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**CHARACTERIZATION OF PULP OZONOLYSIS PRODUCTS**

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## CHARACTERIZATION OF PULP OZONOLYSIS PRODUCTS

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### ABSTRACT

Efforts to reduce the level of chlorinated organics discharged into the environment have sparked interest in ozone bleaching. Pulp ozonation by-products are not as well characterized as the by-products from traditional bleaching practices. It is important to know the composition of ozonation effluents so that their potential toxicity and treatability can be assessed. Information about bleaching mechanisms may also be obtained.

Gas chromatography mass spectrometry was used to determine the identities of low molecular weight pulp ozonolysis products. Derivatization of carbonyl compounds selectively provided information about carbonyl by-products. The effects of different pre-treatments on ozonation by-products were examined.

The small compounds in extracts of ozonated pulp are primarily fatty acids, short-chain and long-chain aliphatic acids and diacids. Only small amounts of monomeric lignin products are formed or survive ozonation. Oxalic and glyoxylic acid (and/or their methyl esters) probably arise from aromatic ring fragmentation. Glyoxylic acid (and/or its methyl ester) is the most abundant aldehyde produced. Derivatization techniques indicate that glyoxal is another important aldehyde. Carbonyl compounds present in small quantities in extracts of ozonated pulp appear to have polar precursors.

### KEYWORDS

Ozonation effluents, pentafluorobenzyl oxime derivatives, ozone by-products, aliphatic acids

## INTRODUCTION

Because of increasing pressure to reduce or eliminate chlorinated organics in effluents and pulps, the paper industry is developing bleaching processes which do not utilize chlorine or chlorine dioxide. Ozonation and oxygen delignification are two such promising techniques. Although there is considerable information regarding by-products from chlorinating pulp (1,2), less is known about the by-products from oxygen-based bleaching. Knowing the components of effluents from these bleaching techniques can be invaluable in assessing the effluents' potential toxicity and evaluating treatment strategies. In addition, the composition of the effluents can help elucidate prevalent reaction pathways.

There are many ways to approach the task of effluent characterization. Functional groups (e.g., carboxyl content), physicochemical properties (e.g., Koc), broad physical and chemical characteristics (e.g., molecular weight distribution and aromaticity versus aliphaticity) can be examined. Specific small products can also be identified. Each approach provides important information about these complex mixtures.

Small compounds are of particular environmental interest because they have a higher potential for toxicity than higher molecular weight material, usually because they are more bioavailable (3). Aldehydes are potentially important because they are produced by reactions of ozone with sites of unsaturation and because some aldehydes are toxic (4).

The distribution of small, gas chromatographable products associated with ozonated pulp is the focus of the work reported here. Emphasis is placed on carbonyl compounds. Information about the fraction of the pulp that is the source of the by-products was sought. Extracts from several different pulps were analyzed by gas chromatography-mass spectrometry (GC/MS). These included extracts from an ozonated northwestern softwood kraft pulp that was pre washed with acid solution, prewashed with alkaline solution or pre-extracted with an organic solvent, and a southern softwood kraft pulp (with and without prior oxygen delignification).

## METHODS

Two unbleached, kraft pulps were examined: a northwestern softwood pulp with kappa number 27.9 and a southern softwood pulp with kappa number 27.6.

Approximately 10 o.d. g pulp samples (acidified to pH=2 with H<sub>2</sub>SO<sub>4</sub> solutions) were ozonated at high consistency (30-35% on o.d. pulp) in a rotoevaporator adapted for ozone application from a Welsbach Model T-28 ozonator. Ozone charges varied from 1.2% to 1.7%, except as otherwise noted. Oxygen delignification was conducted for 1 hour at 110°C, 10% consistency, 2% NaOH and 0.5% MgSO<sub>4</sub>.

Methylene chloride pre-extractions were based on TAPPI Method T204 om-88, except the pulp was not air-dried. Most of the ozonated pulps were Soxhlet extracted overnight in methanol. Water was azeotropically removed from the methanol extracts (to ensure solubilization of all compounds) by rotoevaporation of a ternary mixture of the methanol, the water and chloroform. In the initial analyses, the ozonated pulps were washed with pH = 2 H<sub>2</sub>SO<sub>4</sub> solution and the pulps and the filtrates were extracted with diethyl ether. The methanol and the extracts were concentrated by rotoevaporation.

Methanol and ether extracts were methylated by diazomethane generated by the Fales method (5). The methanol extracts were either derivatized directly or an ethereal solution of diazomethane was added to the methanol extract. It became apparent that methanol extraction in the presence of the acidic solution on the pulp caused methylation of the carboxylic acids, probably by way of an acid-catalyzed Fisher esterification.

Pentafluorobenzyl oxime derivatives were prepared by adding approximately 15 g of *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride to 1 mL of concentrated methanol extracts. After standing overnight at room temperature, the methanol solution was acidified with 2 mL of pH = 1.3 H<sub>2</sub>SO<sub>4</sub> solution and extracted with hexane. Derivatization of standards using these conditions indicates that methylation of acids occurs in this procedure as well.

The samples were analyzed with an HP 5890 II GC equipped with an HP 5971A MSD driven by a G1030A Chemstation. Electron impact (70 eV) spectra were obtained for masses 40 to 400 amu. Identifications

were made by library matches using NBS and EPA/NIH libraries, fragmentation analysis and relative retention times. Glyoxylic acid methyl ester, glyoxal, oxalic acid dimethyl ester and vanillin identifications were confirmed by spectra and retention times of standards.

## RESULTS AND DISCUSSION

### General Characteristics of Ozonation By-Products

In the initial investigations of ozonation by-products from a northwestern softwood pulp, the ozonated, high consistency pulp was washed with acidified water and filtered. The aqueous filtrate was extracted with ether as was the bleached pulp, producing two fractions: a water-soluble, ether-soluble fraction and a water-insoluble, ether-soluble fraction. A control sample underwent the same procedures except no ozone was applied to the pulp. Presumably, the products in the control extracts represent the adsorbed, weakly bound, or acid-labile pulp constituents. Total ion current (TIC) chromatograms from the GC/MS analyses of the four fractions are given in Figure 1.

The two control sample chromatograms showed the expected higher molecular weight, water-insoluble components associated with the untreated pulp and the lack of water-soluble material. The ozonated pulp extracts showed the reverse distribution; more compounds were detected in the water than on the pulp. The ozone shifted the distribution of gas chromatographable compounds from higher molecular weight, water-insoluble compounds to smaller, water-soluble compounds. The changes in distribution of products led to the speculation that the higher molecular weight, water-insoluble constituents in the untreated pulp are precursors to some ozonation by-products, a hypothesis explored more fully below.

Short chain diacids and similar polar chemicals are expected by-products from pulp ozonation. The notoriously poor recovery of these chemical classes out of water prompted the use of methanol as an extraction solvent. In addition, our work with model compounds indicated that a good common solvent for chemicals such as lactones, lignin dimers, and unsaturated aliphatic acids is methanol. Subsequent ozonated pulps were therefore extracted with and derivatized in methanol; the methanol extracts were then analyzed directly by GC/MS. The prevalence of

the short chain acids in the methanol extracts can be seen in Figure 2. By comparison, oxalic acid dimethyl ester in the ether extract, designated in Figure 1a, is a minor peak.

It became apparent that a significant portion of the ozonation components is soluble in methanol but not in water. At least some of the water-insoluble material was also insoluble in nonpolar solvents such as ether and hexane. This poorly solubilized fraction may contain polar, high molecular weight lignin fragments as well as lactones and other muconic acid derivatives. The water-soluble products appear to be mostly aliphatic, judging by gas chromatography (discussed below) and by  $^1\text{H}$  NMR spectra. In addition, while high pressure liquid chromatography of water-soluble products resulted in dozens of fairly well resolved peaks, the water-insoluble fraction was not chromatographable. These observations are consistent with ozone producing large, polar, non-chromatographable lignin fragments as well as producing some smaller, chromatographable compounds, possibly fragments of the aromatic ring. In the case of humic substances, a macromolecular material similar to lignin, ozone reduces the molecular weight, but generally only 5 to 30% of the original organic carbon is reduced below 1,000 daltons (6).

#### Composition of Ozonated Pulp Extracts

Aliphatic acids, ranging from six carbons to 24 carbons, were a significant component in almost all of the extracts of ozonated pulp. The methyl esters of the acids, designated in Figure 2, have very characteristic mass spectra, including strong 74 and 87 peaks (Figure 3). Acids with 17 and 19 carbons were identified and were probably derived from the ozonolysis of unsaturated, longer chain fatty acids. However, the presence of a small peak identified as the methyl ester of octadecenoic acid suggests that full cleavage of the unsaturated fatty acids does not occur at ozone doses used in this study (1%-2% on o.d. pulp). Several diacids were detected (Figure 2). The diacids probably also arose from cleavage of double bonds in fatty acids or, in the case of oxalic acid, from cleavage of the aromatic rings in lignin. Of the longer chain diacids (propanedioic to nonanedioic), nonanedioic acid was the most prominent. The latter compound is likely formed when the double bonds in octadecenoic (oleic), hexadecenoic (palmitoleic), octadecadienoic (linoleic) and/or octadecatrienoic (linolenic) acids are cleaved by ozone.

Oxalic acid dimethyl ester and glyoxylic acid methyl ester peaks were prominent in the chromatograms of the the methanol extracts of ozonated pulp (Figure 2). The analytical method that was used does not distinguish between oxalic acid and its methyl esters or between glyoxylic acid and its methyl ester in the extracts. All of these compounds can form through muconic acid type intermediates upon ozonolysis of aromatics (Figure 4). Their presence indicates the extent to which aromatic ring cleavage occurs. Since the formation of these compounds does not represent delignification per se, their presence in high concentrations may reflect inefficient ozone consumption. Glyoxal is another potential ozonolysis product from aromatics which is discussed more fully below.

Few monomeric lignin fragments were identified in any of the extracts. Vanillin and vanillic acid were the two most prevalent. The ozonation products contrast with chlorination effluents in which aromatics are important constituents (1). Another variation from chlorination effluents is the lack of catechols in the ozonation by-product mixtures. This reflects the fact that ozone does not demethylate aromatic methoxyl groups, while chlorine does (7). The scarcity of lignin monomers is consistent with ozone producing polar, high molecular weight material along with aromatic ring fragments from lignin.

#### By-Products From Different Pulps

The distributions of products from two different softwood pulps were compared. Comparisons were also made between pulps that were washed in acidic solution before ozonation, pulps that were washed in alkaline solution, and pulps that were pre-extracted with methylene chloride prior to ozonation. The TIC chromatograms are shown in Figure 5. There are few unique products in the different methanol extracts. The major differences lay in the relative amounts of the different classes of compounds.

Most of the differences in the distribution of the northwestern and southern pulps reflect the differences in their fatty acids content. Two major chromatographable constituents of the southern softwood pulp effluent were octadecanoic acid (stearic acid) and hexadecanoic acid (palmitic acid) whereas the northwestern softwood pulp produced more compounds in comparable amounts. The differences in the extractives contents of the two sources of pulp is further exemplified by the lack of aliphatic acids in

the southern pulp that are presumed to be fatty acid ozonolysis products in the northwestern pulp, e.g., heptadecanoic and nonanedioic acids. In addition, the 20, 22 and 24 carbon fatty acids detected in the northwestern softwood pulp were not found in the southern softwood pulp.

The alkali wash was expected to remove nonbound polar constituents of the pulp. The chromatograms of the ozonated acid-washed and alkaline-washed southern softwood pulps had only minor differences in the relative distributions of their ozonation products. Although the absolute amounts of products appears to be less in the alkaline washes (samples were concentrated to exact volumes and exact volumes were injected in the gas chromatograph), these results can only be considered semi-quantitative and further verification is necessary. The similar product distributions suggest that no major class of precursors of the ozonation products are more alkali-labile than others. However, the alkaline wash may have affected the distribution of some carbonyl compounds present in small quantities, which is discussed below.

The methanol extracts of ozonated northwestern softwood pulp that was pre-extracted with methylene chloride consistently behaved differently than the other softwood extracts for unknown reasons. Upon methylation with diazomethane, there was significant precipitation of material, which did not occur with the other extracts. However, the chromatograms obtained from the pre-extracted pulp were somewhat similar to the unextracted pulp. Although there was a shift in the distribution of the compounds in the effluent away from fatty acids, there were clearly long chain aliphatic acids present, even after pre-extracting the pulp for 5 hours with methylene chloride (based on TAPPI Method T204 om-88 for extractives analysis). The same general trend was seen in the southern softwood pulp. It is unlikely that ozone breaks covalent bonds to produce acids such as octadecanoic (stearic) acid and hexadecanoic (palmitic) acid. Possibilities are that the methylene chloride extraction is inefficient in removing extractives compared to methanol and/or that ozonation causes a change in fiber morphology that allows more extractives to be removed by organic solvents.

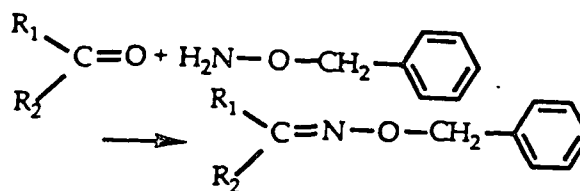
A difference in the aliphatic components of the byproduct mixtures from the pre-extracted pulp and from the unextracted pulp was that the former contained little nonanedioic acid. This indicates that the dicarboxylic acid precursor(s) was effec-

tively removed or reduced. Octadecenoic acid (oleic acid), a very likely precursor to nonanedioic acid, is much less prevalent in the effluent of the pre-extracted pulp than in the effluent of the unextracted pulp.

The precursors of most of the ozonation products of pulps were not readily removed by methods expected to reduce the quantities of polar or nonpolar compounds. More thorough solvent pre-extraction and careful quantitation of the products will more fully address the interesting question of the role of extractives in ozonation by-product formation.

### Carbonyl Compounds

Ozone reacts with double bonds to produce aldehydes, which can frequently be autoxidized to carboxylic acids. Standard GC/MS analyses showed that significant numbers and quantities of carboxylated compounds, some of which were ozone-derived, were present in the extracts of the ozonated pulps. It is reasonable that the corresponding aldehydes of the ozone-derived acids may be present as well. Other carbonyl compounds may also be formed from ozone attack on activated hydrogens (8). One way to selectively look for these compounds is to derivatize them with O-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBOA). PFBOA reacts with aldehydes and, to some extent, ketones, to form the readily identifiable oximes (9,10).



Pentafluorobenzyl oxime derivatives have a signature mass spectrum consisting of a dominant 181 base peak (C<sub>6</sub>F<sub>5</sub>CH<sub>2</sub><sup>+</sup>). Comparing the TIC and the ion chromatogram for mass 181 of the derivatized extract of the southern softwood pulp shows that most of the compounds in the PFBOA-treated extracts are oxime derivatives. Vanillin, identified through standard GC/MS analyses of underivatized extracts, served as a monitor for the production of the oxime derivatives. This was important since the PFBOA derivatization methods used in this work were modified from literature methods (9,10). Figure 6 shows

the chromatogram and mass spectrum of a derivatized vanillin standard and the vanillin oxime from an ozonated pulp sample.

Chromatograms from PFBOA-derivatized extracts of the pulps described in the previous sections are shown in Figure 7. The PFBOA derivatization technique was also used to analyze methanol extracts of the southern pulp which was treated in the following ways: oxygen delignified with a subsequent 0.6 % ozone charge, oxygen delignified with a subsequent 1.0% ozone charge, and methylene chloride-extracted and ozonated at a 1.1 % ozone charge.

There is a remarkable similarity in these chromatograms. They are all dominated by one peak, the oxime derivative of glyoxylic acid methyl ester (Figure 8). This compound was identified in the extracts without PFBOA treatment only after its oxime derivative was detected in this series of experiments. Both PFBOA extracts and underivatized extracts indicate that glyoxylic acid and/or its methyl ester is the most prevalent carbonyl compound in the ozonation extracts. Its predominance in all of the extracts and its similar amount in the extracts (shown in Figure 7) suggest that its major precursor is lignin, since the lignin structures in the different pulps are likely to be similar.

The PFBOA samples show that glyoxal is also an important carbonyl compound (Figure 9). Glyoxal could arise from cleavage of unsubstituted double bonds of muconic acid derivatives (Figure 4). Identification of glyoxal in the underivatized samples is not possible because it elutes with methanol. Formaldehyde is another carbonyl compound of interest. Although it was detected in the PFBOA extracts, it was also present in the blanks in small amounts. In addition, the sample work-up was not conducive to good recovery of formaldehyde. Additional work is underway to confirm the presence of these two compounds in ozonation effluents.

Further examination of the smaller peaks reveals that, as in the underivatized samples, the peaks present are essentially the same in all of the chromatograms. However, there are some minor differences in their magnitude relative to the glyoxylic acid methyl ester derivative. Based on the chromatograms shown in Figure 7, it appears that there are fewer carbonyl precursors in the southern softwood pulp and the alkaline-washed northwestern softwood pulp than in the others. The derivatization technique revealed a small effect of

the alkaline wash that was not apparent in the underivatized extracts. Interestingly, extracting the pulps with methylene chloride did not reduce the carbonyl compounds. These results suggest that some carbonyl precursors are alkali-labile or soluble but resistant to removal by organic solvents.

Oxygen treatment before ozonation does not appear to greatly affect the major reaction pathways that produce carbonyl compounds. This result was somewhat surprising since oxygen treatments tend to alter aromatic structures which seem to be a major source of the small carbonyl compounds (11).

The relatively strong molecular ion of the vanillin oxime, shown in Figure 6, is characteristic of aromatic derivatives (10). Few other oxime peaks exhibited as strong a molecular ion, suggesting that vanillin is the major aromatic aldehyde produced by ozonation. These data are supported by the spectra from the underivatized extracts.

To simplify the task of identifying the oximes and their corresponding parent compounds, it is useful to compare an ion chromatogram for mass 59 which is strongly characteristic of methyl esters. The ion fragment that produces the mass peak at 59 amu is  $-\text{COOCH}_3$ . By comparing the 181 traces and the 59 traces, an idea of the number of compounds that are potentially bifunctional, i.e., contain an aldehyde and a carboxylic group, can be obtained. The ion chromatogram for mass 59 suggests that most of the carbonyl compounds have a carboxylic group, with a few exceptions.

In this study, the PFBOA was added to the methanol extracts of the pulps and the reaction was quenched with acidic water. In literature methods (9,10), the derivatization is performed in water. In the case of a glyoxal standard, the methanol appears to induce the formation of an oxime derivative different from that produced in water. In addition, glyoxylic acid becomes methylated upon acidification in methanol (see Methods). The other standards derivatized in this study (acetone, formaldehyde, vanillin, and methylated glyoxylic acid) produced oxime derivatives with the expected mass spectra. Future work in this area should either be performed in water or provide thorough documentation of the derivative formation in methanol.



## CONCLUSIONS

Pulp ozonation produces basically two types of by-products. One type consists of small, gas chromatographable compounds which are primarily fatty acids, short-chain and long-chain aliphatic acids and diacids. The other type is methanol-soluble and water-insoluble, and possibly contains large, polar lignin fragments.

The precursors of some of the aliphatic acids and diacids are unsaturated fatty acids. In particular, nonanedioic acid is an important product of fatty acid cleavage in ozonated pulps. Even though the contribution of aliphatic acids can be reduced by pre-extraction of the pulp with methylene chloride, complete removal of the fatty acids and their ozonolysis products cannot be effected by methods used in this study. Alkaline washes do not change the distribution of major products relative to one another.

Few monomeric lignin compounds are produced or survive ozonation. Evidence of lignin ozonolysis rests primarily in the presence of oxalic acid and glyoxylic acid (and/or their methyl esters). These compounds are major chromatographable components of ozonation by-product mixtures, based on relative peak sizes in TIC chromatograms. Glyoxylic acid is by far the most abundant aldehyde present. Derivatization by PFTBOA indicates that glyoxal is another important carbonyl by-product.

Carbonyl compounds that are present in ozonated pulp in small quantities relative to glyoxylic acid (methyl ester) have precursors that resist extraction from pulp by methylene chloride. However, alkaline washing prior to ozonation reduces carbonyl compounds. These results suggest that the precursors are polar. In addition, northwestern pulp produces more carbonyl compounds than the southern pulp. Oxygen delignification prior to ozonation does not appear to greatly affect the distribution of carbonyl compounds. These differences in carbonyl content of the different pulps were discernible only in PFTBOA-derivatized extracts, probably due to their small quantities relative to other detected compounds.

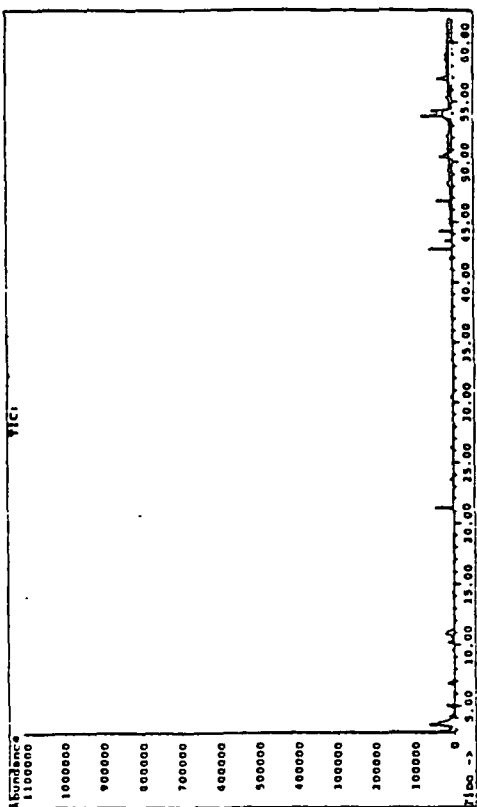
## ACKNOWLEDGEMENTS

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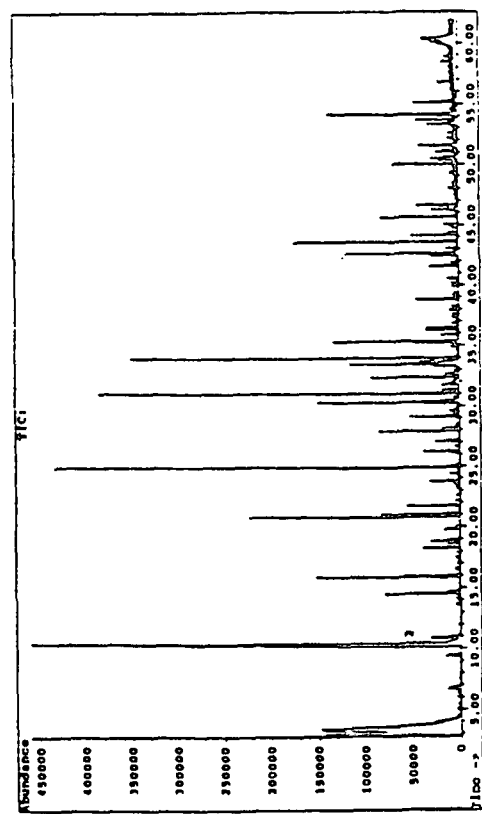
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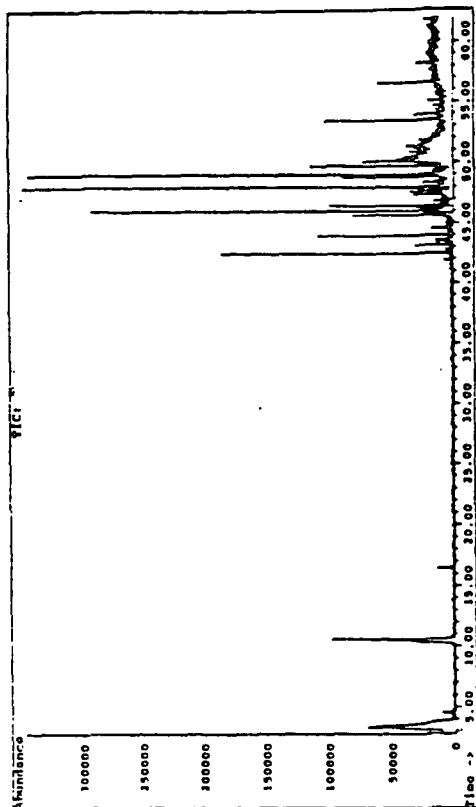
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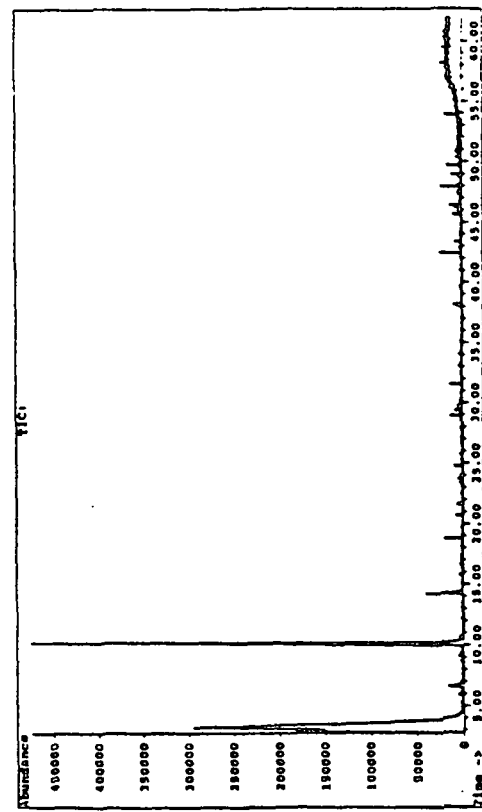
(b)



(a)

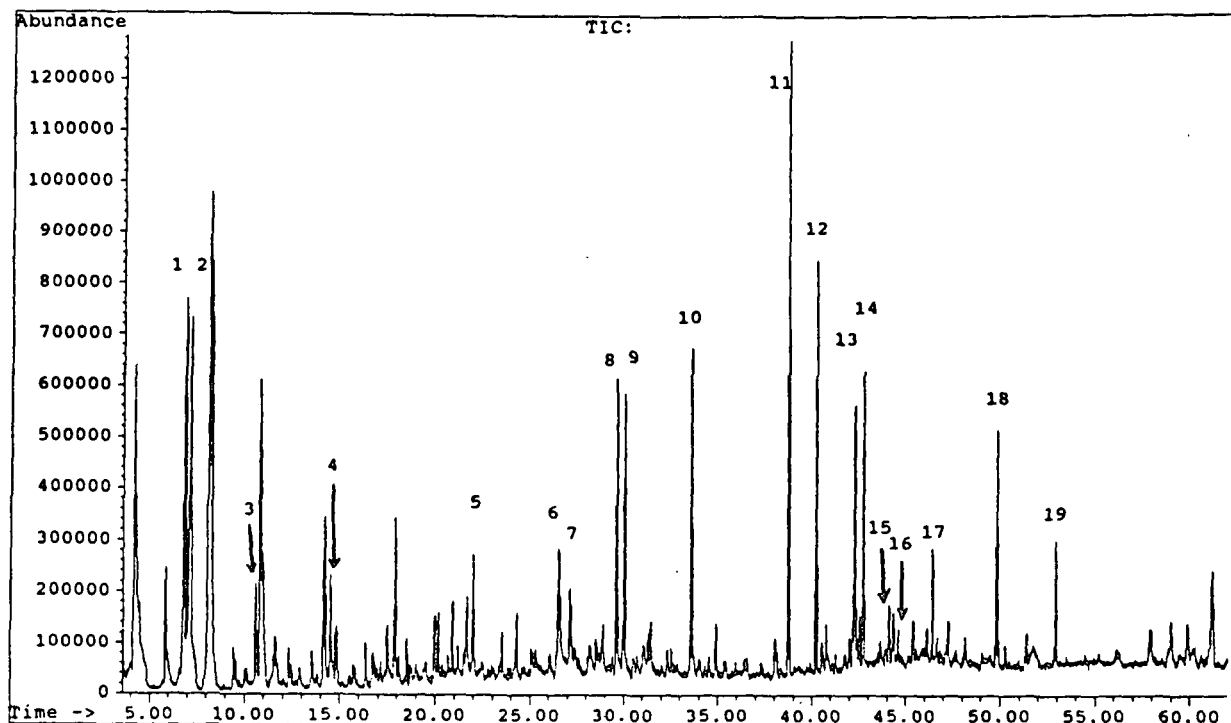


(d)



(c)

Figure 1. TIC chromatograms of methylated ether extracts of a) ozonated pulp filtrate, b) ozonated pulp, c) control pulp filtrate, and d) control pulp.



<u>Peak</u>	<u>Name</u>
1	2-Oxo-ethanoic acid methyl ester (glyoxylic)
2	Ethanedioic acid dimethyl ester (oxalic)
3	Propanedioic acid dimethyl ester (malonic)
4	Butanedioic acid dimethyl ester (succinic)
5	Hexanedioic acid dimethyl ester (adipic)
6	4-Hydroxy-3-methoxy benzaldehyde (vanillin)
7	9-Oxo-nonanoic acid methyl ester
8	4-Hydroxy-3-methoxy benzoic acid methyl ester (vanillic)
9	Nonanedioic acid dimethyl ester (azelaic)
10.	Hexadecanoic acid (palmitic)
11	Hexadecanoic acid methyl ester (palmitic)
12	Heptadecanoic acid methyl ester
13	Octadecanoic acid methyl ester
14	Octadecanoic acid methyl ester (stearic)
15	Nonadecanoic acid methyl ester
16	Nonadecanoic acid methyl ester
17	Eicosanic acid methyl ester (arachidic)
18	Docosanoic acid methyl ester (behenic)
19	Tetracosanoic acid methyl ester (lignoceric)

Figure 2. TIC chromatogram of a methanol extract of ozonated northwestern softwood pulp showing pulp ozonolysis by-products.

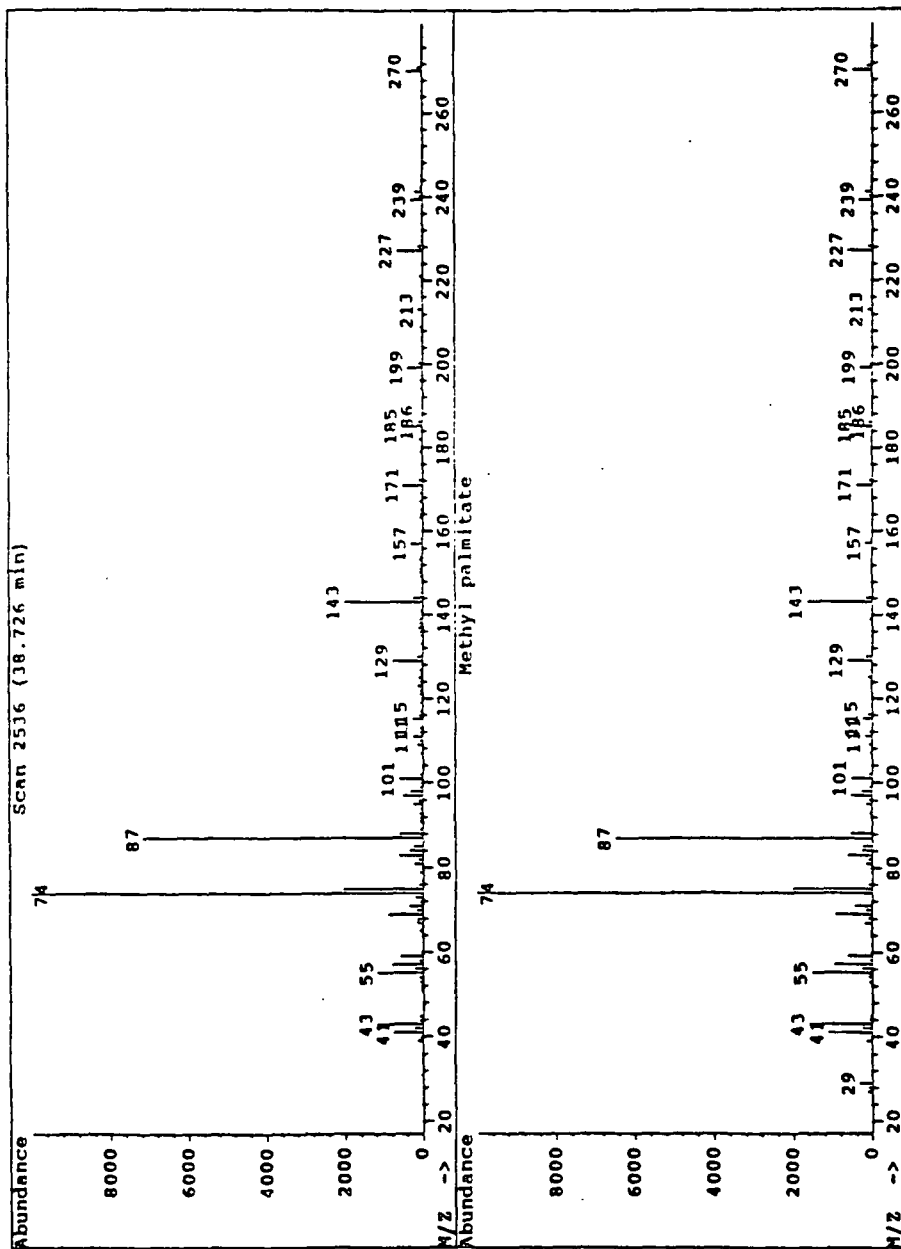


Figure 3. Mass spectra from peak number 11 (Figure 2) and from NIST/EPA/MSCD 54 K Mass Spectral Database.

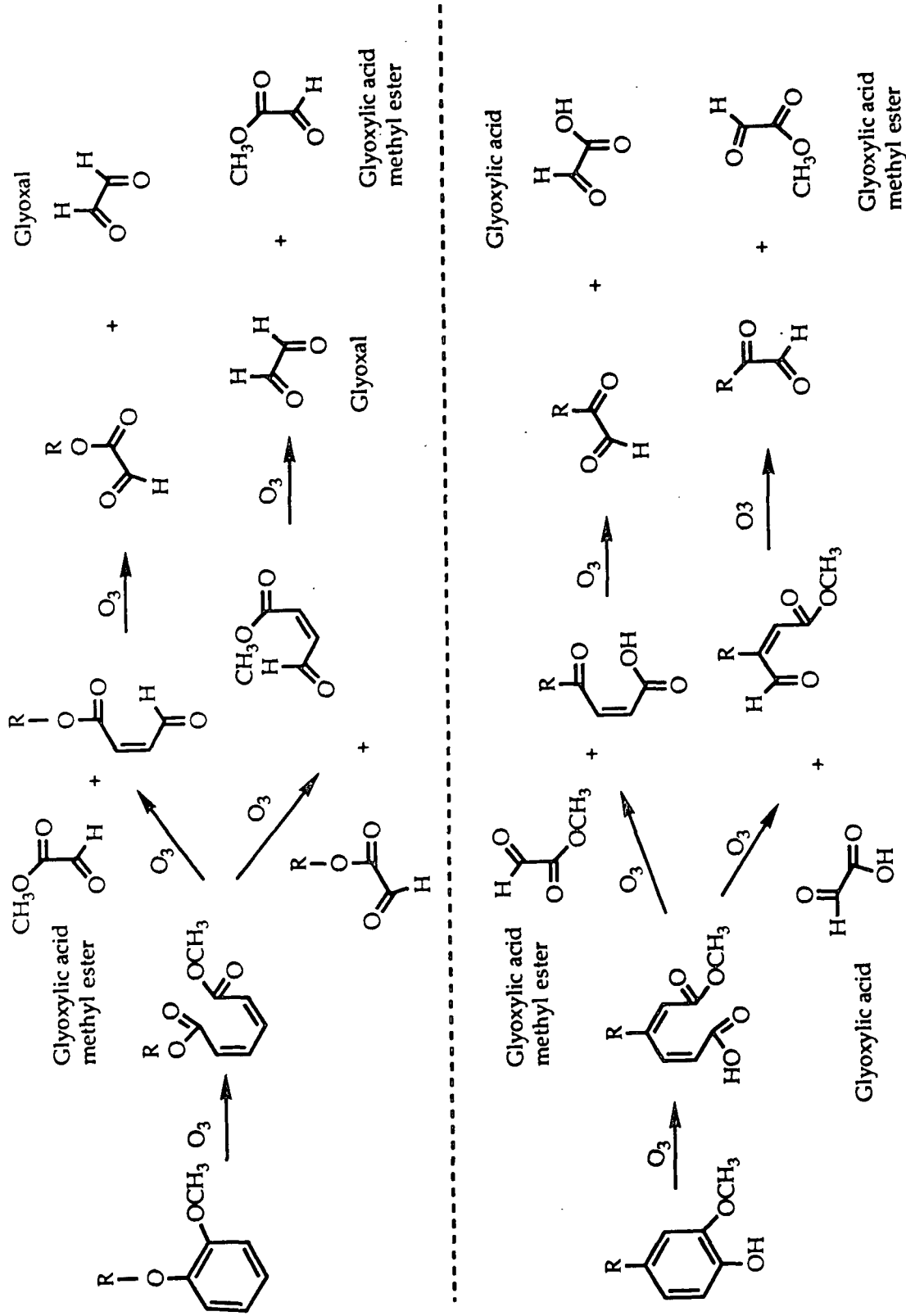
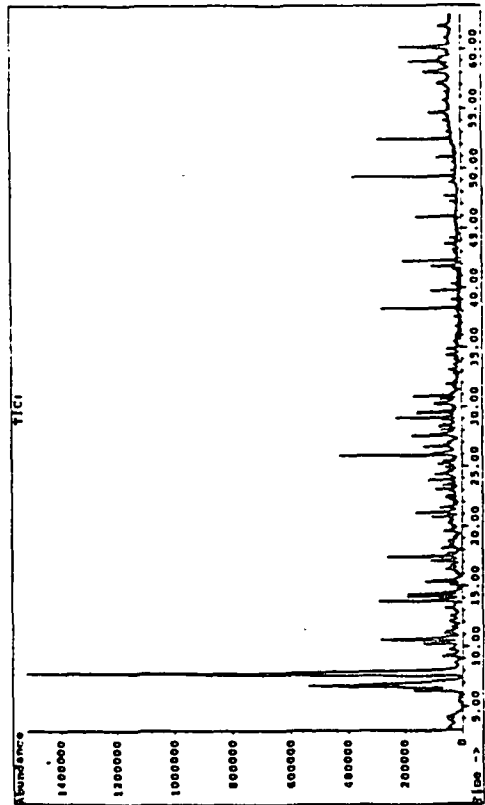
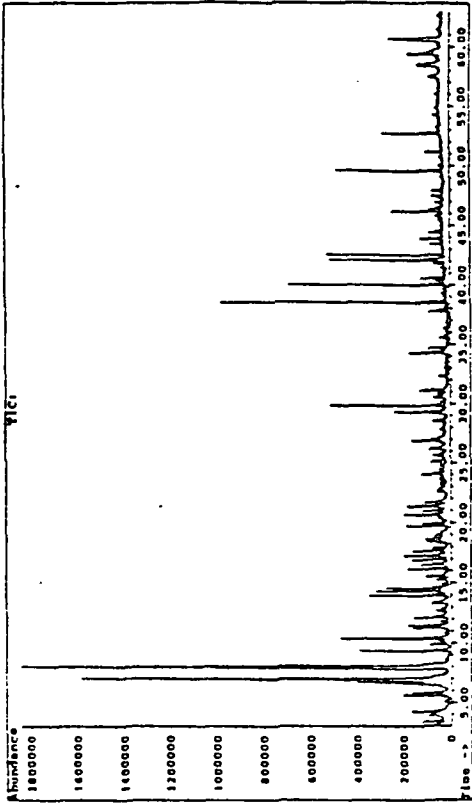


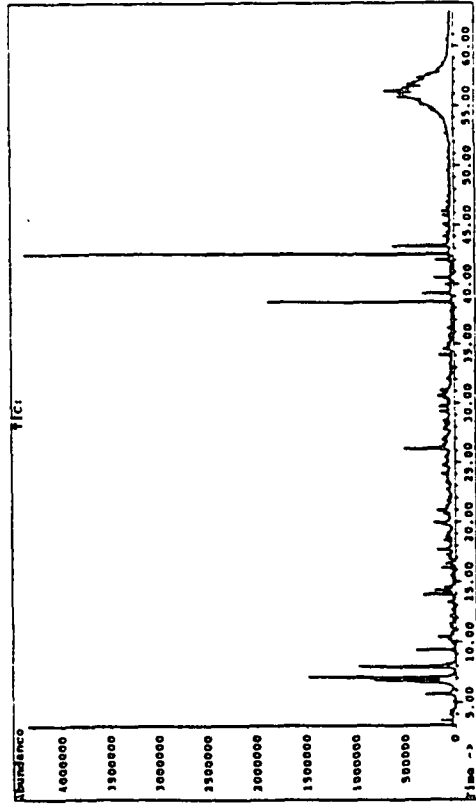
Figure 4. Potential pathways for the formation of carbonyl compounds from ozonation of lignin.



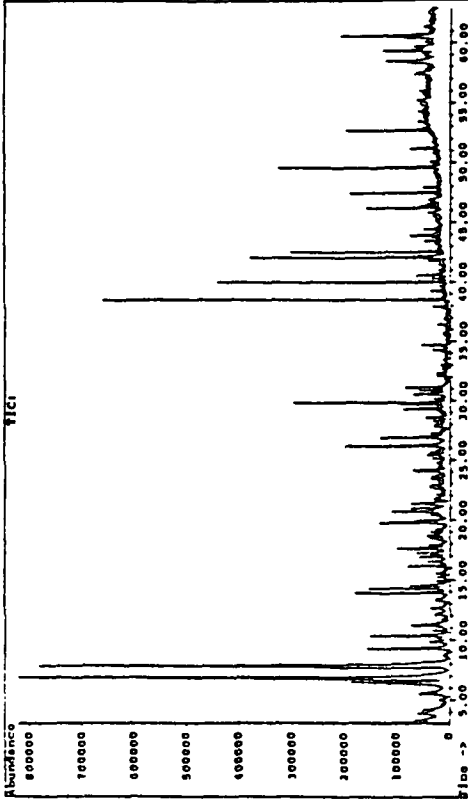
(a)



(b)

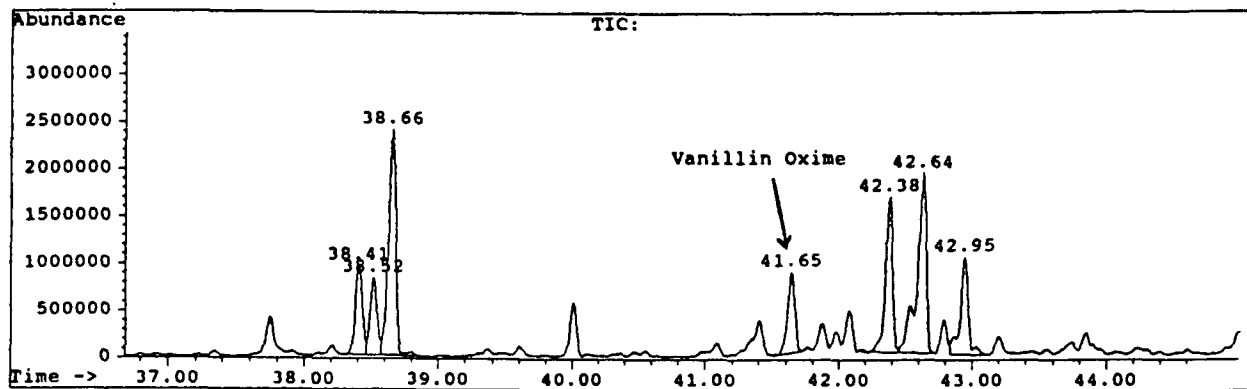


(c)

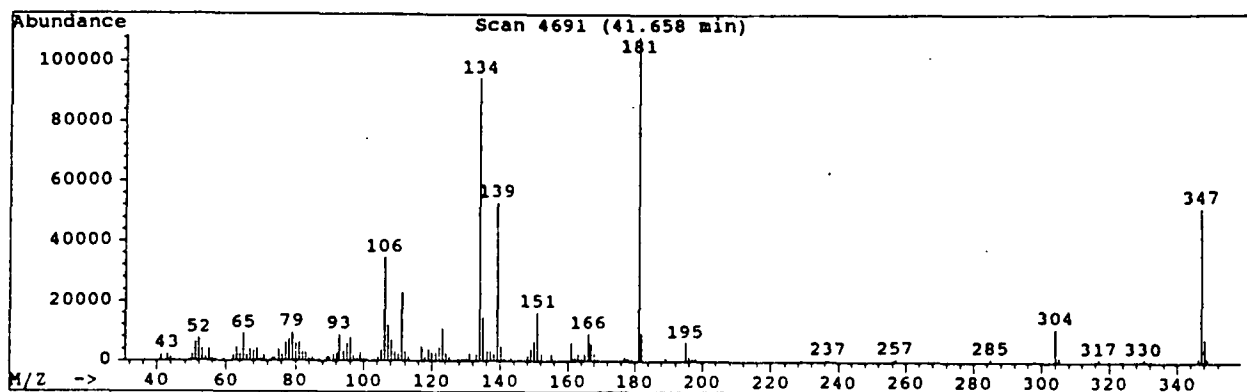


(d)

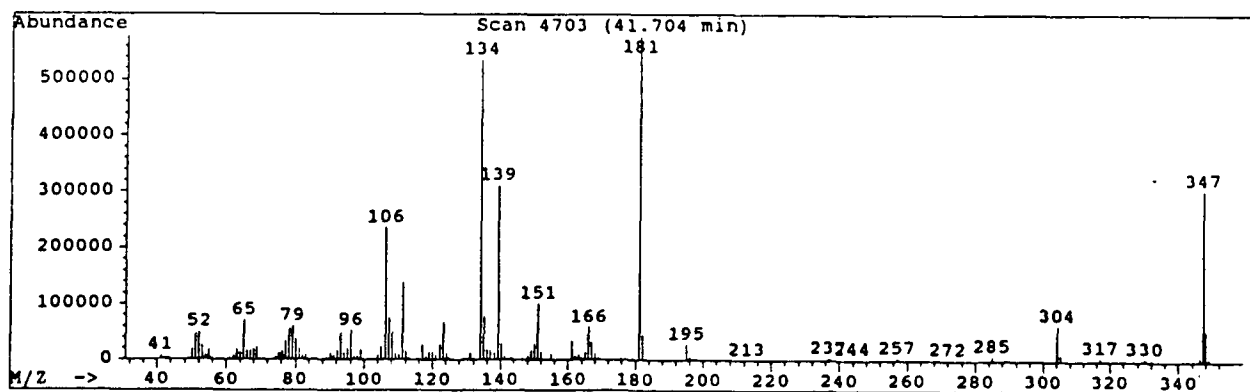
Figure 5. TIC chromatograms of methylated methanol extracts of ozonated pulp, a) southern softwood, prewashed with acid, b) northern softwood, prewashed with acid, c) southern softwood, pre-extracted with methylene chloride, and d) northern softwood prewashed with base.



(a)



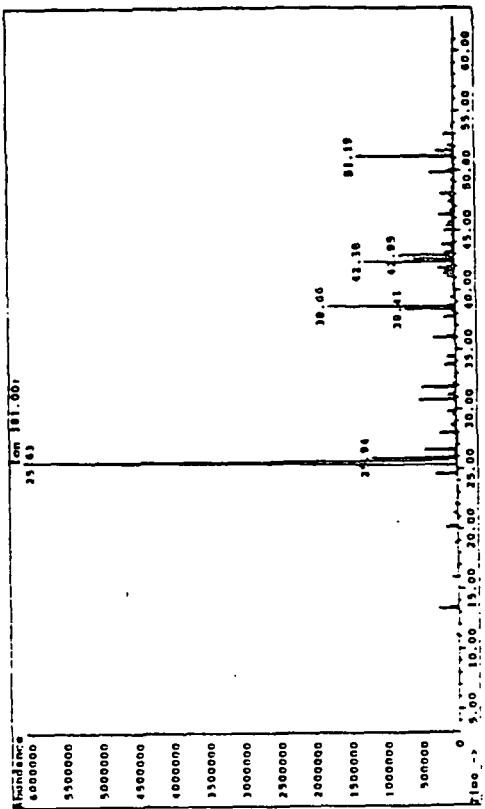
(b)



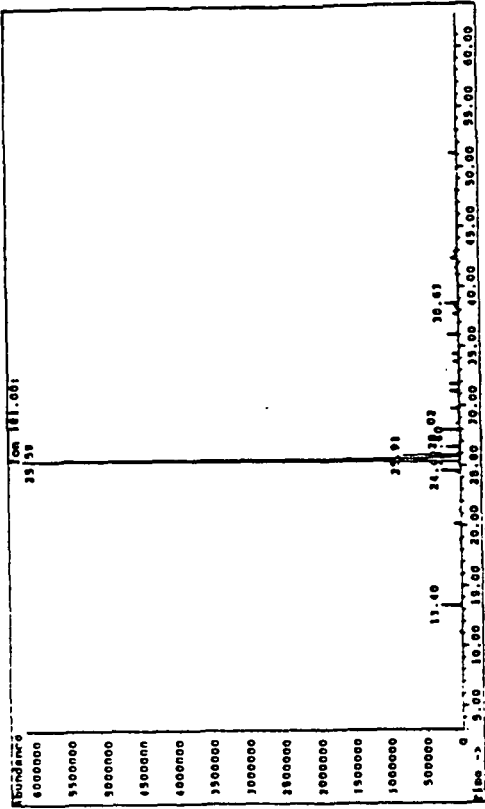
(c)

Figure 6. Vanillin oxime derivatives; a) TIC chromatogram of a PFBOA derivatized extract of an ozonated northwestern softwood pulp, b) mass spectrum of the designated sample peak, and c) mass spectrum of a vanillin standard derivatized in methanol.

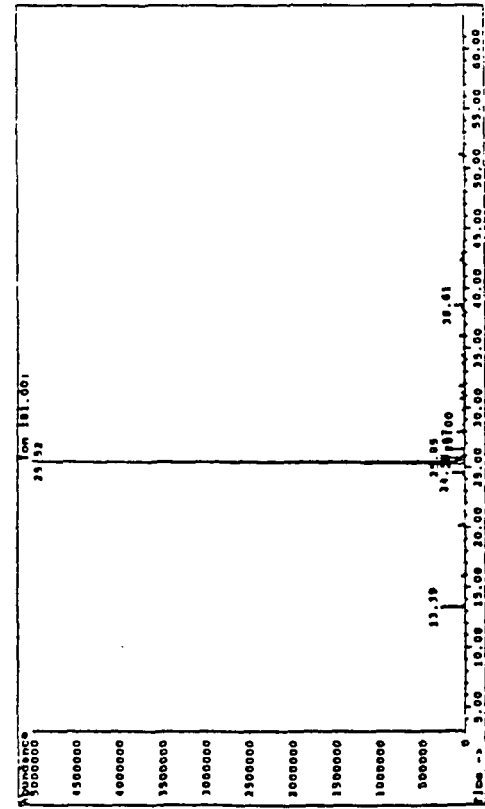




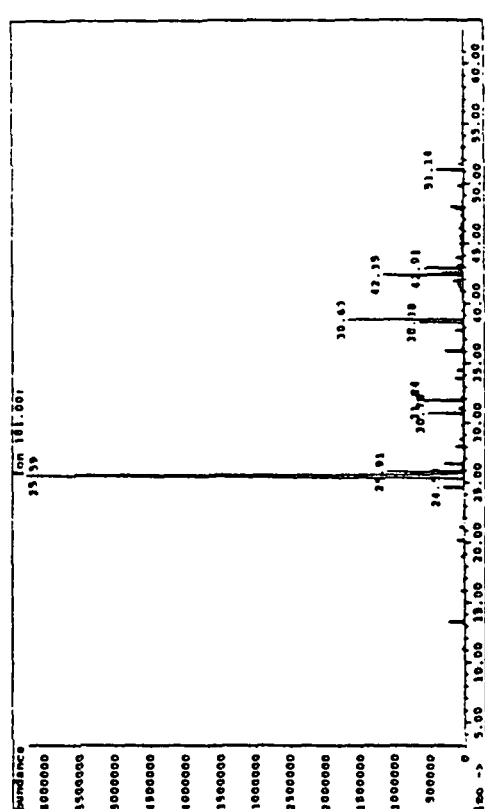
(a)



(b)

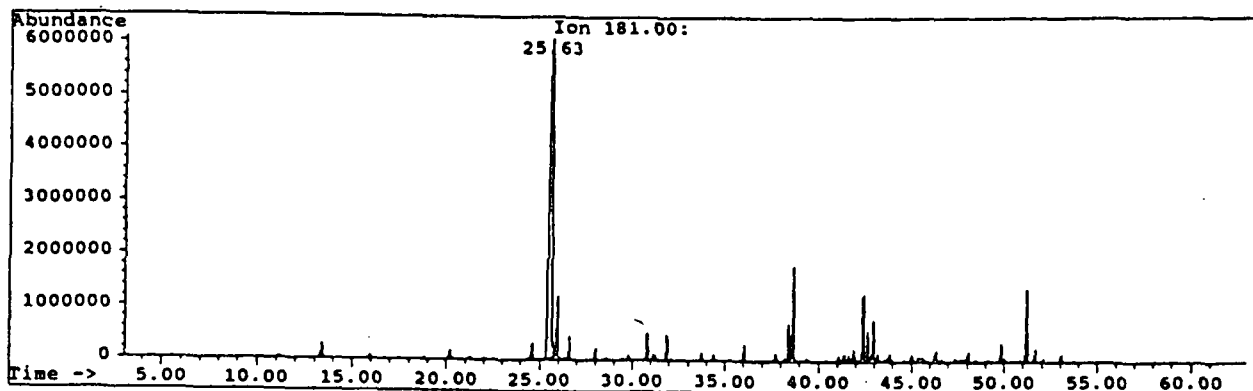


(c)

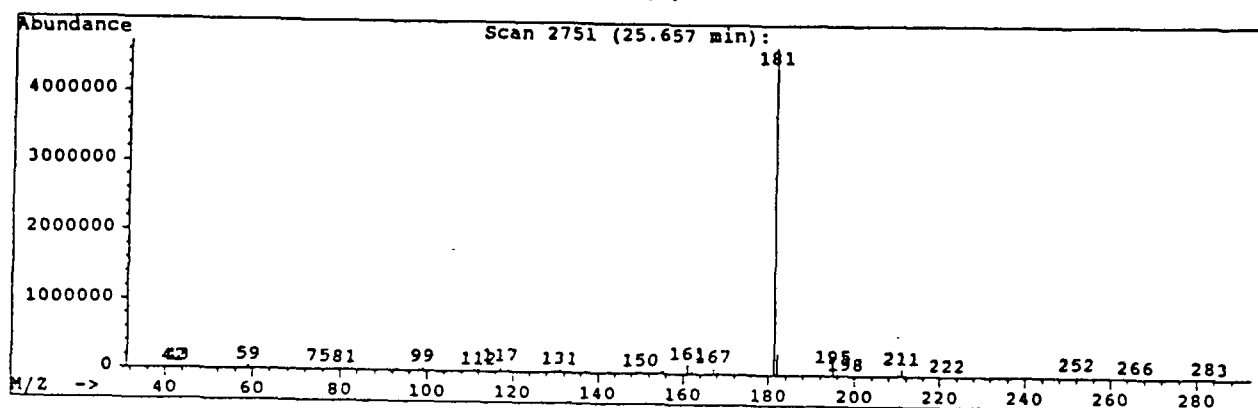


(d)

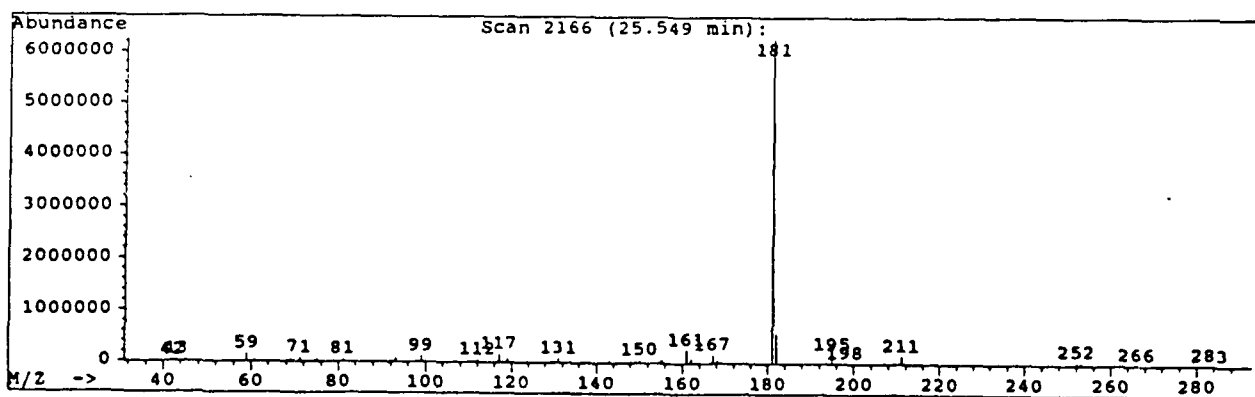
Figure 7. Ion chromatograms (mass = 181) of PFBOA derivatized extracts of ozonated a) southern softwood, prewashed with acid, b) northwestern softwood, prewashed with acid, c) northwestern softwood, pre-extracted with methylene chloride, and d) northwestern softwood prewashed with base.



(a)

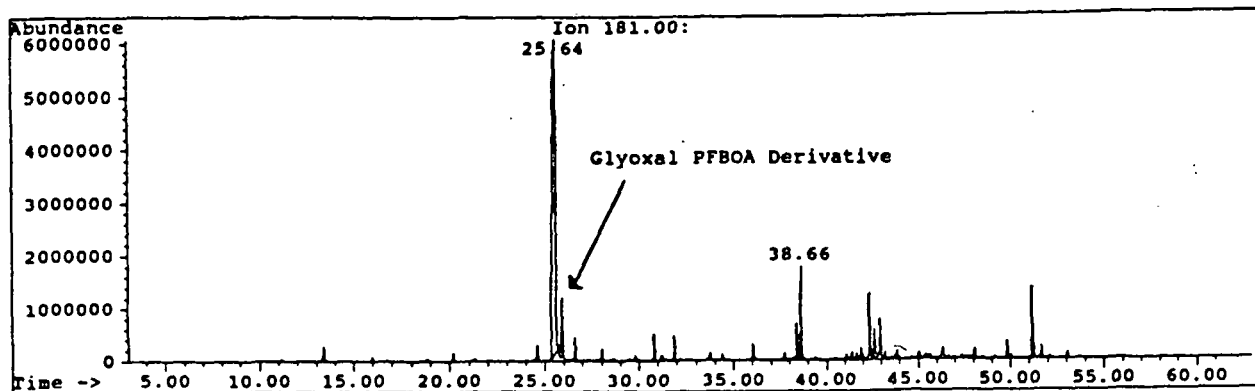


(b)

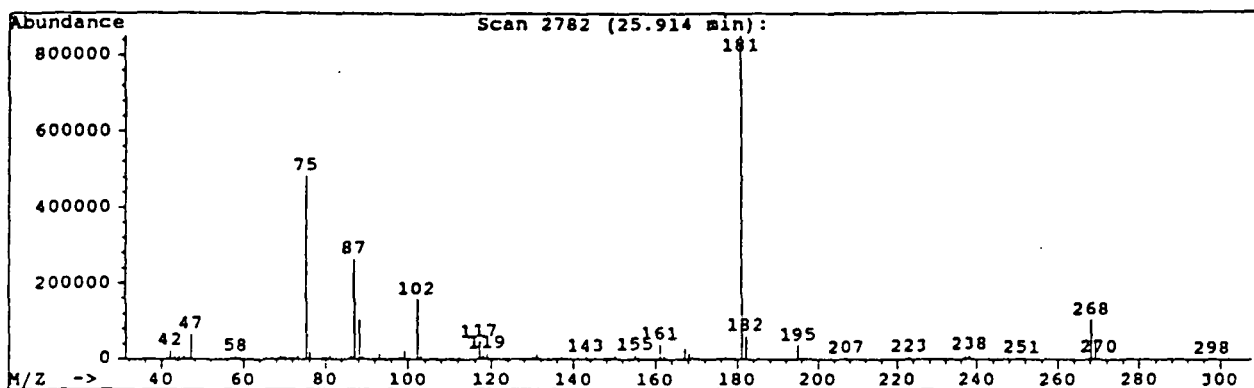


(c)

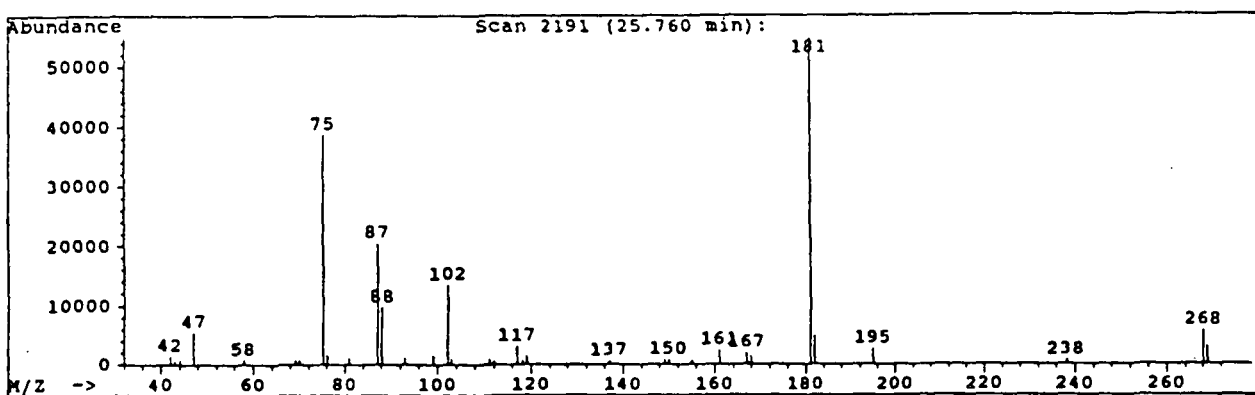
Figure 8. Glyoxylic acid methyl ester oxime derivatives; a) TIC chromatogram of a PFBOA derivatized extract of an ozonated northwestern softwood pulp, b) mass spectrum of the designated sample peak, and c) mass spectrum of a glyoxylic acid methyl ester standard derivatized in methanol.



(a)



(b)



(c)

Figure 9. Glyoxal oxime derivatives; a) TIC chromatogram of a PFBOA derivatized extract of an ozonated northwestern softwood pulp, b) mass spectrum of the designated sample peak, and c) mass spectrum of a glyoxal standard derivatized in methanol.