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Studies on Chlorine Dioxide Modification
of Lignin in Wood

Neil G. Vander Linden

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STUDIES ON CHLORINE DIOXIDE MODIFICATION
OF LIGNIN IN WOOD

A thesis submitted by

Neil G. Vander Linden

B.S. 1964, University of Wisconsin

M.S. 1969, Lawrence University

in partial fulfillment of the requirements
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Appleton, Wisconsin

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TABLE OF CONTENTS

	Page
SUMMARY	1
BACKGROUND	3
Reactions of Chlorine Dioxide and Acidified Chlorite	3
Model Compound Studies	3
Isolated Lignin Studies	8
Lignin <u>In Situ</u> Studies	9
Spectrometric Studies	10
Infrared Spectroscopy	10
Ultraviolet and Visible Spectroscopy	12
Proposed Study	14
RESULTS AND DISCUSSION	15
General Oxidation Results	15
Effect of Reaction on Lignin Content	18
Effect of Reaction on Functional Group Content	18
Effect on Methoxyl Content	24
Carboxyl and Volatile Methoxyl	26
Chlorination	27
Alkaline Cupric Oxide Degradation of Groundwoods	29
Reaction	29
Isolation and Identification	29
Quantitative Analysis of Products	31
Ultraviolet and Visible Spectral Analysis	37
Practical Aspects	37
Basic Theory	38
Cotton Dilution Method	39
Compact Method	41
Absorption Spectra	44

	Page
Infrared Spectral Analysis	49
Oxidation Effects	51
Neutralization Studies	53
Reduction Effects	57
Extent of Reaction	59
CONCLUSIONS	65
EXPERIMENTAL	68
Selection and Preparation of Starting Material	68
Groundwood Extraction	68
Analytical Procedures	69
Chlorine Dioxide Generation	71
Reaction of Groundwood with Chlorine Dioxide	71
Other Groundwood Reactions	72
Infrared Analysis	75
Ultraviolet and Visible Analysis	76
Gas Chromatographic Analysis	77
Mass Spectrometric Studies	78
ACKNOWLEDGMENTS	80
LIST OF ABBREVIATIONS	81
LITERATURE CITED	82
APPENDIX I. SAMPLE CALCULATIONS	85
Calculation of Yield-Basis Lignin Content for 6% Chlorine Dioxide-Reacted Material	85
Calculations to Change from Weight Basis to Molecular Equivalent Basis for 6% Chlorine Dioxide-Reacted Material	85
APPENDIX II. IDENTIFICATION OF CUPRIC OXIDE DEGRADATION PRODUCTS	88
Peaks GW-1 and CD-1	88

	Page
Peaks GW-2 and CD-2	92
Peaks GW-3 and CD-3	92
Peaks GW-4 and CD-4	97
Peak CD-5	101
Peaks GW-6 and CD-6	104
APPENDIX III. SPECIFIC SCATTERING AND ABSORPTION COEFFICIENTS OF WHATMAN COMPACTS	109
Key to Flow Sheets of Program BACS	111
Flow Sheet for Program BACS	112
Computer Program BACS	113
Computer Program VAND	115
APPENDIX IV. EXACT COMPOSITION OF COMPACTS USED FOR REFLECTANCE MEASUREMENTS	117

SUMMARY

White spruce (Picea glauca) groundwood was reacted to completion at 35°C with limited amounts of unbuffered aqueous chlorine dioxide and the nature of the modified lignin was studied in situ. Oxidant amounts employed ranged from 2 to 10% by weight on the oven-dry groundwood resulting in yields of from 96 to 100%.

The effects of the chlorine dioxide reaction on the lignin structure and functional group content were studied using recently developed spectrometric methods complemented by selective reduction and degradation studies and classical analytical procedures. Infrared spectra and difference spectra were obtained using potassium chloride pellets containing finely milled groundwood. Ultraviolet and visible spectra were obtained using a new reflectance method developed for this work. Some materials were subjected to reductive bleaching with sodium dithionite and uranium(III) ion in order to investigate the nature of chromophoric groups. Cupric oxide degradation studies were done to determine the degree of aromatic chlorine substitution and analytical work was done to determine the content of Klason and acid-soluble lignin, methoxyl, organically bound chlorine, carboxyl, and volatile methoxyl.

The results showed that the lignin remaining in situ was extensively modified. For the 6% chlorine dioxide reacted material, the modified lignin was found to contain about 80% aromatic material and 20% ring-oxidized products. About 6% of the aromatic structures and over half of the ring-oxidized structures were found to be chlorinated. About 1.8 equivalents of carboxyl and 0.2 equivalent of volatile methoxyl were found for each equivalent of ring-oxidized material produced. Infrared spectra showed considerable increases in absorption due to carboxyl, carbonyl and small increases in absorption due to ester carbonyl and sodium dithionite-reducible carbonyl, as well as substantial

decreases in the absorption bands associated with the aromatic rings. Ultra-violet spectra also showed decreases in the absorption bands associated with the aromatic rings, whereas the visible spectra showed absorption increases due to chlorine dioxide produced chromophores. About 75% of the absorption due to these chromophores could be removed by sodium dithionite reduction. The remaining 25% could not be removed by either of the two reducing agents employed, leaving a residual absorption stronger than that of the original groundwood.

On the basis of the above, it was concluded that the principal chlorine dioxide oxidation products remaining with the lignin in situ are probably chlorinated and unchlorinated muconic acid derivatives, which account for about 85% of the ring-oxidized material or 18% of the total modified lignin. The remainder of the ring-oxidized material appears to consist of mainly quinone structures and lactones formed from the muconic acids. Finally, about 6% of the aromatic structures are chlorine substituted at the 6-position.

The improved knowledge of the nature of chlorine dioxide modified lignin in situ should prove useful to those involved in the development of chlorine dioxide pulping processes, particularly those involving chlorine dioxide modification of lignin followed by extraction with some other chemical.

BACKGROUND

The following paragraphs summarize current knowledge concerning the oxidation of lignin model compounds, isolated lignins, and lignin in situ by chlorine dioxide and related oxidants. Among the oxidants included are acidified chlorite and elemental chlorine, since in acidic media chlorine dioxide, hypochlorous acid, chlorous acid, and elemental chlorine are all involved whether or not chlorine dioxide or acidified chlorite is used as the oxidizing agent (1). Also included are some results of studies relating to peroxyacetic acid oxidation as there is a considerable similarity in the type of products formed.

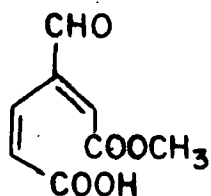
REACTIONS OF CHLORINE DIOXIDE AND ACIDIFIED CHLORITE

MODEL COMPOUND STUDIES

The most comprehensive works on chlorine dioxide and acidified chlorite oxidation of lignin model compounds are those of Sarkanen, et al. (2) and Dence, et al. (3). They studied the reactions of vanillin, vanillyl alcohol, α -methyl vanillyl alcohol, and syringyl alcohol with both oxidants and found the principal products to be derivatives of muconic acid monomethyl esters or p-benzoquinones. Figure 1 shows the compounds isolated and identified along with the respective model compounds from which they were obtained.

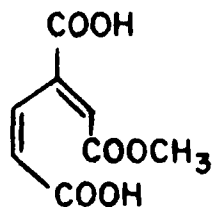
For the most intensely studied model, vanillyl alcohol, the combined yields of the reaction products accounted for only 28% of the substrate, indicating that there may be other as yet unidentified product types.

No muconic acid derivatives were found containing substituted chlorine, leading the authors to speculate that chlorine substitution stabilized the



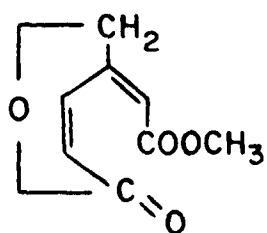
β -formyl muconic acid
monomethyl ester
(from vanillin)

I



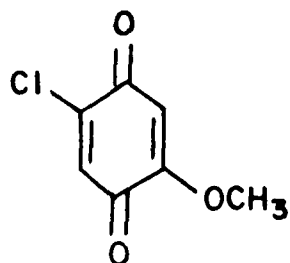
β -carboxy muconic acid
monomethyl ester
(from vanillin)

II



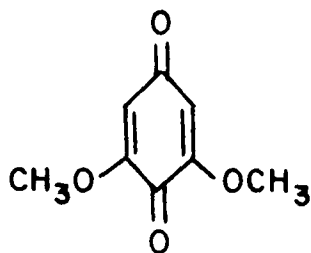
δ -lactone ester
(from vanillyl alcohol)

III



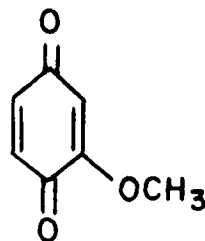
2-methoxy-5-chloro-
p-benzoquinone
(from vanillyl alcohol)

IV



2,6-dimethoxy-
p-benzoquinone
(from syringyl alcohol)

V



2-methoxy-
p-benzoquinone
(from α -methylvanillyl alcohol)

VI

Figure 1. Products Isolated from Model Compounds (2,3)

ring against further attack. The formation of chlorinated products was attributed to the formation of elemental chlorine in the reaction mixture as a result of secondary reactions.

Ishikawa, et al. (4) repeated some of this earlier work (2,3) and confirmed the results of vanillyl alcohol, but suggested that the product identified previously as a β -formyl muconate (I) was more likely a lactol (VII in Fig. 2). They also isolated the chlorinated quinone (IV) from vanillin oxidation and a 1,3-diketone (VIII) and a chlorinated quinone (IX) from syringyl alcohol oxidation.

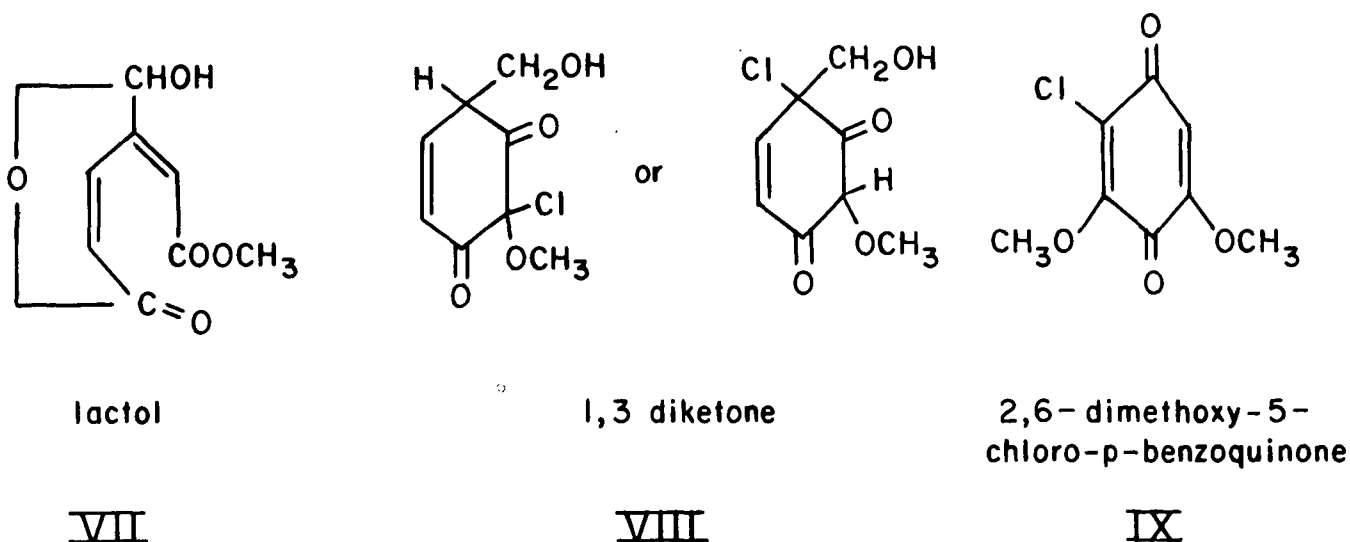
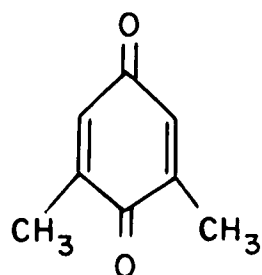


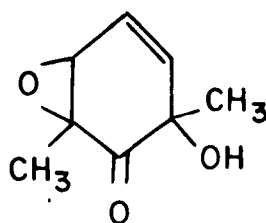
Figure 2. Additional Products from Model Compounds (4)

Lindgren and Ericsson (5) studied the reaction of 2,6-xyleneol and mesitol with chlorine dioxide and found the major products to be the p-quinone (X) and epoxy-ketone (XI) for the former and the p-quinol (XII), epoxy-ketone (XIII), and chlorinated epoxy-ketone (XIV) for the latter (Fig. 3). The epoxy compounds were only isolated from solutions buffered at pH 5, although there was some gas chromatographic evidence that they might be formed as an intermediate in unbuffered solutions.



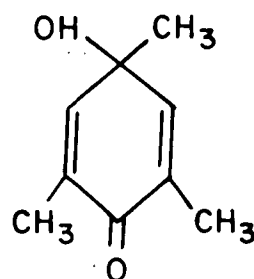
p-quinone

X



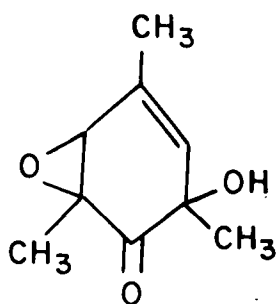
epoxy-ketone

XI



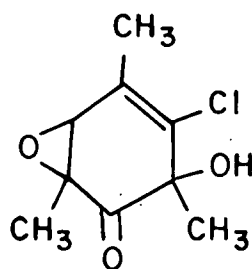
p-quinol

XII



epoxy-ketone

XIII



3-chloro-epoxy-ketone

XIV

Figure 3. Oxidation Products Reported by Lindgren and Ericsson (5)

In another publication (6), Lindgren reported the isolation of the benzene-sulfinic acid adduct of the o-benzoquinone, as well as the p-benzoquinone and muconic acid derivatives, on chlorine dioxide oxidation of guaiacol and pyrocatechol.

In studies of related oxidants, Gess and Dence (7) have shown that chlorination of creosol results in the formation of o-benzoquinones of varying degrees of chlorine substitution and trichloromethyl muconic acid.

Farrand (8) isolated various muconic acid derivatives and quinones from the peroxyacetic acid oxidation of lignin model compounds. The results of his work are summarized in Fig. 4. Farrand's diacid (XVII) is similar in nature to the monomethyl muconic acid derivatives found from the chlorine dioxide oxidation of vanillin. Since these esters are easily hydrolyzed (3), it is conceivable that the diacid and products such as XIX and XX could also be formed in the chlorine dioxide system.

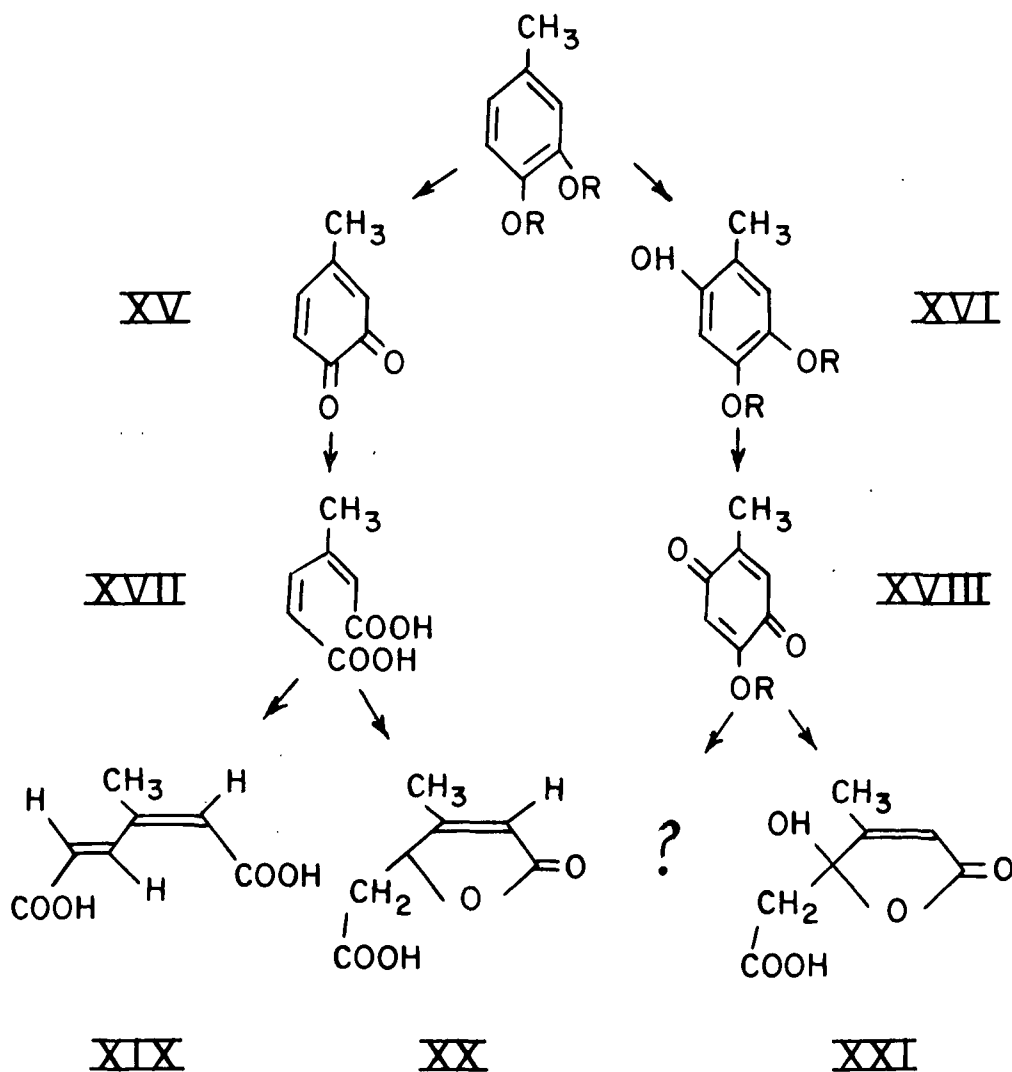


Figure 4. Reaction Scheme for Peroxyacetic Acid Oxidation of Lignin Model Compounds (8)

ISOLATED LIGNIN STUDIES

The most recent and detailed study of chlorine dioxide oxidation of isolated lignins is that of Ishikawa, et al. (4). They reacted pine and birch dioxane lignins with excess oxidant and analyzed the soluble and insoluble lignin degradation products for various functional groups. As expected, on the basis of model compound studies, they found considerable chlorination, demethylation, and production of carboxyl groups. Their results are summarized in Table I.

TABLE I
FUNCTIONAL GROUPS PER C₉ UNIT FOR CHLORINE DIOXIDE-OXIDIZED
PINE DIOXANE LIGNIN

Material	Cl	OCH ₃	CO ₂ CH ₃	COOH	Phenolic OH
Original lignin	0.00	0.93	0.02	0.00	0.30
Insol. oxid. lig.	0.65	0.46	0.27	0.86	0.00
Sol. oxid. lignin	1.31	0.18	0.22	2.10	0.00

Their studies of oxidant consumption and solubilization showed that the consumption leveled off after about an hour, but lignin solution continued for an additional three or four hours. They attributed this phenomenon to the initial formation of methyl esters of muconic acid derivatives followed by a slower ester hydrolysis with the resultant formation of the more soluble diacid derivatives.

The total amount of oxidant consumed by the various isolated lignins was found to be related to the phenolic content and varied from about 1 mole per equivalent for liginosulfonic acid to about 2 moles per equivalent for pine dioxane lignin.

Levitin, et al. (9) studied oxylignins produced from the oxidation of periodate lignin with both acidified chlorite and chlorine dioxide and found the products showed considerable chlorination and demethylation. Ultra-violet spectra of methanol solutions of the oxylignins showed a marked decrease in absorbance in the 280 nm region. Barton (10) obtained similar results in his study of the soluble degradation products from the acidified chlorite oxidation of Indulin.

LIGNIN IN SITU STUDIES

Barton (10) studied the soluble products from the acidified chlorite oxidation of slash pine and isolated two materials which he designated as "chlorite lignin A" and "chlorite lignin B." The former has the empirical formula $C_{26}H_{28}O_{14}Cl$, is free of carbohydrate materials, and appears to contain two methoxyl groups, two carboxyl groups, two hydroxyl groups, and one chlorine atom per unit weight of 600 g. The latter has the empirical formula $C_{21}H_{21}O_{13}Cl_2$ and appears to contain one methoxyl group, two carboxyl groups, and two chlorine atoms per unit weight of 553 g. In view of earlier work by Pearl (11) in which 6-chlorovanillin was isolated from spent liquor from the acidified chlorite oxidation of black spruce, a portion of the chlorine in Barton's oxylignins is probably aromatically substituted.

Barton's attempt at a lignin material balance met with failure. Stone and Kallmes (12) encountered similar problems in attempting to determine a lignin balance on acidified chlorite-treated wood samples. They concluded that there is an appreciable quantity of insoluble lignin derived material which remains with the wood but is not discernible by Klason lignin analysis.

Buchanan (13) found considerable organically bound chlorine in chlorine dioxide-modified wood and found both chlorine and carboxyl groups in the alkali-soluble portion of the modified material. Much of the organically bound chlorine was found to be susceptible to alkaline hydrolysis.

Dence, et al. (3) also studied the chlorine dioxide demethylation of wood meal, along with the previously mentioned studies of model compounds and isolated lignins. They observed that the degree of demethylation was greatest for model compounds, slightly less for isolated lignins, and considerably less for lignin in situ. On the basis of these studies they proposed a scheme showing the kinds of reactions to be expected when lignin is oxidized by aqueous chlorine dioxide. This scheme is shown in Fig. 5.

SPECTROMETRIC STUDIES

In recent years a number of new spectrometric techniques have been developed which make it possible to study lignin in situ. Although these studies do not concern chlorine dioxide oxidation, they are pertinent to this work and will be discussed in the following paragraphs.

INFRARED SPECTROSCOPY

The most important new technique in infrared spectroscopy of lignin is the development of differential spectra by Kolboe and Ellefson (14). They obtained spectra of lignin in situ by placing the material to be investigated in the sample beam of the spectrophotometer and a calculated amount of holocellulose in the reference beam. Thus, they were able to cancel out the absorption due to the carbohydrate material leaving only that due to lignin. They used the technique to compare the spectra of lignin in situ with those of Brauns and

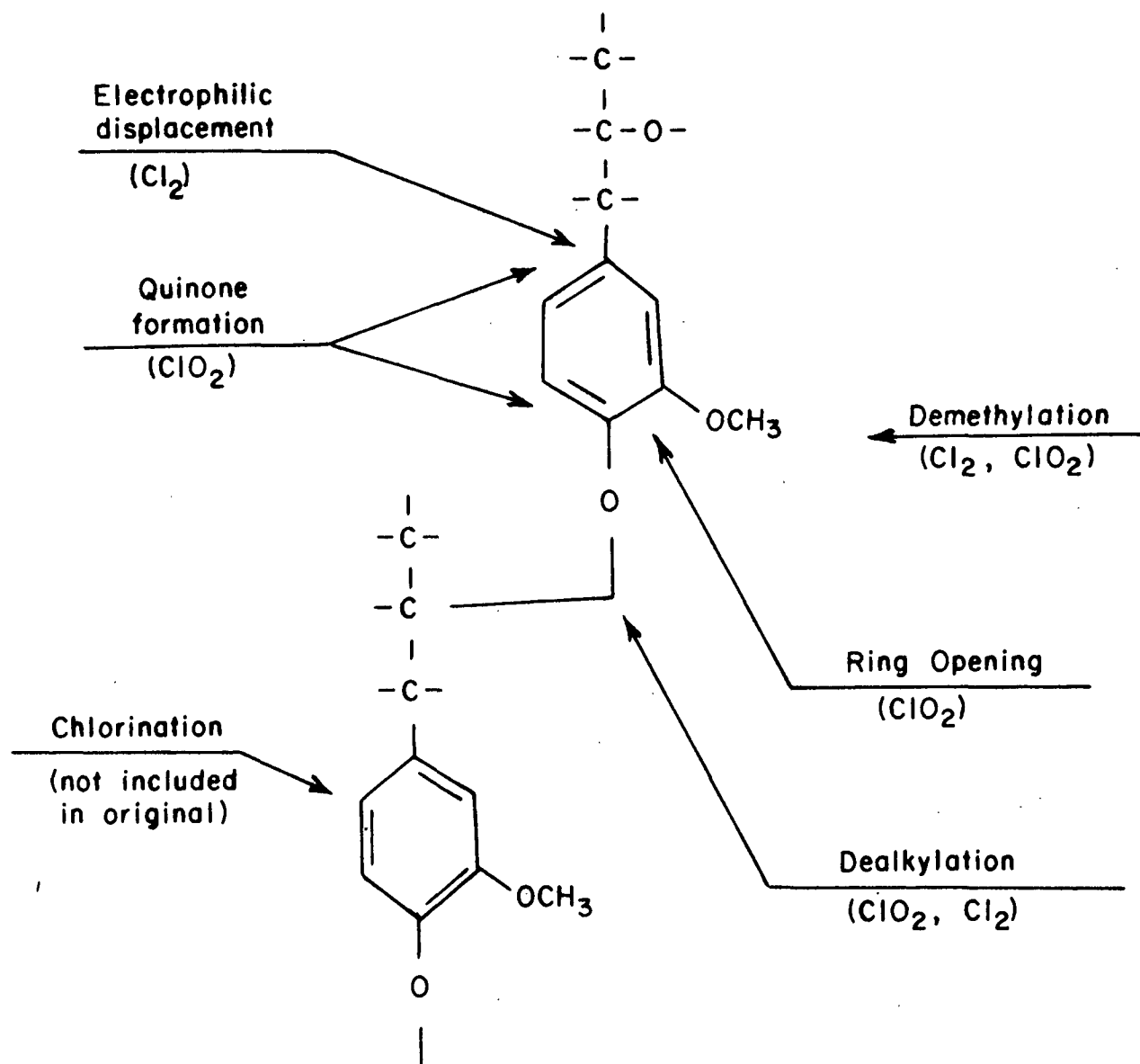


Figure 5. Attack of Lignin by Chlorine Dioxide (3)

Bjorkman isolated lignins and concluded that only small structural changes occur on isolation.

Bolker and Somerville (15) applied the same technique to the study of residual lignin in unbleached pulps. Michell, et al. (16-18) applied the technique to the study of delignification during NSSC pulping. Spectra were measured on thin microtome sections of wood cooked to varying degrees. He modified the technique slightly by placing samples from two successive cooks in the two beams in order to study progressive changes.

ULTRAVIOLET AND VISIBLE SPECTROSCOPY

In the ultraviolet and visible regions of the spectrum two types of techniques have been developed for determining the spectra of lignin in situ.

Bolker and Somerville (19) used KCl pellets containing finely ground sample. They used a dilution method to prepare pellets containing very small but exact amounts of sample and holocellulose and then ran difference spectra such as was discussed for the infrared region.

Polcin and Rapson (20-22) developed various reflectance techniques for the study of lignin absorption in the ultraviolet and visible regions. These reflectance techniques are based on the theory of light scattering as developed by Kubelka-Munk and modified by Van den Akker (23). According to the theory the reflectance of a thick pad, R_{∞} , can be used to calculate the ratio of the absorption coefficient, K , and the scattering coefficient, S , as indicated in Equation (1).

$$K/S = (1-R_{\infty})^2/2R_{\infty} \quad (1)$$

These values were determined for each wavelength of interest. Their difference for a sample before (o) and after (a) a given treatment was called the "decoloration number," \underline{DC}_λ , as shown in Equation (2).

$$\underline{DC}_\lambda = {}^o(K/S)_\lambda - {}^a(K/S)_\lambda \quad (2)$$

For treatments mild enough to have little or no effect on the scattering coefficient this becomes

$$\underline{DC}_\lambda = [{}^o(K_\lambda) - {}^a(K_\lambda)]/S_\lambda \quad (3)$$

It is obvious from Equation (3) that the decoloration number is still dependent on S_λ , which would have to be determined for each wavelength of interest.

Therefore, they conceived a new variable "relative decoloration number,"

$[\underline{DC}]_\lambda$, which is independent of S_λ and therefore a more accurate measure of changes in the chromophoric content of the material. This quantity is defined in Equation (4).

$$[\underline{DC}]_\lambda = [{}^o(K/S)_\lambda - {}^a(K/S)_\lambda]/{}^o(K/S)_\lambda \quad (4)$$

Thus, if chromophores absorbing at the wavelength in question are removed as a result of the treatment, $[\underline{DC}]_\lambda$ is a positive number between 0 and 1. If chromophores are formed during the treatment, $[\underline{DC}]_\lambda$ is a negative number whose magnitude depends on the number of chromophores introduced.

For more drastic treatments, where S_λ is likely to be affected or where the absolute values of K_λ and S_λ are desired, a more complicated procedure must be employed involving the measurement of not only R_∞ , but also the transmittance or R_0 , which is the reflectance of a thin sheet backed by a black background of zero reflectance. This procedure will be discussed more fully later.

These reflectance techniques have been employed by Polcin and Rapson (24-26) and Fleury and Rapson (27) to study the reduction of chromophores in lignin by various reducing agents and to determine the ultraviolet and visible spectra of lignin in situ.

PROPOSED STUDY

In view of the previous discussion it is apparent that very little is known concerning the modification of lignin in situ by chlorine dioxide. Model compound studies have yielded information regarding the types of compounds most likely to be formed, p-benzoquinones, and derivatives of muconic acids, but, to date, no one has given evidence which would either confirm or deny their presence in the modified lignin in situ.

For the above reasons it was decided to apply the recently developed experimental techniques to the study of the changes which occur when lignin in situ is modified through treatment with selected amounts of chlorine dioxide. The reactions were confined to those relatively high yields (95 to 100%) at which the lignin is modified but not yet extensively solubilized. Only the modified lignin remaining with the wood was to be studied.

The results of this work should give a better understanding of the chlorine dioxide-lignin reaction and should be especially useful to those interested in employing chlorine dioxide as a pulping agent, since knowledge of the nature of chlorine dioxide-modified lignin could be useful in determining the optimum amounts of oxidant required or could be used to further develop multistage processes in which chlorine dioxide modifies the lignin prior to extraction with some other chemical.

RESULTS AND DISCUSSION

White spruce (Picea glauca) was chosen as the substrate for this work since it was readily available and could be hand processed in order to obtain a groundwood of known origin and quality. The wood was converted to refiner groundwood and subjected to alcohol-benzene and hot water extraction as indicated in the Experimental section,

Most of the work reported here was done on groundwood reacted with 2, 4, 6, 8, or 10% chlorine dioxide on an oven-dry wood basis as described in the Experimental section. The above values for percentage chlorine dioxide are nominal values used for convenience in the text. In practice, they were slightly lower due to a steady decrease in the concentration of the chlorine dioxide solution during the filling of the reaction bottles. Assuming a linear decrease in concentration with time, the actual values have been estimated from the known initial and final concentrations (6.015 and 5.612 g/liter, respectively) and are given in Table II. Some initial work was also done on groundwood reacted with 3, 6, and 9% chlorine dioxide and some data are reported for the corresponding products. The 2 and 6% chlorine dioxide-reacted materials were selected for more extensive study.

GENERAL OXIDATION RESULTS

The results of the chlorine dioxide oxidation of the groundwood materials are summarized in Table II. On addition of the chlorine dioxide there is an immediate change in color. The initially pink tint then either persists or gradually passes through shades of orange to yellow, depending on the amount of oxidant applied. The time required to exhaust the oxidant appears to be linearly related to the percentage applied for concentrations up to about 8% (Fig. 6).

TABLE II

aqueous chlorine dioxide oxidation of groundwood
(35°C and 3% consistency)^a

O.D. Groundwood, g	Chlorine Dioxide, % o.d. GW ^b	Product Color	Reaction Time, hr-min	Yield, %
39.774	1.86	pink	1-43	99.12
40.797	1.87	pink	1-52	99.20
38.849	1.84	pink	2-01	99.45
	<u>1.86^c</u>		<u>1-52</u>	<u>99.26</u>
39.657	3.79	peach	3-27	99.01
39.580	3.81	peach	3-37	99.06
40.862	3.82	peach	3-46	99.02
	<u>3.81</u>		<u>3-37</u>	<u>99.03</u>
40.133	5.77	orange	4-55	98.67
40.010	5.80	orange	5-03	98.28
39.158	5.83	orange	5-13	98.18
	<u>5.80</u>		<u>5-04</u>	<u>98.38</u>
40.068	7.81	yellow-orange	6-21	d
39.928	7.85	yellow-orange	6-33	97.11
39.627	7.87	yellow-orange	6-48	97.29
	<u>7.84</u>		<u>6-34</u>	<u>97.20</u>
40.213	9.91	yellow	7-05	96.67
40.170	9.92	yellow	7-15	96.63
38.993	9.99	yellow	7-25	96.75
	<u>9.94</u>		<u>7-15</u>	<u>96.68</u>

^aUnbuffered media - final pH ca. 2.0.

^bGW = groundwood.

^cAll underlined figures are averages of previous three entries.

^dYield not determined due to loss of material during processing.

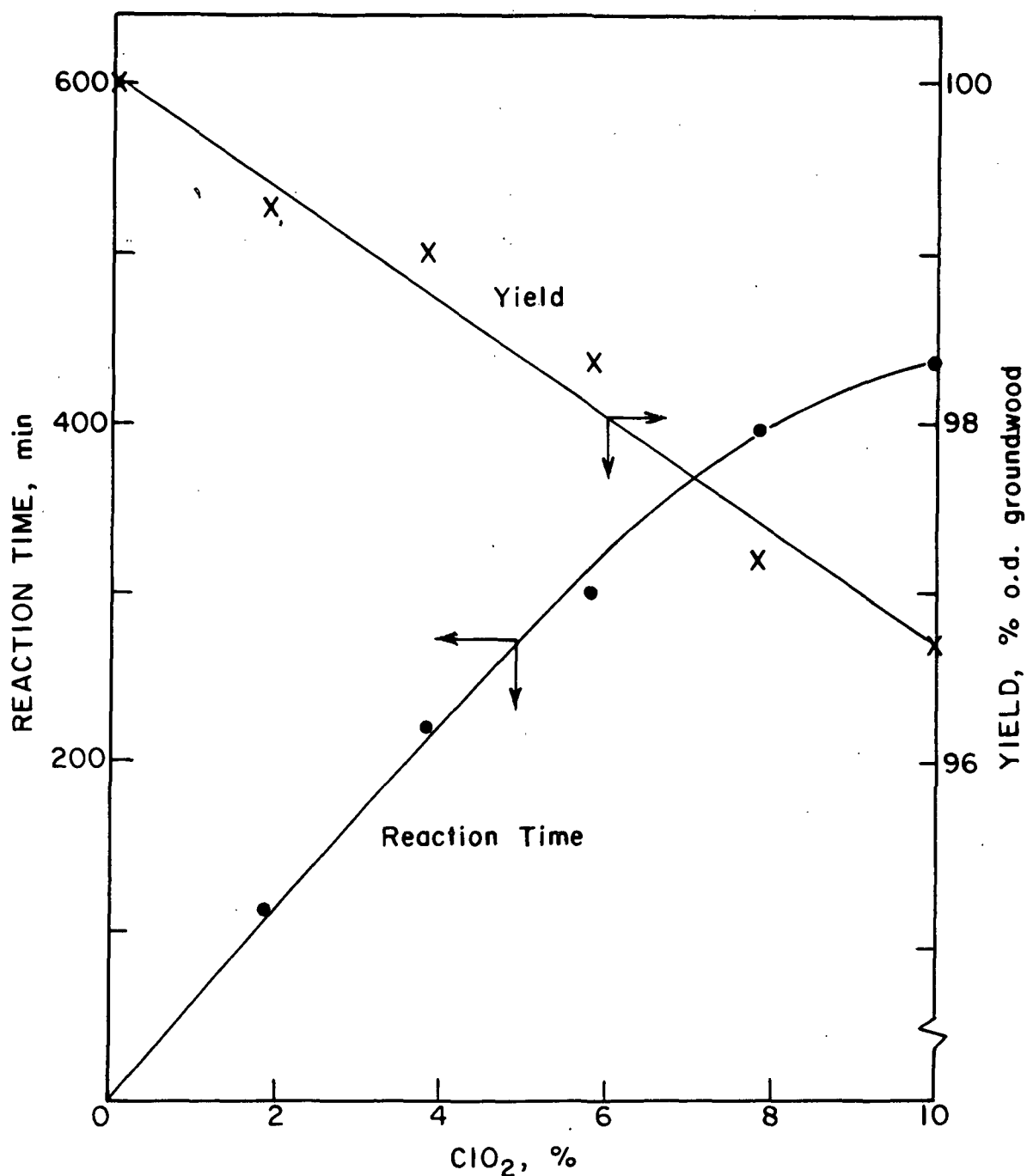


Figure 6. Effect of ClO₂ Concentration on Yield and Reaction Time

Also shown in the figure is the groundwood yield which appears to have a reverse linear relationship with the chlorine dioxide concentration over the range of values investigated. A regression line was fitted through the experimental points and yield values from this line were used to calculate the experimental or yield-basis values for the lignin concentration as described in the Experimental section.

EFFECT OF REACTION ON LIGNIN CONTENT

The reaction with chlorine dioxide has a dramatic effect on the analytical lignin content as shown in Fig. 7. From a comparison of the yield-basis lignin content (calculated by assuming all material lost during the course of the reaction to be lignin) and the Klason plus acid-soluble lignin content, it is quite obvious that these analytical methods do not give a realistic measure of the lignin-derived material present in the chlorine dioxide-reacted materials. Apparently, the lignin in situ has been modified in such a way as to no longer be completely discernible by classical methods.

The lines on the graph are a result of regression analysis. Future references to lignin content in this work all will refer to the values obtained from the yield-basis regression line unless otherwise specified.

EFFECT OF REACTION ON FUNCTIONAL GROUP CONTENT

The original groundwood and the 3, 6, and 9% chlorine dioxide-reacted materials were analyzed for methoxyl and organically bound chlorine contents. The carboxyl content was also determined for the original groundwood and the 6% chlorine dioxide-reacted groundwood. Finally, the volatile methoxyl portion of the total methoxyl liberated as methanol on hot distillation was determined for the 6% chlorine dioxide-reacted material. The results of these analyses are presented in Table III. Information concerning procedures used can be found in the Experimental section.

In order to better visualize the effects of the chlorine dioxide reaction, it is desirable to convert the data in Table III from a weight basis to a molecular equivalent basis. To do this, it is first necessary to make some basic assumptions concerning the nature of the lignin material.

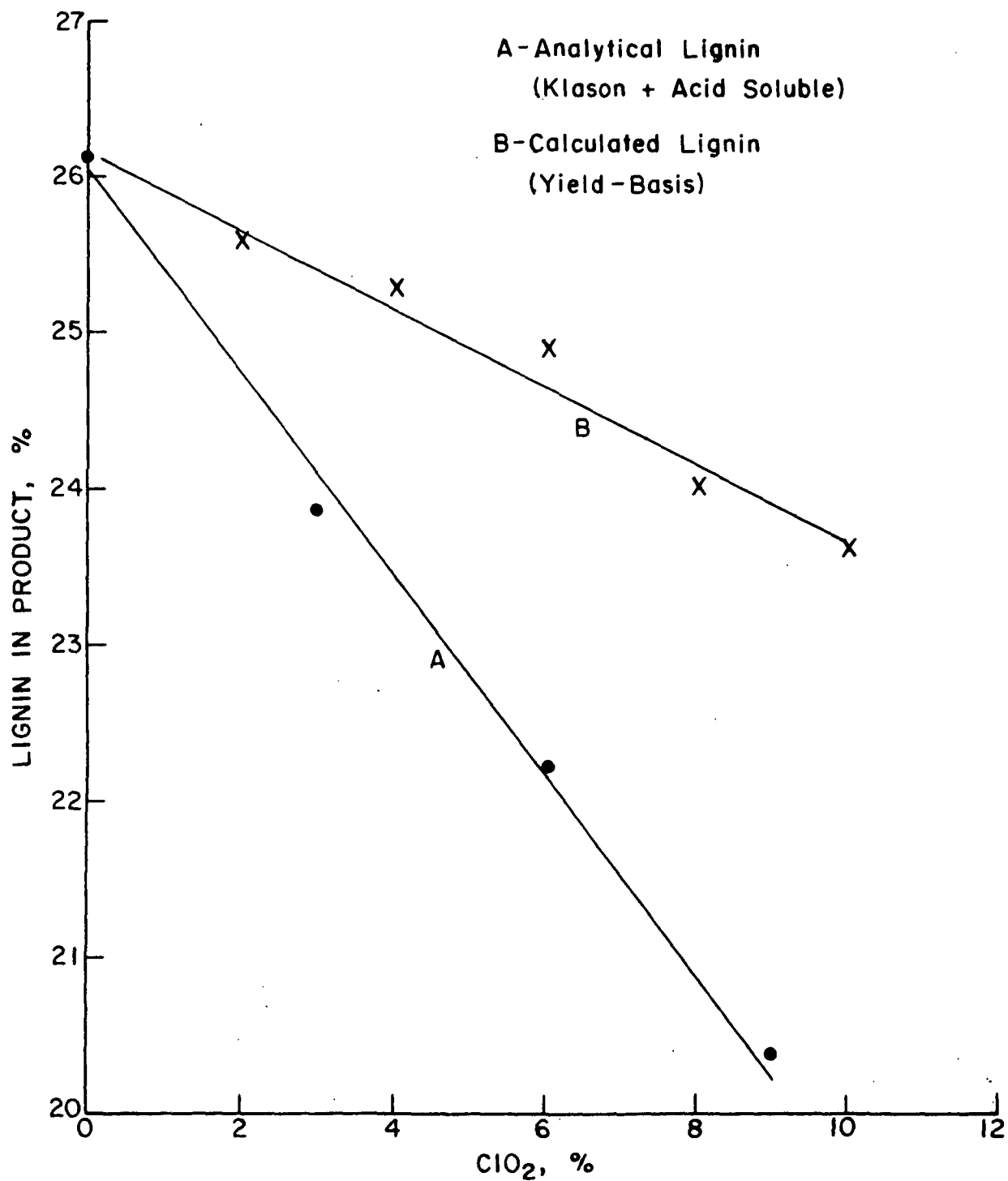


Figure 7. Effect of ClO_2 on Lignin Content

TABLE III

ANALYTICAL RESULTS^a

Chlorine Dioxide Applied	Klason ^b Lignin	Acid- Soluble Lignin	Total Methoxyl	Organically Bound Chlorine	Volatile Methoxyl	Carboxyl, equiv. per 100 g
0.0	25.82	0.33	4.06	0.13	--	0.0036
3.0	23.48	0.36	3.70	0.63	--	--
6.0	20.50	1.70	3.10	0.86	0.675	0.04555 ^c
9.0	17.22	3.14	2.68	1.36	--	--

^aAll values except carboxyl are expressed as percentage of oven-dry groundwood product and are the averages of two determinations.

^bCorrected for ash of about 0.6% for original groundwood and much less for chlorine dioxide-reacted materials.

^cCorrected for carboxyl in unreacted groundwood and is therefore representative of carboxyl produced as a result of the chlorine dioxide oxidation.

It is generally accepted that the basic structural unit for the protolignin is the phenylpropane unit whose formula weight can be estimated on the basis of elemental analysis. Lai and Sarkanen (28) give elemental analyses for two sprucewoods which when converted to a C-9 basis¹ give an average formula weight of 187 g/equiv. For chlorine dioxide-reacted materials the picture is not quite so clear. Obviously the reacted lignin is quite different from the protolignin as evidenced by the methoxyl and chlorine contents. In order to arrive at an approximate value for the number of lignin equivalents in the reacted material it is first necessary to make some assumptions concerning the nature of the modified lignin.

For the purpose of conversion to a molecular equivalent basis it will be assumed that the modified lignin consists of an unreacted portion (amount based on methoxyl content) and an oxidized portion (amount obtained by difference). The unreacted portion will be assumed to have the same formula and formula weight as the protolignin, whereas the oxidized portion will be assumed to be a muconic acid structure whose presence is postulated on the basis of model compound and demethylation studies by Dence, et al. (3) and the results of this work. The formation and structure of the muconic acid derivative is illustrated in Fig. 8. Note that the oxidation results in the loss of one carbon atom and two hydrogen atoms and the gain of two oxygen atoms, for a net increase in formula weight of from 187 to 205 g/equiv. On the basis of the above assumptions, it is possible to estimate the number of unreacted basic lignin units from the methoxyl content, calculate the weight of the unreacted lignin, subtract this from the total lignin weight to obtain the weight of the oxidized portion, correct for chlorine content, and divide by 205 g/equiv. to obtain the number of oxidized structures. A sample calculation can be found

¹ $C_9H_8.5O_2.54OCH_3$ 1.93

in Appendix I. The final results of this transformation are given in Table IV. They are presented both on the basis of 100 equivalents of original lignin (reflecting yield effects) and on the basis of 100 equivalents of product lignin (reflecting percentage composition).

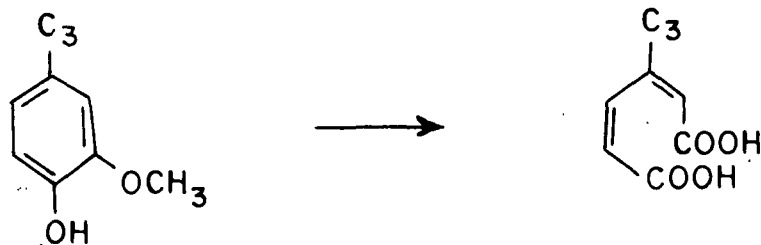


Figure 8. Formation of Muconic Acid Derivative

From the equivalents of unreacted lignin per 100 equivalents of original material it can be estimated by difference that from 2.0 to 2.4 equivalents of chlorine dioxide were consumed for each equivalent of lignin oxidized. Ishikawa, *et al.* (4) noted a consumption of about 2.0 equivalents of chlorine dioxide per equivalent of pine dioxane lignin on reaction with an excess of oxidant. Thus, virtually all of the chlorine dioxide applied can be accounted for as having reacted with the lignin portion of the groundwood, leaving the carbohydrate material relatively unaffected. This is consistent with the following statement by Rapson (29), "Chlorine dioxide has relatively little effect on the carbohydrate components of pulp, unless a large excess of chlorine dioxide is provided, excessively high temperature is used, and the time of reaction is unduly prolonged."

The equivalents of lignin solubilized, as compared to the equivalents of oxidized material remaining *in situ*, does not vary a great deal over the range of chlorine dioxide concentrations applied. This seems to indicate

TABLE IV
FUNCTIONAL GROUP CONTENT PER 100 EQUIVALENTS OF LIGNIN MATERIAL

% O.D. Wood	ClO ₂		Total Equiv. Lignin	Equiv. Unreac. Lignin	Equiv. Oxid. Lignin	Equiv. Sol. Lignin ^a	Equiv. ^b Methoxyl	Equiv. Bound Chlorine	Equiv. Carboxyl	Equiv. Volatile Methoxyl
	Equiv.									
0.0	0.0		100.0	100.0	0.0	0.0	93.6	0.0 ^c	2.57	--
3.0	34.2 ^d		100.0	90.8	9.2	7.8	90.8	10.9	--	--
	31.7		92.8	84.3	8.5	7.2	84.3	10.1	--	--
6.0	72.4		100.0	80.0	20.0	14.2	80.0	16.8	36.4 ^e	1.74
	63.4		87.6	70.1	17.5	12.4	70.1	14.7	31.9 ^e	1.53
9.0	117.0		100.0	73.9	26.1	23.1	73.9	29.9	--	--
	95.1		81.2	60.0	21.2	18.8	60.0	24.2	--	--

^aTotal material lost to solution obtained by difference from total equiv. lignin.

^bIncludes volatile methoxyl and any methoxyl associated with carbohydrate. The latter should be fairly small as carbohydrate methoxyl is usually associated with the uronic acids and IR and titrimetric data show only small amounts of acid to be present.

^cAssumed to be zero for the original groundwood. All other values corrected for the chlorine found in the original groundwood (2.6 equiv./100 equiv. lignin).

^dFor modified lignins two rows of data are given, the top row based on 100 equiv. of modified lignin and the bottom row based on 100 equiv. of original lignin.

^eCorrected for carboxyl in unreacted groundwood.

that the chlorine dioxide probably does not preferentially attack the less condensed structures which would be more easily solubilized.

Effect on Methoxyl Content

The steady decrease in methoxyl content with increased concentrations of chlorine dioxide can be more readily visualized in graphical form (Fig. 9). With the exception of the initial region (0 to 3% chlorine dioxide) the loss of methoxyl is in a direct linear relationship with the amount of oxidant applied. A comparison of the data for the 9% chlorine dioxide-reacted material with data reported in the literature for much higher amounts of oxidant seems to indicate that the linear relationship would not apply for amounts in excess of 9% (Table V).

TABLE V
COMPARATIVE DATA ON METHOXYL LOSS

Source	Equiv. ClO ₂ per Equiv. Lig.	Orig. OCH ₃ Lost, %	OCH ₃ in Oxid. Lignin, %	Equiv. OCH ₃ per 100 Equiv. Oxid. Lignin	Temp., °C
This work (9% ClO ₂)	0.95	36.7	11.2	0.74	35
Dence (3) (groundwood)	3.00	33-39	--	--	Room temp.
Barton (10) (sol. lignin prod.)	7.00 ^a	--	10.5	0.75	75-80
Ishikawa (4) (insol. dioxane lig.)	3.50	--	9.6	0.73 ^b	30

^aSodium chlorite (pH 4.5).

^bIncludes 0.27 equivalent reported as methyl ester which would analyze as methoxyl using Institute Procedure 18.

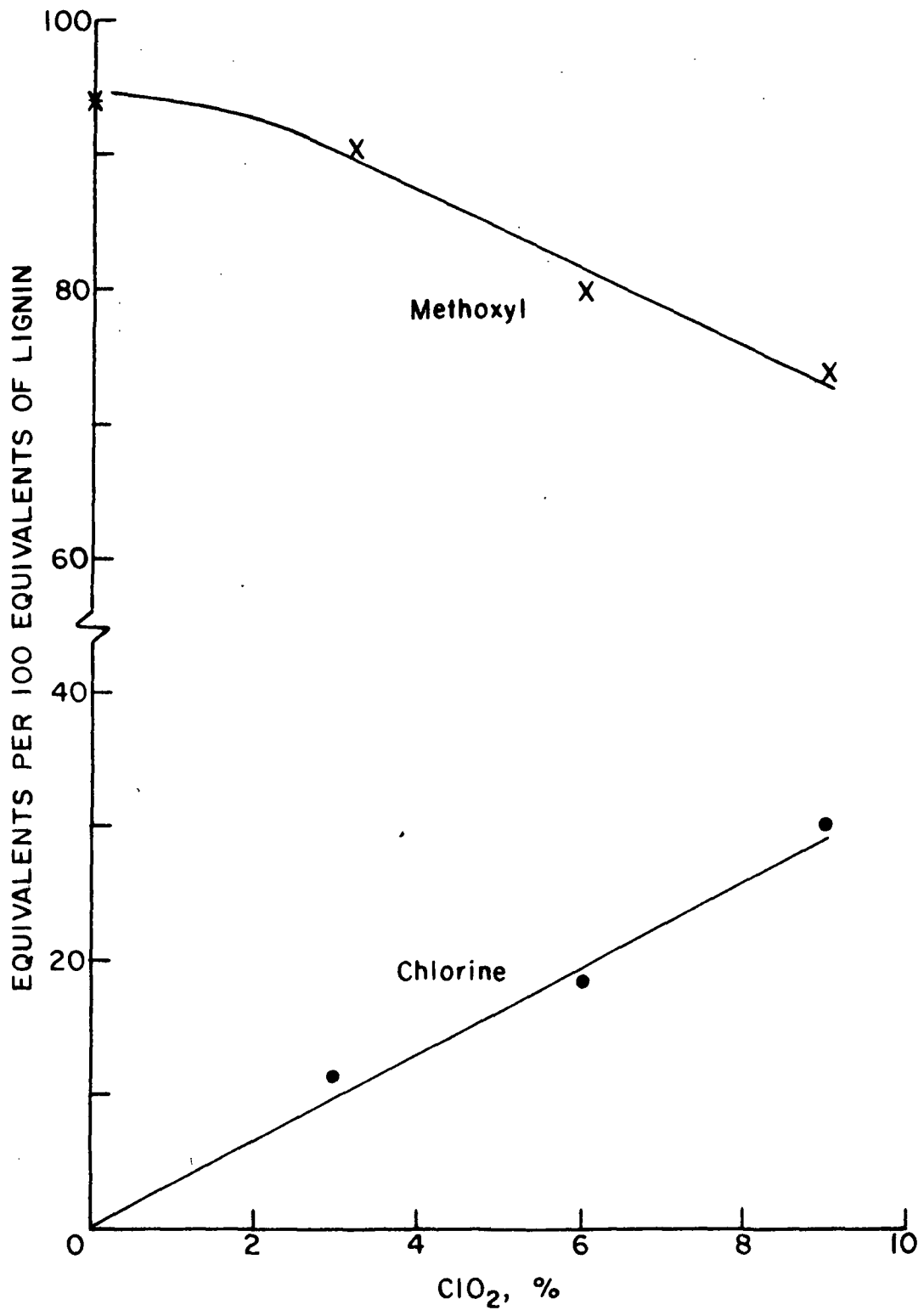


Figure 9. Effect of ClO_2 on Methoxyl and Chlorine Contents

The agreement between the results obtained on application of 9% chlorine dioxide and those obtained by others for much higher amounts of oxidant indicates that demethylation ceases to be as important for chlorine dioxide amounts above this level.

Carboxyl and Volatile Methoxyl

Concurrent with the loss in methoxyl there is an increase in carboxyl content. For the 6% chlorine dioxide-reacted material there are about 1.8 carboxyl groups produced for each equivalent of oxidized lignin material remaining in situ (Table IV). This is consistent with ring rupture found previously for lignin model compounds (2-4,6).

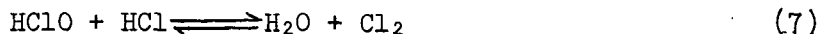
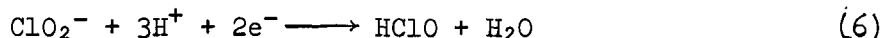
Unlike the products reported for model compounds, however, the products formed from lignin in situ do not appear to retain the methoxyl group as an ester. This was confirmed by hot distillation studies using the method described by Dence, et al. (3). It was found that only about 1.7 equivalents of methanol were produced for each 100 equivalents of modified lignin subjected to hot distillation. Dence, et al. found that 80-85% of the methoxyl present as a methyl ester of muconic acid or as a methoxyquinone was liberated as methanol under these conditions; thus, there are probably no more than about 2.2 equivalents of nonaromatic or volatile methoxyls per 100 equivalents of 6% chlorine dioxide-reacted lignin.

The above results would also seem to limit the quantity of p-quinone structures in the oxidized lignin, as all of these isolated in model compound studies contained a methoxyl group.

Chlorination

As indicated in Tables III and IV and in Fig. 9, the amount of organically bound chlorine increases in a direct linear relationship with the amount of chlorine dioxide applied. The 29.9 equivalents of chlorine per 100 equivalents of oxidized lignin found for the 9% chlorine dioxide-reacted material is considerably less than the corresponding values of 38 and 65 equivalents per 100 equivalents of lignin reported by Ishikawa, *et al.* (4) and Barton (10), respectively. Apparently, unlike the demethylation reaction, the chlorination reaction continues to be of importance for chlorine dioxide applications in excess of 9%. Quite probably some part of the lignin material is susceptible to chlorination, yet is no longer as susceptible to the type of oxidative degradation which results in loss of methoxyl.

As previously mentioned, the chlorination is thought to be due to elemental chlorine which is formed via secondary reactions in both the acidified chlorite and chlorine dioxide systems (1).



The equilibrium shown in Equation (7) is highly dependent on pH as indicated in Fig. 10. Considering the final pH of 2.0 for the 6% chlorine dioxide reaction, a substantial amount of chlorine could be formed during the course of the reaction.

On the basis of work reported in the literature, the organically bound chlorine could be expected to be substituted on aromatic structures (3,4,10), quinones (3,4), or muconic acid derivatives (7). In order to determine the

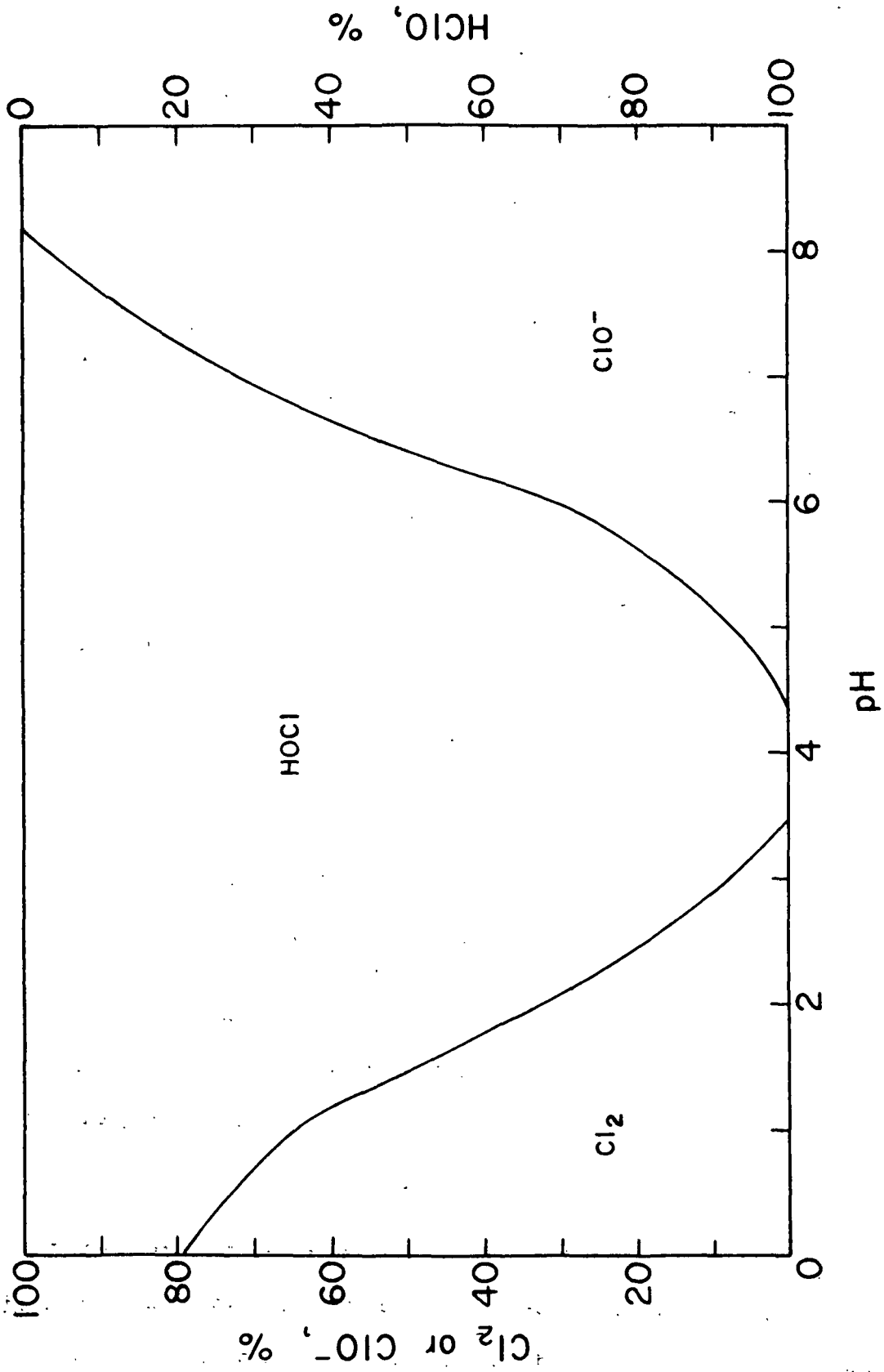


Figure 10. Composition of a 0.01N Solution of Chlorine in Water at Various pH's (30)

relative importance of these various possible structures, alkaline cupric oxide degradation studies were done on the 6% chlorine dioxide-reacted lignin and are reported in the following section.

ALKALINE CUPRIC OXIDE DEGRADATION OF GROUNDWOODS

REACTION

Both the original groundwood and the 6% chlorine dioxide-reacted groundwood were subjected to alkaline cupric oxide degradation for three hours at 170°C. The amounts of reactants and yields obtained are summarized in Table VI.

TABLE VI
CUPRIC OXIDE DEGRADATION

Sample	O.D. Groundwood, g	Lignin, g	2N NaOH, ml	CuO(H ₂ O), g	Yield, g ether sol.
Original groundwood	14.0	3.66	160	26.5	1.60
6% ClO ₂ - reacted groundwood	14.7	3.62	160	26.5	1.45

The reaction products were worked up as indicated in the Experimental section and the ether solubles were ultimately dissolved in 100 ml of acetone for chromatographic analysis.

ISOLATION AND IDENTIFICATION

The chromatograms of the ether-soluble products from the cupric oxide degradation of the original groundwood and the 6% chlorine dioxide-reacted material are given in Fig. 11A and 11B, respectively. The two letters in the peak labels refer to the material degraded, original groundwood (GW) or 6%

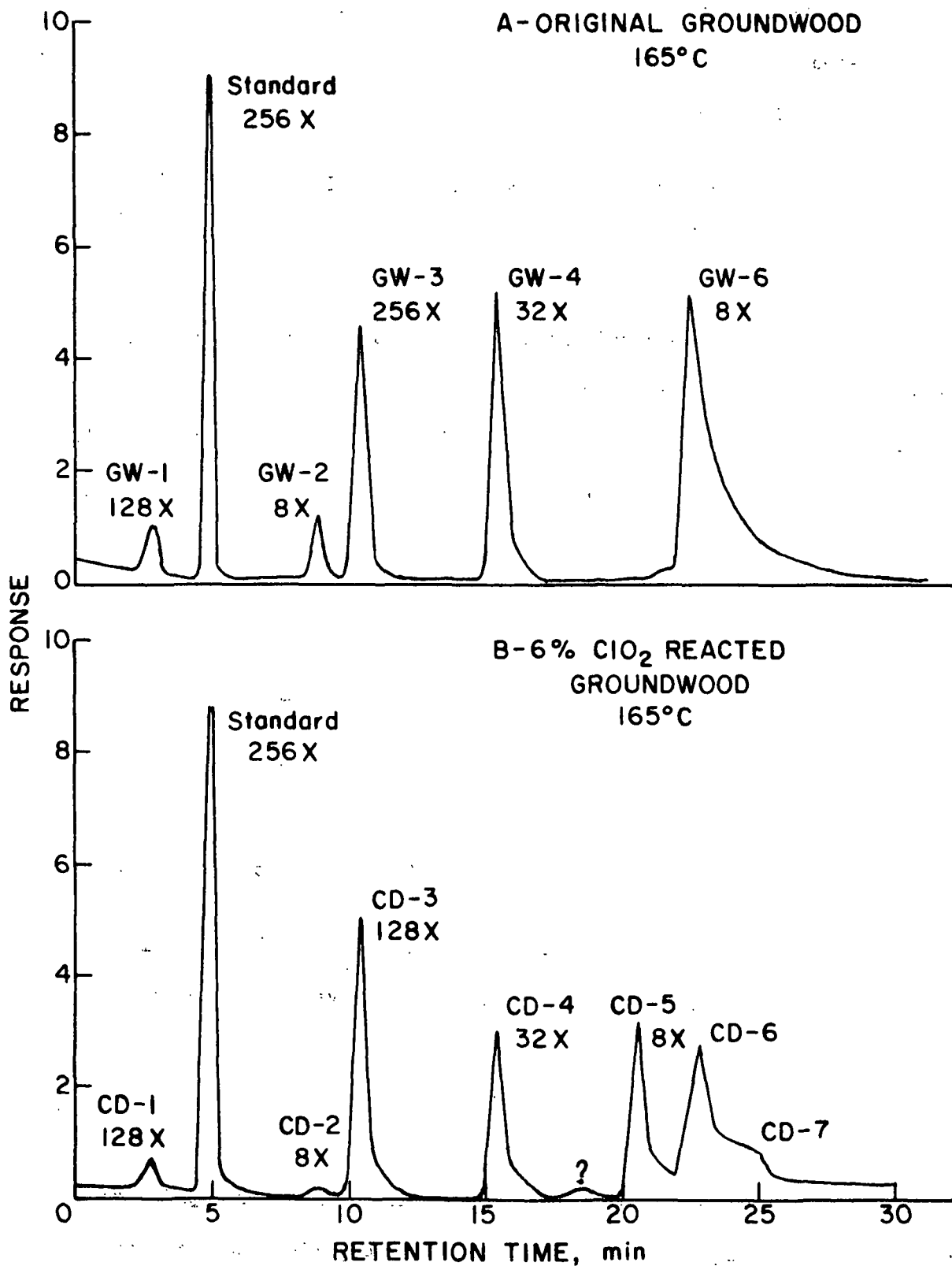


Figure 11. Chromatographs of CuO Oxidation Products

chlorine dioxide-reacted groundwood (CD), and the number relates to the order of peak appearance.

The identity of the substances in the various peaks was determined by comparison of retention time with those of known compounds (Table VII), by running chromatographs of mixtures of knowns and unknowns (single peaks obtained in all cases), and where possible, by comparison of the mass spectrum of the unknown with that of the known. The last technique was only possible for major peaks where there was sufficient sample to obtain a meaningful mass spectrum. The identities of the various peaks and the procedures employed in establishing the identity are presented in Table VIII. A detailed analysis of the various mass spectra, including probable disintegration patterns, is given in Appendix II.

The shoulder labeled CD-7 has not been identified. Its retention time is similar to that of 5-chlorovanillin, but could not be determined accurately because of vanillic acid interference. An attempt to remove the vanillic acid by extraction with potassium bicarbonate solution at pH 8.0 resulted in the removal of Peak CD-7 along with that of vanillic acid. Thus, it appears that Peak CD-7 contains an acid and is therefore not 5-chlorovanillin.

QUANTITATIVE ANALYSIS OF PRODUCTS

The quantitative results of the gas chromatographic analysis of the major products are summarized in Tables IX and X. The vanillin and acetovanillone yields for the original groundwood compare favorably with the 15.9 and 3.85% yields obtained by Pepper, et al. (31) for the same material.

The chlorine dioxide reaction results in a substantial reduction in the yields of all the degradation products. It is interesting to note that the

TABLE VII
RETENTION TIMES AND RESPONSE FACTORS^a

Sample	Retention Time, min	Response Factor ^b
Guaiacol	2.8	--
<u>p</u> -Hydroxybenzaldehyde	8.5	--
Vanillin	10.4	1.40
Acetovanillone	15.3	1.43
6-Chlorovanillin	20.5	0.95
Vanillic acid	22.1	0.89
5-Chlorovanillin	24.6	0.89
Unknown GW-1	2.9	--
Unknown CD-1	2.8	--
Unknown GW-2	8.8	--
Unknown CD-2	9.1	--
Unknown GW-3	10.5	--
Unknown CD-3	10.4	--
Unknown GW-4	15.4	--
Unknown CD-4	15.4	--
Unknown CD-5	20.7	--
Unknown GW-6	22.5	--
Unknown CD-6	22.8	--
Unknown CD-7	24.8	--

^aChromatographic conditions listed in Experimental section.

^bRelative to p-dibromobenzene standard.

TABLE VIII
IDENTIFICATION OF CHROMATOGRAPHIC PEAKS

Peak	Identity	Identification Procedure		
		Retention Time	Mixture with Known	Mass Spectra
GW-1	Guaiacol	X	X	X
CD-1	Guaiacol	X	X	X
GW-2	<u>p</u> -Hydroxybenzaldehyde	X	X	
CD-2	<u>p</u> -Hydroxybenzaldehyde	X	X	
GW-3	Vanillin	X	X	X
CD-3	Vanillin	X	X	X
GW-4	Acetovanillone	X	X	X
CD-4	Acetovanillone	X	X	X
CD-5	6-Chlorovanillin	X	X	X
GW-6	Vanillic acid	X	X	X
CD-6	Vanillic acid	X	X	X
CD-7	?	X	X	

TABLE IX
YIELDS OF MAJOR PRODUCTS FROM CUPRIC OXIDE DEGRADATION^a

Sample	Vanillin	Aceto- vanillone	6-Chloro- vanillin	Vanillic Acid	Ether Sol.
Original groundwood	16.0	3.0	--	2.5	43.7
6% ClO ₂ - reacted groundwood	9.55	2.0	0.91	1.7	40.0

^aAll data expressed as weight percentage of lignin degraded.

TABLE X

CUPRIC OXIDE DEGRADATION PRODUCTS

Sample	Undegraded Composition ^a			Degradation Products			
	Lignin	Methoxyl	Chlorine ^b	Vanillin	Aceto- vanillone	Vanillic Acid	6-Chloro- vanillin
Proto- c lignin	100.0 ^e	93.6	0.0	19.6	3.36	2.80	0.0
6% ClO ₂ - reacted c lignin	100.0 ^f	80.0	16.8	12.4	2.40	1.99	0.964
6% ClO ₂ - reacted d lignin	87.6 ^f	70.1	14.7	10.9	2.11	1.75	0.847

^aBased on o.d. wood.^bAssumed zero for protolignin; other values corrected for 2.6 equivalents of chlorine in wood.^cPer 100 equivalents of protolignin.^dPer 100 equivalents of 6% chlorine dioxide-reacted lignin.^eEquivalent weight = 187 from elemental analysis data published by Lai and Sarkanen (28).^fAverage equivalent weight of 197 from calculations made previously (Appendix I).

percentage loss in yield is approximately the same (33 to 39%) for all three major products. Since the various products vary only in the nature of the side chain, and the relative yields have been shown to be sensitive to the degree of oxidation of the side chain (32), it appears that the chlorine dioxide has not caused any significant changes in the nature of the side chains of those lignin structures which are the precursors of the cupric oxide degradation products. Thus, the loss in yield is more likely associated with changes in the aromatic ring structures.

One obvious change is a reduction in the number of aromatic structures. Using the equivalents of nonvolatile methoxyl as an estimate of the aromatic content (Table X), the following revised yields can be calculated on an equivalent basis.

For the protolignin:

$$(19.6/93.6) \times 100 = \underline{20.9\%} \text{ vanillin yield.}$$

For the 6% chlorine dioxide-reacted lignin:

$$[(12.4 + 0.96)/80.0] \times 100 = \underline{17.2\%} \text{ vanillin yield.}$$

Relative yield:

$$(17.2/20.9) \times 100 = \underline{82.2\%}.$$

The relative yield of 82.2% is quite close to the relative yield of 84% reported by Leopold (33) for methylated and unmethylated lignins. This, along with the failure of Ishikawa, *et al.* (4) to find any free phenolic groups in chlorine dioxide-reacted pine dioxane lignin, makes it plausible that the cause of the additional loss in yield is the selective attack on the free phenolic groups by the chlorine dioxide.

From the data in Table X it can be calculated that the 0.964 equivalent of 6-chlorovanillin produced account for less than 6% of the bound chlorine known to be present in the 6% chlorine dioxide-reacted material. However, if it is assumed that the ratio of vanillin to 6-chlorovanillin obtained (13 to 1) applies to all aromatic structures, it is possible to estimate the total number of chlorine-substituted aromatic moieties to be about 5.55. This could account for approximately 33% of the organically bound chlorine known to be present.

In order to determine the fate of the remaining chlorine, the aqueous phase from the cupric oxide degradation was titrated with silver nitrate using a silver-silver chloride electrode. It was found that 75% of the organically bound chlorine was now present in the aqueous phase as chloride ion.

Braddon and Dence (34) studied the alkaline hydrolysis of various chlorine-substituted compounds (1 hour, 0.5M NaOH, 60°C) and found that for substituted aromatic compounds less than 5% of the chlorine was hydrolyzed, while for chlorine-substituted quinones, muconic acids, and propane side chains the hydrolysis was almost complete. Van Buren and Dence (35) have shown that both 6-chlorovanillin and 5-chlorovanillin lose very little chlorine (about 2%) under alkaline cupric oxide degradation conditions similar to those employed in this work. Thus, it appears that 75% of the bound chlorine is attached to nonaromatic moieties.

Kempf and Dence (36) found a similar situation in their studies of chlorination followed by alkali extraction. They discovered that from 50 to 90% of the organically bound chlorine was removed from the pulp during the alkaline extraction. They attributed the major portion of the chloride ion

in the alkaline solution to the hydrolysis of β -chlorodibasic acids formed through the oxidation of chlorinated aromatic units.

If the chloride found in this work comes from chlorinated diacids, it can be estimated from the data in Table IV and the 75% yield that about 69%² of the acids could be chlorinated. This is consistent with infrared results to be discussed later.

ULTRAVIOLET AND VISIBLE SPECTRAL ANALYSIS

PRACTICAL ASPECTS

Measurement of lignin absorption spectra in situ is complicated by numerous experimental problems related to the nature of the lignin carbohydrate system and the strong absorption of lignin in this region of the spectrum. The literature disclosed three possible techniques. The first technique (19) involved obtaining a difference spectrum from transmittance measurements on potassium chloride pellets containing very small amounts (about 100 micrograms) of finely milled groundwood and holocellulose, respectively. Spectra obtained using this technique were unsatisfactory and difficult to reproduce. The second technique (21) involved measuring the transmittance of very thin handsheets (about 0.001 g/cm²) and the reflectance of a thick pad of groundwood and the subsequent calculation of the specific absorption coefficients via application of the Kubelka-Munk theory as discussed in the following section. This method was found to be unsatisfactory due to problems in forming the thin handsheets and in determining the basis weight of the sheet area used for the

² $[(0.75)(16.8)]/[36.4/2] \times 100 = 69.$

transmittance measurement. The third technique (22) was the cotton dilution method which will be discussed later. Though not completely satisfactory, this method provided the basis for a new technique developed for use in this work.

BASIC THEORY

The basic theory behind both the cotton dilution method and the method employed in this work is that first developed by Kubelka-Munk and later modified by Van den Akker (23). The basic relations involved for a multicomponent sheet of paper are the following:

$$sW = s_1W_1 + s_2W_2 + \dots + s_nW_n \quad (8)$$

$$kW = k_1W_1 + k_2W_2 + \dots + k_nW_n \quad (9)$$

$$k/s = (1 - R_\infty)^2/2R_\infty \quad (10)$$

$$sW = (1/b) [\sinh^{-1}(b/T) - \sinh^{-1}b] \quad (11)$$

$$sW = (1/b) \operatorname{ctnh}^{-1}[(1 - aR_0)/bR_0] \quad (12)$$

where \underline{s} , \underline{s}_1 , \underline{s}_2 , \underline{s}_n = specific-scattering coefficients of composite sheet, Component 1, Component 2, and Component n , respectively

\underline{k} , \underline{k}_1 , \underline{k}_2 , \underline{k}_n = respective specific-absorption coefficients

\underline{W} , \underline{W}_1 , \underline{W}_2 , \underline{W}_n = respective basis weights

\underline{R}_∞ = reflectance of a pile of many layers or a single thick layer, the thickness being sufficiently great that no change in reflectance is observed on changing the backing from black to white

\underline{T} = transmittance of a single sheet

\underline{R}_0 = reflectance of a single sheet backed by a black body of zero reflectance

$$\underline{a} = [(1/\underline{R}_\infty) + \underline{R}_\infty]/2$$

$$\underline{b} = [(1/\underline{R}_\infty) - \underline{R}_\infty]/2.$$

Equations (8) and (9) assume the additivity of \underline{s} and \underline{k} for a multicomponent system. According to Hecht (37) this assumption is valid if the concentration of absorbing materials is small and the scattering is predominated by the basis material. This condition is fulfilled in the cotton dilution method described in the following section.

COTTON DILUTION METHOD

Polcin and Rapson (22) diluted the groundwood with cotton linters and adapted the above equations to the new system. For a composite sheet of cotton linters and groundwood, Equations (8) and (9) become:

$$s = s_o C_o + s_p C_p + s_l C_l \quad (13)$$

$$k = k_o C_o + k_p C_p + k_l C_l \quad (14)$$

The ratio of \underline{k} to \underline{s} can then be expressed as:

$$k/s = (k_o C_o + k_p C_p + k_l C_l) / (s_o C_o + s_p C_p + s_l C_l) \quad (15)$$

where \underline{k} , \underline{k}_o , \underline{k}_p , \underline{k}_l = specific absorption coefficients for the composite sheet, pure cotton, groundwood polysaccharides, and lignin, respectively

\underline{s} , \underline{s}_o , \underline{s}_p , \underline{s}_l = corresponding specific scattering coefficients

\underline{C}_o , \underline{C}_p , \underline{C}_l = corresponding weight fractions of components³.

Two assumptions were made to simplify the above relations.

(a) The scattering process occurs mainly in the cotton fibers and

when $\underline{C}_o \gg \underline{C}_p$ and \underline{C}_l , the sum:

$$s_o C_o + s_p C_p + s_l C_l \doteq s_o \quad (16)$$

³Under the conditions of Polcin and Rapson (22), $\underline{C}_o = 0.96$, $\underline{C}_p = 0.03$ and $\underline{C}_l = 0.01$.

(b) The absorption power of the pure polysaccharide is very low in comparison to that of the lignin, i.e., $k_{\frac{C}{P-P}} \neq 0$, and therefore can be neglected. Then Equation (15) will take the following form:

$$(k_o C_o + k_l C_l) / s_o = k/s \quad (17)$$

then

$$k_l = [(k/s)s_o - k_o C_o] / C_l \quad (18)$$

or, for a given wavelength of light:

$$(k_l)_\lambda = [(k/s)_\lambda (s_o)_\lambda - (k_o)_\lambda C_o] / C_l \quad (19)$$

The $(s_o)_\lambda$ and $(k_o)_\lambda$ values are determined via reflectance and transmittance measurements on pure cotton handsheets using Equations (10) and (12). This need only be done once for a series of samples. Thereafter, one need only know the $(R_\infty)_\lambda$ and composition of the groundwood-cotton sheets in order to calculate $(k_l)_\lambda$.

Though this method is far superior to the thin sheet method mentioned previously, it still requires the formation of handsheets in which the various components are uniformly distributed throughout the sheet so that concentration values do in fact reflect accurately the composition of the material exposed to the light beam. In practice, the sheets formed do not have an ideal distribution of groundwood throughout the sheet. There are fiber bundles and other heterogeneities visible to the naked eye, plus a certain amount of two-sidedness. Actual measurements made during the course of this study showed variations in R_∞ of up to 10% when different areas of the same sheet were exposed to the light beam. Another drawback of this technique is the requirement for

lignin analyses on the sheets after measurement as the formation process makes it extremely difficult to form sheets with an exact predetermined composition.

COMPACT METHOD

An improved procedure designed to overcome some of the problems inherent in the use of handsheets was developed for the present work. This method is called the compact method and involves the milling of the diluent and the groundwood material on the Wiley mill, mixing the desired amounts of the two materials in small glass bottles on the mixer-mill, and forming compacts of the finely milled material under pressure (details in Experimental section). Other minor changes were made compared with the method of Polcin and Rapson (22). These include the use of Whatman No. 40 filter paper as the diluent and the revision of the second assumption (p. 40) to assume that the polysaccharide portion of the groundwood has the same absorption coefficient as the Whatman paper ($k_p = k_o$). Equation (19) then becomes

$$(k_l)_\lambda = [(k/s)_\lambda (s_o)_\lambda - (k_o)_\lambda (C_o + C_p)]/C_l \quad (20)$$

where $(k_l)_\lambda$ = the specific absorption coefficient of the lignin in the groundwood at wavelength λ

$(k/s)_\lambda$ = the ratio of the specific absorption and scattering coefficients obtained from the reflectance of the compact via Equation (10)

s_o and k_o = the specific scattering and absorption coefficients of the Whatman No. 40 component [obtained from measurements of the reflectance and transmittance of Whatman sheets via Equations (10) and (11) and corrected for compacting effects as noted in Appendix III].

The specific absorption coefficients obtained using the compact method are much lower than those reported for dioxane solutions of isolated lignin (22) and in between the values obtained by Polcin and Rapson (21,22) using

the thin handsheet and cotton dilution techniques (Table XI). The difference between the values obtained using the compact method and those reported for solutions of isolated lignin are most likely due to concentration effects and inhomogeneity in the solid state. Differences between the results of this work and those reported by Polcin and Rapson (21,22) for reflectance methods are not as easily explained. Initial work using methods identical to those of Polcin and Rapson (21,22) gave the values reported in Table XI, which are similar in magnitude to those obtained using the compact method.

TABLE XI
SPECIFIC-ABSORPTION COEFFICIENTS FROM VARIOUS SOURCES

Source and Method	Specific-Absorption Coefficient, cm^2/g		
	280 nm	400 nm	500 nm
Compact (this work)	8,000	650	85
Cotton dilution (this work)	10,500	1,600	^a
Thin sheet (this work)	10,100	1,600	^a
Cotton dilution (<u>22</u>)	38,000	3,000	200
Thin sheet (<u>21</u>)	1,700	500	74
Dioxane solution (<u>22</u>)	48,000	3,500	2,000

^aVirtually zero and in some cases slightly negative.

The low values obtained do not limit the usefulness of the procedure as the results are sufficiently reproducible (Fig. 12) to give at least a semi-quantitative measure of the absorption changes.

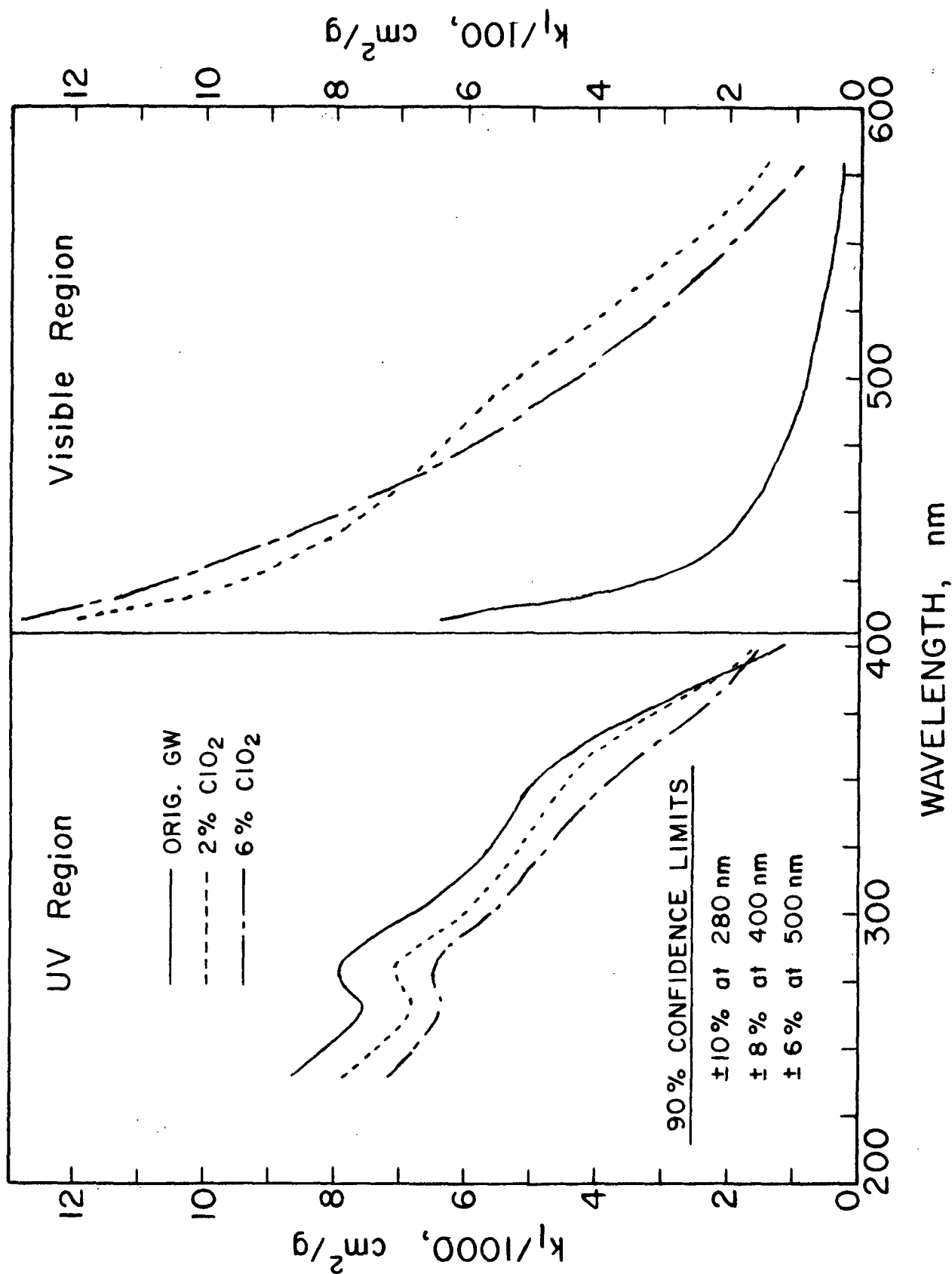


Figure 12. Effect of Chlorine Dioxide on Specific-Absorption Coefficient of Lignin in Groundwood

ABSORPTION SPECTRA

The ultraviolet and visible absorption spectra of the original groundwood and the 2 and 6% chlorine dioxide-reacted materials as obtained via the compact method are given in Fig. 12. In the short wavelength region (240 to 350 nm) the three curves are similar, but displaced toward lower absorption intensity with increased chlorine dioxide application. The absorption maximum at 280 nm has been associated with the aromatic ring (25) and losses here are probably a reflection of decreased aromaticity. The absorption shoulder in the 350 nm region has been related to carbonyl groups in conjugation with the aromatic ring (25), thus losses here could be indicative of either destruction of the carbonyl group or the aromatic ring.

At the longer wavelengths (360 to 580 nm) the chlorine dioxide-reacted materials absorb more intensely than the original groundwood, indicating that additional chromophores are formed during the reaction with chlorine dioxide. This is consistent with the visual color changes noted previously in Table II. Inspection of the spectra of the 2 and 6% chlorine dioxide-reacted materials reveals that there are at least two types of chromophores formed, one absorbing more strongly from 400 to 450 nm and the other absorbing more strongly from 450 to 580 nm. The latter is more prominent in the spectrum of the 2% chlorine dioxide-reacted material and is therefore most likely an intermediate product which is susceptible to further oxidation by additional chlorine dioxide.

In order to gain more information concerning the nature of the chromophores formed during the chlorine dioxide reaction, the original groundwood and the 2 and 6% chlorine dioxide-reacted materials were subjected to reductive bleaching by 6 electron equivalents of uranium(III) ion and sodium dithionite

(sodium hydrosulfite) as indicated in the Experimental section. The spectra of the reduced materials are given in Fig. 13-15.

The spectra of the original groundwood shows an almost complete removal of the absorption shoulder at 350 nm by the uranium(III), which reacts rapidly with essentially all aldehydic, ketonic, or quinoidic carbonyls (26,27). There is also a substantial decrease in absorption throughout the visible region of the spectrum.

Since the sodium dithionite is only capable of reducing simple quinones, coniferaldehyde structures, and flavones (26,38), its effect on the groundwood absorption was not as pronounced. It did, however, reduce the absorptivity by about half as much in the 350-nm region, indicating the presence of a considerable number of coniferaldehyde structures among the conjugated carbonyls of white spruce lignin. In the visible region of the spectrum the sodium dithionite is only slightly less effective than the uranium(III), indicating that the chromophores absorbing in this region are most likely quinonoids. These results are consistent with those reported by Polcin and Rapson (26) for western hemlock and eastern spruce groundwoods.

For the chlorine dioxide-reacted materials, the uranium(III) proved to be comparatively less effective at all wavelengths. In the visible region of the spectrum it was even less effective than the sodium dithionite, especially for the 6% chlorine dioxide-reacted material. The cause of this anomalous behavior is not known. It seemed conceivable that complexes of uranium or some other metal with chlorine dioxide oxidation products could have affected the absorption spectra, but spectrographic analyses showed no observable uranium line or unusual concentrations of other metals (Table XII).

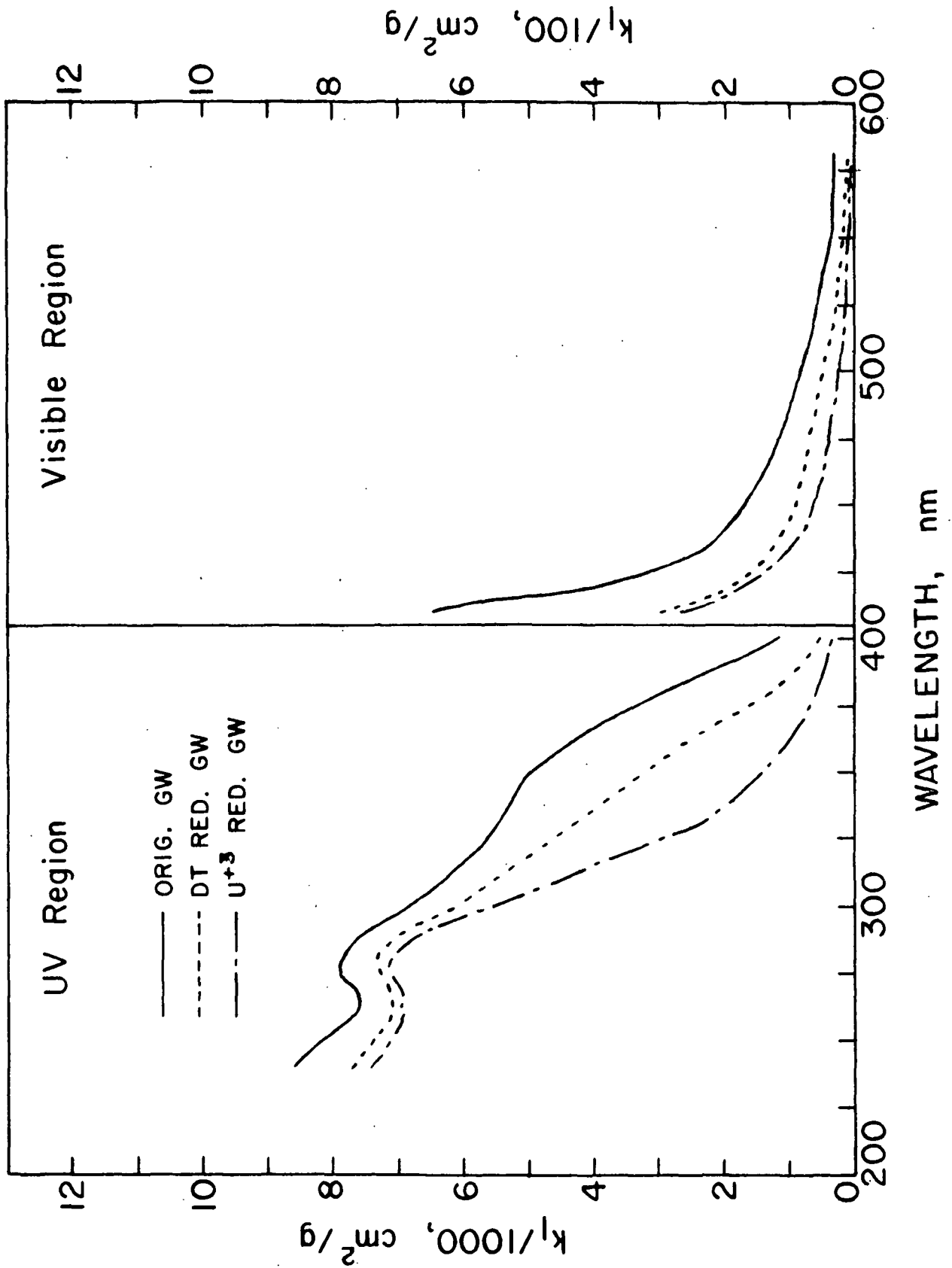


Figure 13. Effect of Reduction on Specific-Absorption Coefficient of Lignin in Original Groundwood

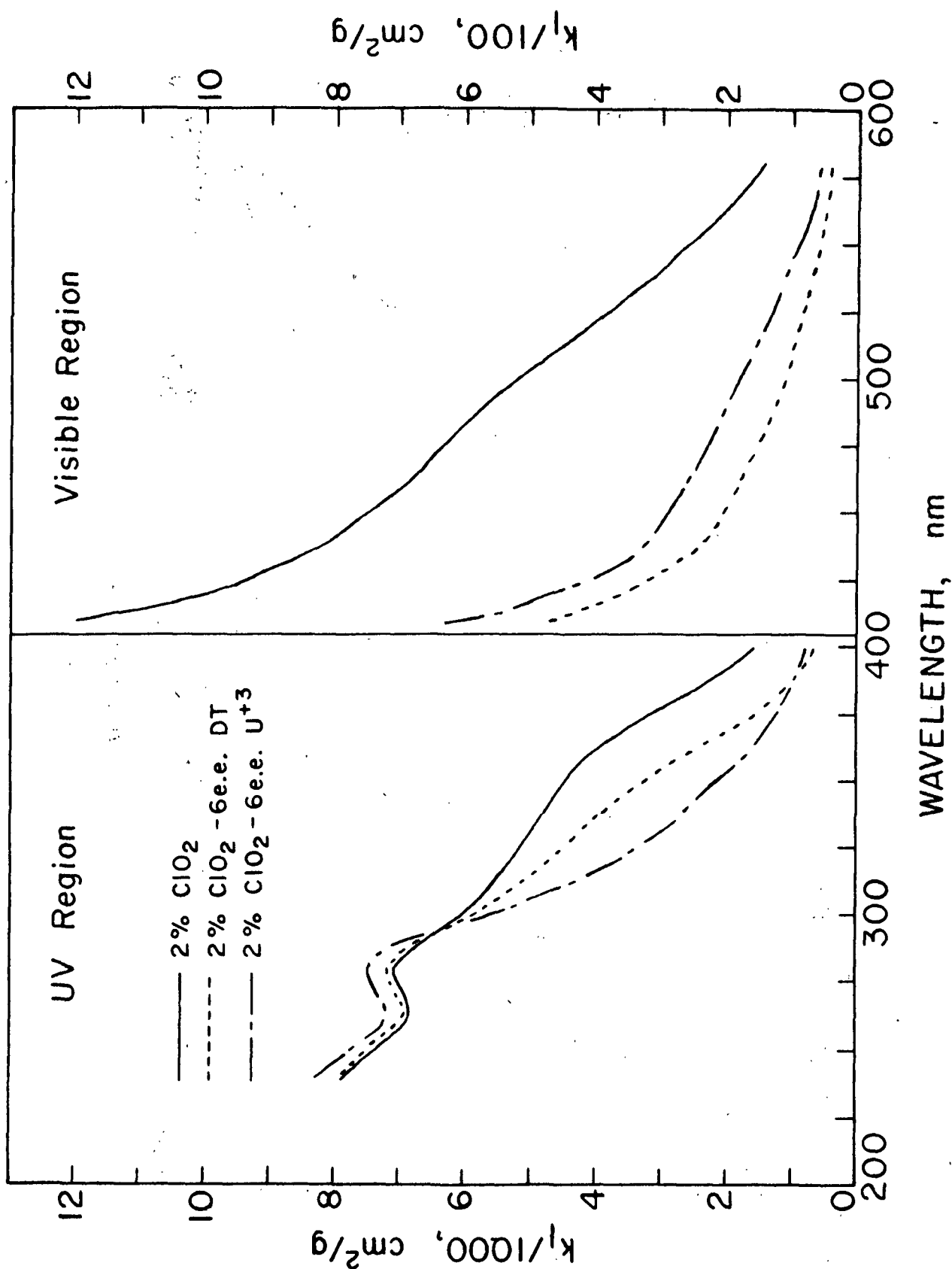


Figure 14. Effect of Reduction on Specific-Absorption Coefficient of Lignin in 2% ClO_2 -Reacted Groundwood

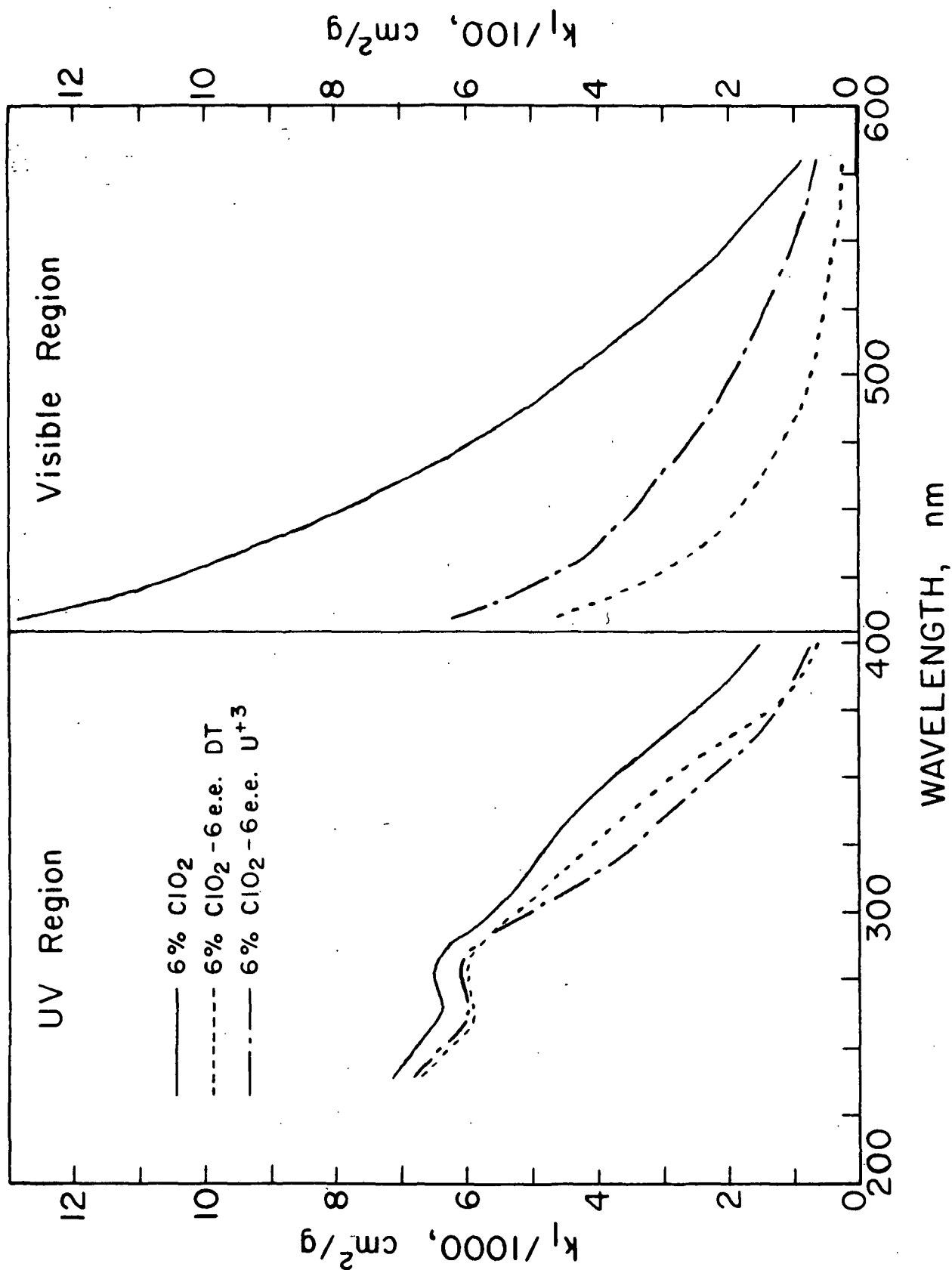


Figure 15. Effect of Reduction on Specific-Absorption Coefficient of Lignin in 6% ClO_2 -Reacted Groundwood

TABLE XII
SPECTROGRAPHIC ANALYSES FOR VARIOUS METALS

Sample	Iron, %	Nickel, %	Sodium, %	Uranium, %
6% ClO ₂ ground-wood	0.0100	0.00016	0.0069	--
6% ClO ₂ ground-wood DT reduced	0.0012	0.000073	0.0048	--
6% ClO ₂ ground-wood U(III) reduced	0.00099	0.00012	0.0049	No line observed

The sodium dithionite was about as effective in reducing the chlorine dioxide-reacted materials as it was in reducing the original groundwood. In the visible region of the spectrum most of the absorption attributable to the chlorine dioxide reaction products was removed, indicating that the majority of the chromophores absorbing in this region are probably quinones. This is consistent with the results of model compound studies previously mentioned (3,4,6).

INFRARED SPECTRAL ANALYSIS

Infrared spectra of the various materials were obtained using potassium chloride pellets prepared as indicated in the Experimental section. For comparisons of products from reaction of groundwood with varying amounts of chlorine dioxide, pellets were prepared containing known amounts (2 to 3 mg) of sample and the absorbances of the various peaks were determined via the base-line method (39). To relate the absorbances to the lignin content the horizontal line through the 1820 cm⁻¹ maxima was used as the base, and to compare relative aromatic contents the line passing through the 1820 and the 1550 cm⁻¹ maxima was used as the base (Fig. 16). Absorbances were divided by the lignin content to obtain absorbance/mg lignin.

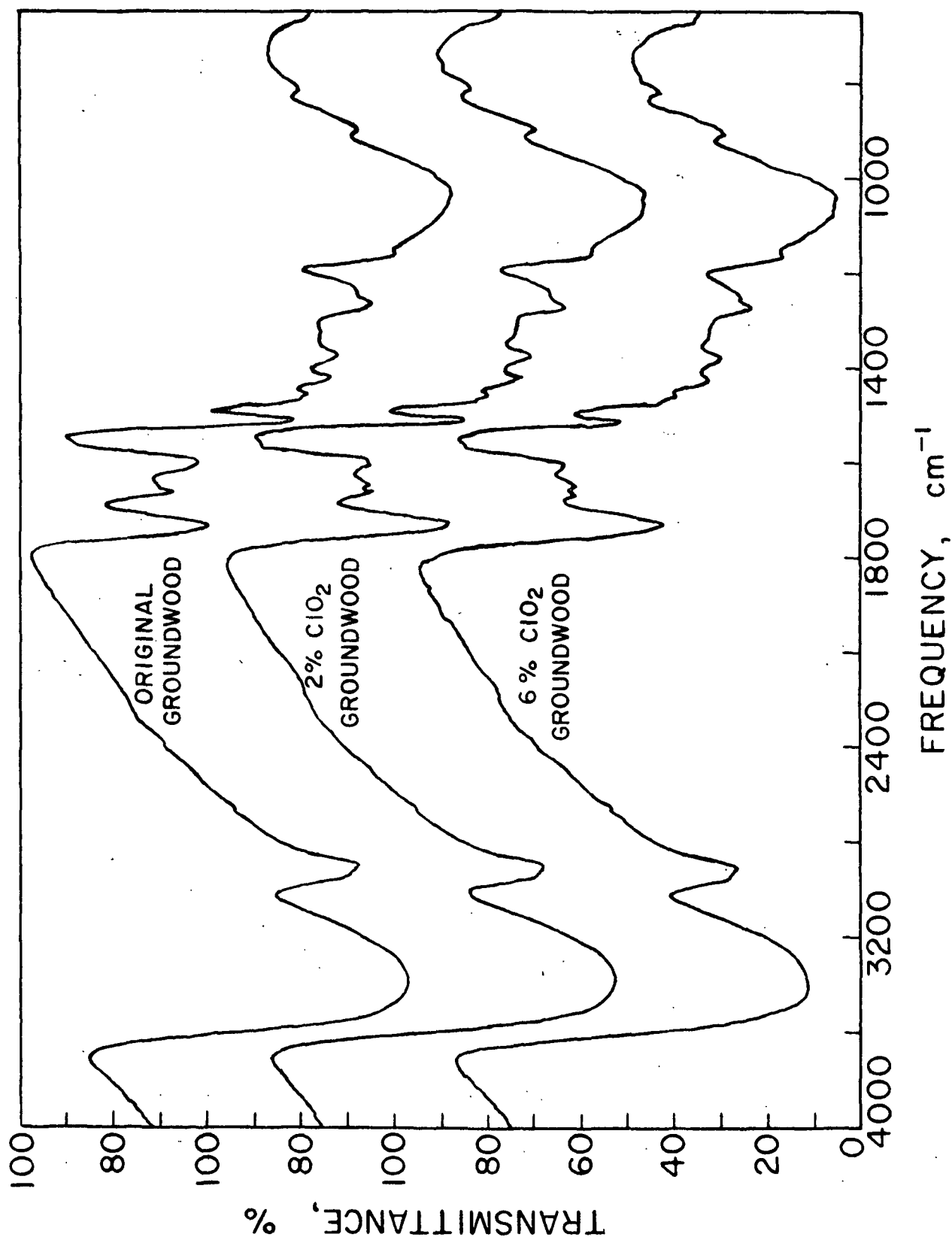


Figure 16. Infrared Spectra of Original Groundwood and Chlorine Dioxide-Reacted Groundwoods

For comparisons between groundwoods reacted with the same amount of chlorine dioxide, then subjected to relatively mild alkaline or reductive treatments, the aromatic absorption at 1510 cm^{-1} was assumed to be unaffected and was used as an internal reference.

OXIDATION EFFECTS

Though the spectra of the original groundwood and the 2 and 6% chlorine dioxide-reacted materials are similar (Fig. 16), there are significant changes in the following: absorption due to carbonyl (1650 to 1800 cm^{-1}), aromatic rings (1510 and 1600 cm^{-1}), C-H deformation (1300 to 1500 cm^{-1}), and aryl-alkyl ethers and phenols (1200 to 1300 cm^{-1}).

These changes can be better visualized in the difference spectra, obtained by placing pellets containing equivalent amounts (same absorption at 2900 cm^{-1}) of the materials of interest in the two beams of the spectrophotometer. Such a spectrum showing the differences between the original groundwood and the 6% chlorine dioxide-reacted material is given in Fig. 17.

The 6% chlorine dioxide-reacted groundwood absorbs more intensely throughout the 1650 to 1800 cm^{-1} region with a maximum near 1710 cm^{-1} , shoulders near 1720 and 1750 cm^{-1} , and some general increase in the 1650 to 1700 cm^{-1} region. The nature of these carbonyl absorption bands will be discussed more fully later.

The small absorption maximum near 1640 cm^{-1} could be due to a conjugated carbonyl, carbon-carbon double bonds, or interference from water.

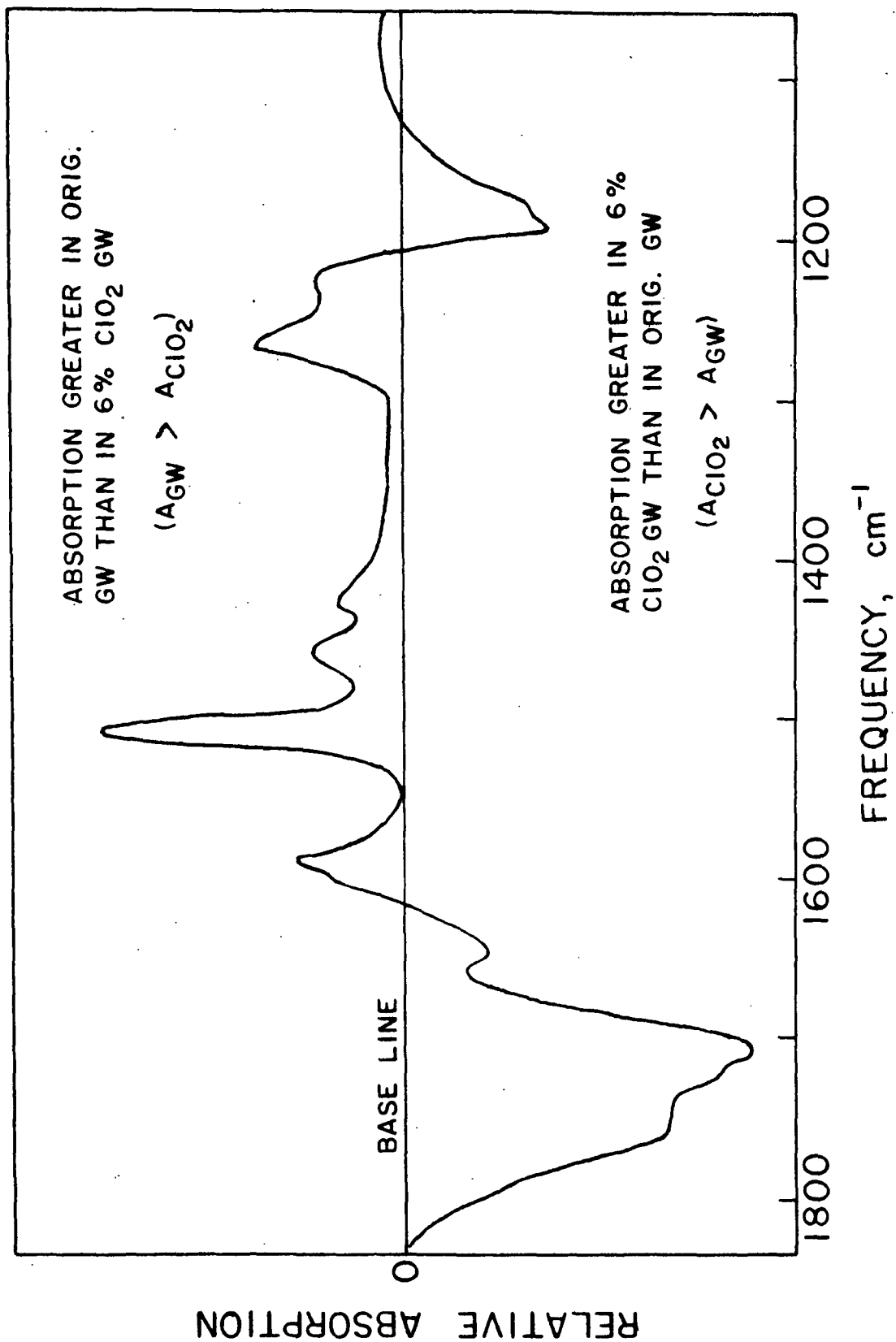


Figure 17. Infrared Difference Spectrum Showing Effect of 6% Chlorine Dioxide Reaction

The increased absorption in the C-O stretch region (1180 to 1200 cm^{-1}) is not easily related to a specific functional group. It is worth noting, though, that absorption in this region is found in the infrared spectra of a number of muconic acid derivatives isolated by Farrand (8) in his study of the peroxy-acetic acid oxidation of lignin model compounds.

Absorption losses are evident in the two absorption bands due to the aromatic rings at 1510 and 1600 cm^{-1} . There are also minor absorption losses in the 1400 to 1500 cm^{-1} region which can be related to demethylation (40) and moderate losses at 1200 to 1300 cm^{-1} where the aryl-alkyl ethers and phenols absorb (40).

NEUTRALIZATION STUDIES

Spectra of the original groundwood and the 6% chlorine dioxide-reacted groundwood, after neutralization with 0.2N sodium hydroxide to pH 9.2, are given in Fig. 18. From the relative intensities of the peaks at 1730 cm^{-1} (where carboxyl absorbs) and 1600 cm^{-1} (where carboxylate ion absorbs) it is possible to estimate the amount of carboxyl groups in the materials, assuming an insignificant amount of sample is solubilized during the treatment. The latter assumption is quite reasonable for the original groundwood, but is a bit less certain for the chlorine dioxide-reacted groundwood, as about 12% of this material dissolved in boiling water during the demethylation studies reported previously. This subject will be discussed further in the following paragraphs.

A comparison of the relative intensities of the 1600 and 1730 cm^{-1} peaks before and after neutralization (Fig. 16 and 18) shows only a slight change for the original groundwood, indicating very little carboxyl is present.

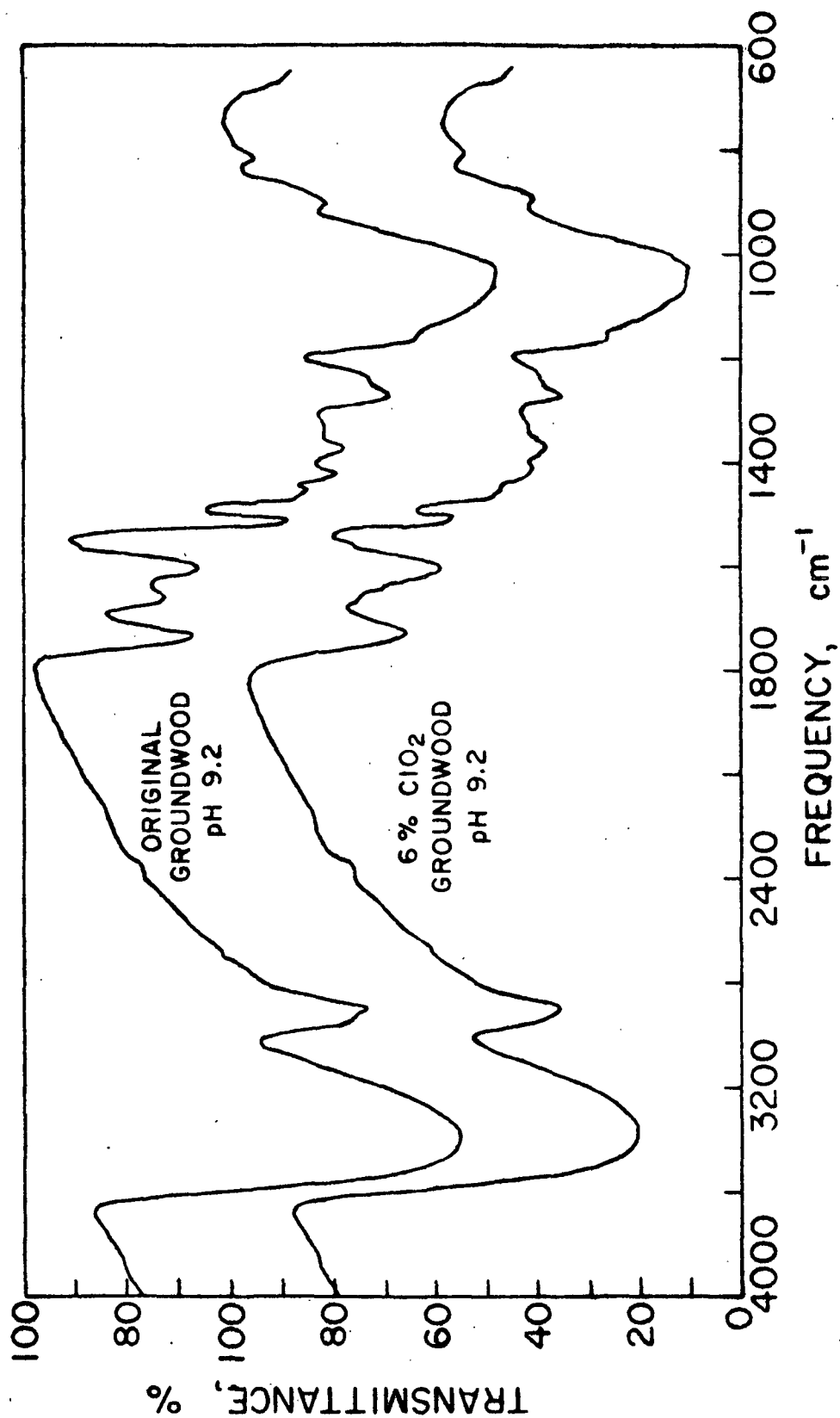


Figure 18. Infrared Spectra of Neutralized Groundwoods

Apparently, the major portion of the uronic acids was lost during the hot-water extraction. A similar comparison for the 6% chlorine dioxide-reacted material shows a dramatic change in the relative intensities of the above-mentioned peaks. Almost all of the additional carbonyl absorption resulting from the chlorine dioxide oxidation has been shifted from the 1730 cm^{-1} region to the 1600 cm^{-1} region, indicating that it is mostly carboxyl in nature.

The changes due to neutralization of the 6% chlorine dioxide-reacted material are much more evident in the difference spectrum shown in Fig. 19a. Notice the absorption loss in the carbonyl region with a corresponding gain in the carboxylate region. The only other peaks in the region from 1150 to 1800 cm^{-1} are small increases in the 1400 cm^{-1} region which are also due to carboxylate ion and some absorption loss in the 1200 cm^{-1} region which could be related to OH bending in the acid or to ionization of some phenols. The absence of any other differences for example at 1510 cm^{-1} , confirms the validity of the assumption made previously concerning the loss of only insignificant amounts of material to the solution during the neutralization treatment.

The residual absorption in the 1730 cm^{-1} region for the 6% chlorine dioxide-reacted groundwood (Fig. 18) can be almost entirely accounted for as nonionizable carbonyl present in the original groundwood, as both curves in Fig. 18 show about the same degree of absorption in this region.

The difference spectrum of these two materials (Fig. 19b) does show the chlorine dioxide-reacted groundwood to contain a small amount of nonionizable absorption at 1698 cm^{-1} and 1765 cm^{-1} which is not found in the original groundwood. The former is in the region where conjugated ketones or chlorinated quinones might absorb and the latter is at about the

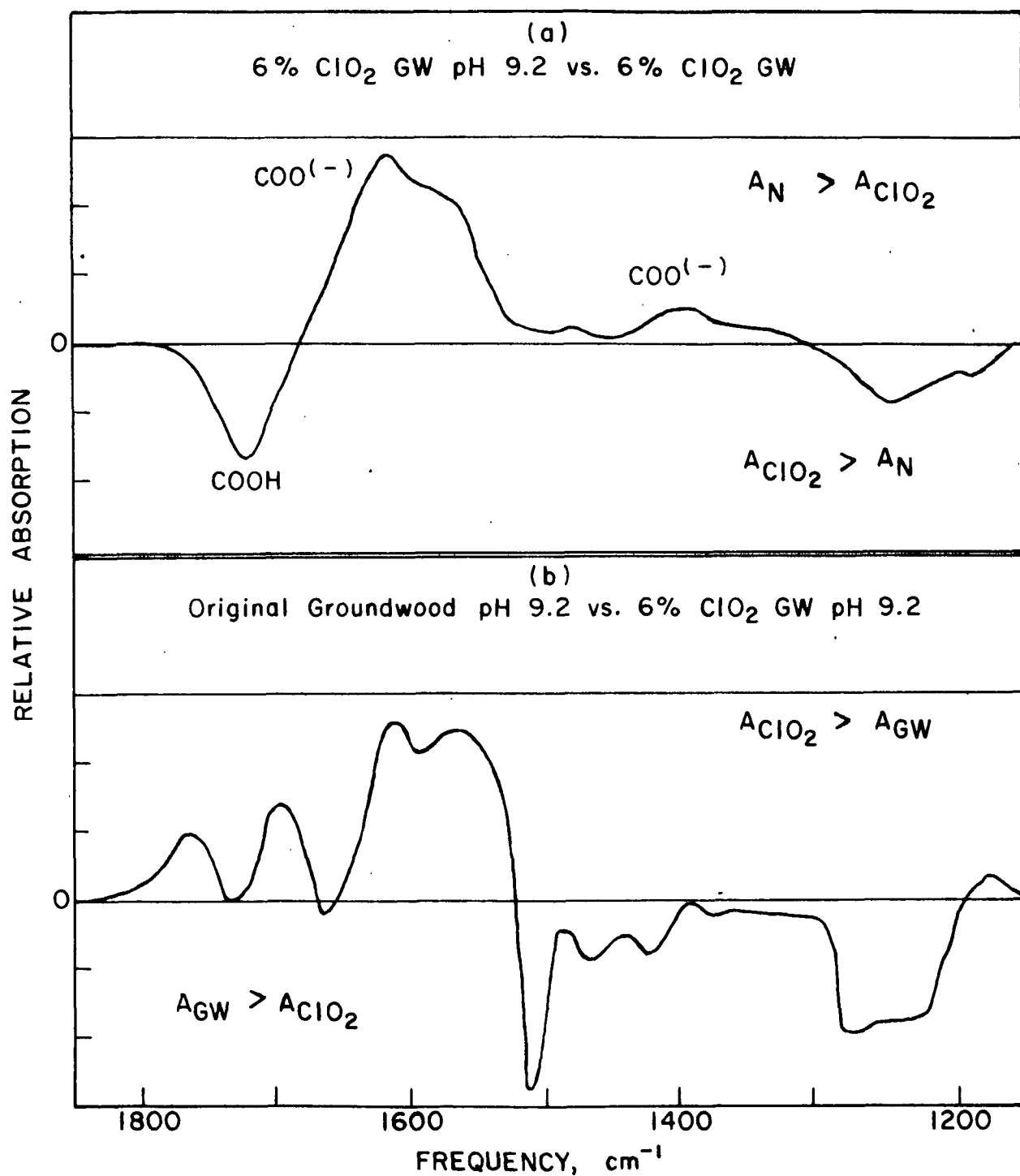


Figure 19. Difference Spectra Showing Effects of Neutralization

frequency noted by Farrand (8) for γ -lactone acids isolated from peroxyacetic acid oxidation of lignin model compounds.

The two absorption peaks in Fig. 19b at about 1560 and 1614 cm^{-1} are due to the carboxylate ions from the chlorine dioxide produced acids. They are seen more clearly in the neutralization difference spectrum for the chlorine dioxide-reacted material (Fig. 19a) where they are not partially offset by differences in the aromatic absorption at 1600 cm^{-1} . The main absorption is at 1615 cm^{-1} with an absorption shoulder at 1560 to 1570 cm^{-1} . According to Bellamy (41), the sodium salt absorbing in the 1560 to 1570 cm^{-1} region is most likely attached to a hydrocarbon residue, while that absorbing near 1615 cm^{-1} is most likely attached to a carbon atom which is chlorine substituted. Thus, it appears that more than half of the acid structures are chlorinated, which is consistent with the previously mentioned chlorination studies.

REDUCTION EFFECTS

The difference spectra showing the results of sodium dithionite and uranium(III) reduction of the original groundwood and the 6% chlorine dioxide-reacted groundwood are shown in Fig. 20. The reduced original groundwood shows a sharp decrease in absorption at 1660 cm^{-1} , which is the absorption band attributed to α -carbonyl, coniferaldehyde, and simple quinone structures in lignin (26). The dithionite is about 65% as effective as the uranium(III) in reducing the absorption at 1660 cm^{-1} , indicating that 35% of the conjugated carbonyls in the lignin are of the α -carbonyl type. The dithionite and uranium(III) both cause a decrease in the aromatic ring absorption near 1600 cm^{-1} , confirming that the carbonyls reduced were conjugated to the aromatic ring (26).

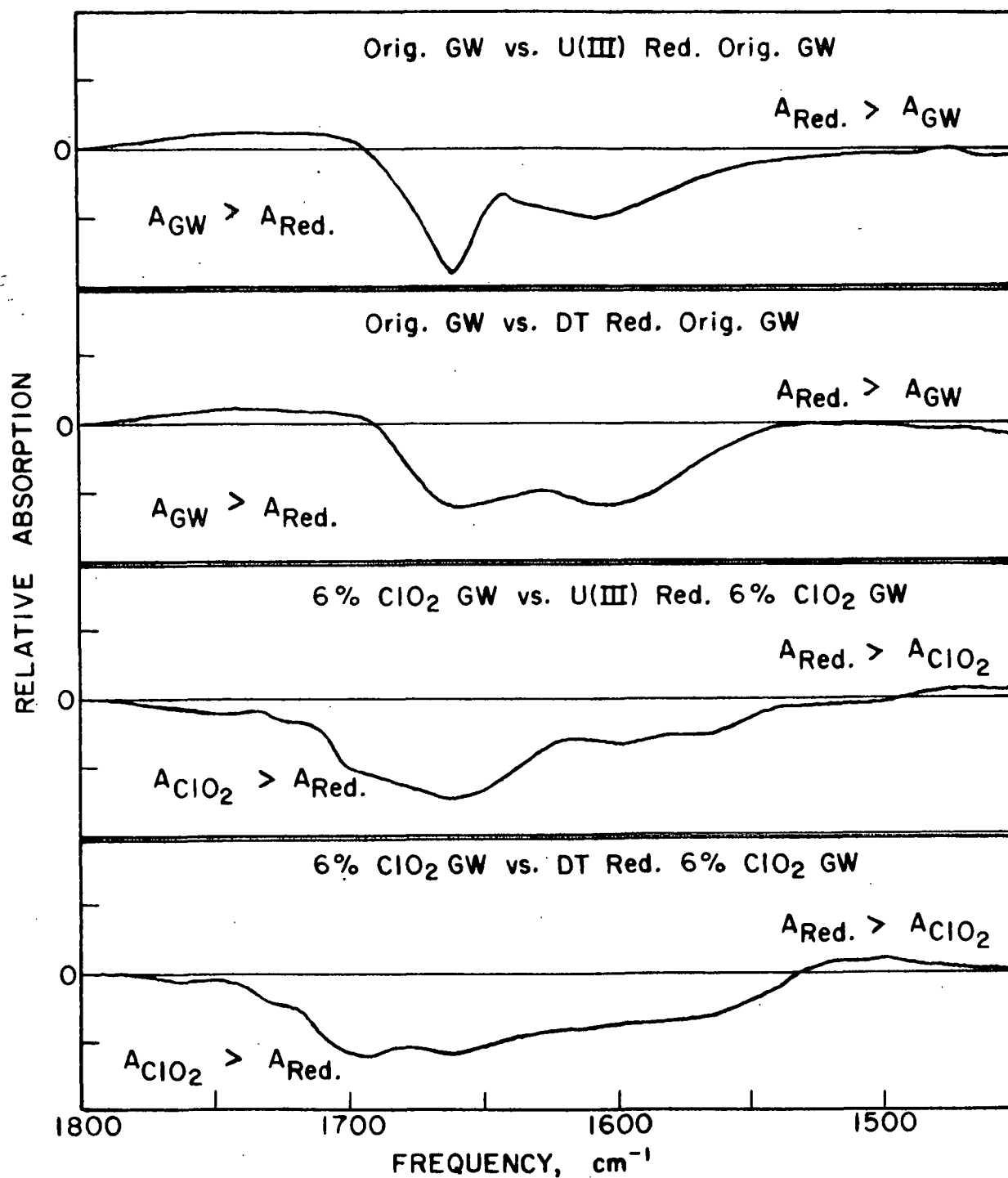


Figure 20. Difference Spectra Showing Effects of Reduction

The effects of the reduction on the 2 and 6% chlorine dioxide-reacted materials were not as specific as those noted for the original groundwood. Absorption losses were noted throughout the region from 1550 to 1730 cm^{-1} , the main effect being in the 1640 to 1730 cm^{-1} region (Fig. 20). Thus, in addition to reducing carbonyls which were present in the original groundwood, both sodium dithionite and uranium(III) reduce some carbonyls which are products of the chlorine dioxide oxidation. With the exception of the 1660 cm^{-1} region the two reductants are about equally effective. The difference at 1660 cm^{-1} is most likely due to the α -carbonyl from the original groundwood which is only reducible by the uranium(III). The remaining functional groups reduced are quinones absorbing over a wide range of frequencies due to varying degrees of chlorine substitution. As noted previously, both chlorinated and unchlorinated quinones have been isolated as major reaction products in the chlorine dioxide oxidation of lignin model compounds (3,4,6). This is also consistent with the absorption increases noted previously for the visible region of the spectrum.

EXTENT OF REACTION

In order to obtain a semiquantitative picture of the changes due to the various treatments, the absorbance per milligram of yield-basis lignin was calculated at selected frequencies. The results of this calculation are given in Table XIII.

The data are based on the assumption that at the yield levels obtained in this work (96 to 100%), the chlorine dioxide selectively attacks the lignin leaving the carbohydrate fraction relatively unchanged. This is substantiated by the fact that previous workers have shown cellulose (42) and wood carbohydrate (29,43) to be only slightly modified after reaction with much higher concentrations of chlorine dioxide than were applied in this work.

TABLE XIII

RELATIVE ABSORBANCE PER MILLIGRAM OF YIELD BASIS LIGNIN
FOR SELECTED MATERIALS

Sample	Frequency, cm^{-1}			
	1730	1660	1600	1510
Orig. GW unreacted	0.331	0.257	0.323	0.575 ^a
Orig. GW DT red.	0.362	0.182	0.249	0.575 ^b
Orig. GW uran. red.	0.355	0.143	0.266	0.575 ^b
2% ClO_2 untreated	0.478	0.267	0.272	0.522 ^a
2% ClO_2 uran. red.	0.455	0.152	0.238	0.522 ^b
6% ClO_2 untreated	0.608	0.313	0.303	0.446 ^a
6% ClO_2 DT red.	0.545	0.248	0.256	0.446 ^b
6% ClO_2 uran. red.	0.580	0.198	0.257	0.446 ^b
Orig. GW pH 9.2	0.306	--	--	0.575 ^b
6% ClO_2 pH 9.2	0.330	--	--	0.446 ^b

^a Calculated from IR spectra of known weights of sample.

^b Assumed as basis for calculation of other entries.

It is also assumed that the molar absorptivity for the aromatic ring compounds is unaffected by the treatments and that there is no loss of aromatic material during the neutralization and reduction procedures. Both assumptions are probably valid for the neutralization and reduction procedures as there is no significant change in the 1510 cm^{-1} region of the difference spectra, as

can be noted in Fig. 19a and 20. In the case of the chlorine dioxide reaction, however, there exists the possibility that chlorine substitution of the aromatic rings might have altered the extinction coefficient. The effect is probably small, though, as degradation studies showed that less than 6% of the rings are chlorinated and the effect of chlorine substitution on the extinction coefficient has been shown to be small in cases where the ring contains ether groups (44,45).

While the 1510 cm^{-1} absorbances calculated using the 1820 cm^{-1} maximum as a base line are adequate for use as internal standards in relating the absorbances of the various peaks to the lignin content (Table VIII), a base line more closely associated with the 1510 cm^{-1} peak should be used in more accurately determining the aromatic content. For this reason the 1510 cm^{-1} absorbances for the original groundwood and 6% chlorine dioxide-reacted groundwood were also calculated using the line passing through the 1820 and 1550 maxima as base line. On this basis the original groundwood had an absorbance of 0.514 unit per mg lignin and the 6% chlorine dioxide-reacted groundwood had an absorbance of 0.382 unit per mg lignin.

If we assume the absorbance of 0.514 for the original groundwood to correspond to 100% aromatic structures with an equivalent weight of 187 g and use the relative absorbance at 1510 cm^{-1} as a measure of the percentage of aromatic units in the oxidized lignin, the aromatic lignin content of the 6% chlorine dioxide material can be calculated. If it is further assumed that all of the remaining lignin material consists of ring rupture products with an equivalent weight of 205 (as described on p. 18, 21, and 22), then it is possible to calculate the ring oxidized lignin content. The results of these calculations are given in Table XIV along with the analytical values for methoxyl, carboxyl,

chlorine, and volatile methoxyl reported earlier (Table IV). The correlation between the aromatic equivalents as estimated from the infrared absorbance at 1510 cm^{-1} (78.1) and the nonvolatile methoxyl content ($80.0 - 1.7 = 78.3$) is quite good lending credence to the validity of the procedures.

TABLE XIV
COMPOSITION OF 6% CHLORINE DIOXIDE-REACTED LIGNIN

Structural Component	Equivalents per 100 Equivalents Lignin
Aromatic structures	78.1 ^a
Ring oxidized structures	21.9
Methoxyl	80.0
Carboxyl	36.4
Chlorine	16.8
Volatile methoxyl	1.7

$$^a [0.382/0.514] \times 100 \times \frac{197}{187} = 78.1.$$

The absorbance given in Table XIII for the 1730 cm^{-1} region can be used to estimate the relative amounts of carboxylic acid products as compared to other carbonyls which absorb in this region. The change in absorbance between the original groundwood (0.331) and the 6% chlorine dioxide-reacted groundwood (0.608) shows an increase of 0.277 unit due to chlorine dioxide-produced structures. The corresponding increase in these materials at pH 9.2 is 0.024 unit. Thus, $0.024/0.277 \times 100$ or about 8.7% of the groups are noncarboxyl and by difference about 91.3% are carboxyl.

Another estimate of the % carboxyl can be obtained from the equivalents of ring oxidized material and equivalents of carboxyl given in Table XIV for the 6% chlorine dioxide-reacted material. Assuming two carbonyl groups per ring oxidized equivalents, it can be calculated that $[36.4/(21.9 \times 2)] \times 100$ or about 83% of the carbonyl would be carboxyl.

The second estimate is probably the better of the two as the first one is bound to be on the high side as all noncarboxylic absorption outside of the 1730 cm^{-1} region was ignored. In any case it has been shown that most of the carbonyl formed from the oxidation is carboxyl.

From the data in Table XIII for the 1660 cm^{-1} region, it can be seen that the absorbance changes on application of reducing agents are quite similar in magnitude for all three groundwood materials [about 0.11 for uranium(III) and 0.075 for dithionite]. This seems to indicate that the functional groups being reduced are mainly from the original groundwood. The higher residual absorbance after uranium(III) reduction for the 6% chlorine dioxide-reacted groundwood is indicative of the production of a nonreducible group as a result of the chlorine dioxide oxidation. This is in the region where the carbon-carbon double bonds of muconic acid derivatives would absorb. The higher relative absorbance at 1600 cm^{-1} as compared to 1510 cm^{-1} for the uranium reduced 6% chlorine dioxide-reacted material as compared to the corresponding unreacted groundwood (0.257/0.446 versus 0.266/0.575) indicates that some nonreducible groups are produced which absorb in the 1600 cm^{-1} region also.

From the above discussion of the infrared spectra, it can be concluded that the principal reaction between lignin and chlorine dioxide involves the degradation of the aromatic ring with the resultant formation of a ring oxidized product containing about 1.8 carboxyl groups per equivalent, and that a substantial portion of these ring oxidized products are chlorinated.

There is also evidence for the formation of small amounts of esters (probably lactones) as well as quinones, which are also at least partially chlorinated.

CONCLUSIONS

On the basis of this work, certain conclusions can be made concerning the nature of lignin in situ after reaction with limited amounts of unbuffered aqueous chlorine dioxide. These conclusions are summarized in the following paragraphs and illustrated in the reaction scheme shown in Fig. 21.

Even when the chlorine dioxide applied is limited so as to obtain yields in excess of 98%, the lignin material remaining in situ is extensively modified and is no longer completely discernible by classical analytical procedures. About 20% of the modified lignin is ring oxidized material which appears to consist mainly of muconic acid derivatives such as E and I. Together they account for about 85% of the degraded aromatic rings. The monoethyl esters such as B and F are not present in significant amounts, although they may be intermediates in the formation of the diacids.

The modified lignin contains substantial amounts of organically bound chlorine, about 75% of which appears to be attached to ring oxidized structures, most likely muconic acid structures such as I. The remaining chlorine is probably attached to aromatic rings at the 6-position such as in C.

Quinonoid structures such as D and G, and lactone structures such as H also appear to be present in small amounts. In addition, there are some chromophoric groups produced in small amounts which are not reducible by either sodium dithionite or uranium(III) ion and are therefore most likely not quinones.

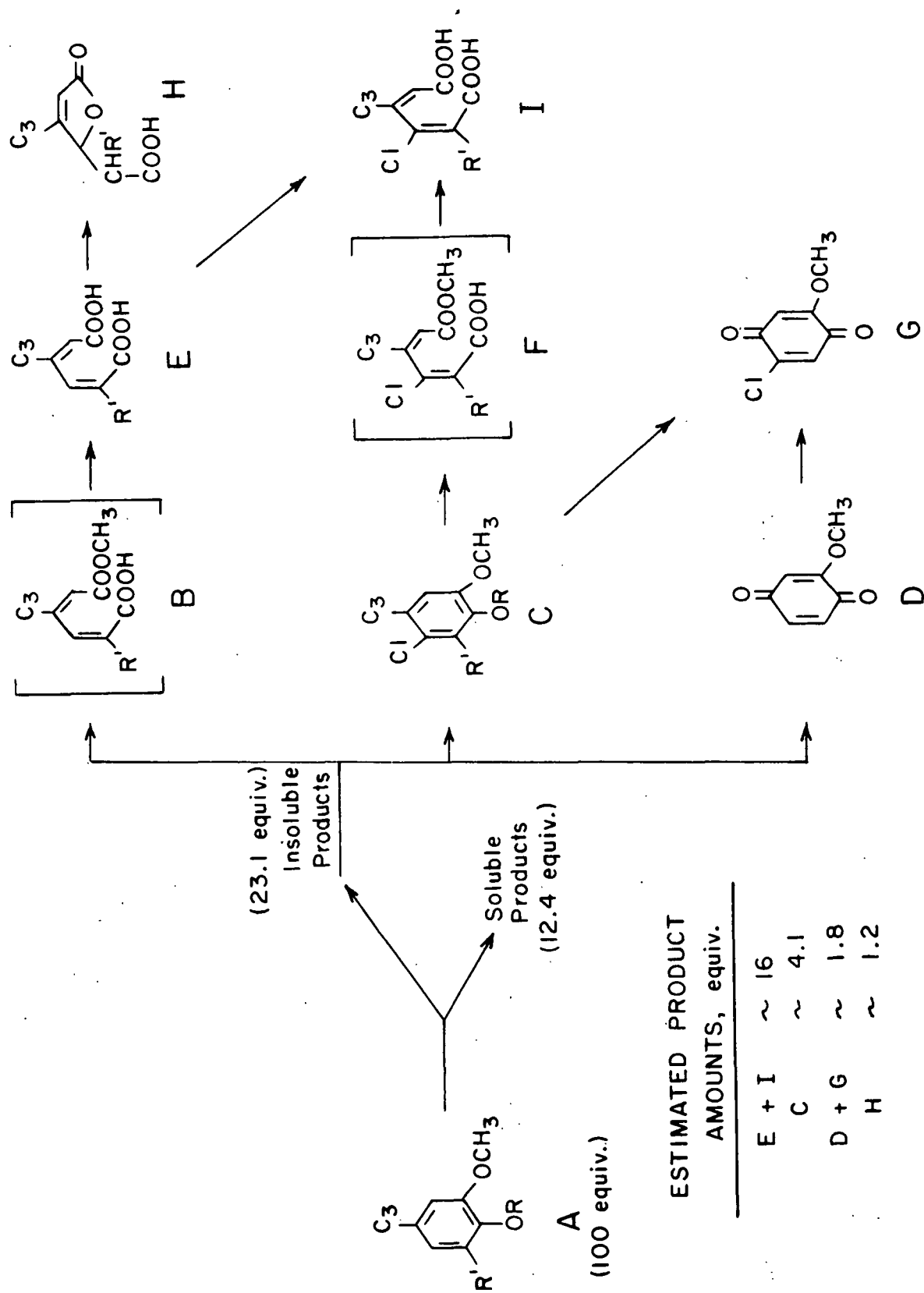


Figure 21. Reaction Scheme for ClO_2 Oxidation of Lignin

It has also been shown during the course of this work that meaningful ultraviolet and visible spectra of lignin in situ can be obtained via reflectance measurements on compacts of finely milled groundwood diluted with cellulosic material.

EXPERIMENTAL

SELECTION AND PREPARATION OF STARTING MATERIAL

Two twenty-year-old plantation grown white spruce (Picea glauca) trees were cut from the lot at The Institute of Paper Chemistry. After stripping off the branches, two four-foot bolts were cut from the stump end. These bolts ranged from three to six inches in diameter and contained a heartwood core, as determined by resin emission, or from 0.75 to 2.0 inches.

The selected bolts were peeled to remove the bark and the outer growth ring; the knots were bored out, the bolt was split lengthwise, and the heartwood was routed out. The remaining sapwood was chipped in the Institute chipper and hand screened to remove obvious impurities. The chips were then processed into refiner groundwood at the Kimberly-Clark Corporation Research and Engineering Center in Neenah, Wisconsin.

GROUNDWOOD EXTRACTION

The refiner groundwood was air dried in a forced circulation drier at room temperature and passed through the large Wiley mill (No. 5 screen). The milled material was then charged in 80-gram portions into a large Soxhlet extractor and continuously extracted with a mixture of alcohol and benzene (1 to 2) for twelve hours. The heating mantle on the solvent flask was adjusted to give about two siphons per hour.

After completion of the alcohol-benzene extraction, the material was air dried and batch extracted in a beaker with hot (80°C) water for five hours. It was then filtered, washed, air dried, and stored at ambient temperature in the dark in plastic bags.

ANALYTICAL PROCEDURES

The following is a list of analytical procedures employed in the course of this study:

- (a) Lignin Content. The lignin content of the various samples was determined by classical methods as well as estimated on the basis of yield. The former was done using the Klason lignin determination (Institute Method 428) and the acid-soluble lignin determination based on measurement of the absorbance of the Klason filtrate after dilution to 500 ml (absorptivity of lignin assumed to be 105 liters/g-cm) (46). The yield basis lignin contents were estimated by assuming all material lost as a result of the chlorine dioxide reaction was lignin. Thus, if 100 grams of groundwood containing 26% lignin were reacted with chlorine dioxide to give 98 grams of product, it was assumed that 2 grams of lignin were lost and the new lignin content was estimated to be $24/98 \times 100 = 24.5\%$.
- (b) Methoxyl. The methoxyl content of the groundwood samples was determined using Institute Method 18.
- (c) Carboxyl. Two methods were used for the determination of carboxyl groups. In the first a suspension of 2.0 grams o.d. groundwood in 50 ml of distilled water was titrated with 0.2N sodium hydroxide, with agitation after each incremental addition of base. The pH was determined using a Corning Model 12 pH meter and a plot of pH versus milliliters of base was made and the end point determined by the maximum slope method.

The second method employed was the calcium acetate method described by Meesook and Purves (47), with the exception that potentiometric methods were used to determine the hydrogen ion liberated by calcium ion exchange.

- (d) Volatile Methoxyl. Methoxyl groups liberated as methanol on hot distillation of an aqueous suspension of groundwood at pH 7 were determined as described by Dence, et al. (3).
- (e) Organically Bound Chlorine. The amount of organically bound chlorine in the groundwood samples was determined via combustion in a Schöniger flask followed by a Volhard titration of the liberated chloride.
- (f) Inorganic Elements. Trace amounts of inorganic elements were determined by standard spectrometric techniques using an Institute modified Bausch & Lomb Spectrograph (1 1/2 meter grating).
- (g) Chlorine Dioxide Concentration. The chlorine dioxide solutions were analyzed according to the method of Ernest (48). Both the neutral and acid end points were determined in order to verify the absence of free chlorine.
- (h) Chloride Concentration. The aqueous phase from the cupric oxide degradation studies was analyzed for chloride ion by potentiometric titration with silver nitrate using a silver-silver chloride reference electrode.

CHLORINE DIOXIDE GENERATION

The procedure used to generate the chlorine dioxide was a modification of that described by Ernest (48). Seventy grams of sodium chlorate and sixty-seven grams of crystalline oxalic acid were mixed in a 500-ml round bottom flask in a 60°C water bath. Next, 167 ml of a solution, in the proportion of 400 ml of distilled water to 120 ml of concentrated sulfuric acid, was added. The apparatus was assembled under a hood taking care to moisten all ground glass connections. The chlorine dioxide generated was passed through a trap containing a saturated solution of sodium chlorite in order to convert any free chlorine to chlorine dioxide and was then collected in a five-liter bottle of cooled (8°C) water situated in a bucket of crushed ice. The chlorine dioxide solutions were analyzed and utilized shortly after generation.

REACTION OF GROUNDWOOD WITH CHLORINE DIOXIDE

A weighed amount (about 40 g) of groundwood material was placed in a two-liter bottle along with a measured amount of distilled water. The slurry was allowed to stand overnight to assure uniform wetting. Next, the additional amount of distilled water required to give a final consistency of three percent was added and the slurry was thoroughly mixed. Finally, the required amount of chlorine dioxide (2 to 10% by weight on o.d. groundwood) solution was added via pipet and the bottle was capped and vigorously shaken. The bottles were placed in a hot-water bath at 35°C and were removed and thoroughly shaken at least once every thirty minutes. As the reaction neared completion (from two to eight hours depending on the chlorine dioxide concentration) the bottles were opened and tested with potassium iodide-starch test paper. The reaction was considered complete thirty minutes after obtaining a negative test. The bottle was then

removed from the bath, the contents filtered on a Buchner funnel, and washed with 800 ml of distilled water. The material was then returned to the bottle and allowed to diffusion wash with 1800 ml of distilled water overnight. It was then filtered onto a tared filter paper and washed with an additional 1000 ml of distilled water. The pads were air dried in a forced circulation drier at ambient temperature, weighed, crumbled into plastic bags, and stored in the dark. The next day duplicate samples were removed in order to determine the moisture content.

OTHER GROUNDWOOD REACTIONS

The original groundwood and the 2 and 6% chlorine dioxide-reacted groundwoods were subjected to reductive bleaching and the original groundwood and the 6% chlorine dioxide-reacted groundwood were subjected to alkaline cupric oxide degradation. The procedures employed are discussed in the following paragraphs:

- (a) Sodium Dithionite Reduction. The unreacted groundwood and the 2 and 6% chlorine dioxide-reacted groundwoods were reduced with 6 electron equivalents of sodium dithionite using the methods of Polcin and Rapson (26). One gram of groundwood, 5 ml of phosphate buffer (pH 6.2) and 6.75 ml of water were placed in an Erlenmeyer flask in a water bath at 60°C and allowed to come to equilibrium. The required amount of dithionite solution was then added bringing the total volume up to 25 ml. Both the original and final pH values of the slurries were found to be between 6.0 and 6.4. When the reaction was completed the slurries were filtered on a Buchner funnel and thoroughly washed with distilled water. They were then suspended in 0.1N hydrochloric acid and allowed to soak

for five minutes. The slurries were again filtered and washed with distilled water and then dried in the vacuum oven overnight at 50°C. They were then stored in a manila envelope in a desiccator over phosphorous pentoxide.

- (b) Uranium(III) Reduction. The unreacted and the 2 and 6% chlorine dioxide-reacted groundwoods were reduced with uranium(III) ion according to the procedures of Polcin and Rapson (26). A solution of 0.5N uranyl sulfate was prepared by dissolving the required amount of uranyl sulfate in one liter of 3.5N hydrochloric acid. The uranium(III) solutions were prepared by passing the uranyl sulfate solution through a zinc reductor column just prior to addition to the pulp slurry. One gram of groundwood was suspended in 44 ml of distilled water in a three neck round bottom flask and the flask was placed in a water bath at 60°C. Then, under an inert atmosphere of nitrogen gas, and with vigorous stirring, 13.2 ml of 5N hydrochloric acid and 12 ml of uranium(III) solution were added. The pulp slurry was then stirred for two minutes then the action of the uranium(III) was stopped by the addition of 30 ml of 6.8N potassium acetate. The mixture was stirred for an additional 6 minutes, then removed from the bath and allowed to cool to room temperature. It was then filtered on a Buchner funnel and washed with 80 ml of 0.05M disodium dihydrogen ethylenediaminetetraacetate dihydrate (EDTA). The material was then suspended in a mixture of 15 ml of 0.2M EDTA and 30-ml water and heated for

15 minutes at 85-95°C under an inert atmosphere. After filtering and washing with distilled water, the last step was repeated two more times. The sample was then suspended in 0.1N hydrochloric acid for 5 minutes. Next it was filtered and washed with distilled water and then dried in the vacuum overnight at 50°C. The samples were then stored in manila envelopes in a desiccator over phosphorous pentoxide.

- (c) Cupric Oxide Degradation of Groundwoods. Unreacted and 6% chlorine dioxide-reacted groundwoods were degraded in alkaline cupric oxide using a modified version of the procedure of Pearl and Beyer (49). In each case a portion of groundwood containing approximately 3.65 g of lignin (yield-basis) was reacted with 26.5 g of hydrated cupric oxide ($\text{CuO} \cdot \text{H}_2\text{O}$) and 160 ml of 2N sodium hydroxide for three hours at 170°C in a stainless-steel bomb. On completion of the reaction, the bomb was cooled to room temperature, after which the contents were removed, filtered, and washed with 2% sodium hydroxide solution until the washings were colorless. The material was then washed twice with 25-ml portions of ether. The combined filtrate and washings were then acidified with concentrated sulfuric acid to pH 2, care being taken to cool and vigorously stir the solution during neutralization. The acidified solution was extracted continuously with ether in a liquid-liquid extractor for 72 hours, after which the ether solution was washed four times with 20-ml portions of concentrated sodium sulfate, dried with anhydrous magnesium

sulfate, and filtered. It was then evaporated to dryness in a stream of filtered air and the residue dissolved in 100 ml of C.P. acetone. Two ten-milliliter portions of the acetone solution were evaporated to dryness in tared weighing bottles in the vacuum oven at 35°C in order to determine the total yield of ether solubles.

INFRARED ANALYSIS

Infrared spectra were obtained from transmittance measurements made on potassium chloride pellets (BDH infrared grade) containing finely pulverized groundwood. To prepare the pellets the Wiley milled (80 mesh) groundwood was placed in a stainless-steel capsule and ground for six periods of five minutes on the mixer-mill, care being taken to cool the material between periods of grinding in order to prevent overheating. Next, the finely powdered material was dried for 24 hours in the vacuum oven at 40°C. About 2.2 mg of this material was thoroughly mixed with about 250 mg of potassium chloride and a pellet was formed using a conventional pellet press and die, allowing six minutes under vacuum and ten minutes at ten tons force. Pellets made entirely of potassium chloride were also prepared as a reference. For normal infrared spectra, the pellet containing 100% potassium chloride was placed in the reference beam and the groundwood-containing pellet in the sample beam. For difference spectra, pellets containing equivalent amounts (same absorption at 2900 cm^{-1}) of the two materials of interest were placed in the reference and sample beams.

Preliminary infrared spectra were obtained on the Perkin-Elmer Model No. 700 infrared spectrophotometer and more detailed studies were done on the Perkin-Elmer Model No. 621 infrared spectrophotometer.

ULTRAVIOLET AND VISIBLE ANALYSIS

The specific absorption coefficients of the lignin fraction of the various groundwood materials were determined using a new method based upon the procedure employed by Polcin and Rapson (22).

A Beckman Model DK-2 spectrophotometer equipped with an integrating sphere was used to obtain transmittance and reflectance measurements on sheets of Whatman No. 40 filter paper, reflectance measurements on compacts of Wiley milled (80 mesh) Whatman No. 40 paper, and reflectance measurements on compacts of Wiley milled (80 mesh) groundwood diluted to about a 1% lignin concentration with the milled Whatman No. 40 paper.

To avoid errors due to nonuniformity of the sheets of filter paper, transmittance measurements were made at 340 nm on twenty-two tabs cut from eleven sheets of filter paper and the average was calculated. That sheet having a transmittance nearest the average was then selected for measurements over the entire range of wavelengths of interest (240 to 580 nm). The selected sheet was also placed at the head of a pack of twelve sheets for the measurement of reflectance. A die, 3.71 cm² in area, was used to punch out the area of the sheet which was in the light beam in order to determine basis weight.

The remainder of the Whatman No. 40 paper from the box from which the eleven sheets were taken at random for the transmittance measurements, was disintegrated in the Wiley mill (80 mesh). The groundwood samples were likewise disintegrated and mixtures of milled groundwood and milled Whatman No. 40 paper were prepared to contain about 1% lignin. The exact compositions of these mixtures are given in Appendix IV. After shaking for four periods of

one minute on the large mixer-mill in small glass bottles, the powdered mixtures were emptied into a brass die (3.5 cm in diameter) and pressed against a silvered plate for two minutes at one ton total force. The pressed compacts were removed from the die and placed in small manila envelopes (care being taken to label the plate side of the compact).

Reflectance measurements were made at four different positions on the plate side of the compacts using a magnesium oxide compact as a reference. These data, along with data on the absolute reflectance of the magnesium oxide, the concentrations of compact components, and the 100% line of the reflectance curve were recorded on computer cards and processed as indicated in computer programs BACS and VAND, which are given in Appendix III. A complete discussion of the adaptation of the procedure of Polcin and Rapson (22) by the author is given in the Results and Discussion section of this thesis.

GAS CHROMATOGRAPHIC ANALYSIS

All chromatographic analyses were done on the Varian Model 1520 gas chromatograph using the conditions listed in Table XV.

TABLE XV

CHROMATOGRAPHIC CONDITIONS

Instrument	Varian 1400
Column	10% S.E. 30 on Chromosorb G, AW, DMCS, 1/4" x 6', S.S.
Temperature	165°C isothermal
Flow rate	27.3-ml helium per min
Range	10 ⁻¹¹
Injector temperature	200°C
Detector temperature	225°C

Chromatograms were run on acetone solutions of the ether solubles from the cupric oxide degradation studies, as well as acetone solutions of various knowns (vanillin, guaiacol, acetovanillone, 5-chlorovanillin, 6-chlorovanillin, syringaldehyde, vanilloyl, methyl ketone, vanillic acid, and p-hydroxybenzaldehyde). Where quantitative results were desired, solutions were prepared containing 1% of the known and 1% p-dibromobenzene as an internal standard. All of the knowns used were recrystallized chromatographically pure compounds obtained from Dr. Irwin Pearl and the Analytical Department.

MASS SPECTROMETRIC STUDIES

In order to confirm the tentative identification of the chromatographic peaks, as determined by relative retention times, mass spectra were obtained whenever there was sufficient sample to give a meaningful disintegration pattern. The instrument used was a Du Pont Instruments Model 21-491 spectrometer interfaced via a jet separator with a Varian Model 1440-1 gas chromatograph equipped with a flame ionization detector. The gas chromatographic and beam monitor responses were recorded with a Hewlett-Packard Model 7128A recorder. The mass spectra were recorded with a Century GPO 460 recorder. Table XVI summarizes the conditions utilized for this work.

TABLE XVI
CONDITIONS FOR MASS SPECTROSCOPY

Interface temperature	290°C
Block temperature	3 00°C
Oven temperature	108°C
Source temperature	195°C
Frequency	30 Hz
Sensitivity	7.5
Scan	10 sec/decade
Chart speed	4 inches/sec
Pressure prior to sample entry	<u>ca.</u> 1×10^{-7} torr

ACKNOWLEDGMENTS

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LIST OF ABBREVIATIONS

Abs., absolute

AW, acid washed

Chromosorb G, flux calcined diatomite support for chromatographic column

Comp., compact

DMCS, dimethyldichlorosilane treated

DT, dithionite

Equiv., equivalent(s)

GW, groundwood

Insol., insoluble

Lig., lignin

m/e, mass/charge

N, neutralized

o.d., oven-dry

Oxid., oxidized

Red., reduced

S.E. 30, methyl silicone liquid phase for chromatographic column

Sol., soluble

S.S., stainless steel

Unreac., unreacted

Uran., uranium(III) ion

What., Whatman No. 40

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APPENDIX I

SAMPLE CALCULATIONS

CALCULATION OF YIELD-BASIS LIGNIN CONTENT FOR 6%
CHLORINE DIOXIDE-REACTED MATERIAL

On reaction with chlorine dioxide, 1000 g of original groundwood, containing 261.5 g of lignin (Table III) and, by difference, 738.5 g of carbohydrate produce 980 g (Fig. 8) of 6% chlorine dioxide-reacted material. If only lignin material is lost to solution the product composition is:

$$\text{Lignin} = 261.2 - 20.0 = 241.2 \text{ g}$$

$$\text{Carbohydrate} = 738.5 \text{ g}$$

$$\% \text{ Lignin (on product)} = 241.2 / (241.2 + 738.5) = \underline{24.64\%}$$

CALCULATIONS TO CHANGE FROM WEIGHT BASIS TO MOLECULAR EQUIVALENT
BASIS FOR 6% CHLORINE DIOXIDE-REACTED MATERIAL

Using 1000 g of the 6% chlorine dioxide-reacted material as a basis:

$$\text{Lignin} = 246.4 \text{ g} \quad (\text{from above})$$

$$\text{Methoxyl} = 31.0 \text{ g} \quad (\text{Table III})$$

$$\text{Chlorine} = 8.6 \text{ g} \quad (\text{Table III})$$

and

$$\text{Equiv. methoxyl} = 31.0 / 31.0 = \underline{1.00}$$

$$\text{Equiv. chlorine} = 8.6 / 35.5 = \underline{0.242}$$

If it is assumed that the equiv. of unreacted lignin are equal to the equiv. methoxyl, then:

$$\text{Equiv. unreacted lignin} = \underline{1.00}$$

$$\text{Weight unreacted lignin} = \underline{187 \text{ g}}$$

Then, by difference:

$$\text{Weight oxidized lignin} = 246.4 - 187 = \underline{59.4} \text{ g}$$

Correcting for the weight of substituted chlorine (which is not accounted for in the assumed equiv. weight of 205 g),

$$\text{Weight oxidized lignin} = 59.4 - 8.6 = \underline{50.8} \text{ g}$$

and

$$\text{Equiv. oxidized lignin} = 50.8/205 = \underline{0.248}$$

and

$$\text{Equiv. total lignin} = 1.00 + 0.248 = \underline{1.248}$$

$$\text{Average equiv. weight} = 246.4/1.248 = \underline{197}$$

and

$$\text{Methoxyl per equiv.} = 1.00/1.248 = \underline{0.80}$$

$$\text{Chlorine per equiv.} = 0.242/1.248 = \underline{0.194}$$

Converting to a basis of 100 equiv. of product material:

Total lignin	100
Unreacted lignin	80
Oxidized lignin	20
Methoxyl	80
Chlorine	16.8 (corrected for 2.6 equiv. in original groundwood)

Converting to a basis of 100 equiv. of substrate lignin:

To produce 1000 g of product at 98% yield one needs:

$$1000/0.98 = 1020.4 \text{ g of substrate groundwood}$$

or

$$1020.4 \times 0.2615 = \underline{266.8} \text{ g substrate lignin}$$

then there are:

$$266.8/187 = \underline{1.427} \text{ equiv. substrate lignin}$$

as calculated above there are:

$$\underline{1.248} \text{ equiv. product lignin}$$

thus

$$\text{product lignin/substrate lignin} = 1.248/1.427 = \underline{0.876}$$

Thus, all values calculated on the basis of 100 equiv. of product lignin can be converted to the basis of 100 equiv. of substrate lignin through multiplication by 0.876.

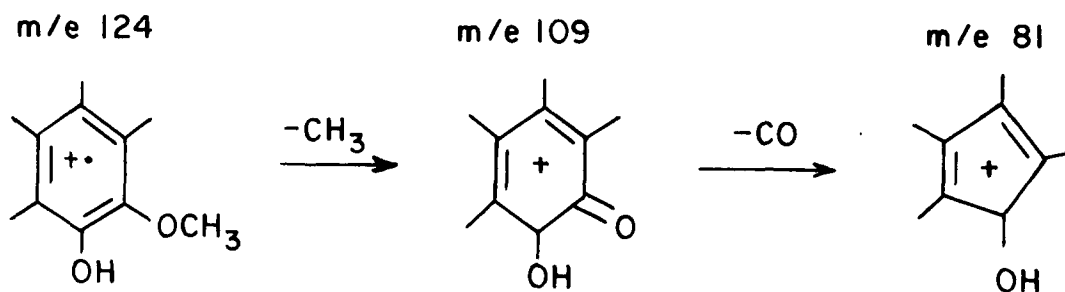
APPENDIX II

IDENTIFICATION OF CUPRIC OXIDE DEGRADATION PRODUCTS

The chromatograms of the ether-soluble alkaline cupric oxide degradation products from the unreacted and 6% chlorine dioxide-reacted groundwoods are given in Fig. 22. Where sufficient sample was available, the substances in the various peaks were identified via mass spectroscopy as indicated in the Experimental section. A detailed analysis of the various mass spectra including probable disintegration patterns is given in the following sections.

PEAKS GW-1 AND CD-1

The mass spectrum (Fig. 23) of the known guaiacol showed a base peak corresponding to the parent ion at $m/e = 124$ and strong fragment ions at $m/e = 109$ and 81 . The initial fragmentation pattern most likely involves the loss of a methyl group followed by the loss of a molecule of carbon dioxide as illustrated in the following figure.



For the unknown GW-1 (Fig. 24) the base peak is also the ion at $m/e = 124$ and the fragment ions at $m/e = 109$ and 81 are also prominent. Thus, it is evident that GW-1 contains substantial amounts of guaiacol. Since the spectrum also shows some peaks not prominent in the spectrum of the known, it is possible

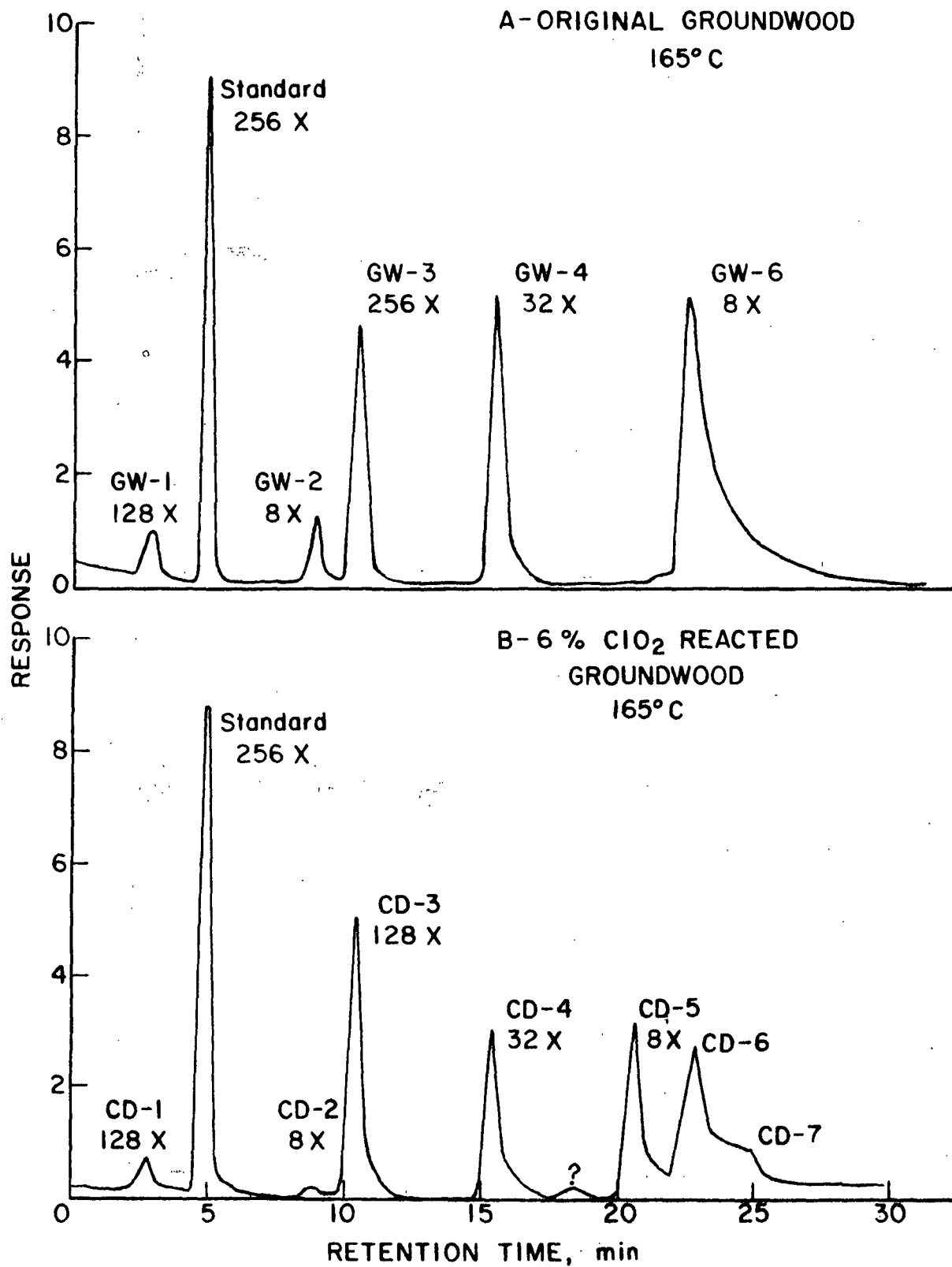


Figure 22. Chromatographs of CuO Oxidation Products

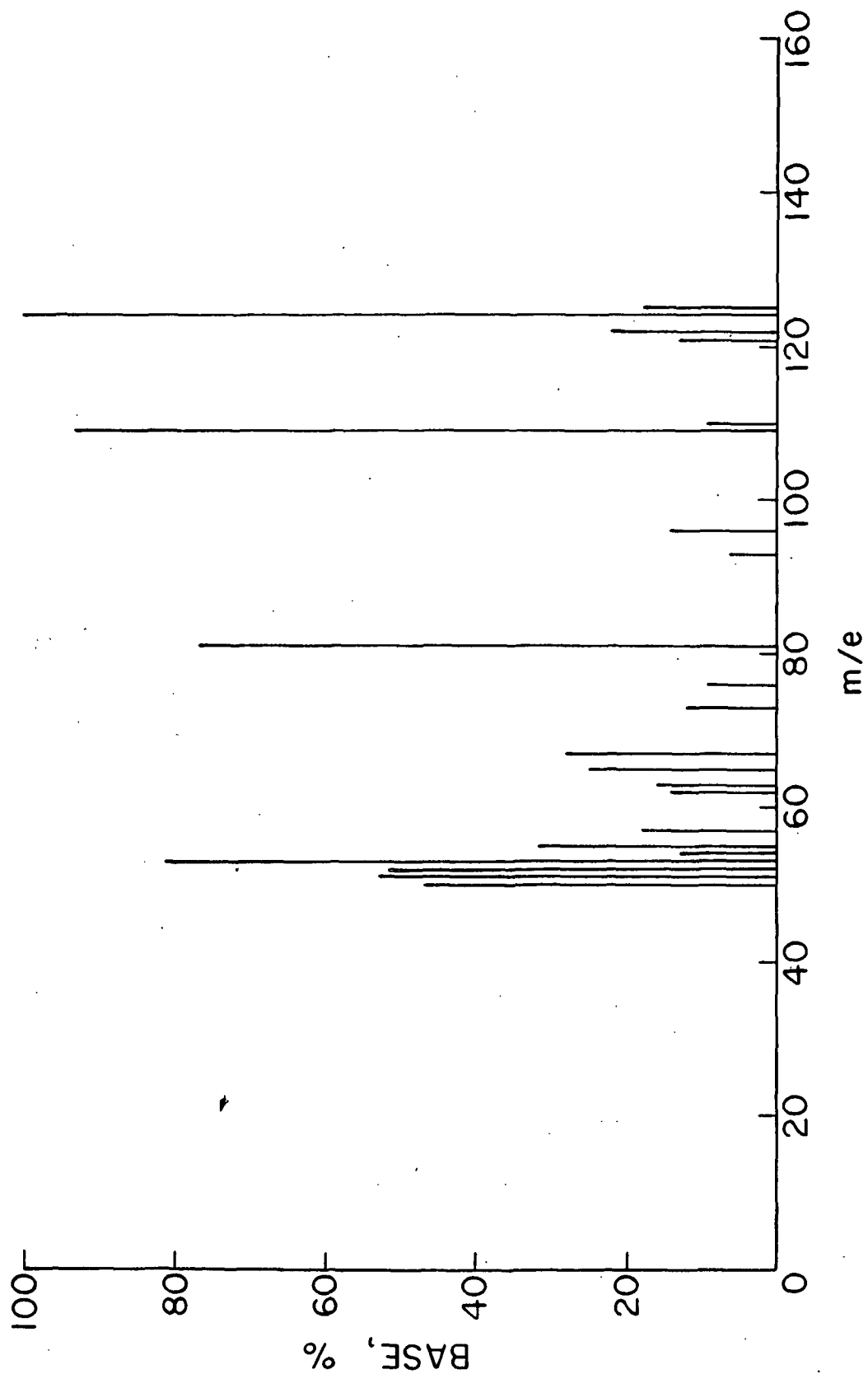


Figure 23. Mass Spectrum of Guaiacol Known

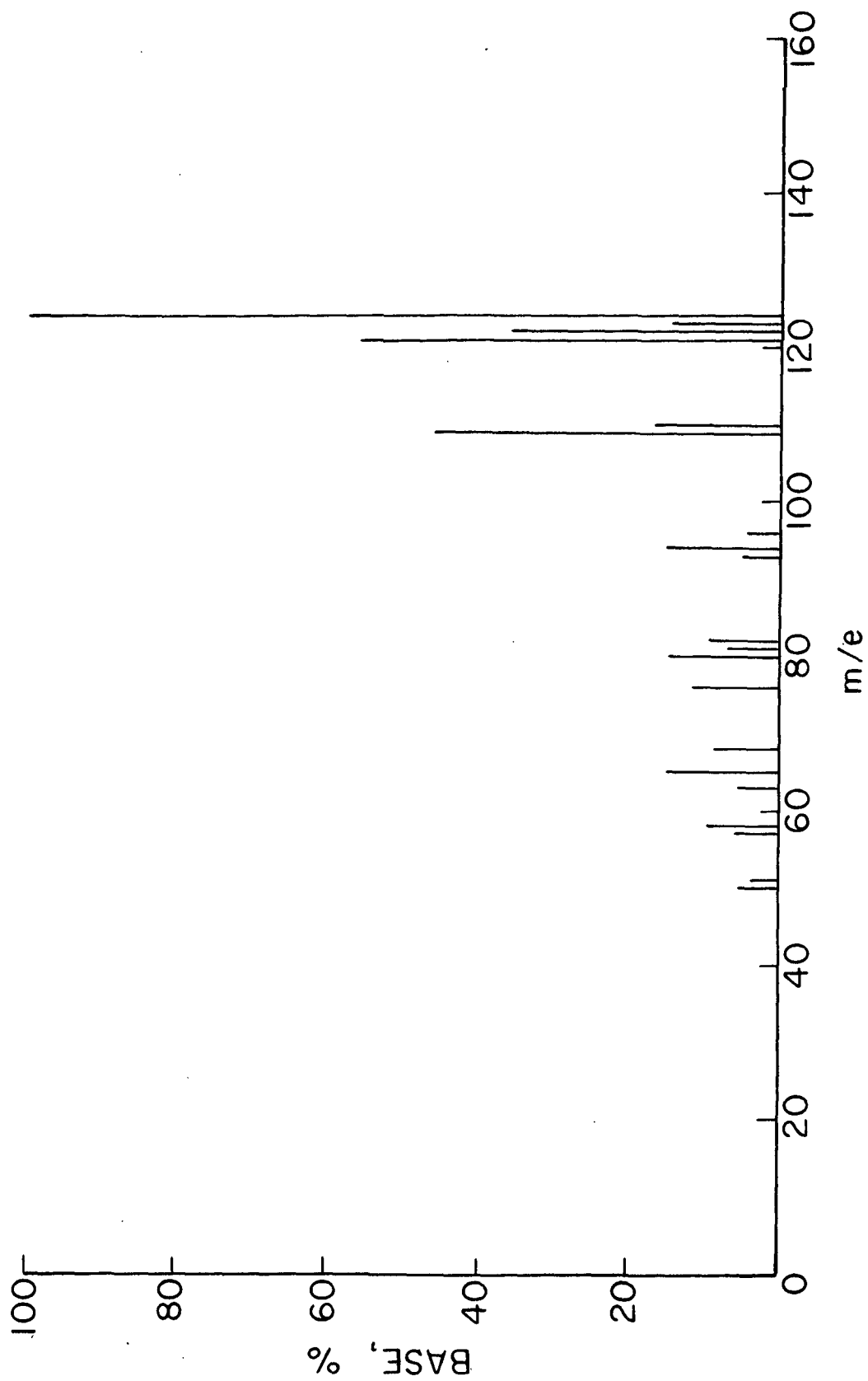


Figure 24. Mass Spectrum of Unknown GW-1

that small amounts of impurity are present. One probable impurity is acetone, since the guaiacol peak comes before the solvent tail has completely disappeared.

Unknown CD-1 did not contain sufficient sample to obtain a meaningful mass spectrum, but is most likely guaiacol as it is chromatographically similar to both the guaiacol known and GW-1 and was formed under conditions similar to those involved in the formation of GW-1.

PEAKS GW-2 AND CD-2

These peaks did not contain sufficient sample for mass spectroscopic analysis. On the basis of chromatographic similarities, they are most likely p-hydroxybenzaldehyde.

PEAKS GW-3 AND CD-3

The mass spectrum (Fig. 25) of vanillin shows a base peak at $m/e = 152$ corresponding to the parent ion and other prominent ion fragments at $m/e = 151$, 123, 109, and 81. On the basis of the above it would appear that the initial disintegration pattern is as shown in Fig. 26.

The spectra of both unknowns GW-3 and CD-3 (Fig. 27 and 28) show the same base peak corresponding to the parent ion at $m/e = 152$, as well as the major fragmentation peaks at $m/e = 151$, 123, 109, and 81. Thus, both of these unknowns must contain vanillin. The almost complete agreement of the other minor peaks in the spectra indicate that very little if any impurity is present.

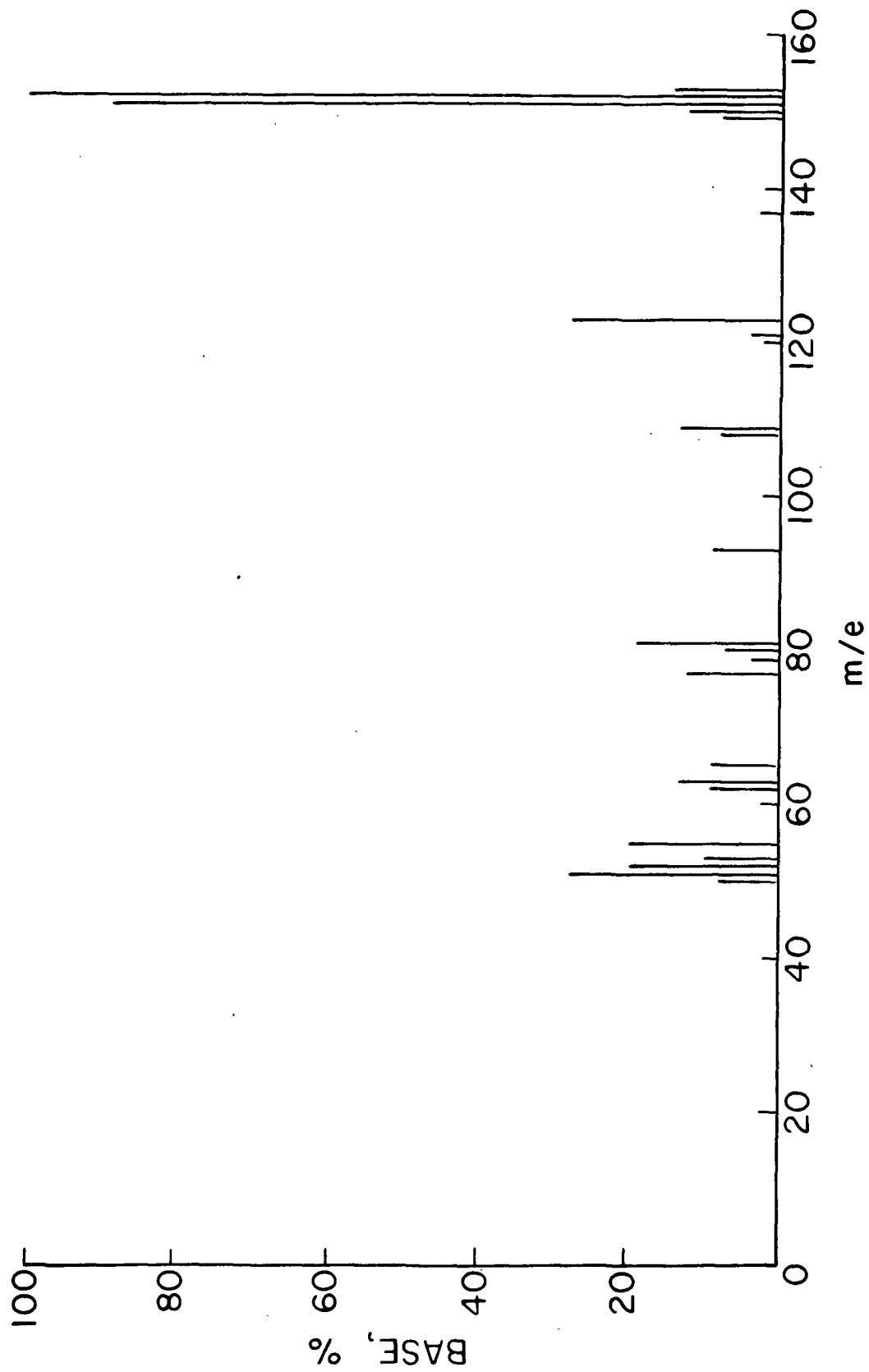


Figure 25. Mass Spectrum of Vanillin Known



Figure 26. Probable Initial Disintegration Pattern of Vanillin

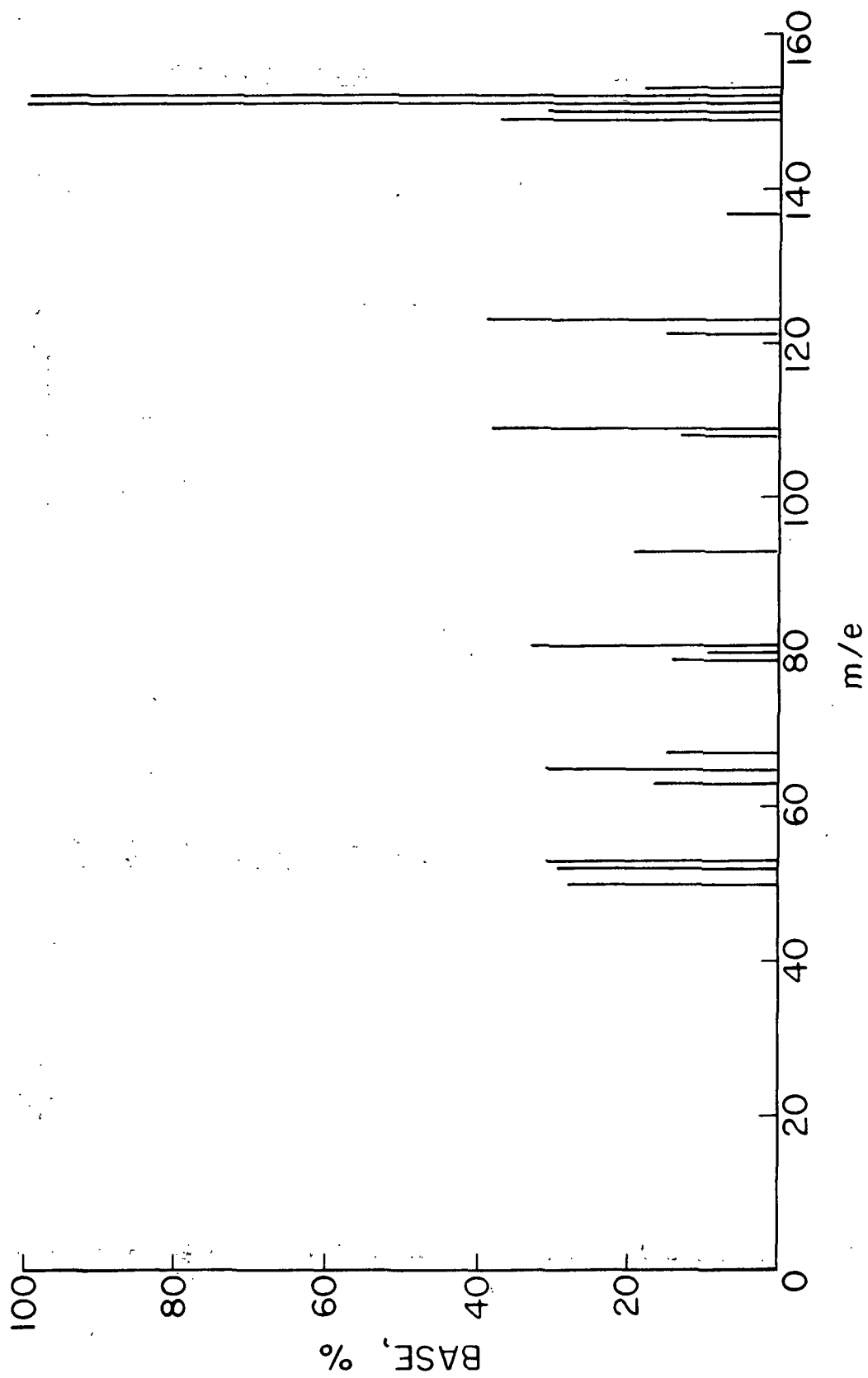


Figure 27. Mass Spectrum of Unknown GW-3

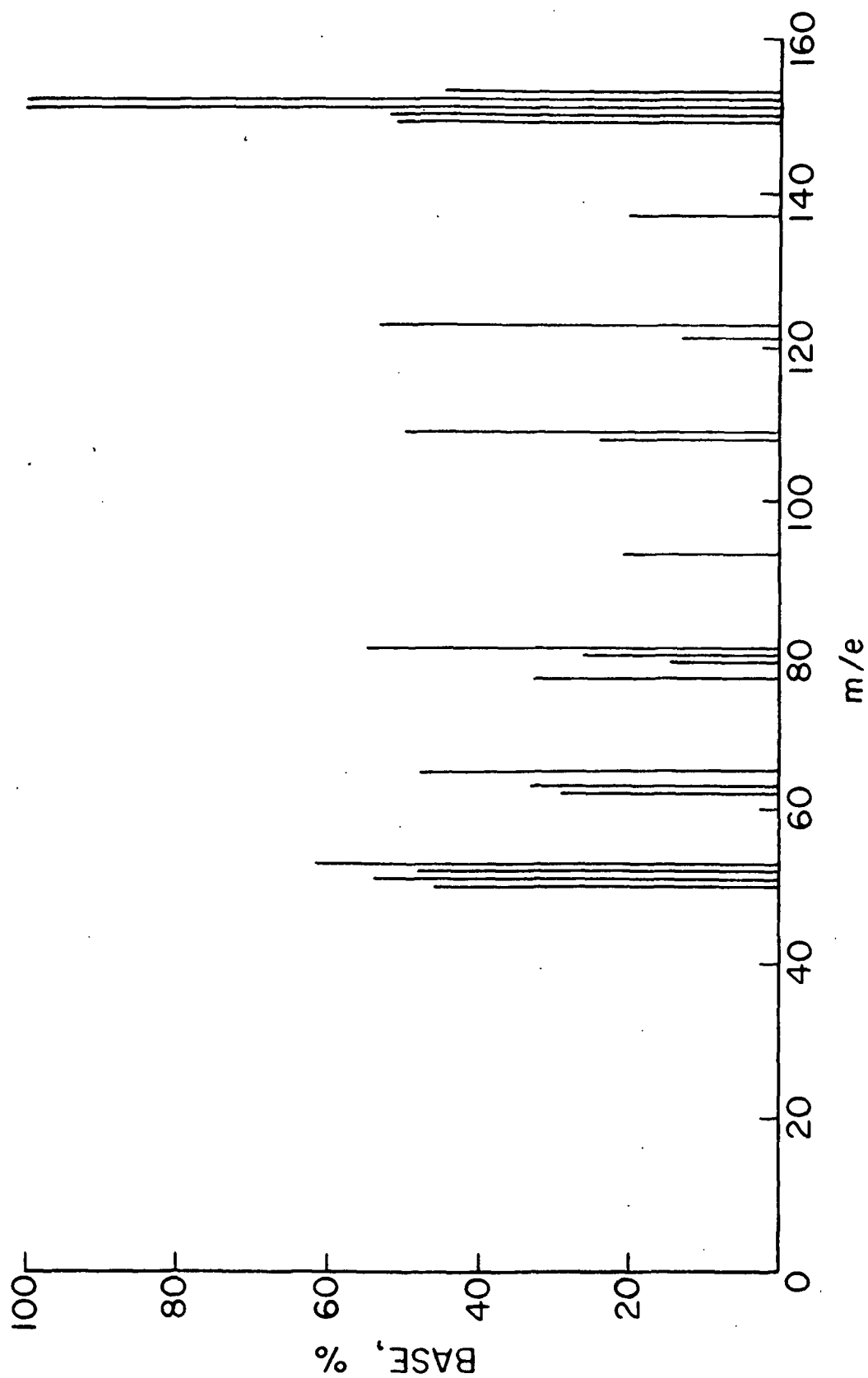
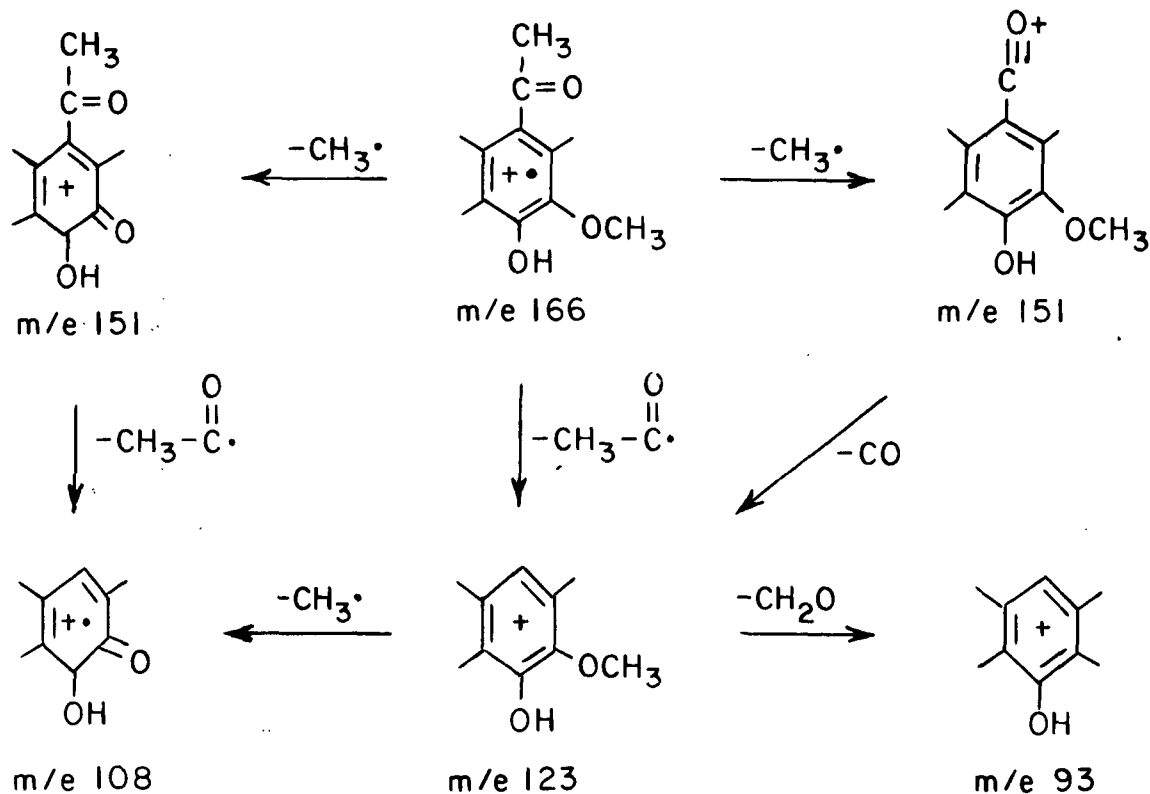


Figure 28. Mass Spectrum of Unknown CD-3

PEAKS GW-4 AND CD-4

The mass spectrum (Fig. 29) of acetovanillone shows a strong parent ion at $m/e = 166$, a very strong base peak at $m/e = 151$, and prominent ion fragments at $m/e = 123$, 108 , and 93 . These peaks can be explained by an initial disintegration pattern such as the following:



In both unknowns, GW-4 and CD-4 (Fig. 30 and 31), there is a strong parent ion at $m/e = 166$, a base peak at $m/e = 151$, and prominent ion fragments at $m/e = 123$, 108 , and 93 . Thus, both unknowns are shown to contain substantial amounts of acetovanillone. The rest of the spectra show no strong anomalous peaks, indicating that only small amounts of impurities could be present.

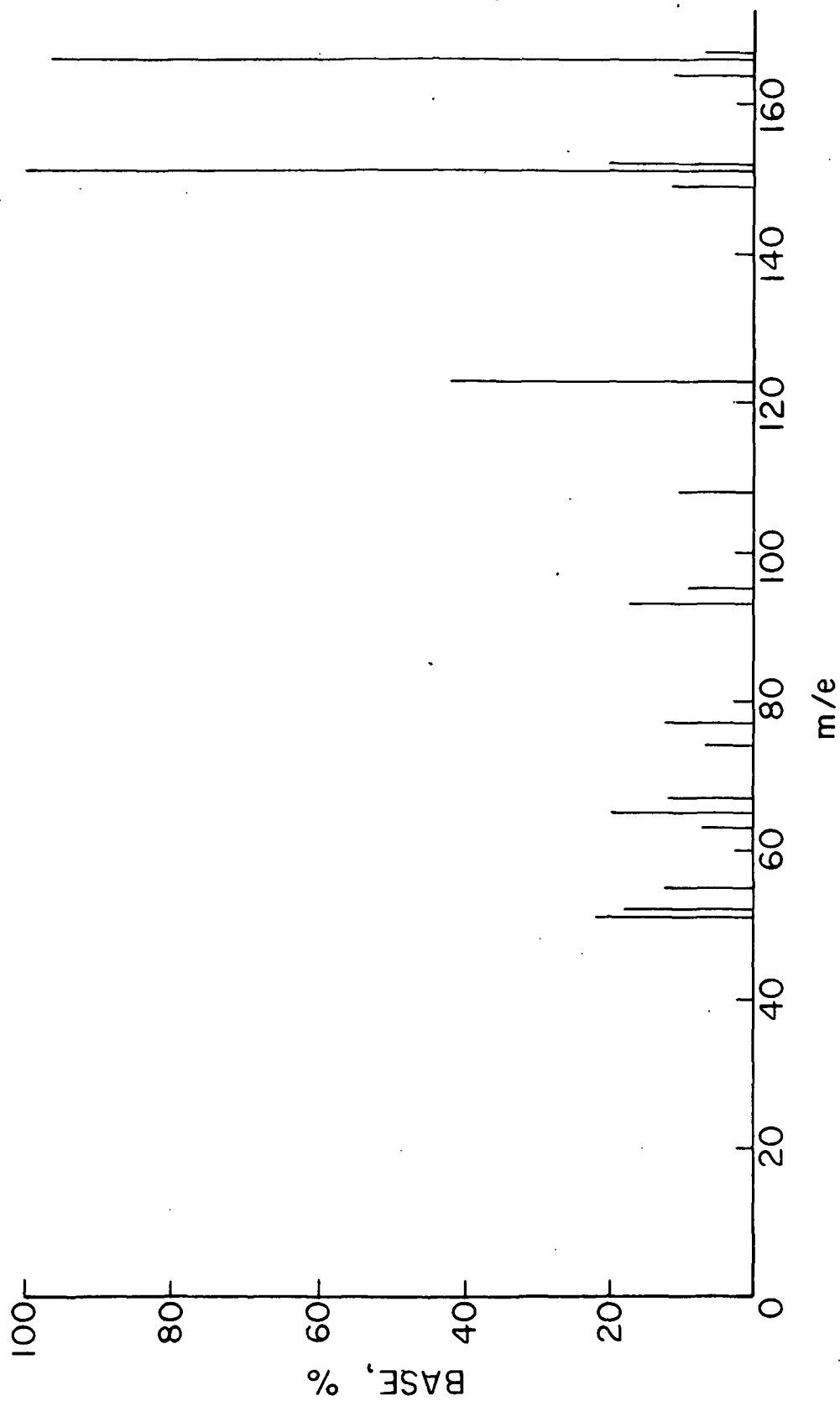


Figure 29. Mass Spectrum of Acetovanillone Known

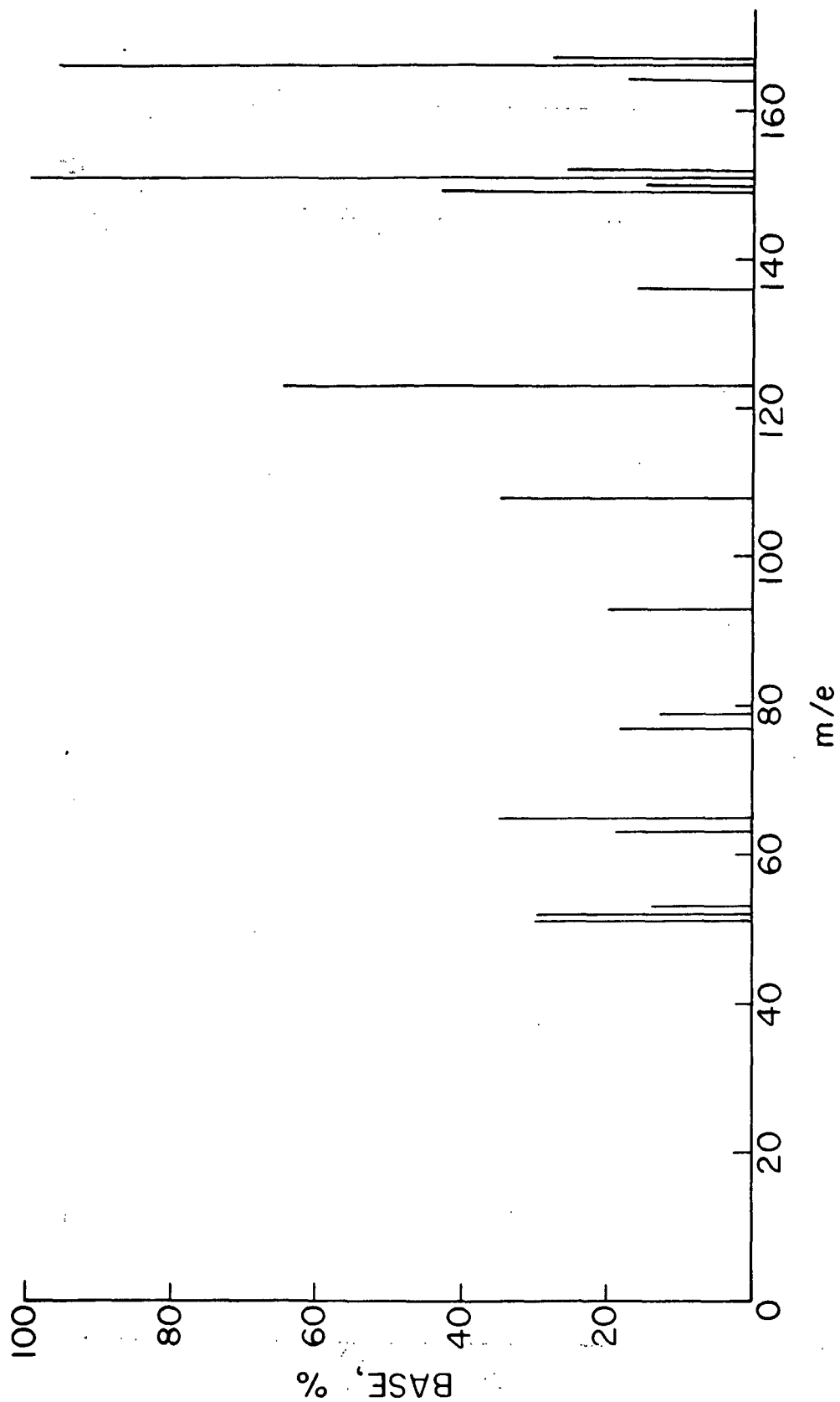


Figure 30. Mass Spectrum of Unknown GW-4

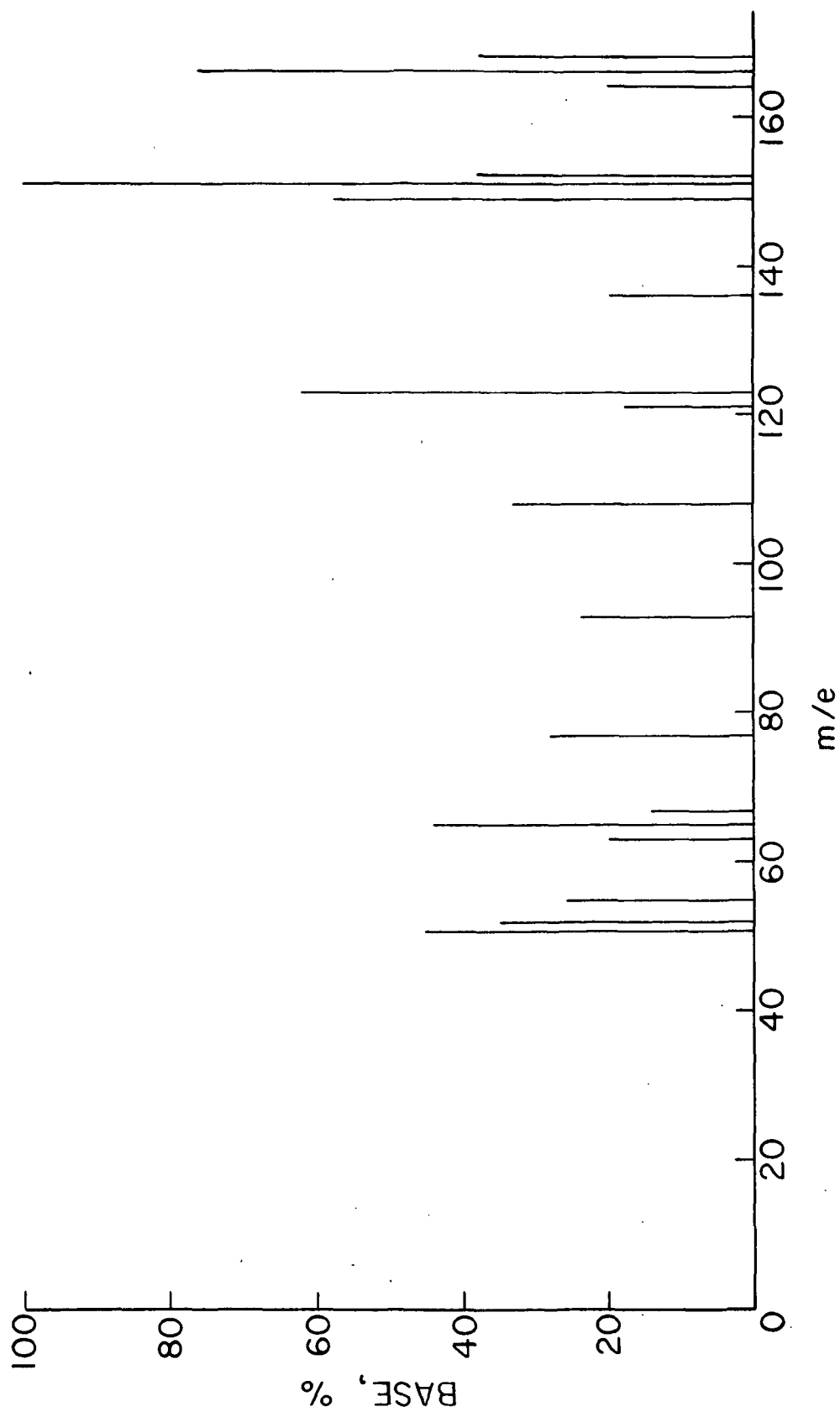
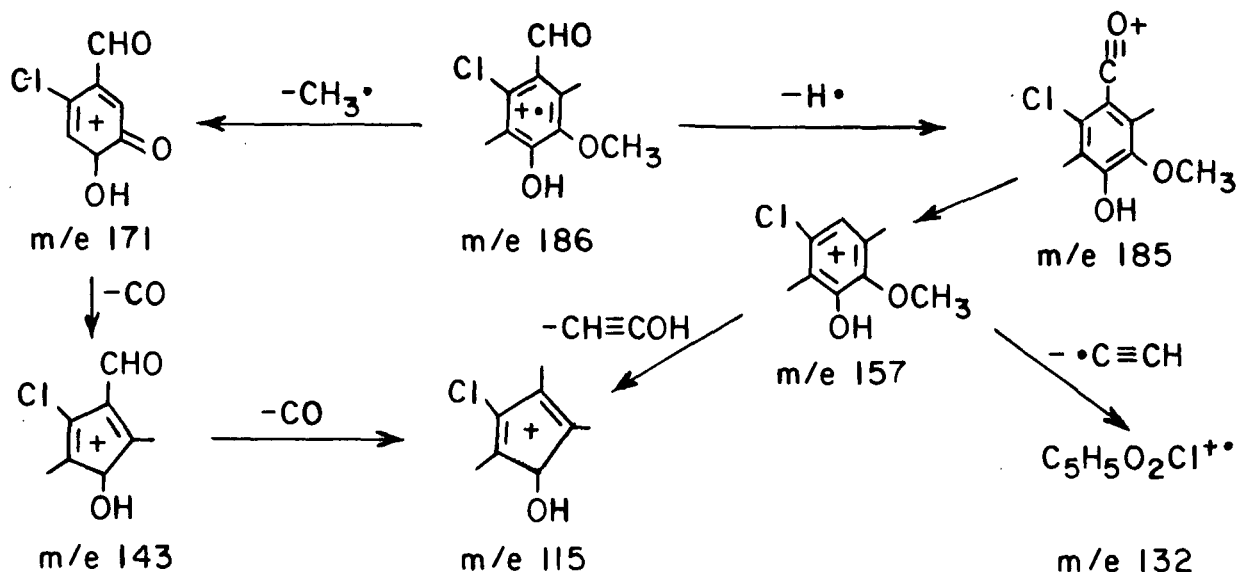


Figure 31. Mass Spectrum of Unknown CD-4

PEAK CD-5

The mass spectrum of the known 6-chlorovanillin (Fig. 32) shows a base peak corresponding to the parent ion at $m/e \approx 186$, a very strong peak at $m/e = 185$, and other prominent peaks at $m/e = 188, 187, 184, 171, 170, 157, 143, 142, 132$, and 115 . The following figure shows the probable disintegration pattern:



By subtracting 34 from the m/e values for the 6-chlorovanillin, most of the m/e values noted for vanillin are obtained, indicating that the chlorine remains attached while the rest of the molecule fragments such as vanillin does.

The most prominent ions in the spectrum of the unknown CD-5 (Fig. 33) are the parent ion at $m/e = 186$ and the base peak at $m/e = 185$. Also prominent are ion fragments at $m/e = 188, 187, 184, 183, 171, 170, 157, 151, 149, 144, 143, 142, 132, 123, 121, 117$, and 115 . The four relatively weak peaks at $151, 149, 123$, and 121 can be ascribed to a small amount of acetovanillone impurity. The rest of the peaks fit nicely with the disintegration pattern of the known 6-chlorovanillin, with the exception of the 117 peak which might be the result of the fragment at 132 losing a methyl group. Thus, it is evident that unknown CD-5 contains substantial amounts of 6-chlorovanillin.

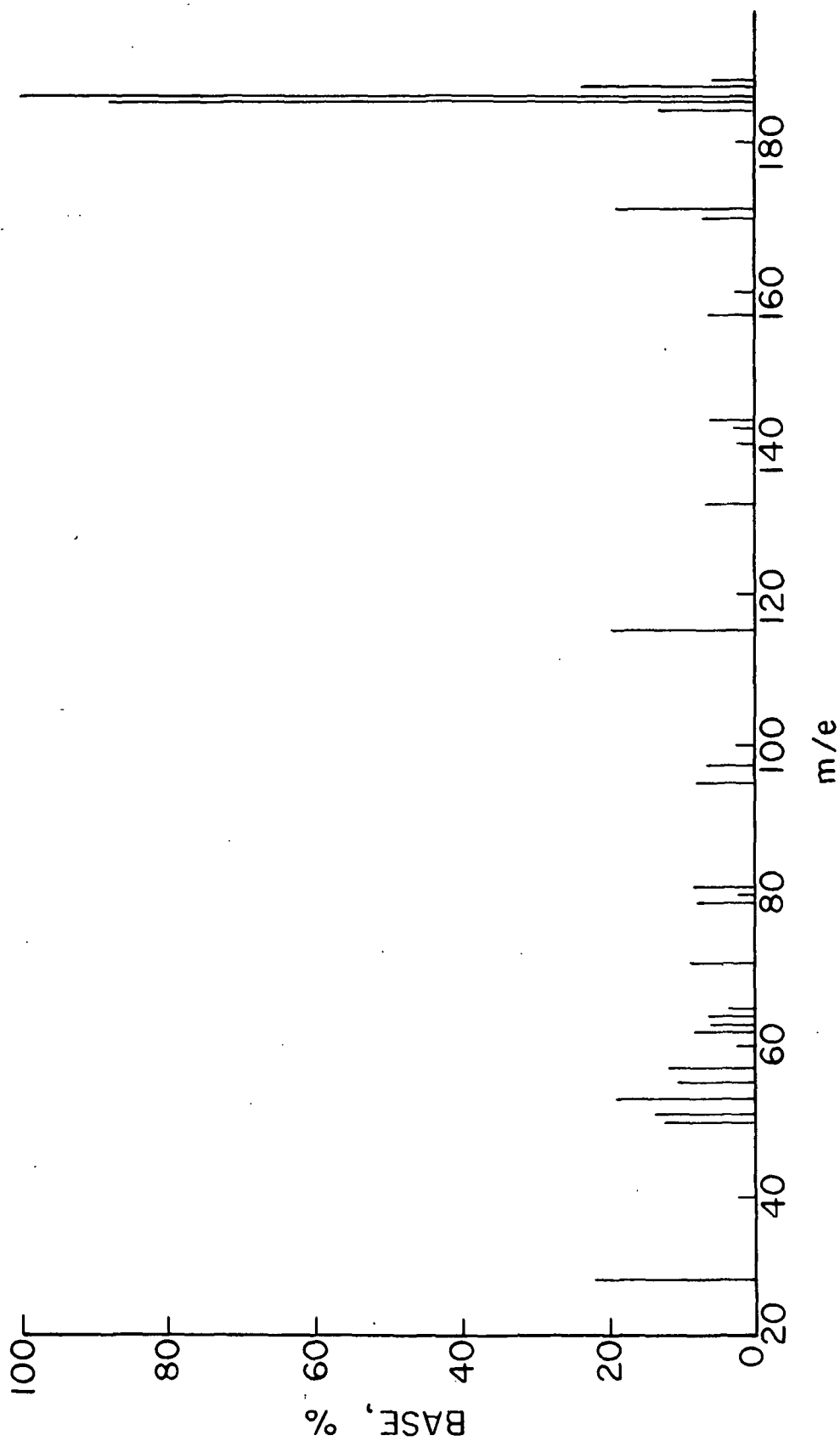


Figure 32. Mass Spectrum of 6-Chlorovanillin Known

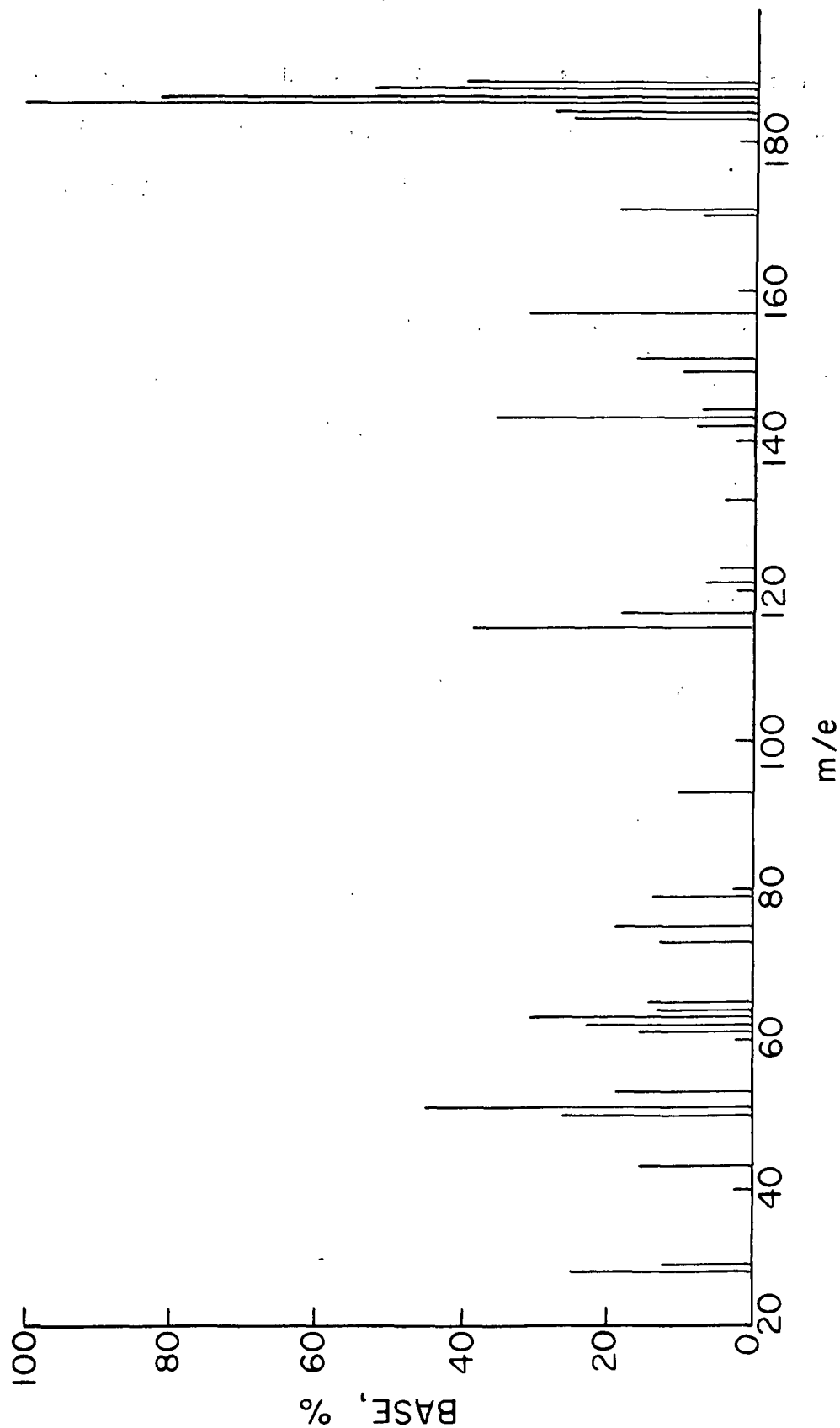


Figure 33. Mass Spectrum of Unknown JD-5

PEAKS GW-6 AND CD-6

The mass spectrum of vanillic acid (Fig. 34) shows a base peak corresponding to the parent ion at $m/e = 168$ and other prominent ions at $m/e = 153, 151, 125, 124, 123, 121, 109, 93, 83, 81,$ and 79 . The probable disintegration pattern is shown in Fig. 35.

The spectra of unknowns GW-6 and CD-6 (Fig. 36 and 37) show base peaks corresponding to the parent ion at $m/e = 168$ and other prominent ions at $m/e = 153, 151, 125, 124, 123, 121, 109, 97, 93, 83, 81,$ and 79 . Thus, these two unknowns are shown to contain substantial amounts of vanillic acid. The remainder of the spectra show some minor variations which may be due to small amounts of impurities.

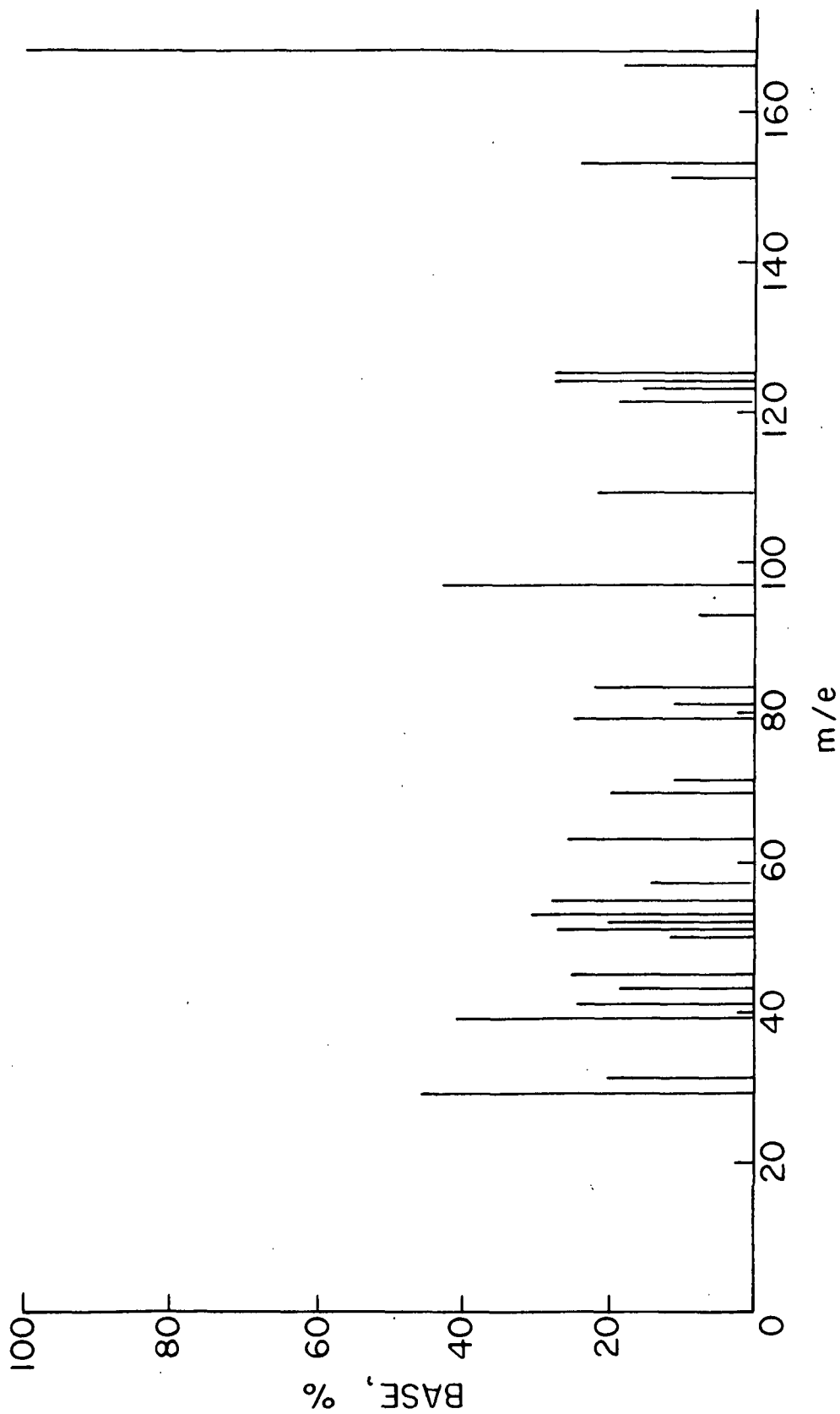


Figure 34. Mass Spectrum of Vanillic Acid Known

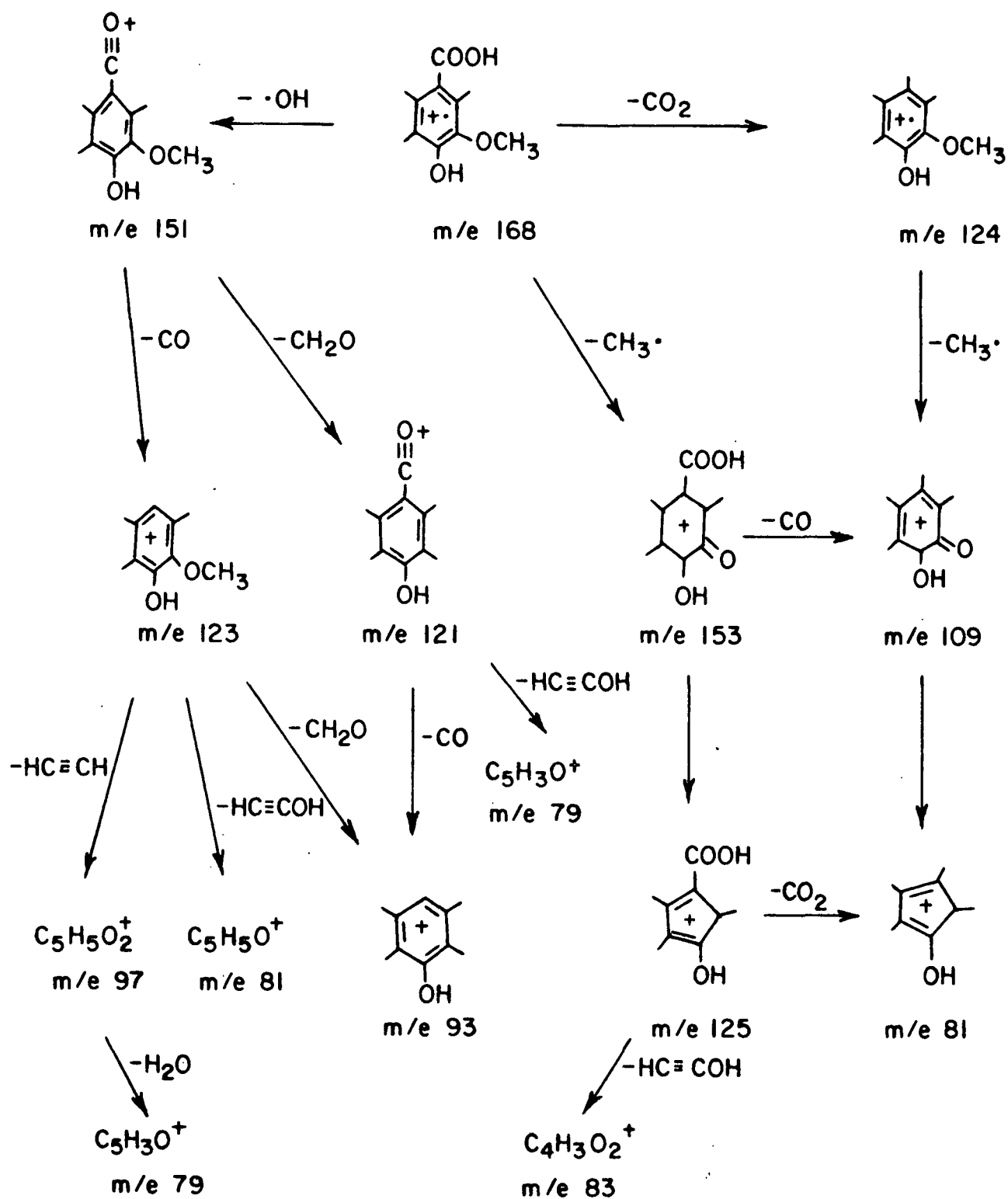


Figure 35. Probable Initial Disintegration Pattern of Vanillic Acid

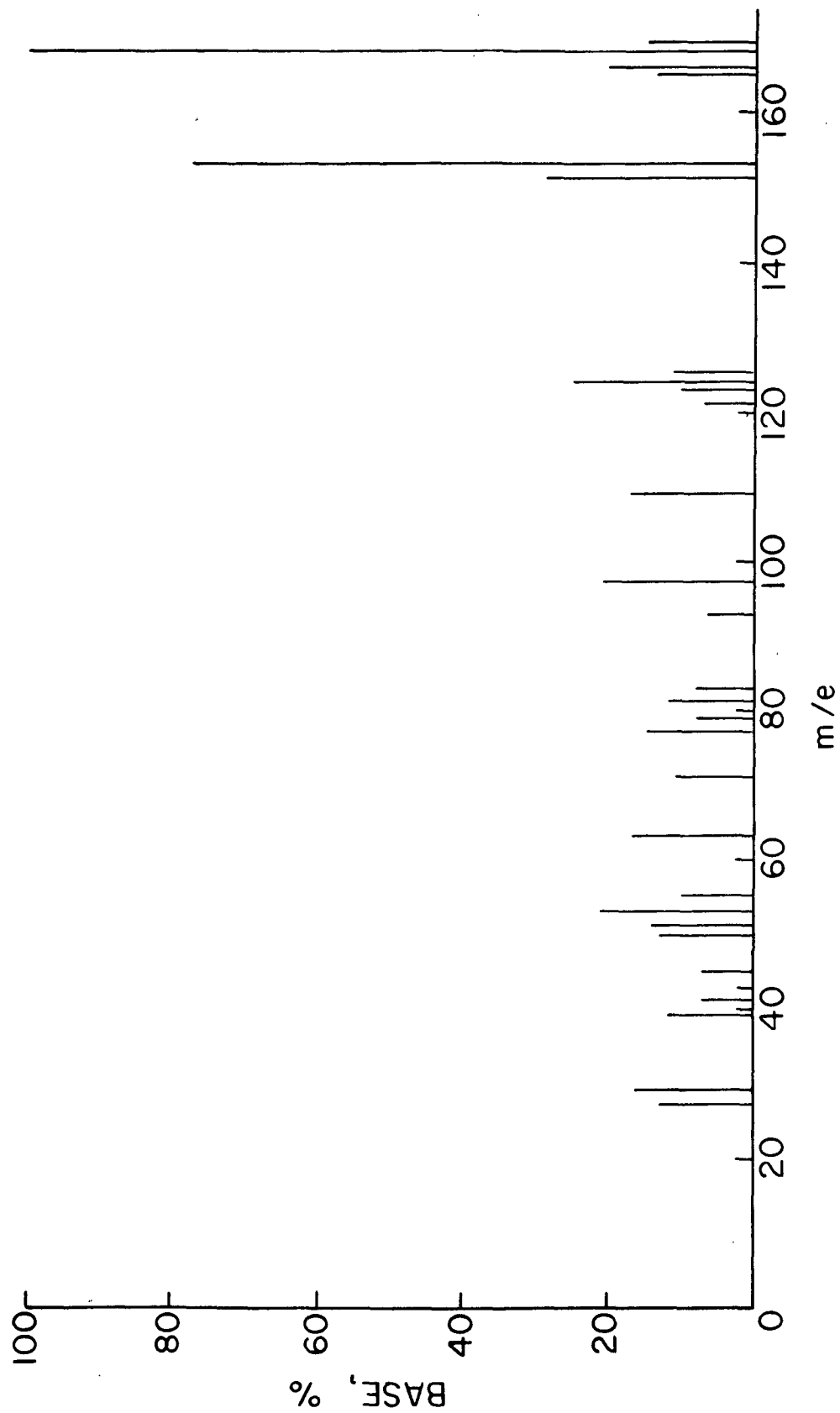


Figure 36. Mass Spectrum of Unknown GW-6

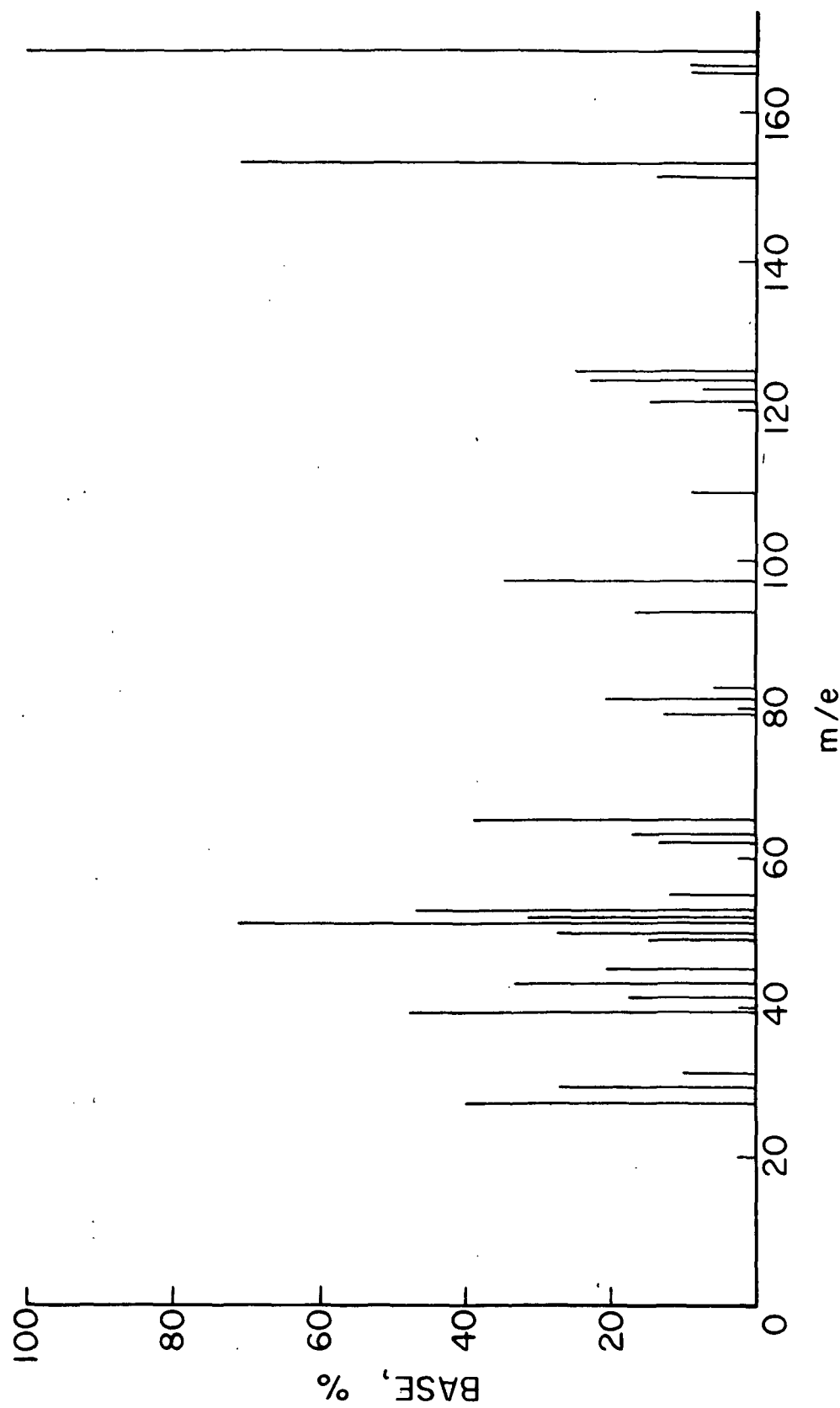


Figure 37. Mass Spectrum of Unknown CD-6

APPENDIX III

SPECIFIC ABSORPTION AND SCATTERING COEFFICIENTS
OF WHATMAN COMPACTS

The specific-scattering and -absorption coefficients of the sheets of Whatman paper were determined via measurement of reflectance, transmittance, and basis weight as indicated in the previous section. These values were then corrected for the effects of milling and compacting according to the following procedure.

1. The reflectance of the compact was measured and the ratio of the specific-absorption and -scattering coefficients was calculated as follows:

$$(k_{\underline{c}}/s_{\underline{c}}) = 1 - R_{\infty})^2 / 2R_{\infty}.$$

2. It was then assumed that $k_{\underline{c}}$ was equal to the specific-absorption coefficient of the Whatman sheets, $k_{\underline{o}}$, and the corresponding values of $s_{\underline{c}}$ were calculated (Fig. 38).
3. It was next assumed that the variation of $s_{\underline{c}}$ with wavelength was similar to that of the specific-scattering coefficients of the sheets, $s_{\underline{o}}$, and the values given by the two straight lines fitted through the data were taken as a better estimate of $s_{\underline{c}}$.
4. Using the $s_{\underline{c}}$ values given by the straight lines, new values of $k_{\underline{c}}$ were calculated.
5. These corrected values were used to calculate the specific-absorption coefficients of the lignin materials via computer programs BACS and VAND as explained on the following pages.

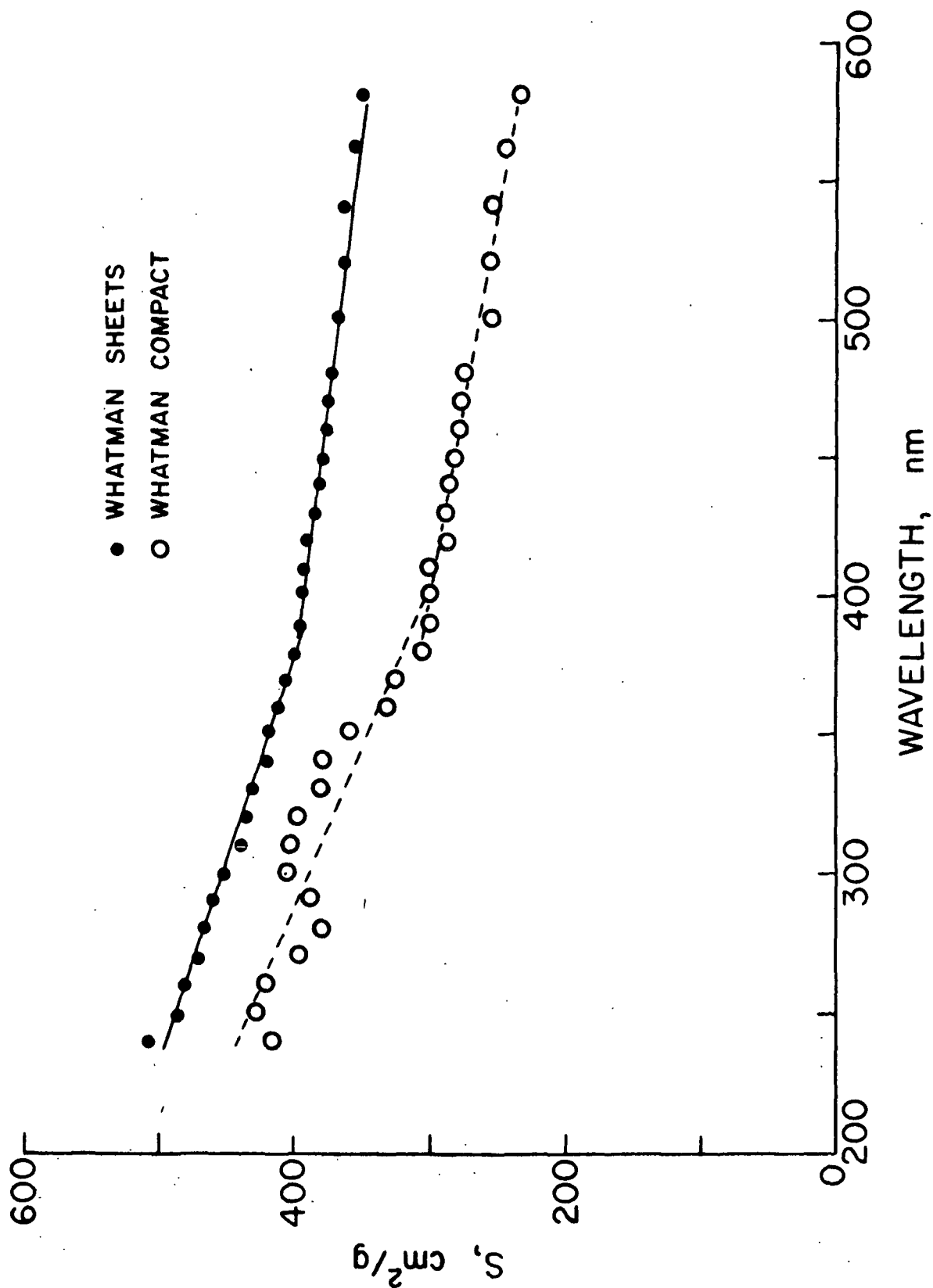
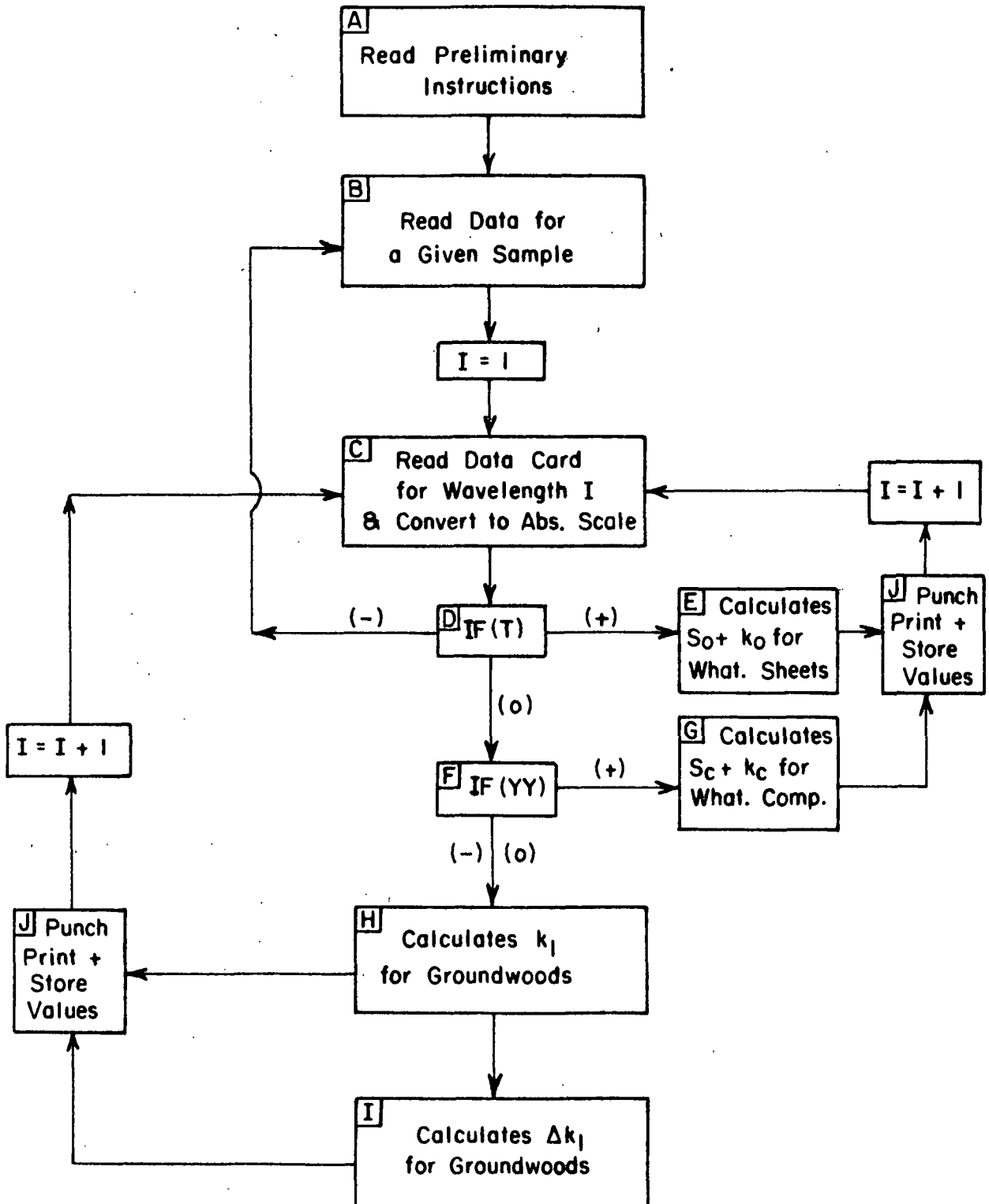


Figure 38. Scattering Coefficients of Whatman No. 40

KEY TO FLOW SHEETS OF PROGRAM BACS

- A. Read in of preliminary data which are common to all samples including Whatman sheets, Whatman compacts, and groundwood compacts.
- B. Read in data which are common to all wavelengths but particular to a given sample: concentration, sample identification, etc.
- C. Read in data particular to a given wavelength: reflectance, transmittance, etc. I index identifies wavelength; I=1, $\lambda=240$; I=2, $\lambda=240$; etc. Data are corrected to the absolute scale by correcting for the 100% line and the absolute reflectance of the MgO reference compacts.
- D. T value routes sample through proper circuit.
T(+) for Whatman sheets.
T(-) for the card following the read in of the final wavelength for a given sample. This tells the computer to return to B and begin to read in data for a new sample.
T(0) for all compacts.
- E. Uses the Kubelka-Munk relations to calculate the specific-absorption and -scattering coefficients for the Whatman sheets.
- F. YY differentiates between Whatman compacts and groundwood compacts.
YY(+) Whatman compacts.
YY(- or 0) groundwood compacts.
- G. Calculates the specific-absorption and -scattering coefficients of Whatman compacts on the basis of assumptions made concerning milling and compacting effects.

FLOW SHEET FOR PROGRAM BACS



COMPUTER PROGRAM BACS

```

C      THIS PROGRAM CALCULATES THE SCATTERING AND ABSORPTION
C      COEFFICIENTS DIRECTLY FROM THE KUBELKA-MUNK RELATION.
      DIMENSION IDESIG(3)
      DIMENSION XXK(31,35)
      DIMENSION SS(31,35)
      DIMENSION UK(31,35)
      DIMENSION DKL(31,35)
      DIMENSION XX(31)
      DOUBLE PRECISION ROO,T,W,ABSR,ABST,CONW,B,A,X,SW,XKW,S,XK
      IORDR=5
      IOPRT=6
      IOPCH=7
C      STORE WAVELENGTH VALUES FOR THE X COORDINATE.
      XX(1)=240.0
      I=1
50     I=I+1
      IF(I-31) 53,53,11
53     IF(I-26) 51,51,52
51     IF(I-13) 54,64,54
64     XX(I)=XX(I-1)
      GO TO 50
54     XX(I)=XX(I-1)+10.000
      GO TO 50
52     XX(I)=XX(I-1)+20.000
      GO TO 50
C      READ IN PRELIMINARY DATA FOR A GIVEN SAMPLE
11     WRITE(IOPRT,1)
      1 FORMAT(1H ,18X,2HSW,16X,2HKW,18X,1HS,18X,1HK,/,88H SPECIMEN
      USCATTERING POWER  ABSORBING POWER  SPEC. SCAT. COEFF.  SPEC.
      IABSP. COEFF.      ,T95,'UK(I,J)',T112,'DKL')
202    READ(IORDR,3) CONW,W,Q,CL,CO
      3 FORMAT(F6.4,4X,4(F8.6,4X))
      READ(IODR,40) J,Z,YY
40     FORMAT(16,4X,F6.4,4X,F6.4)
      W=W/CONW
      I=1
C      READ DATA FOR A GIVEN WAVELENGTH.
21     READ(IORDR,2) IDESIG,ABSR,ABST,T,ROO
      2 FORMAT(3A2,2(F6.4,4X),2(F6.2,4X))
C      CONVERT ROO AND T TO ABSOLUTE SCALE.
      ROO=0.01*ABSR*ROO/ABST
      T=0.01*ABSR*T/ABST
      IF(T) 202,4,5
4      IF(YY) 14,14,29
C      CORRECT VALUE OF WHATMAN 40 SCAT. COEFF. FOR COMPACTING
C      EFFECTS.
29     SK=(1.0-ROO)*(1.0-ROO)/(2.0*ROO)
      IF(Q) 27,26,28
26     IF(I=17) 24,24,23

```

```

24 SS(I,J)=-0.875*XX(I)+652.0
   GO TO 22
23 SS(I,J)=-0.3222*XX(I)+430.80
22 XXK(I,J)=SK*SS(I,J)
   GO TO 25
27 SS(I,J)=XXK(I,20)/SK
   XXK(I,J)=XXK(I,20)
   GO TO 25
28 XXK(I,J)=SK*SS(I,20)
   SS(I,J)=SS(I,20)
25 WRITE(IOPCH,120) IDESIG,SS(I,J),XXK(I,J),I,J
120 FORMAT(3A2,5X,F12.6,10X,F12.6,10X,I3,5X,I3)
   WRITE(IOPRT,121) IDESIG,SS(I,J),XXK(I,J)
121 FORMAT(1H ,3A2,41X,F14.6,6X,F14.6)
   I=I+1
   GO TO 21
C   CALCULATE SW=F(T,ROO).
5   B=0.5*(1.0/ROO-ROO)
   A=0.5*(1.0/ROO+ROO)
8   X=B/T
   SW=1.0B*(ALOG(X+SQR T(**2+1.0))-ALOG(B+SQR T(B**2+1.0)))
9   XKW=A*SW-SW
   IF(W) 99,10,12
10  WRITE(IOPRT,110) IDESIG,SW,XKW
110 FORMAT(1H ,3A2,2(5X,F14.6))
   GO TO 21
12  S=SW/W
   XK=XKW/W
   XXK(I,J)=XK
   SS(I,J)=S
   WRITE(IOPCH,13) IDESIG,SS(I,J),XXK(I,J),I,J
13  FORMAT(3A2,5X,F12.6,10X,F12.6,10X,I3,5X,I3)
   WRITE(IOPRT,133) IDESIG,SW,XKW,SS(I,J),XXK(I,J)
133 FORMAT(1H ,3A2,4(5X,F14.6))
   I=I+1
   GO TO 21
C   CALCULATE SPECIFIC ABSORPTION COEFFICIENT OF LIGNIN.
14  SK=(1.0-ROO)*(1.0-ROO)/(2.0*ROO)
   XXKL=((SK*SS(I,30))-(XXK(I,30)*CO))/CL
17  UK(I,J)=XXKL
C   DETERMINATION OF THE ABSORPTION CHANGE DUE TO REACTION.
   DKL(I,J)=UK(I,J)-UK(I,1)
   WRITE(IOPCH,35) IDESIG,UK(I,J),I,J
35  FORMAT(3A2,10X,F12.6,10X,I3,10X,I3)
   WRITE(IOPRT,135) IDESIG,UK(I,J),DKL(I,J)
135 FORMAT(1H0,3A2,T91,F12.6,4X,F8.2)
   I=I+1
   GO TO 21
END

```

COMPUTER PROGRAM VAND

```

C   THIS PROGRAM PLOTS THE SPECIFIC ABSORPTION COEFFICIENTS
C   OF LIGNIN IN GROUNDWOOD AND ABSORPTION DIFFERENCES BE-
    TWEEN DIFFERENT GROUNDWOOD SAMPLES.
    DIMENSION IDESIG(3)
    DIMENSION Y(31)
    DIMENSION YA(31)
    DIMENSION YB(31)
    DIMENSION YC(31)
    DIMENSION YD(31)
    DIMENSION YE(31)
    DIMENSION YF(31)
    DIMENSION YG(31)
    DIMENSION YH(31)
    DIMENSION XX(31)
    DIMENSION UK(31,35)
    IORDR=5
    IOPRT=6
    IOPCH=7
    DO 100 I=1,31
101  FORMAT(F5,1)
100  READ(IORDR,101) XX(I)
    J=1
    1 READ(IORDR,110) Z
110  FORMAT(F4.1)
    DO 120 I=1,31
    READ(IORDR,121) IDESIG,UK(I,J)
120  WRITE(IOPRT,123) IDESIG,UK(I,J),J
123  FORMAT(1H ,3A2,5X,F12.6,5X,I3)
121  FORMAT(3A2,10X,F12.6)
    WRITE(IOPRT,130) IDESIG,J
130  FORMAT(1H ,3A2,10X,I2)
    IF(Z) 2,3,3
    3 J=J+1
    GO TO 1
    2 READ(IORDR,140) JJ,KK,LL,YMIN,YMAX,YPMIN,YPMAX,Q
140  FORMAT(3(I3,4X),4(F8.2,4X),F4.1)
    READ(IORDR,141) YQMIN,YQMAX,YZMIN,YZMAX
    READ(IORDR,141) YSMIN,YSMAX,YTMIN,YTMAX
141  FORMAT(4(F8.2,5X))
    DO 4 I=I+1
    Y(I)=UK(I,JJ)
    YA(I)=UK(I,KK)
    YB(I)=UK(I,LL)
    YC(I)=YA(I)-Y(I)
    YD(I)=YB(I)-Y(I)
    YE(I)=YB(I)-YA(I)
YF(I) YF(I)=YC(I)/Y(I)
    YG(I)=YD(I)/Y(I)
    4 YH(I)=YE(I)/YA(I)
    M=0

```



```
CALL PLOT(XX,Y,17,220.,420.,YMIN,YMAX,0,M)
CALL PLOT(XX,YA,17,220.,420.,YMIN,YMAX,0,M)
CALL PLOT(XX,YB,17,220.,420.,YMIN,YMAX,1,M)
WRITE(IOPRT,150) JJ,KK,LL
150 FORMAT(3(12,21))
M=0
CALL PLOT(XX(18),Y(18),14,390.,590.,YPMIN,YPMAX,0,M)
CALL PLOT(XX(18),YA(18),14,390.,590.,YPMIN,YPMAX,0,M)
CALL PLOT(XX(18),YB(18),14,390.,590.,YPMIN,YPMAX,1,M)
WRITE(IOPRT,150) JJ,KK,LL
M=0
CALL PLOT(XX,YC,17,220.,420.,YQMIN,YQMAX,0,M)
CALL PLOT(XX,YD,17,220.,420.,YQMIN,YQMAX,0,M)
CALL PLOT(XX,YE,17,220.,420.,YQMIN,YQMAX,1,M)
WRITE(IOPRT,150) JJ,KK,LL
M=0
CALL PLOT(XX(18),YC(18),14,390.,590.,YZMIN,YZMAX,0,M)
CALL PLOT(XX(18),YD(18),14,390.,590.,YZMIN,YZMAX,0,M)
CALL PLOT(XX(18),YE(18),14,390.,590.,YZMIN,YZMAX,1,M)
WRITE(IOPRT,150) JJ,KK,LL
M=0
CALL PLOT(XX,YF,17,220.,420.,YSMIN,YSMAX,0,M)
CALL PLOT(XX,YG,17,220.,420.,YSMIN,YSMAX,0,M)
CALL PLOT(XX,YH,17,220.,420.,YSMIN,YSMAX,1,M)
WRITE(IOPRT,150) JJ,KK,LL
M=0
CALL PLOT(XX(18),YF(18),14,390.,590.,YTMIN,YTMAX,0,M)
CALL PLOT(XX(18),YG(18),14,390.,590.,YTMIN,YTMAX,0,M)
CALL PLOT(XX(18),YH(18),14,390.,590.,YTMIN,YTMAX,1,M)
WRITE(IOPRT,150) JJ,KK,LL
IF(Q) 5,2,2
5 CALL EXIT
END
```

APPENDIX IV

EXACT COMPOSITION OF COMPACTS USED FOR
REFLECTANCE MEASUREMENTS

TABLE XVII

COMPOSITION OF COMPACTS FOR REFLECTANCE MEASUREMENTS

Groundwood Sample	Electron Equiv. Uran.(III)	Electron Equiv. Dithionite	Ovendry Wood, g	Ovendry What. 40, g
Unreacted (G1)	0	0	0.0689	1.4557
Unreacted (G2)	0	0	0.0696	1.4695
Unreacted (GD1)	0	6	0.0694	1.4714
Unreacted (GD2)	0	6	0.0691	1.4608
Unreacted (GU1)	6	0	0.0696	1.4716
Unreacted (GU2)	6	0	0.0685	1.4473
2% ClO ₂ (21)	0	0	0.0715	1.4718
2% ClO ₂ (22)	0	0	0.0722	1.4855
2% ClO ₂ (2D1)	0	6	0.0710	1.4613
2% ClO ₂ (2D2)	0	6	0.0718	1.4779
2% ClO ₂ (2U1)	6	0	0.0714	1.4693
2% ClO ₂ (2U2)	6	0	0.0706	1.4526
6% ClO ₂ (61)	0	0	0.0728	1.4505
6% ClO ₂ (62)	0	0	0.0720	1.4353
6% ClO ₂ (6D1)	0	6	0.0740	1.4750
6% ClO ₂ (6D2)	0	6	0.0736	1.4656
6% ClO ₂ (6U1)	6	0	0.0734	1.4618
6% ClO ₂ (6U2)	6	0	0.0732	1.4573