dioxane lignin. Their pyrograms are included in Appendix II. It can be noted that the carbohydrate-related peaks are generally found at retention times of 12 to 13 min or less. This is especially evident in the hemicellulose and holopulp pyrograms and is borne out by inspection of the lower yield pulp samples (Fig. 7-8) which have less lignin.

Levoglucosan pyrolysis was included since there is abundant evidence (9) that a major mechanism operating in cellulose pyrolysis involves formation of levoglucosan which, in part, degrades further. It is clear that pyrolysis of cotton linters is not a very adequate "model" for pyrolysis of cellulose in the kraft pulps. In particular, the peaks at 14 and 16 min appear to have little, if any, relevance to the pulp pyrograms.

The pyrogram of dioxane lignin contains the main lignin-related peaks evident in the pulp pyrograms. There are sizeable differences in relative intensities of these peaks, however. This must reflect, in part, the substantial modification of the residual lignin during kraft pulping. The absence of

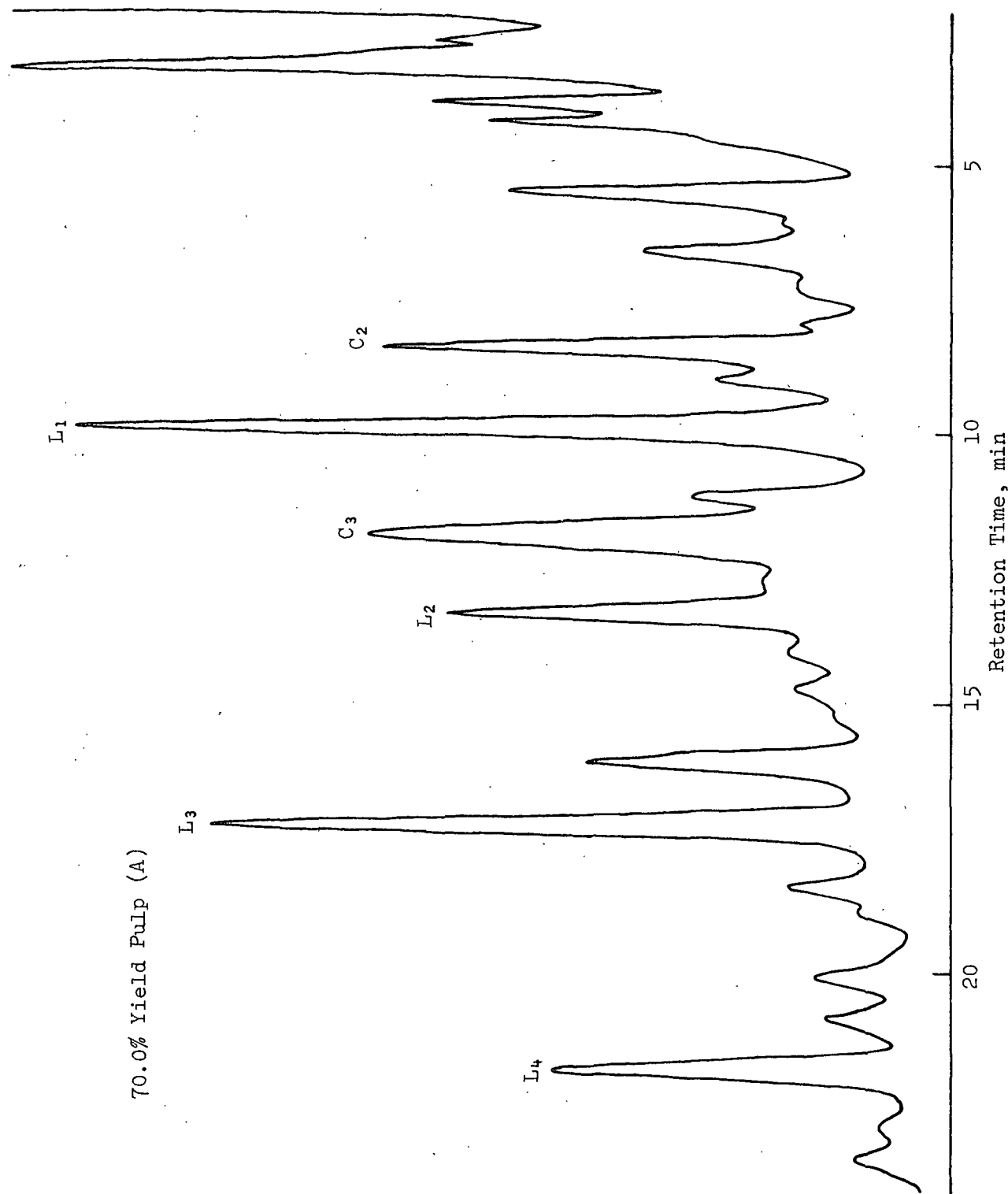
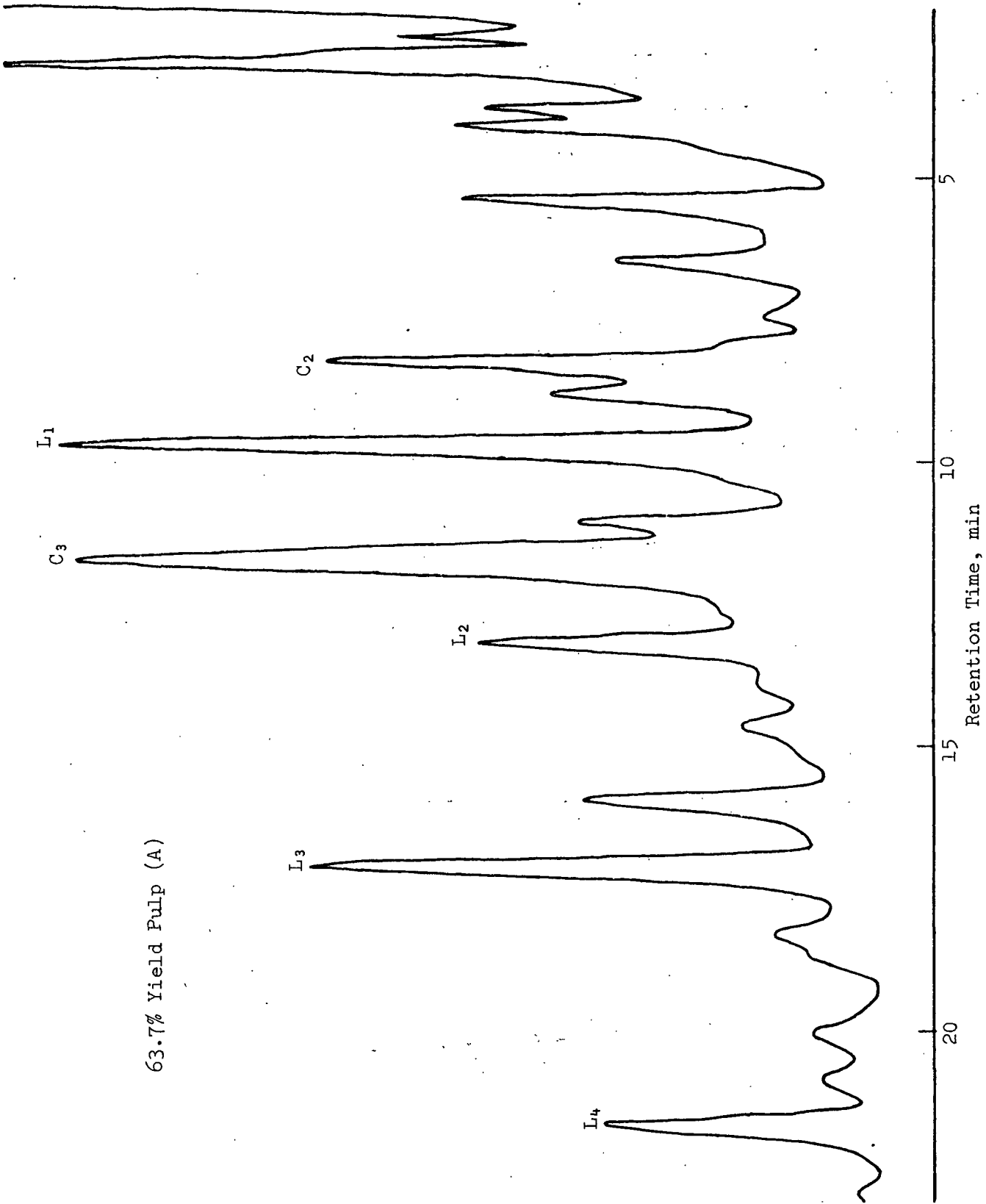


Figure 5. Pyrogram of 70.0% Yield Kraft Pulp - Series A



63.7% Yield Pulp (A)

Figure 6. Pyrogram of 63.7% Yield Kraft Pulp - Series A

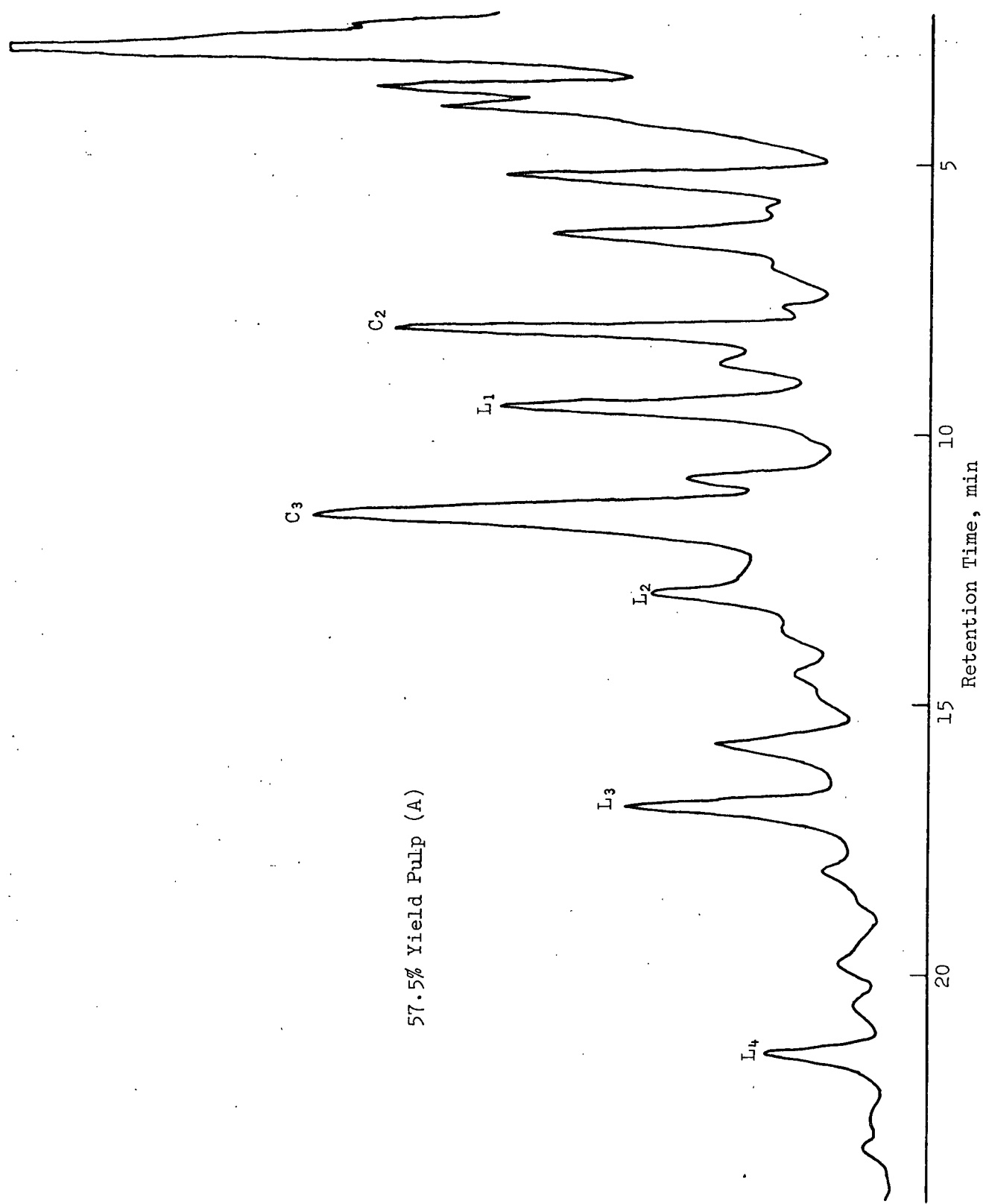


Figure 7. Pyrogram of 57.5% Yield Kraft Pulp - Series A

54.4% Yield Pulp (A)

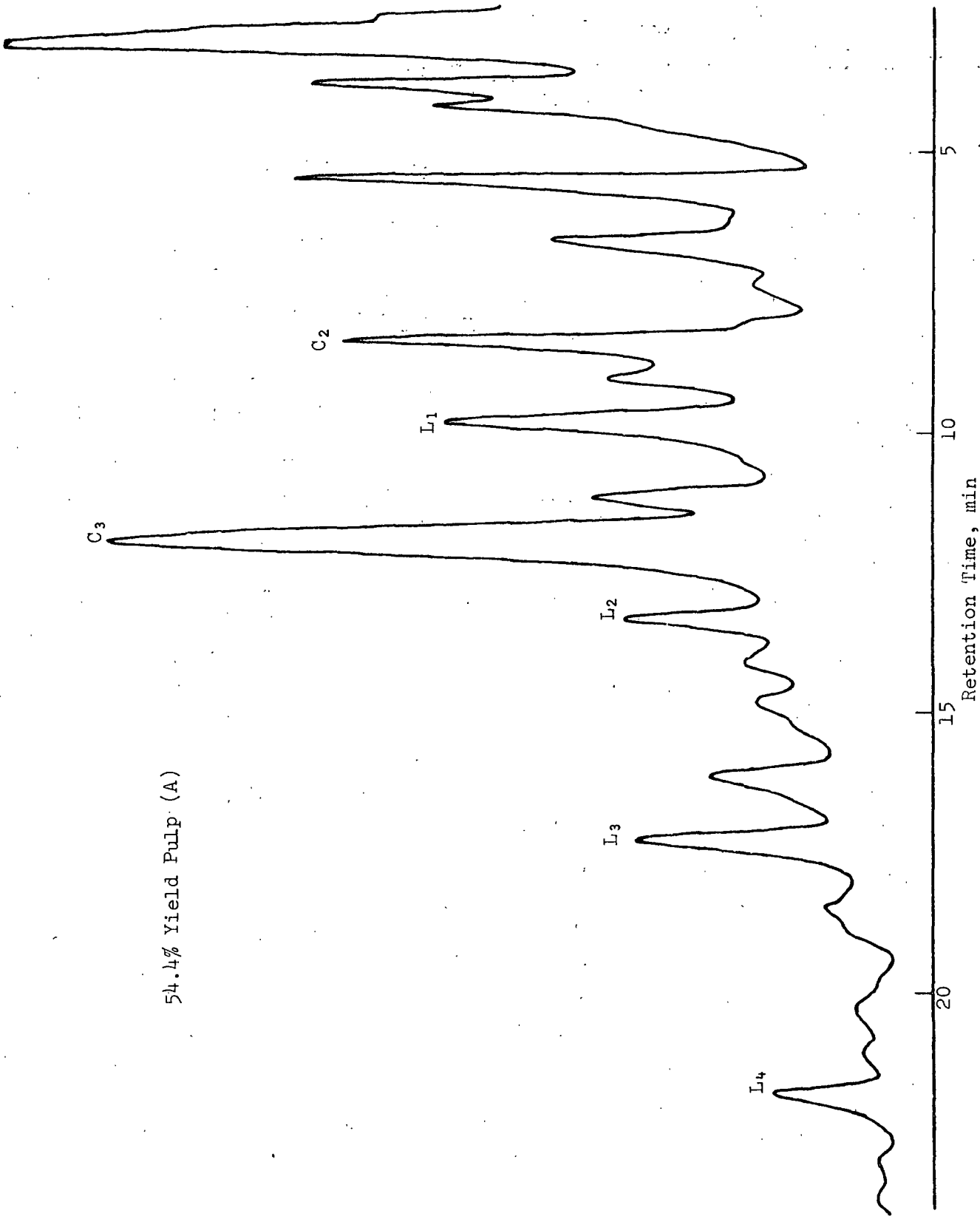


Figure 8. Pyrogram of 54.4% Yield Kraft Pulp - Series A

significant peaks at early retention times in the dioxane lignin pyrogram is noteworthy, and the pulp pyrograms appear to be the same in this respect.

#### CORRELATION WITH YIELD AND LIGNIN CONTENT

The 3L parameter which is based on three lignin peaks and two carbohydrate peaks appears to have promise as an indicator of pulp yield. As was mentioned earlier in the report, the relationship between pulp yield and pulp composition will not be the same for different wood species and will also be strongly dependent on the particular process variables. In the kraft process, for example, these variables would be expected to include temperature, alkalinity, and sulfidity. This means that the success of the pyrolysis method or any other method that reflects the composition of the pulp will depend on the use of reference pulps prepared from the same wood species using the same cooking process parameters that are used to make the pulps to be tested.

Figure 9 shows the relationship between pulp yield (Series A pulps) and the 3L parameter. Each data point is the average of at least three separate determinations. The experimental data are included in Appendix I. The data approximate a linear relationship rather well over this yield range (54-70%). Curvature would not be surprising, however, in view of results summarized in Fig. 1. The question of linearity over this yield range could only be clarified by pyrolysis of a greater number of samples. However, the plot illustrates that the method has real potential as a means of characterizing pulps at different yield levels.

Significant deviation is noted for the point representing the 57.4% yield pulp. It should be noted, however, that this is due more to an uncertainty concerning the yield value than the 3L parameter. Based on the cooking

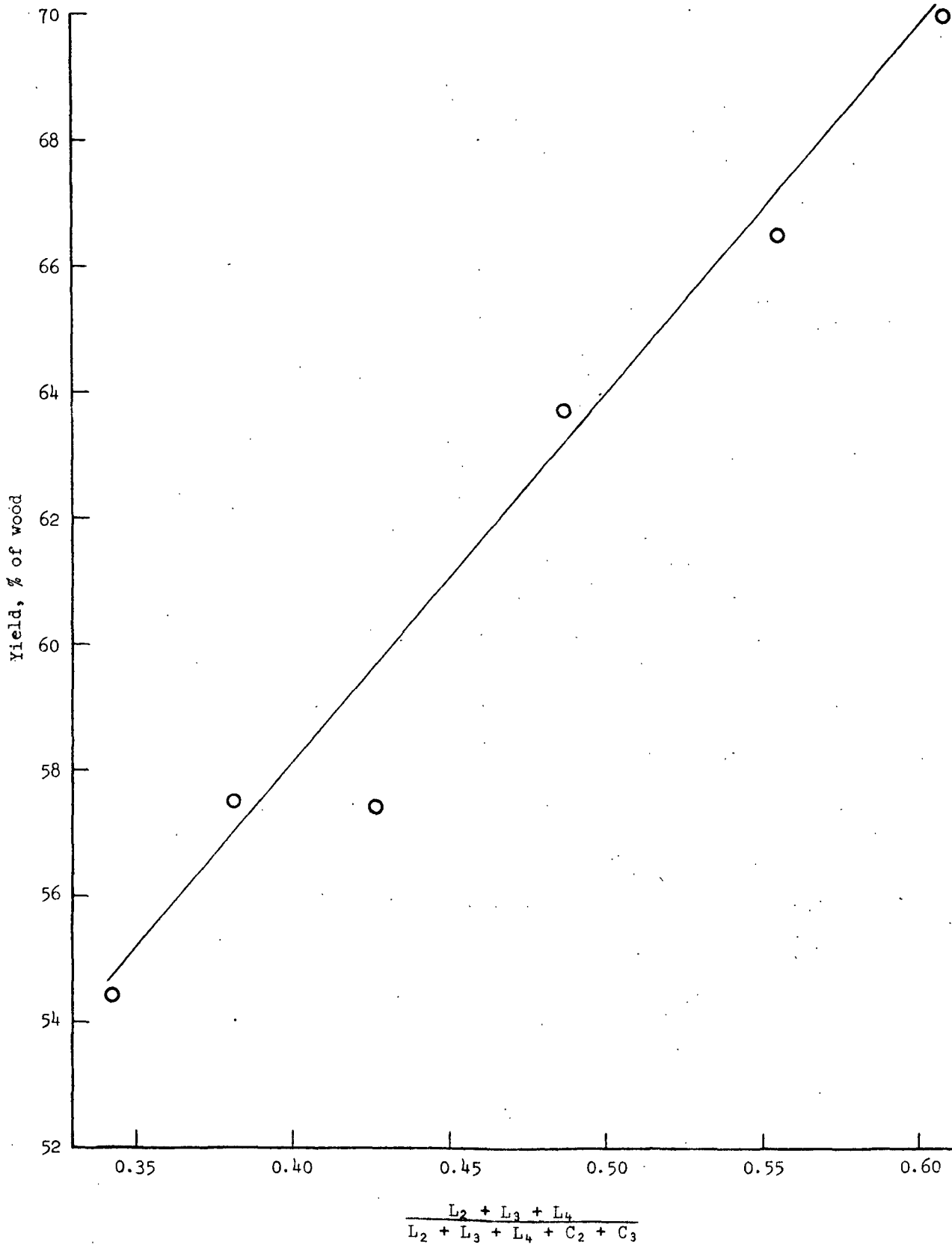


Figure 9. Relationship Between Pulp Yield and the 3L Value for Kraft Pulps of Series A

time for this pulp, the yield was expected to be approximately 60%. Further, the lignin content of this pulp (14.9%) is significantly higher than the 57.5% yield pulp (13.1%) which was cooked longer. This point will be further elaborated below.

Figure 10 shows that the 3L parameter obtained from the pyrograms of kraft pulps correlates well with the lignin content of those pulps. Lignin content here is the sum of Klason and acid-soluble lignin. This finding provides experimental support that the 3L parameter has been properly chosen to reflect the relative amount of lignin in a series of pulps. It also supports the assumption that there is not significant cross-contamination of the five chosen peaks, i.e., L<sub>2</sub>, L<sub>3</sub>, and L<sub>4</sub> represent lignin while C<sub>2</sub> and C<sub>3</sub> represent carbohydrate material.

It will also be noted that the troublesome pulp (57.4% yield) referred to above now falls into line with the other pulps in Fig. 10. It is represented by the point at 14.9% lignin.

Thus, it can be concluded that the 3L parameter obtained from pulp pyrograms is a good measure of lignin content for kraft pulps in the yield range 54-70%. Since lignin content is related to pulp yield, the 3L parameter can also be a useful indicator of yield with the aid of reference data from standard pulps.

#### PYROGRAMS OF KRAFT PULPS - SERIES B

A brief mention will be made of pyrolysis experiments involving a different series of kraft pulps. These pulps were used in the early orienting stage of the investigation. When confidence was acquired with the technique, it was decided to place emphasis on pulps covering a higher yield range (above 55%)

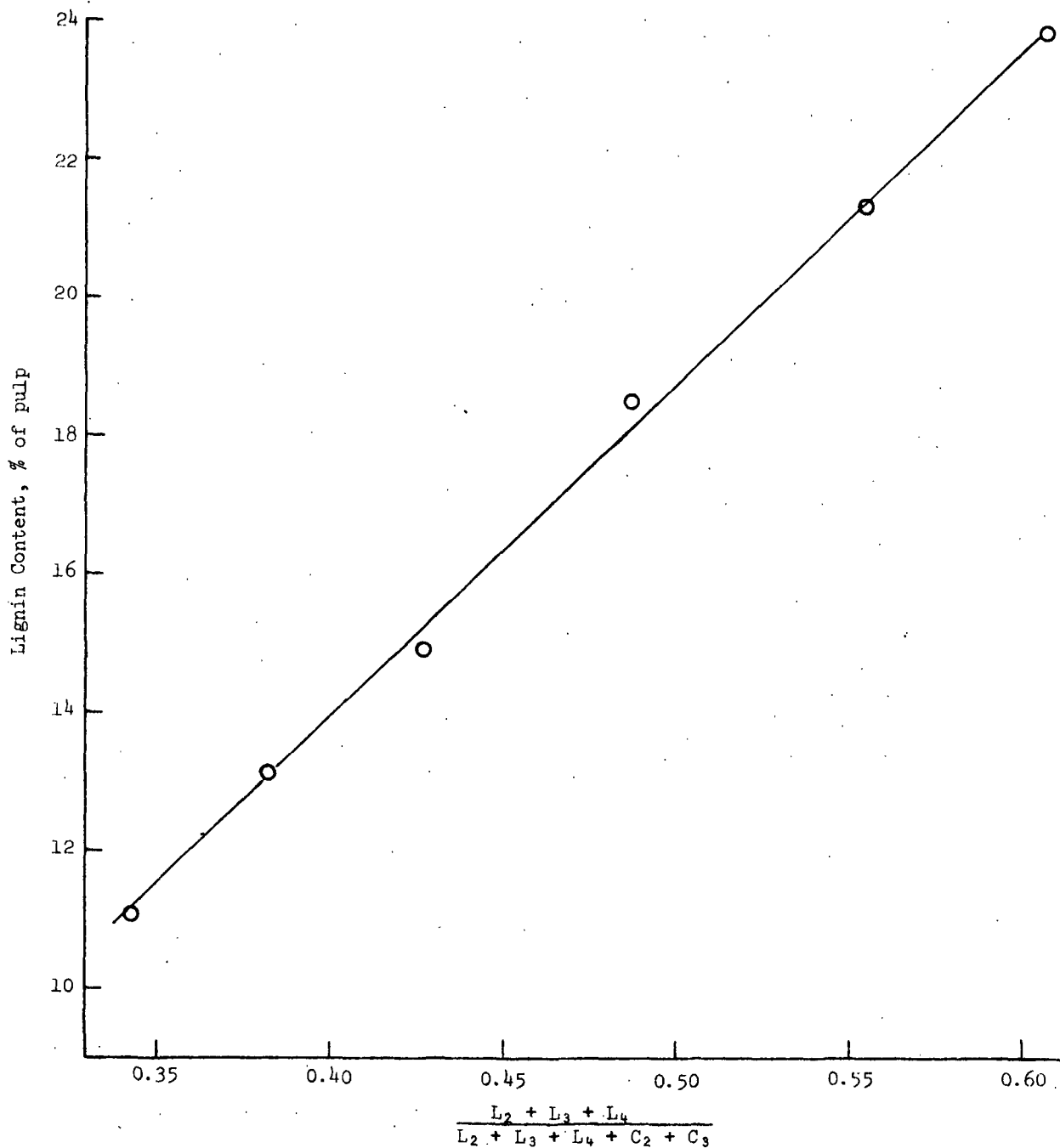


Figure 10. Relationship Between Lignin Content (Klason + Acid-Soluble) and the 3L Value for Kraft Pulps of Series A

where problems with the use of Kappa number as a yield indicator are most acute. The work on pulps in this higher yield range (Series A) has already been discussed.

Representative pyrograms of four pulps of Series B (yield range 50-61%) are shown in Fig. 11-13. The same general features noted earlier are again evident. The 3L parameter was obtained from these pyrograms in the usual way, and the data plotted versus pulp yield as shown in Fig. 14. Since much of these data come from pyrograms obtained in the earlier stages of the work, the precision was not quite as good (within  $\pm 4.4\%$ ) as the data from pulps of Series A.

It would be reasonable to expect accuracy to diminish as the lignin content drops to rather low values. This may, in part, explain the deviation of the point representing the 50.8% yield pulp. On the other hand, the relationship in Fig. 14 may well be curved rather than linear. The data are too limited to determine this.

The plot of the 3L parameter versus lignin content for this limited series of pulps is shown in Fig. 15. In this case, a linear relationship is viewed more likely than in Fig. 14. In other words, the 3L parameter is a measure of relative lignin content and will be linearly related to yield only if lignin content is so related to yield.

#### INFLUENCE OF HEMICELLULOSES ON PULP PYROGRAMS

One of the hopes that developed in the early stages of the research was that one or more peaks in the pyrograms might be representative only of hemicellulose content. This was reinforced slightly by the success achieved in the chromatographic separation of products. In order to explore this possibility, available hemicellulose samples, including a glucuronoxylan and a glucomannan

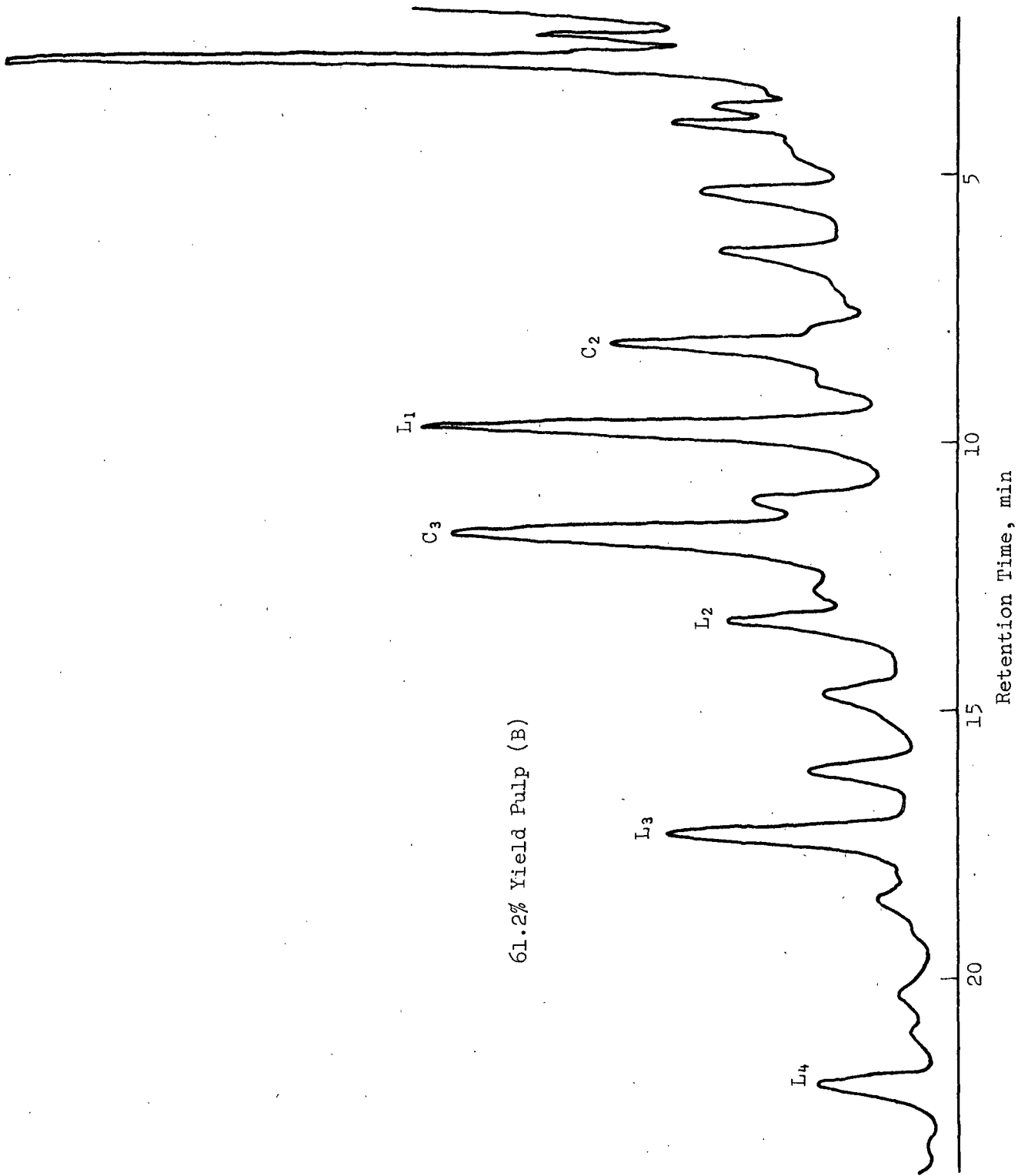


Figure 11. Pyrogram of 61.2% Yield Kraft Pulp - Series B

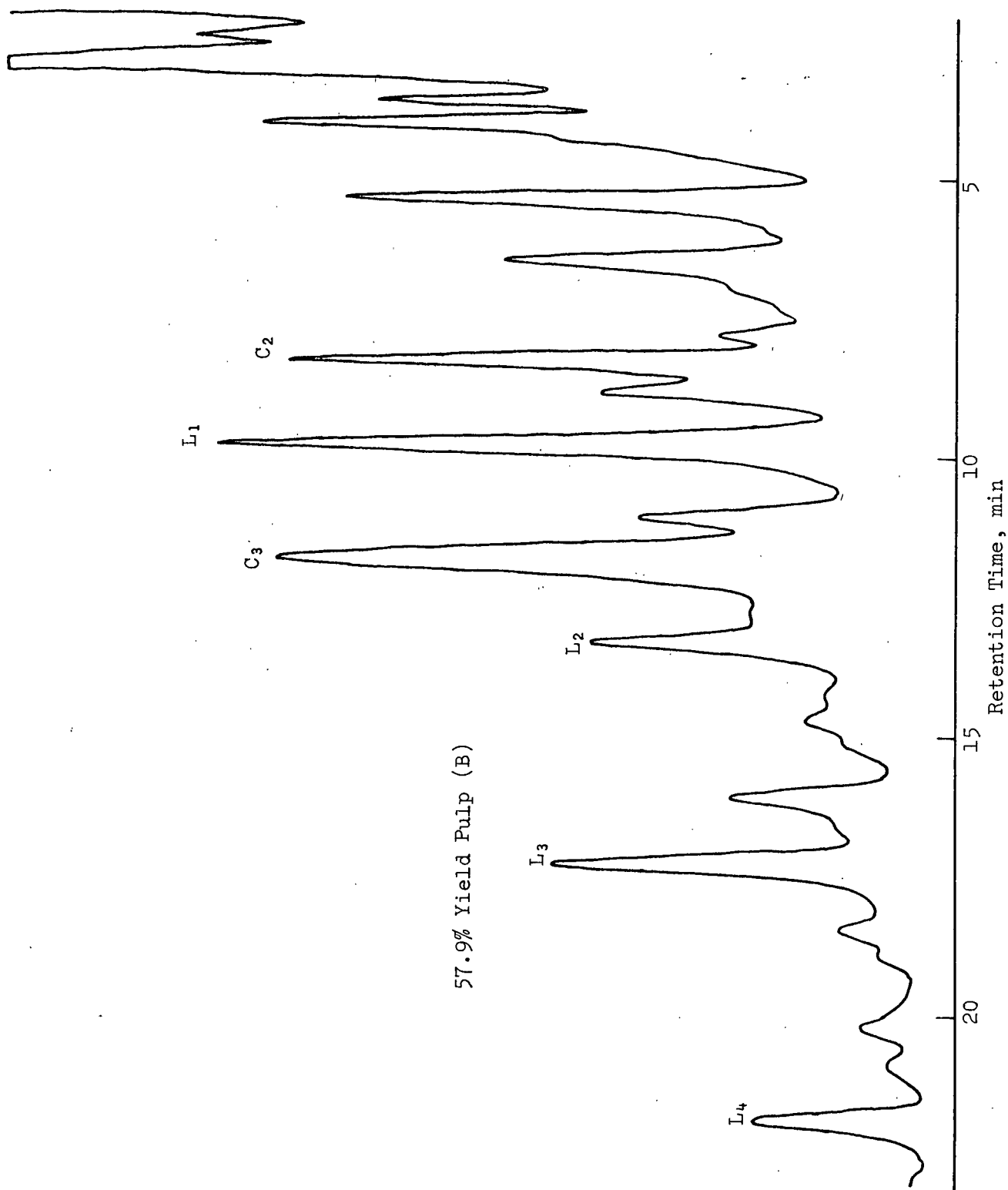


Figure 12. Pyrogram of 57.9% Yield Kraft Pulp - Series B

53.5% Yield Pulp (B)

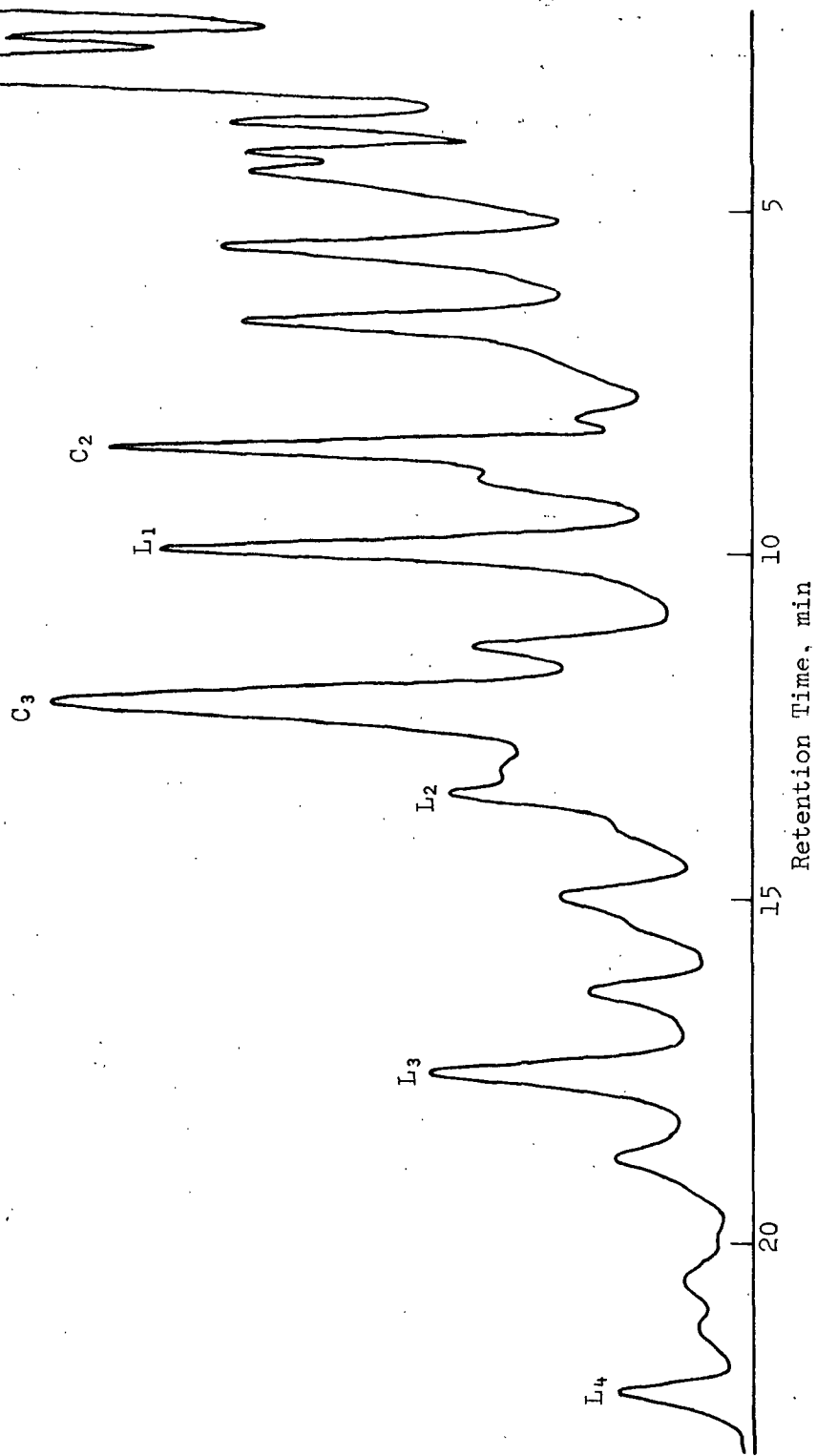


Figure 13. Pyrogram of 53.5% Yield Kraft Pulp - Series B

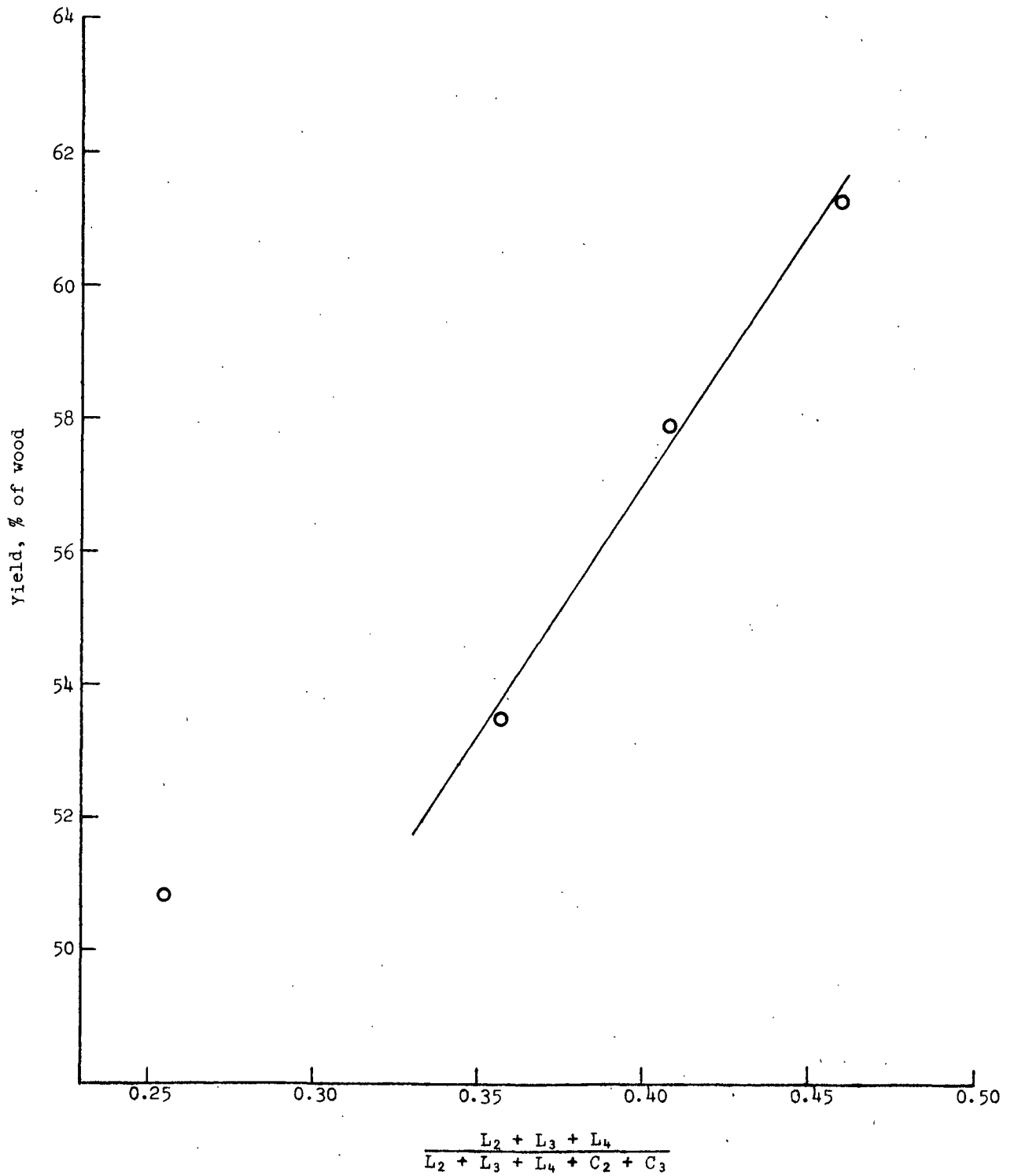


Figure 14. Relationship Between Pulp Yield and the 3L Value for Kraft Pulps of Series B

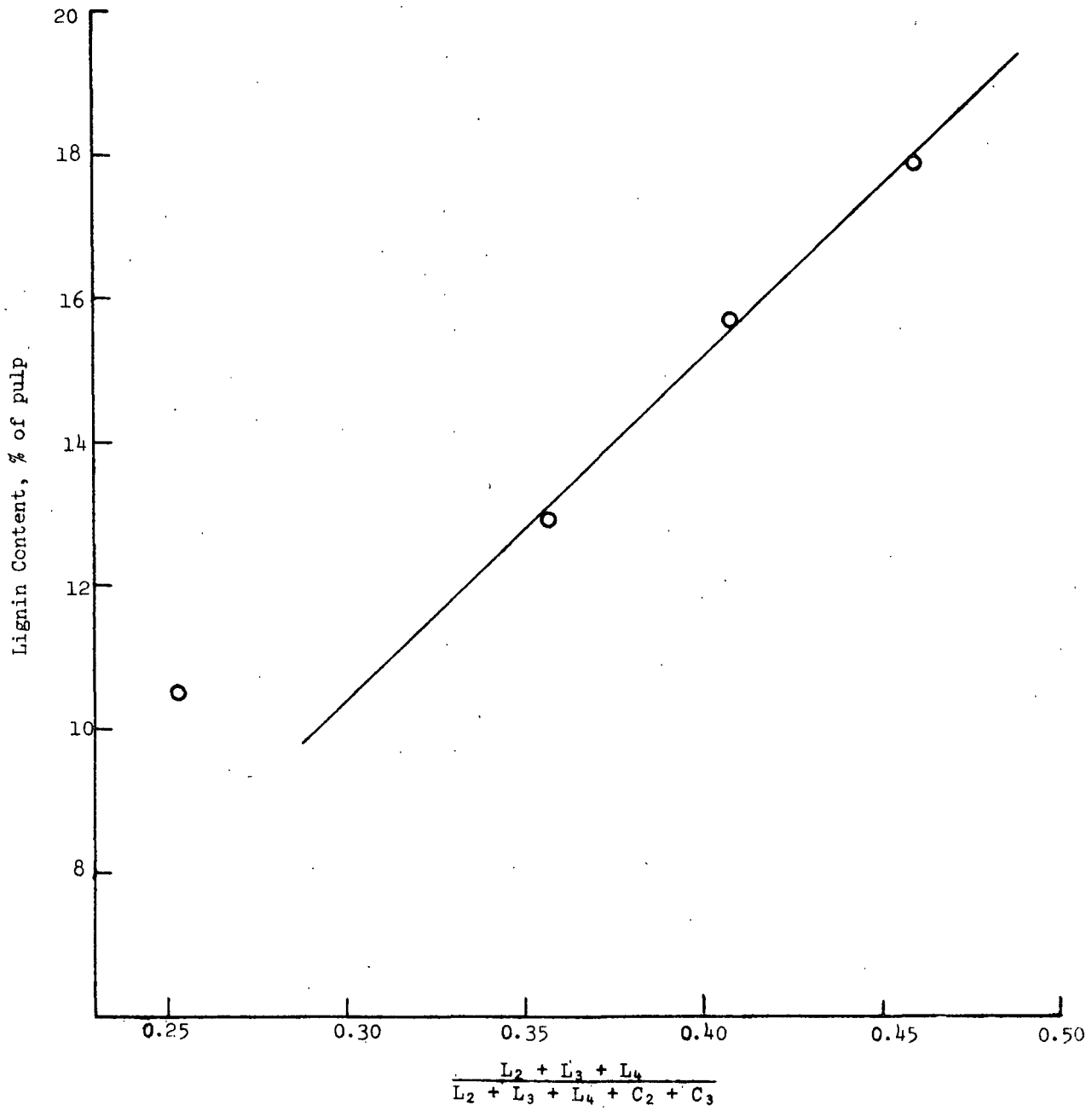


Figure 15. Relationship Between Lignin Content (Klason + Acid-Soluble) and the 3L Value for Kraft Pulps of Series B

along with a holopulp, were all subjected to pyrolysis. The curves are included in Appendix II (Fig. 16-21).

Peaks are evident at retention times comparable to the carbohydrate peaks in the pulp pyrograms. For example, the fir holopulp pyrogram (Fig. 18) has two major peaks at 8.9 and 12.5 minutes which correspond very closely to the C<sub>2</sub> and C<sub>3</sub> peaks from the pulps. The higher content of hemicellulose in the holopulp has not resulted in any dramatic difference in the pyrolysis products compared with those of the kraft pulps.

A series of pyrolyses were run on pulp-hemicellulose mixtures to see what effect deliberate enrichment would have on the pyrolysis products. The only consistent change in the pyrograms was enhancement of the C<sub>2</sub> and C<sub>3</sub> peaks. Table III illustrates how this change affects the 3L parameter. The experimental 3L values may be compared with values calculated on the basis of the lower lignin contents after hemicellulose addition and the correlation shown in Fig. 10. The agreement in the 3L values between Runs 74, 76, 77B and 78, all of which had about the same level of added hemicellulose, is a further illustration of the reproducibility of the pyrolysis method.

TABLE III  
EFFECT OF ADDED HEMICELLULOSE ON PULP PYROGRAMS

Run No.	Sample <sup>a</sup>	Lignin Content, %	3L, exptl.	3L, calc.
59	A-5	13.1	0.384	--
74	A-5 + 11% GM	11.8	0.354	0.356
76	A-5 + 12% X	11.7	0.358	0.353
77B	A-5 + 10% X	11.9	0.366	0.358
78	A-5 + 10% X	11.9	0.331	0.358
77A	A-5 + 24% X	10.6	0.342	0.332

<sup>a</sup>Pulp A-5 is 57.5% yield; GM - glucomannan; X - xylan.

The difference in lignin content between the pulp and the pulp + 10% hemicellulose can be translated into a corresponding yield difference. Reference to Fig. 9 would indicate that a pulp giving a 3L value of 0.352 (average of runs incorporating 10% hemicellulose addition) would be at a yield of 55.5%. Thus, there is a high probability that the method can distinguish between two pulps of 57.5% and 55.5% yields. In other words, the difference between the experimental values of 0.352 (our "55.5% yield" pulp containing the 10% added hemicellulose) and 0.381 (average value for the 57.5% yield pulp) is about 8% and is well beyond the average error of  $\pm 3\%$  noted for the method. It would also appear that a smaller difference in yield could be distinguished with high probability.

#### CONSIDERATIONS ON THE USE OF THE PYROLYSIS METHOD IN A MILL LABORATORY

A pyrolysis method has been described in this report which provides a means of characterizing ("fingerprinting") a kraft pulp in terms of relative amounts of lignin and carbohydrate present. Since pulp composition can be empirically related to yield by use of reference pulps, the method also has merit as an indicator of pulp yield. What are the necessary factors and potential problems which need to be considered prior to possible application of the method in a mill laboratory?

Some of these include the cost of the necessary equipment, the time required for analyses, the problem of obtaining representative samples of pulp for pyrolysis, the need for pyrograms from standard pulp samples of known yield, possible wide variations in wood species used in the pulping process, and the effect of inorganic impurities.

The cost of the equipment used for the pyrolyses described in this report is estimated at about \$7,000. This would include the flame ionization gas chromatograph, a suitable strip-chart recorder and the pyrolysis unit. This would not seem to be excessive if the method was successful in contributing to better process control.

The time required to run a pyrolysis and complete the resulting pyrogram is about 25 minutes. At that point the pyrogram can be removed, a base line drawn, measurements of peak heights obtained, and the 3L parameter calculated. While the latter is being done, the temperature of the GC oven is rapidly programmed up to 330°C. The heater is turned off and the oven opened to cool to 70°C. When it has cooled, a new pyrolysis can be initiated. This would be roughly an hour after the previous pyrolysis began. Once minimal experience has been gained with the method it should not be necessary to weigh the sample. The method depends on relative peak heights, and it has been shown that the ideal sample size is between 1 and 2 mg. If by accident an excessive amount of sample is introduced, this will be apparent simply by the size of the peaks and the run can be repeated. It should be possible to run samples nearly twice as rapidly with a second gas chromatograph.

Another matter alluded to above was the possible problem of obtaining a representative pulp sample since such very small quantities are pyrolyzed. One approach, closely resembling the course taken in this work, would be to carefully screen several grams of a pulp sample and remove any undercooked fragments followed by a milling procedure to homogenize the sample and reduce fiber size.

It has already been mentioned that use of the method for evaluating the yield of pulp samples will depend on calibration. The calibration undoubtedly will have to be performed using pulps prepared in laboratory-scale cooks using conditions that closely approximate those used in the mill. These pulps, of course, should be made from the wood species important to the mill operation. A sufficient number of pulps should be studied over the yield range of interest to permit a satisfactory correlation between the 3L parameter and yield. For any single reference pulp, the average 3L value of at least three pyrolyses should be used in developing the correlation.

It is recognized that in many pulp mills the wood furnish is subject to considerable variation even during a single day. It is conceivable that differences in the relative amounts of juvenile and mature wood could, because of differences in lignin content, confuse the interpretation of a pulp pyrogram. It should be emphasized that we have tested the method only with southern pine. The ease of extending the method to hardwood pulps is uncertain and this question needs further research. The pyrograms may well be more complex because of the likelihood of syringyl-based pyrolysis products in addition to those seen in softwood pyrograms.

Another possibly troublesome factor was thought to be the presence of inorganic impurities. It is known (20) that inorganic additives in amounts of 2-5% can cause significant differences in the relative amounts of the pyrolysis products of cellulose and lignin. We briefly studied the effect of added calcium chloride and sodium carbonate on pulp pyrograms. The indicated levels of addition were achieved on a larger scale by adding the necessary amount of dissolved salt to 2.5 g of pulp and then freeze drying the aqueous suspension. The resulting material was used in the pyrolyses.

As shown in Table IV, the influence of sodium carbonate at the 2.3% add-on level is considerable. It appears to enhance the guaiacol peak ( $L_1$ ) and depress the amounts of the carbohydrate ( $C_2$  and  $C_3$ ) and creosol ( $L_2$ ) peaks. The effect is more dramatic on the 1L parameter. Addition of calcium chloride at the 0.55% level appears to exert a slight effect on the 3L value. However, two pyrolyses were also run on samples containing 2.8% calcium chloride. This caused a drastic change in the pyrogram appearance especially in the region of the  $L_1$ ,  $L_2$ ,  $C_2$ , and  $C_3$  peaks. The change was so great that it was impossible to calculate a meaningful 3L value.

TABLE IV  
EFFECT OF ADDED INORGANIC SALTS  
ON PULP PYROGRAMS

Run No.	Sample <sup>a</sup>	3L <sup>b</sup>	1L <sup>c</sup>
98	A-3 pulp	0.481	0.374
93	A-3 + 2.3% $\text{Na}_2\text{CO}_3$	0.522	0.492
94	A-3 + 2.3% $\text{Na}_2\text{CO}_3$	0.509	0.491
101	A-3 + 0.55% $\text{CaCl}_2$	0.507	0.374
102	A-3 + 0.55% $\text{CaCl}_2$	0.499	0.360

<sup>a</sup>Percentages are added amounts of the salt on the basis of the weight of the pulp.

<sup>b</sup> $(L_2 + L_3 + L_4)/(L_2 + L_3 + L_4 + C_2 + C_3)$ .

<sup>c</sup> $L_1/(L_1 + C_2 + C_3)$ .

The tentative conclusion that emerges from this limited study involving salt addition is that inorganic substances at levels of approximately 2.5% can cause significant and possibly major variations in the 3L (or 1L) parameter which is the basis of the pulp pyrolysis method.

#### POSSIBLE FUTURE WORK

Further study of the application of the pyrolysis method to other high-yield pulps would seem to be warranted. In particular, semichemical pulps at yield levels as high as 85% could be investigated. The greater complexity expected for pyrograms of hardwood pulps should be checked and the applicability of the method to these pulps assessed. It is possible that the method will be applicable to pulps prepared from mixtures of hard and softwoods, and this should be examined carefully in future research. It would also be wise to examine the influence on pulp pyrograms of other inorganic materials at reasonable concentration levels.

### CONCLUSIONS

Pyrolysis-gas chromatography provides a method of characterizing high-yield kraft pulps in terms of pulp composition, i.e., the relative amounts of lignin and carbohydrate present. A correlation has been shown between pulp yield and a parameter (3L value) obtained from the pyrograms. It should be possible to use the parameter as an indicator of pulp yield in a mill laboratory if the relationship is calibrated with pulps prepared at known yield levels using the appropriate pulping conditions and wood species.

#### ACKNOWLEDGMENTS

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APPENDIX I  
PYROLYSIS DATA FROM PULP SAMPLES

TABLE V

SUMMARY OF PYROLYSIS DATA

Run No.	Pulp Yield, %	3L Value	3L, mean <sup>a</sup>	1L Value	1L, mean <sup>a</sup>
SERIES A					
41	70.0	0.619		0.488	
42	70.0	0.599		0.477	
52	70.0	0.599	0.608 ± 1.3%	0.444	0.460 ± 3.5%
54	70.0	0.615		0.459	
69	70.0	0.602		0.477	
43	66.5	0.549		0.444	
44	66.5	0.538		0.420	
105	66.5	0.569	0.555 ± 2.2%	0.440	0.434 ± 1.7%
106	66.5	0.566		0.434	
45	63.7	0.491		0.407	
46	63.7	0.491		0.385	
98	63.7	0.481	0.487 ± 0.6%	0.374	0.390 ± 3.5%
99	63.7	0.487		0.377	
100	63.7	0.485		0.408	
47	57.4 <sup>b</sup>	0.419		0.292	
63	57.4	0.423	0.427 ± 1.9%	0.302	0.305 ± 3.3%
64	57.4	0.440		0.320	
58	57.5	0.390		0.274	
59	57.5	0.384	0.381 ± 2.1%	0.269	0.267 ± 2.2%
60	57.5	0.369		0.259	
50	54.4	0.346		0.244	
103	54.4	0.352	0.342 ± 2.6%	0.263	0.253 ± 4.3%
104	54.4	0.330		0.238	
SERIES B					
26	61.2	0.449		0.409	
32	61.2	0.487	0.460 ± 3.9%	0.454	0.420 ± 5.5%
36	61.2	0.444		0.396	
38	57.9	0.423		0.352	
39	57.9	0.381	0.408 ± 4.4%	0.324	0.346 ± 3.8%
40	57.9	0.420		0.357	
34	53.5	0.381		0.313	
35	53.5	0.356	0.358 ± 4.2%	0.302	0.298 ± 4.4%
37	53.5	0.337		0.278	
70	50.8	0.268		0.214	
71	50.8	0.253	0.254 ± 3.5%	0.193	0.204 ± 3.9%
72	50.8	0.243		0.206	

<sup>a</sup>The mean value of 3L and 1L for each pulp is listed along with the average error expressed as a percentage of the mean.

<sup>b</sup>The pulp yield may be misleading; the lignin content is significantly higher than would be expected at this yield (see Table I).

APPENDIX II

PYROGRAMS OF RELATED MATERIALS

The results of pyrolyses at 400°C are given on the following pages (Fig. 16-21) for cellulose, levoglucosan, fir holopulp, a glucuronoxylan, a glucomannan and a dioxane lignin.

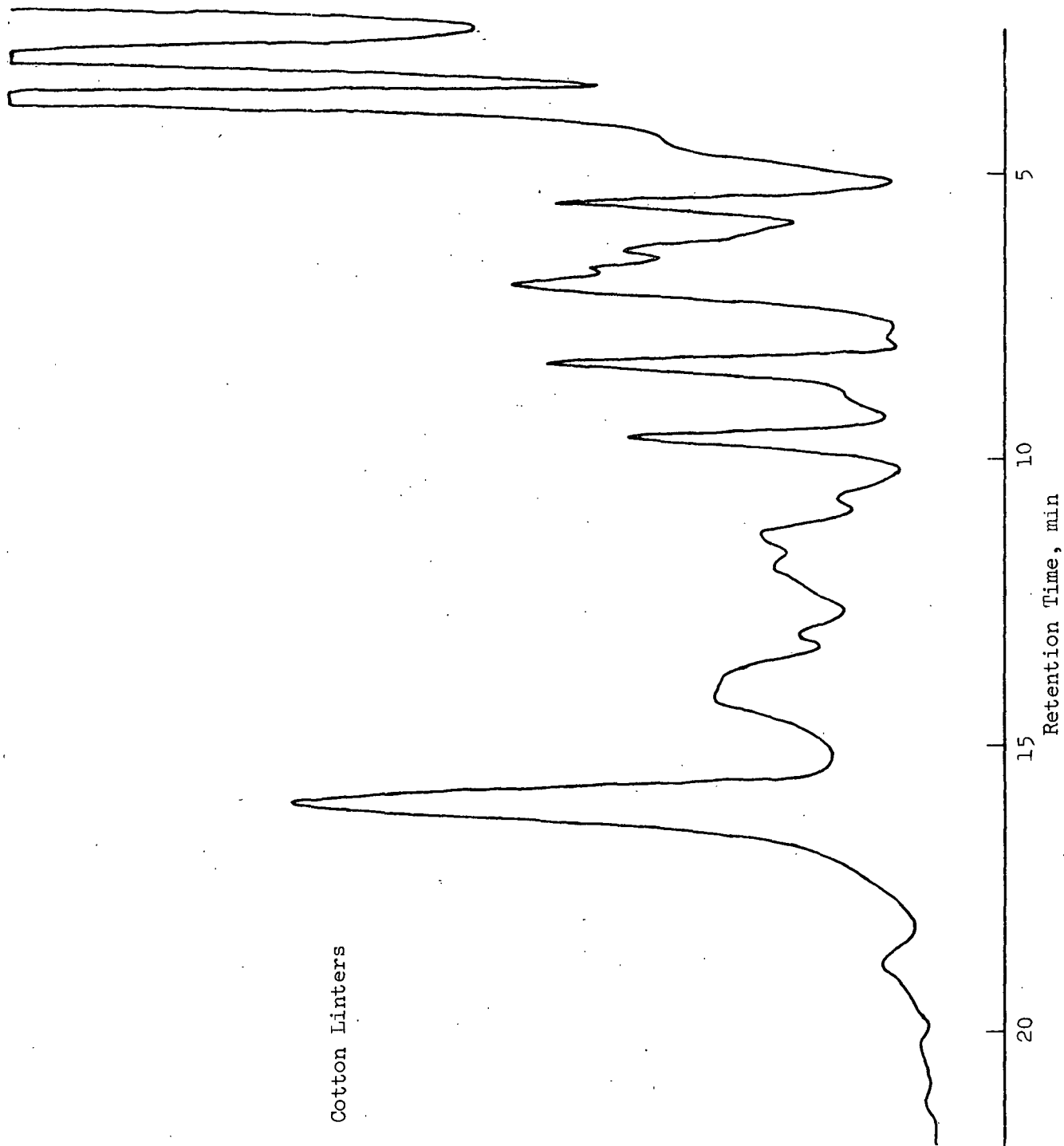


Figure 16. Pyrogram of Cotton Linters

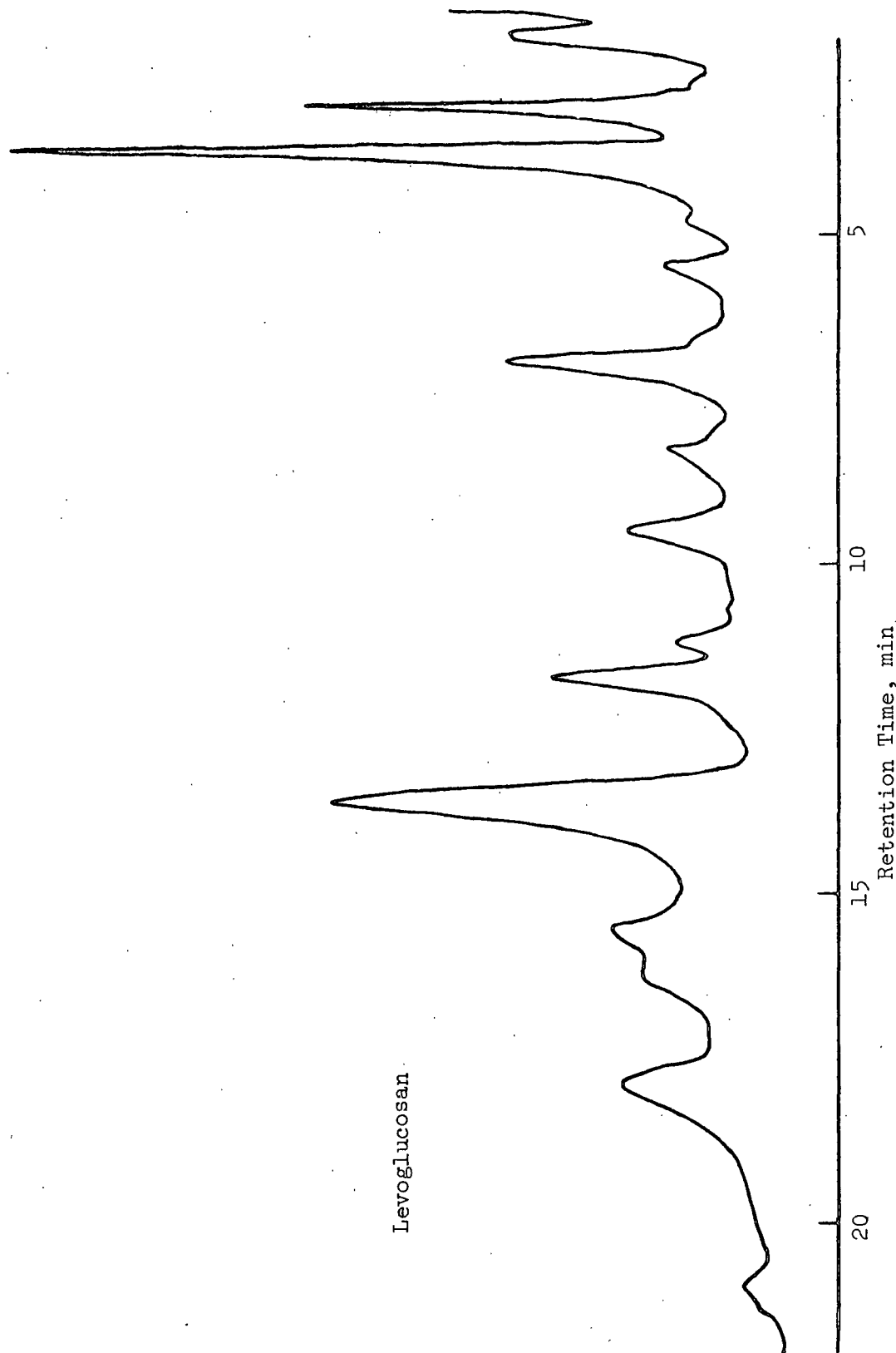
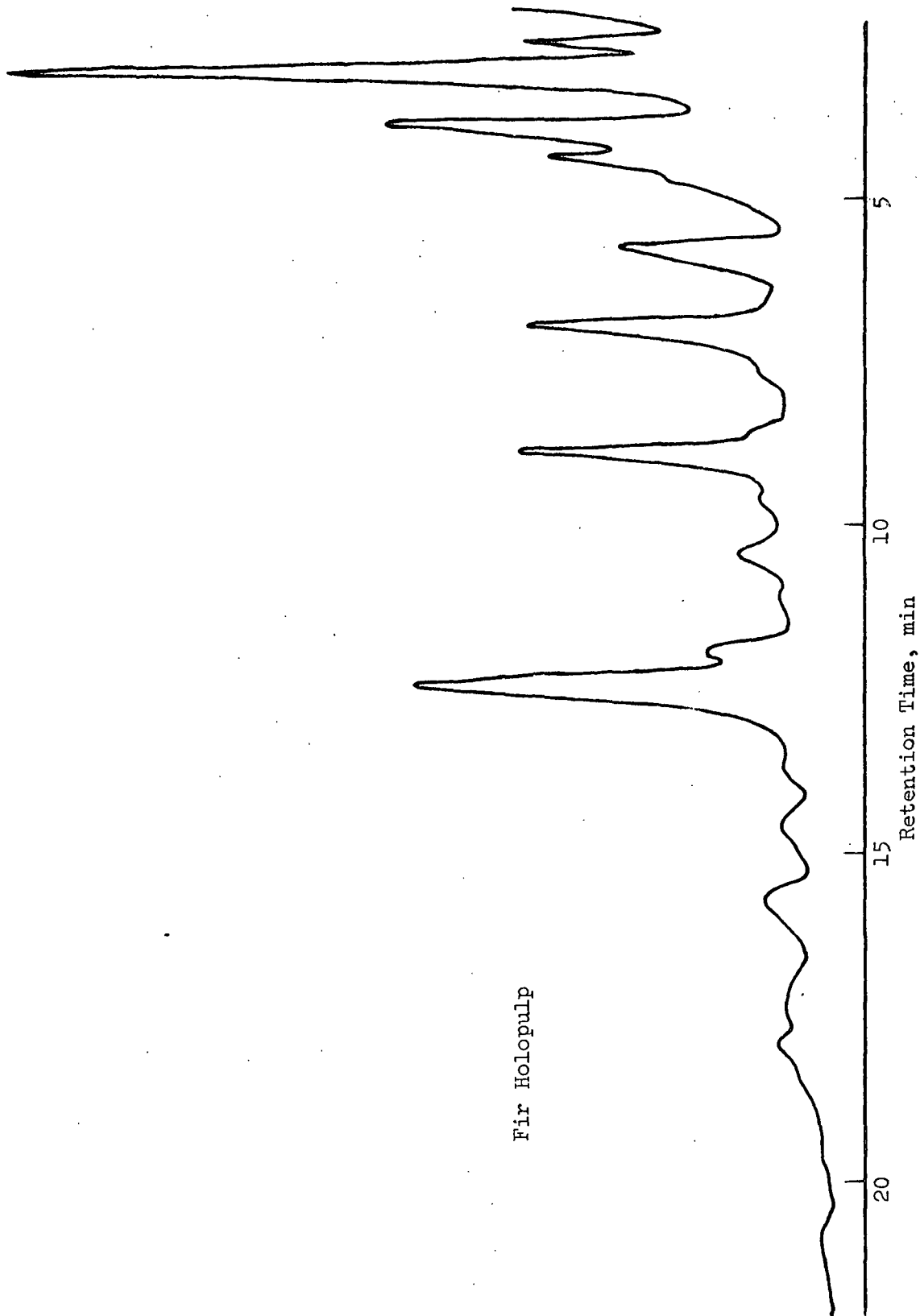


Figure 17. Pyrogram of 1,6-Anhydro-D-Glucopyranose (Levoglucozan)



Fir Holopulp

Figure 18. Pyrogram of a Fir Holopulp

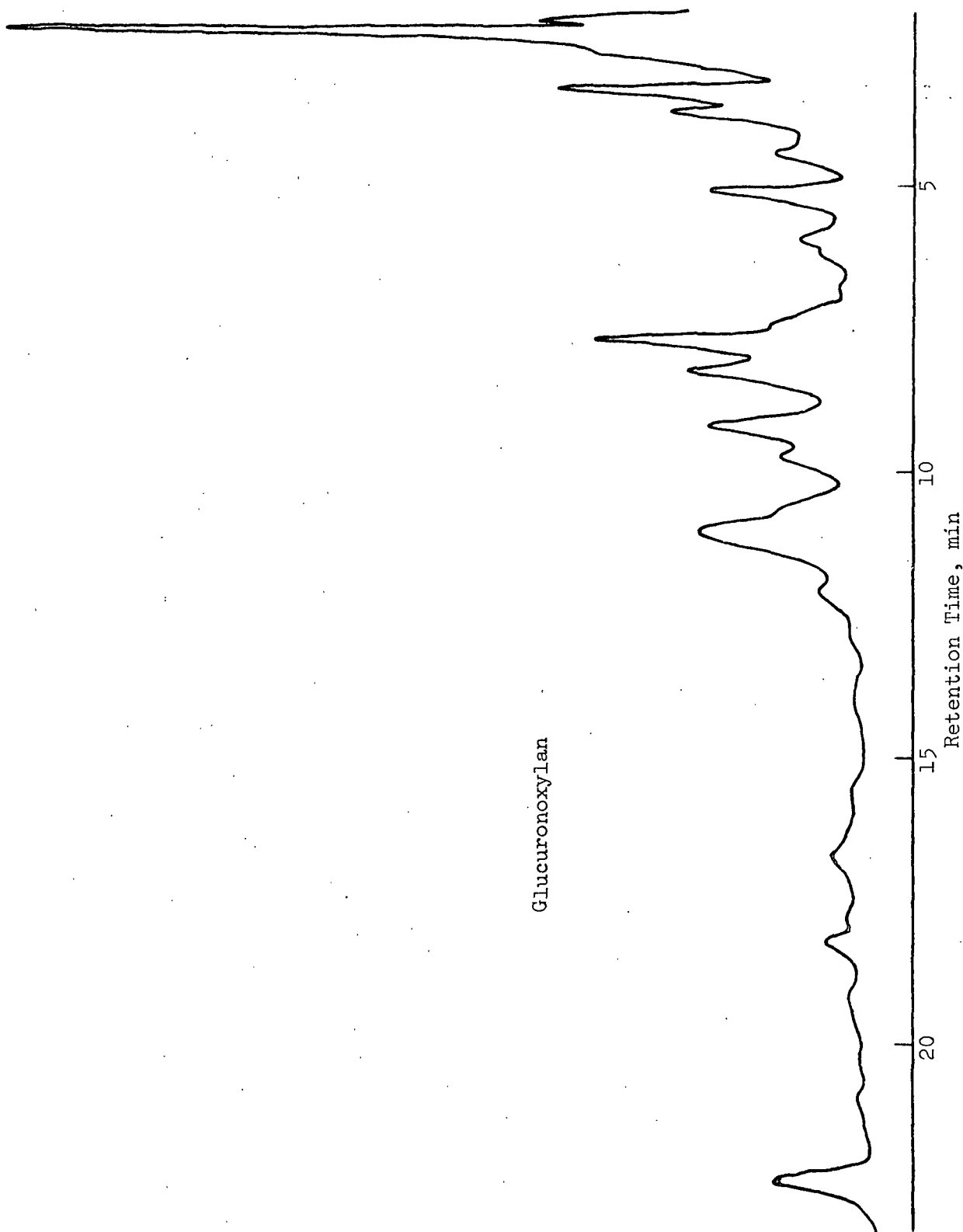


Figure 19. Pyrogram of a Glucuronoxylan Isolated from Yellow Poplar Heartwood

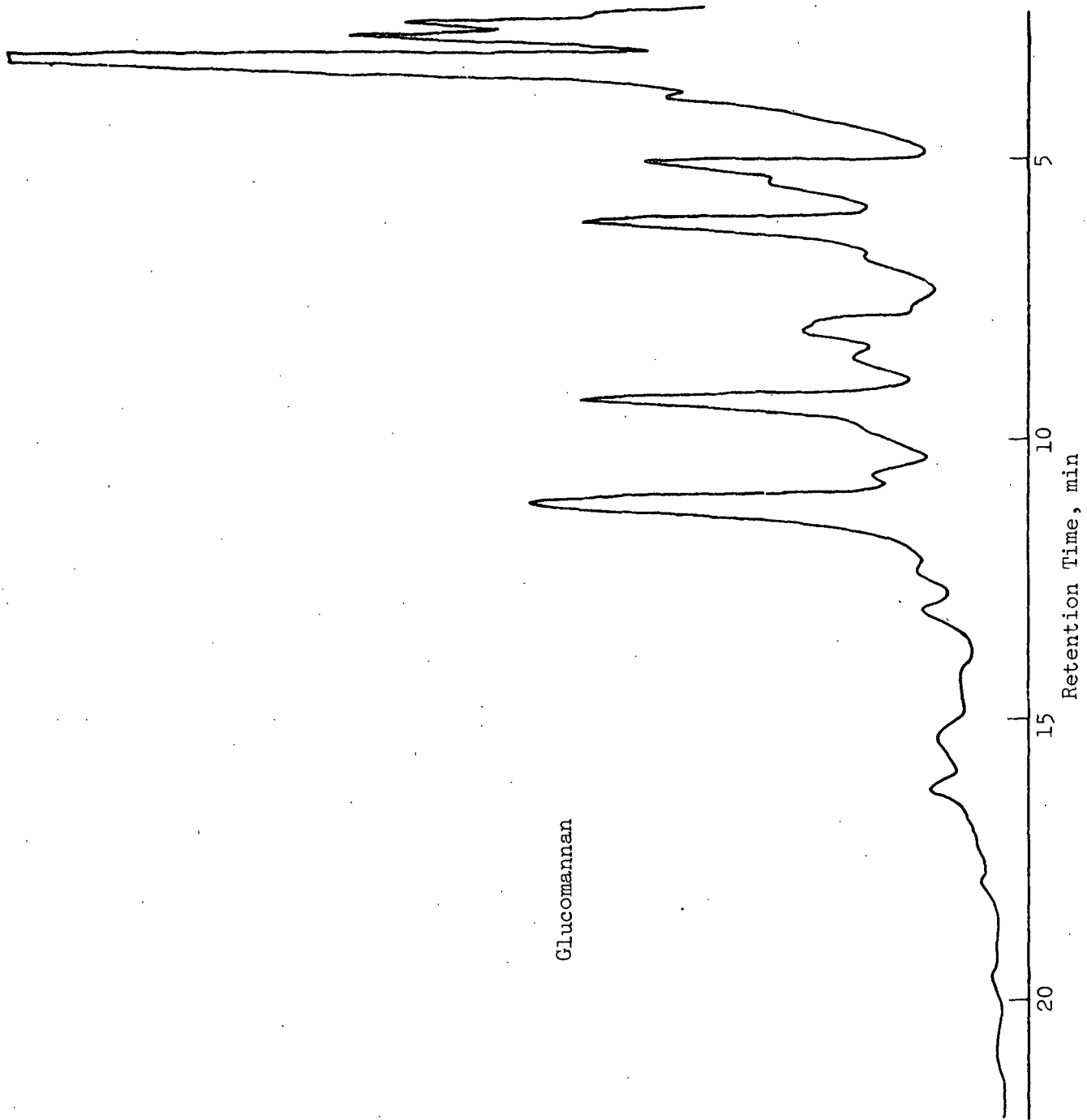


Figure 20. Pyrogram of a Glucomannan Isolated from Engelmann Spruce

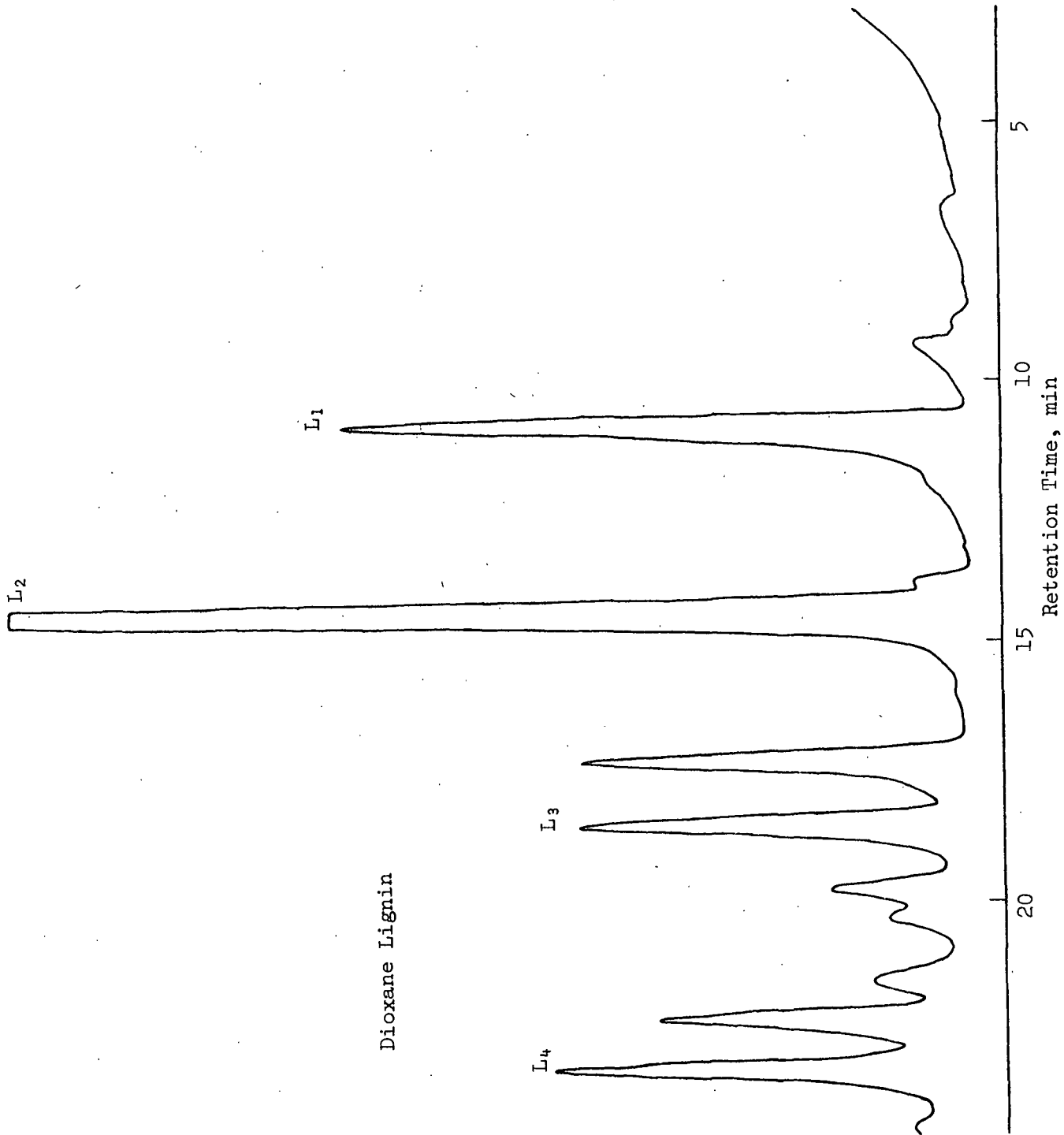


Figure 21. Pyrogram of a Dioxane Lignin Isolated from Loblolly Pine