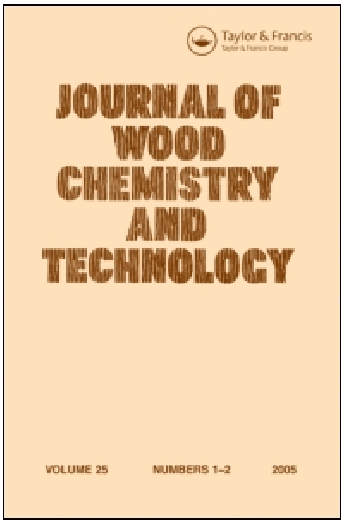
This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



# Journal of Wood Chemistry and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

# The Formation of Oxalic Acid During Bleaching of Kraft Pulp

J. A. Krasowski[a]; J. Marton[a]
[a] Laurel Research Center, Westvaco Corporation, Laurel, MD

**To cite this Article** Krasowski, J. A. and Marton, J.(1983) 'The Formation of Oxalic Acid During Bleaching of Kraft Pulp', Journal of Wood Chemistry and Technology, 3: 4, 445 — 458
**To link to this Article: DOI:** 10.1080/02773818308085175
**URL:** http://dx.doi.org/10.1080/02773818308085175

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 3(4), 445-458 (1983)

# THE FORMATION OF OXALIC ACID DURING BLEACHING OF KRAFT PULP

J. A. Krasowski and J. Marton
Laurel Research Center
Westvaco Corporation
Johns Hopkins Rd.
Laurel, MD 20707

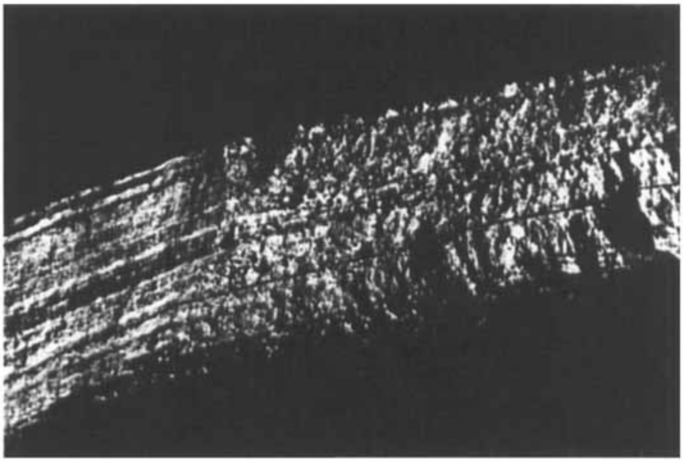
## ABSTRACT

Calcium oxalate scaling is a major practical problem in a paper mill, especially in the evaporators, pulp digesters, and the bleach room. The sources of oxalic acid were determined by analysis of mill samples. In the unbleached pulp mill, the source of oxalic acid is the wood. In addition, a major amount of oxalic acid was found to be formed in the bleach room. A laboratory bleaching study was undertaken to establish a quantitative relationship betweeen bleaching conditions and oxalic acid production. Hardwood kraft pulp was bleached using three sequences. The amount of oxalic acid produced was dependent upon the available lignin content of the pulp (Kappa number) and not the oxidant concentration or reaction temperature.

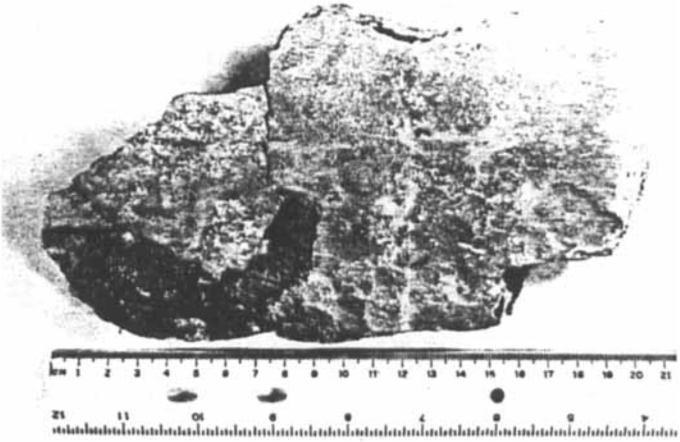
## INTRODUCTION

Calcium oxalate is known to be a major component of the incrustations and scale found in pulp mills, especially when high levels of calcium are present in the mill waters. This material tends to form very hard, porcelain-like deposits that can clog stock lines and washer screens if not removed periodically (Figure 1). Calcium oxalate scale has been found at various mill locations, including refiner plates, pipe lines, evaporators and heat exchangers[1]. Another problem caused by oxalic acid is an inter-

0277-3813/83/0304-0445$3.50/0



SIDE VIEW (2X)



TOP VIEW

FIGURE I

SAMPLE OF CALCIUM OXALATE HARD SCALE
TAKEN FROM A PAPER MILL STOCK PIPE

ference in rosin sizing. Cobb and Lowe[2] found that an aluminum oxalate complex forms and depletes the available aluminum so that the aluminum rosinate complex is not formed. The magnitude of the interference is dependent upon the concentration of the oxalate ion in the white water[3].

Oxalic acid is naturally occurring in both plants and animals as an end-product of metabolism. An interestingly analogous medical problem is that calcium oxalate is a main constituent of urinary calculi (kidney stones). The precipitate forms in neutral or alkaline urine in the presence of abnormally high oxalate excretion.

Trees like many other plants contain oxalic acid. In a study by Samuelson and others[4], analysis of kraft black liquor has shown that oxalic acid is dissolved during pulping. It was suggested that the oxalic acid dissolved during kraft cook was formed from the degradation of the carbohydrates, as it is well known that treatment of carbohydrates with hot alkali produces oxalic acid.

The composition of the material dissolved during bleaching of pine kraft pulp has been determined by Pfister and Sjostrom[5]. Oxalic acid was found to be one of the minor components in bleaching liquors. The reactions in the degradation of lignin during the chlorination stage have been studied using model compounds, pine kraft lignin and pine kraft pulp[6-8]. Extensive oxidation of the lignin was indicated by the large amount of oxalic acid found in the spent liquors. Above studies suggest that there are several possible sources of oxalic acid in the pulp mill: the pulping furnish, and oxidative degradation of carbohydrates and lignin during pulping and bleaching.

## Scope of Present Studies

During preliminary investigations, an analysis of mill samples has indicated that there are considerable amounts of oxalic acid in the pulps and filtrates obtained at each bleaching stage. An analysis of bark samples has indicated that there is one to two orders of magnitude more oxalic acid in bark than in wood. With the increased use of whole tree chips, a suspicion arose that a principal cause for oxalate deposits may be due to the increased level of oxalic acid entering with the bark in the pulping furnish. Further analysis of bleach room samples showed that there is an increase in the amount of oxalic acid found as the bleaching sequence proceeds. It was not clear as to whether the oxalic acid was being formed during the final bleaching stage (possibly due to oxidation of the carbohydrate and lignin material) or whether this increase was due to an accumulation of oxalic acid in the system caused by recycling of the mill waters.

In order to answer the above questions, a laboratory study was conducted with the purpose of establishing a quantitative relationship between bleaching conditions and oxalic acid production and of determining whether a degradation of the cellulose or the lignin is a major source. Hardwood kraft pulp was bleached (Figure 2) using three sequences: (a) chlorination, extraction, calcium hypochlorite, and chlorine dioxide ($CEH_{Ca}D$); (b) chlorination, extraction, sodium hypochlorite, and chlorine dioxide ($CEH_{Na}D$); and (c) chlorination, extraction, chlorine dioxide, extraction, and chlorine dioxide (CEDED). The levels of the bleaching chemicals were varied to simulate high, low, and medium mill conditions. The laboratory data were compared with mill observations in order to reach generally applicable conclusions.

## RESULTS AND DISCUSSION

### Oxalic Acid in Mill Samples

The results obtained for bark chips and bark-free wood chips are shown in Table 1. The amount of oxalic acid found in the bark was one to two orders of magnitude higher than that found in the wood. Assuming that whole tree chips contain about 15% bark and that a mixture of whole tree chips and debarked wood chips is used for the pulp furnish, the amount of oxalic acid in the furnish should be about 0.6 - 1.0 kg/metric ton (at a pulp yield of 45%).

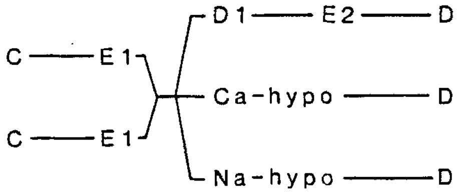


FIGURE 2

OUTLINE OF BLEACHING SEQUENCE

## TABLE 1

Oxalic Acid and Calcium Content of Bark and Wood Chips

| | Oxalic Acid<br>kg/metric ton | | Calcium<br>kg/metric ton | |
|---|---|---|---|---|
| | Bark | Wood | Bark | Wood |
| Hardwood | 9-15 | 0.1-0.3 | 4-5 | 0.3-0.6 |
| Pine | 4-10 | 0.1-0.4 | 1-5 | 0.3-0.5 |

## TABLE 2

Oxalic Acid Content of Mill Samples

| Hardwood Pulp | Oxalic Acid (kg/metric ton) |
|---|---|
| Brown Stock | 0.1-0.6 |
| Chlorination | 0.1-0.9 |
| Extraction | 0.1-0.8 |
| Hypochlorite, Ca $(OCl)_2$ | 0.4-1.2 |
| Dioxide | 0.4-1.5 |
| Paper Mill Decker | 0.3-1.0 |

The results obtained for oxalic acid determinations on mill samples are shown in Table 2. The amount that was found in the brown stock pulp (0.1 - 0.6 kg/ton) indicates that 40-80% of the oxalic acid that was calculated to be in the wood furnish was removed during the kraft pulping process. An apparent increase in the oxalic acid content of the pulp with bleaching is indicated in Table 2. However, this increase could be due to either a formation of oxalic acid or an accumulation of oxalic acid in the system by recycling of mill waters. The processing conditions and interactions influencing the formation and deposition of calcium oxalate scale, and the effect of recycle of mill waters, are being reported in a separate paper[9].

## Formation of Oxalic Acid During Laboratory Bleaching

The data obtained in the laboratory bleaching study are averaged for each stage and presented in Table 3. A t-test on the C-stage data indicated that there is not a significant difference in the amount of oxalic acid produced as a function of % $Cl_2$ added over the range of 1.9 - 2.6% $Cl_2$. The variation in the results may be attributable to the nonuniformity of the heterogenous reaction between the chlorine and the pulp. This has also been suggested in the literature[6,7].

The amount of oxalic acid formed during the extraction stages ($E_1$ and $E_2$) was 0.2 kg/ton which can be considered a negligible amount because the experimental variation was found to be ± 0.1 kg/ton. The residual lignin content of the unbleached pulp was about 2.5% (Kappa No. 16) and was reduced to about 0.8% (Kappa No. 5) after the first caustic extraction; in other words, about 17 kg of lignin were removed per metric ton of pulp in the C-stage. Thus, the oxalic acid yield in chlorination was about 3% of the lignin removed, assuming that only lignin is oxidized.

The first $ClO_2$ stage produced 0.3 kg of oxalic acid/ton and the two hypochlorite stages, calcium and sodium, also produced 0.3 kg of oxalic acid/ton. The final oxidative stage did not produce a significant amount of oxalic acid. These values were obtained by calculating group averages. A linear regression analysis of the data within each of the second oxidative stages showed that the quantity of oxalic acid produced was not

## TABLE 3

Oxalic Acid Content at the Various Bleaching Stages
(kg/metric ton)

| Bleaching Stage | Pulp | Bleaching Filtrate | Total | Amount Formed |
|---|---|---|---|---|
| | | CEDED Sequence | | |
| Brown Stock | 0.40 | - | 0.40 | - |
| C | 0.24 | 0.68 | 0.92 | 0.52 |
| $E_1$ | 0.11 | 0.27 | 0.38 | 0.14 |
| $D_1$ | 0.10 | 0.30 | 0.40 | 0.29 |
| $E_2$ | 0.12 | 0.02 | 0.14 | 0.04 |
| $D_2$ | 0.08 | 0.03 | 0.11 | -0.01 |
| | | | | 0.98 |
| | | CEHD with $H_{Ca}$ Sequence | | |
| C | 0.24 | 0.68 | 0.92 | 0.52 |
| E | 0.11 | 0.27 | 0.38 | 0.14 |
| $H_{Ca}$ | 0.18 | 0.19 | 0.37 | 0.26 |
| D | 0.14 | 0.11 | 0.25 | 0.07 |
| | | | | 0.99 |
| | | CEHD with $H_{Na}$ Sequence | | |
| C | 0.24 | 0.68 | 0.92 | 0.52 |
| E | 0.11 | 0.27 | 0.38 | 0.14 |
| $H_{Na}$ | 0.26 | 0.11 | 0.37 | 0.26 |
| D | 0.09 | 0.06 | 0.15 | -0.11 |
| | | | | 0.81 |

Average values of all conditions pertinent to each stage dependent upon the amount of these three bleaching agents applied to the pulp. The calculated slopes of the lines were nearly zero. Instead of a concentration dependency, there appears to be a random fluctuation in the data; the standard deviation was found to be ± 0.2 kg/ton for the second oxidation stage. Bleaching of pulp is a complex combination of heterogeneous and homogeneous reactions that is dependent on how well the pulp is mixed. This may explain the scatter in the data and the independence of the formation of oxalic acid on the concentration of applied oxidant.

There are two possible sources for the formation of oxalic acid: the oxidative degradation of lignin and/or cellulose. It has been shown in the literature[6] that upwards of 50% of the chlorine applied to lignin is consumed in oxidative reactions. The yield of oxalic acid was 0.5 to 3% of the lignin that was removed by chlorinating unbleached pulps, and 9% when lignin was chlorinated. The formation of oxalic acid has been attributed to the oxidation of the aromatic moieties in lignin. The other two oxidizing agents used to bleach the pulp in this study, hypochlorite and chlorine dioxide, can also react to produce oxalic acid from lignin[10]. Oxidative degradation of the cellulose also may produce oxalic acid and this should be accompanied by a decrease in the average molecular weight of the cellulose[11].

In this study, oxalic acid was produced during the first two oxidative stages. The initial lignin content of the pulp was about 2.5% and was reduced to about 0.8% after the first caustic extraction. The amount of lignin present after the second oxidative stage, H or $D_1$, was reduced to practically zero. If an oxalic acid yield is calculated based on the amount of lignin removed, 3% was produced in the C, H and $D_1$ stages. The amount produced during the final $D_2$ stage was not significant.

During all of the stages, the concentration of oxidant (and temperature in the C-stage) was varied, but the amount of oxalic acid produced was not dependent on the changes within the stage. The yield as stated above can be better correlated with the available lignin content of the pulps. A reaction scheme that has been suggested in the literature[6,10,11] for the reaction of a chlorine containing agent with lignin shows that there is a competition between chlorination and oxidation reactions. A pathway involving a three-step process has been proposed[8] for the oxidation of lignin to produce oxalic acid (and other dicarboxylic acids). (Figure 3)

Oxidative degradation of the pulp can be measured by a decrease in pulp viscosity. It is well known that the viscosity of the pulp is very dependent on the concentration of applied bleaching agents. The oxalic acid production in this study was independent of the viscosity change, suggesting very low correlation between oxalic acid formation and the degradation of the cellulose. (Pulp viscosity was studied in a parallel investigation using the same pulp samples[12].) Therefore, it is believed that the primary source of oxalic acid is from the oxidation of lignin and that the oxidation of cellulose is a secondary source, at most.

## Distribution of Oxalic Acid Between Pulps and Filtrates

The oxalic acid content of the studied pulps was the highest at the brown stock (Table 3). Assuming that the bark content of the chips going into the digester is about 10%, the chips should contain about 1.3 kg of oxalic acid/ton of wood. The brown stock pulp contained about 30% of the oxalic acid that was probably in the chips.

The oxalic acid content in the filtrates was the greatest at the C-stage where 0.7 kg/ton were removed from the system (Table 3). It must be remembered that deionized water was being used for the wash water and that over 90% of the water was pulled off of the chlorination slurry by vacuum filtration before the wash water was added. In the bleach room, displacement-type washing may be used, and if the wash water contains a high level of Ca and a high pH, then a pH shock could cause the precipitation of calcium oxalate on the fibers and washer screens, thereby reducing the washing efficiency.

The amount of oxalic acid carried by the C filtrate, is 50-60% of the total amount of oxalic acid found from brown stock to final stage. It is important to remove this filtrate from the system as this results in the largest single decrease in oxalic acid. The amount of oxalic acid carried

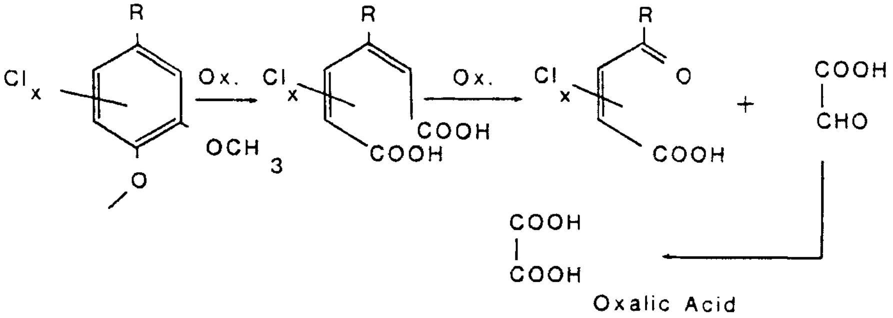


FIGURE 3

Formation of Oxalic Acid From Lignin

by each of the other filtrates is 20% or less of the total amount. All of the filtrates taken together removed about 90% of the total amount of oxalic acid found.

## CONCLUSIONS

The largest single source of oxalic acid is bark which contains 4 - 15 kg oxalic acid/metric ton, depending on the species. If the wood furnish contains 5-10% bark, the unbleached pulp could contain as much as 0.4 - 0.8 kg oxalic acid/ton of pulp from this source. However, as much as 70% of the oxalic acid that can be expected in the brown stock is removed during the pulping and brown stock washing. The oxalic acid content of the brown stock typically has been found to be 0.1 - 0.6 kg/ton.

A mass balance on the data obtained from the samples taken from the laboratory bleaching study has shown that oxalic acid is produced during bleaching; there are 0.8 - 1.0 kg of oxalic acid formed per ton of pulp. This additional amount, taken together with the amount found in the brown stock (0.4 kg/ton), increased the amount of oxalic acid found in the system to 1.2 -1.4 kg/ton which is a 3 - 4 fold increase in the amount of oxalic acid found in the system relative to the unbleached pulp used. The majority of the oxalic acid was formed in the C-stage (0.5 kg/ton), and the remainder was formed in the H- (or $D_1$) stage (0.3 kg/ton). Negligible amounts were formed in the E and $D_2$ stages. The final D-stage pulp contained only 0.1 kg oxalic acid/ton or about 7% of the total amount of oxalic acid in the system. The amount of oxalic acid in the final stage pulp may vary depending on the oxalic acid content of the brown stock and the washing efficiency at each of the stages. The total amount of oxalic acid produced was not found to be dependent on the bleaching sequence (CEDED or CEHD), because the majority was formed in the C-stage.

It is inferred that oxalic acid is produced by the oxidation of lignin and not cellulose. About 3% of the lignin was converted to oxalic acid in each of the first two oxidations. This is the same order of magnitude as reported by Van Buren and Dence[7] for chlorination studies. The amount of oxalic acid produced was dependent upon the available lignin content of the pulp and not the temperature or oxidant concentration. The last oxidative stage produced negligible amounts of oxalic acid as the lignin content of the pulp was reduced to practically zero.

Efficient washing can reduce the magnitude of the problems caused by oxalate. The filtrates in the laboratory study removed 85-90% of the total oxalic acid found (both entering and formed). The C-stage filtrates alone removed 50% of the total. The reuse of the filtrates must be done with care to avoid the accumulation of oxalic acid and its precipitation with calcium ions at the higher pH's.

The oxalate content in the last D filtrates was two times higher in the $H_{Ca}$ sequence than in the $H_{Na}$. The calcium oxalate crystals that are suspended in the waters of the bleach room and the paper mill and the calcium oxalate crystals that are formed from dissolved oxalic acid are the primary source of the oxalate scale problems. The calcium oxalate that is adsorbed on the fibers is a secondary source. High calcium concentrations in the waters caused by the use of calcium hypochlorite (and other sources of Ca such as hard water and incomplete sedimentation at calcification of green liquor) intensify the problem of scale formation.

High bark content in the furnish, inefficient washing, recycling of the wash waters and Ca-hypo bleaching are the factors most likely to cause putty and scaling in the bleachroom.

## EXPERIMENTAL

### Laboratory Bleaching of Pulp

Never-dried regular mill hardwood kraft pulp was used in this study. The three bleaching sequences CEDED, $CEH_{Ca}D$, and $CEH_{Na}D$, that were followed are briefly outlined in Figure 2. The brown stock pulp was divided into eight 500 gram (oven dry basis) portions, and treated with $Cl_2$ and caustic. The chlorinations were done in duplicate and then blended after the extraction so that there would be a sufficient quantity of pulp for sampling at each of the subsequent stages. The chlorinations were at two concentrations of applied $Cl_2$: at 1.92% $Cl_2$ and 2.56% $Cl_2$, two temperatures 25°C and at 45°C. All of the C-stage pulps were at 2% solids during bleaching. After bleaching the pulp slurry was filtered under vacuum and the pulp was washed with 6 liters of deionized water.

Each of the C-stage pulps was then treated with sodium hydroxide at a concentration of 65% of the $Cl_2$ concentration. All of the E-stages were at 73°C for 45 minutes, 10% solids, followed by a dilution to 4% solids and filtering, then washing with 6 liters of water. The pulps that were treated under identical condition were mixed together and divided into 9 portions,to make a total of 36. Three of these were treated with $ClO_2$, three with $Ca(ClO)_2$, and three with NaClO. The $D_1$-stage pulps were treated with NaOH followed by $ClO_2$. The H-stage pulps were treated with $ClO_2$ for the final stage. Samples were taken from each of the stages: pulps and filtrates.

The amount of applied oxidant (expressed as % $Cl_2$) in the third stage was varied from 0.52 to 3.55 for the sodium and calcium hypochlorites, and from 0.20 to 1.35% $ClO_2$. The amount of applied oxidant in the last stage was adjusted to obtain a brightness target of 90.

### Analysis of Pulp and Filtrates for Oxalic Acid

Both pulp and filtrate samples were made slightly alkaline using 1 N NaOH in order to prevent a sublimation loss of the free oxalic acid during drying. The pulps and filtrates were oven dried at 105°C. A 2 g portion of the o.d. pulp was treated with 50 ml of 10% $H_2SO_4$ in anhydrous ethanol (by volume). The residues from drying 50 ml portions of the filtrate samples were placed in 125 ml erlenmeyer flasks and agitated vigorously overnight (16-20 hours) on a mechanical shaker at ambient room temperature in order to form the diethyl ester of oxalic acid. The solvent was separated from the sample by either decanting or filtering, and the volume was measured to correct for the amount of alcohol that was wetting the pulp samples. An equal volume of water was added to the alcohol in a separatory funnel and the diethyl oxalate was extracted four times with chloroform (one 10 ml volume and three 5 ml volumes). The chloroform was dried over $MgSO_4$ and the volume was recorded. This extraction procedure is similar to a published method used for tobacco analysis where methyl esters of dicarboxylic acids were made[13].

The diethyl oxalate was quantitated via gas chromatography using a 0.1% SP-1000 on 80/100 Carbopack C, 6' x 1/8" S.S. column (Supelco, Inc., Bellefonte, PA) The gas chromatograph was a Model 5830A (Hewlett-Packard, Avondale, PA), which was temperature-programmed from 165°C to 180°C at 0.9°C/minute with a $N_2$ carrier flow of 30 cc/minute. All solvents and chemicals were reagent grade or better purity and used without further purification.

### Analysis of Bark Chips and Bark-Free Wood Chips

Samples were oven dried, ground in a small blender jar and treated as above for oxalic acid.

## ACKNOWLEDGMENT

The authors acknowledge the help and valuable advice of Mr. M. B. Ringley of Westvaco Charleston Research Center in planning of the bleaching experiments.

## REFERENCES

1. B. Hultman, C. Nilsson, and S. Sjoberg, Svensk Papperstidn, 84 (18), R 163 (1981).
2. R. M. K. Cobb and P. V. Lowe, TAPPI, 38, 49 (1955).

3. J. Marton and T. Marton, unpublished.
4. L. Lowendahl, G. Peterson and P. Samuelson, TAPPI, 59, 118 (1976).
5. K. Pfister and E. Sjostrom, Paperi Puu, 61 (4a), 220 (1979); 61 (4) 367 (1979).
6. J. Gierer and L. Sundholm, Svensk Paperstidn, 74, 345 (1971).
7. J. B. Van Buren and C. W. Dence, TAPPI, 53 (12), 2246 (1970).
8. J. M. Gess, and C. W. Dence, TAPPI, 54, 1114 (1971).
9. K. L. Wendell and J. Marton, (to be published).
10. H. M. Chang and A. A. Allan, Lignin, p. 463-469. K. V. Sarkanen and C. H. Ludwig (ed.), Wiley Interscience, N. Y., 1971.
11. L. E. Larson and H. deV. Partridge, Chapter 5 in The Bleaching of Pulp. R. P. Singh (ed.), 3rd Ed., TAPPI Press, Atlanta, 1979.
12. M. B. Ringley, (to be published).
13. W. A. Count and J. G. Hendel, J. Chromatogr. Sci., 16, 314 (1980).