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### Ultrafiltration and Pyrolysis Gas Chromatography Mass Spectrometry of Chlorolignins in Pulp Mill Effluent

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## ULTRAFILTRATION AND PYROLYSIS GAS CHROMATOGRAPHY MASS SPECTROMETRY OF CHLOROLIGNINS IN PULP MILL EFFLUENT

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Investigations on the effluent of a German pulp mill on the river Rhine using ultrafiltration and pyrolysis gas chromatography mass spectrometry have shown the presence of several chlorinated 2-methoxyphenols, which probably originate from chlorinated lignin or liginosulfic acid. Chlorinated phenolic pyrolysis products identified were 2-methoxy-6-chlorophenol, 2-methoxy-4-methyl-6-chlorophenol, 2-methoxy-dichlorophenol, 2-methoxy-4-vinyl-6-chlorophenol, 2-methoxy-4-(chloropropyl)phenol, 2-methoxy-4-(prop-2-enyl)-6-chlorophenol, 2-methoxy-4-(propan-2-one)-6-chlorophenol, 2-methoxy-3,5,6-trichlorophenol, 2-methoxy-4-vinyl-3,5,6-trichlorophenol. Monochlorinated 2-methoxyphenols were the dominant chlorinated pyrolysis products, smaller amounts of di- and trichloromethoxyphenols were also detected. 2-Methoxyphenols (guaiacols) were the dominant lignin pyrolysis products, only small amounts of 2,6-dimethoxyphenols (syringols) were detected. This indicates the origin from soft wood. A Py-(GC)-(MS)-TIC-chromatogram of reference spruce milled wood lignin is comparable with the TIC-chromatogram of pulp mill effluent MW-fraction >10,000, showing many similar compounds. The ultrafiltration fraction 1000 < MW <10,000 showed a remarkably empty TIC-chromatogram, with 2-methoxyphenol and 2-methoxy-6-chlorophenol as the only significant phenolic peaks. This may indicate a high degree of oxidation/chlorination of lignin in this fraction.

**KEY WORDS:** Pyrolysis gas chromatography mass spectrometry, ultrafiltration, chlorolignins, chloroguaiacols, pulp mill effluent.

### INTRODUCTION

There is considerable interest in the environmental effects of the large quantities of pulp mill effluents discharged annually,<sup>1</sup> particularly in the role of organochlorine compounds.<sup>2</sup> A study of adsorbable organic halogen (AOX) levels in waste waters of major industries along the Rhine has demonstrated that paper mills are a major cause of organochlorine pollution in this river.<sup>3</sup> It has been estimated that 0.25 million tonnes of organically bound chlorine are released each year from pulp mills worldwide.<sup>1</sup> Lindstrom, Nording and Osterberg<sup>2</sup> have shown that 70% of the organic chlorine in spent chlorination liquor and 95% in spent alkaline extraction liquor is composed of high molecular weight compounds (MW >1000).

Low and high molecular weight compounds in pulp mill effluent have different toxicological properties. Pulp mill effluent was found to be mildly toxic to fish and other water organisms; several low molecular weight mutagens have been identified.<sup>1</sup> High molecular weight compounds in pulp mill effluent are probably biologically inactive, because they cannot penetrate cell membranes of organisms.<sup>1</sup> There is however considerable interest in the degradation of these compounds (chemically, biochemically or physically) in the aquatic environment, which may lead to the formation of toxic chlorinated phenolic compounds of low molecular weight.<sup>1,2</sup>

A variety of analytical methods have been used in the analysis of macromolecules in natural and waste water, including extraction methods,<sup>7</sup> XAD-adsorption,<sup>8</sup> elemental analysis,<sup>1,4,5</sup> functional group analysis,<sup>4,5</sup> chemical degradation techniques,<sup>4,5</sup> colorimetry, UV-spectrometry,<sup>7</sup> fluorescence spectrometry, NMR,<sup>4,5</sup> IR,<sup>4,5</sup> reversed phase HPLC,<sup>9</sup> gel permeation chromatography<sup>10</sup> and ultrafiltration.<sup>4,5</sup> A few applications of pyrolysis gas chromatography mass spectrometry in the analysis of river water and drinking water have been reported.<sup>8,10</sup>

Elemental analysis and functional group analysis (methoxyl-, carboxyl- and hydroxyl-groups) give supplementary information in structural studies, but are not major techniques in structure elucidation. Chemical degradation studies, especially oxidative techniques, are very valuable methods in the study of monomeric substructures of chlorinated lignin, from which models of the original chlorolignin polymer can be postulated.<sup>2,4,5</sup> A disadvantage of oxidative degradation of lignin is the conversion of the propane side chains of the phenylpropane monomers into carboxy or formyl groups, which means the loss of side chain information from the native lignin polymer. <sup>13</sup>C-NMR has also been used in investigations on chlorinated high molecular weight material in spent bleach liquors. However, this technique gives complex spectra, in which carbon-chlorine bonds are difficult to distinguish.<sup>4,5</sup>

Ultrafiltration is a very useful technique to obtain information on the molecular weight distribution of dissolved organic material giving more sophisticated fingerprints of the water types examined. The molecular weight distribution of a macromolecular compound class can be considered a third analytical dimension, additional to the identity/structure and quantity of the compound class studied.

Pyrolysis GC-MS is an analytical approach which can give significant structural information on the composition of mixtures of macromolecules in water samples.<sup>10</sup> Carbohydrates,<sup>11</sup> lignins,<sup>12</sup> fatty acids<sup>13</sup> and proteins<sup>14</sup> can be distinguished by their pyrolysis products and estimates can be made of the quantitative composition of the mixture. The technique is rapid, requires minimal sample preparation and, when applied to lignin, preserves phenylpropane side chain information.

The aim of this study was to obtain qualitative information on the macromolecular composition of pulp mill effluent, and to establish the suitability of ultrafiltration in combination with pyrolysis gas chromatography mass spectrometry for the investigation of high molecular weight compounds in pulp mill effluent. To our knowledge the combination of ultrafiltration and pyrolytic analysis of pulp mill effluent has never been reported before.

## EXPERIMENTAL

### *Materials*

Spruce milled wood lignin (MWL) was a gift from Dr O. Faix from the Institut für Holzchemie und Chemische Technologie des Holzes, Hamburg. Reference water samples were taken from the Drentsche Aa, a small and unpolluted Dutch river. Samples of pulp mill effluent were obtained from a pulp mill on the river Rhine, and stored in plastic containers. It was assumed that hydrophilic lignins do not adsorb readily on an apolar container material.

### *Ultrafiltration*

Water samples (10 litre) were decanted after sedimentation of suspended matter and processed in a Spectrum Spiro/Por ultrafiltration system. Cross flow filters with molecular weight cut offs of 1000 and 10,000 daltons were used to separate the dissolved macromolecules into a low molecular weight fraction (Fraction L) and two higher molecular weight fractions (Fraction M: 1000–10,000 daltons and Fraction H: > 10,000 daltons). The fractions M and H were concentrated to 1 litre in the ultrafiltration cell. After concentration these fractions were washed twice by dilution to 10 litre with water and re-concentration to 1 litre. 1 ml of concentrate was freeze dried and redissolved in 100  $\mu$ l water. The total concentration factor of the procedure steps was 50:1.

### *Analytical Methods*

DOC measurements were performed by wet digestion of the dissolved organic material by potassium persulphate at elevated temperature (70–90 °C) and infrared detection of the CO<sub>2</sub> formed. Prior to digestion, the water samples were filtered through a glass fibre filter, carbonates and volatile organics were removed by acidification and gas stripping.

AOX measurements were performed by Schöninger combustion of organic material adsorbed on active carbon and detection of the hydrogen chloride by a microcoulometric titration in a Ag/AgCl-cell.<sup>15</sup> Prior to combustion, the inorganic chloride adsorbed on the active carbon was washed out with a sodium nitrate solution. The carbon/chloride ratio was calculated from the corresponding DOC- and AOX-values, giving the number of carbon atoms per chlorine atom.

### *Pyrolysis Gas Chromatography Mass Spectrometry*

Curie point pyrolysis was performed with a FOM 3-LX pyrolysis unit.<sup>16</sup> Samples of 25  $\mu$ g (5  $\mu$ l aqueous suspension of 5 mg/ml) were transferred to a disposable ferromagnetic wire, and dried under reduced pressure. The wire was inserted into a clean glass liner, which was placed in the pyrolysis unit. The glass liner was

**Table 1** DOC- and AOX-results, Carbon/chloride ratio

<i>Sample</i>	<i>DOC (mg/l)</i>	<i>AOX (mg/l)</i>	<i>Carbon/chloride ratio</i>
<i>Drentsche Aa</i>			
Fraction L	2.89 (41%)	0.036 (49%)	237
Fraction M	3.72 (53%)	0.023 (32%)	468
Fraction H	0.38 (5%)	0.013 (19%)	83
Total	6.99 (100%)	0.073 (100%)	283
<i>Pulp mill effluent</i>			
Fraction L	58.9 (48%)	2.3 (23%)	76
Fraction M	29.9 (24%)	4.7 (48%)	19
Fraction H	34.9 (28%)	2.8 (29%)	37
Total	123.7 (100%)	9.8 (100%)	37

surrounded by a ceramic tube kept at 180 °C, which in turn was surrounded by a high frequency coil. The wire was inductively heated within 0.1 sec. to its Curie point temperature (610 °C), at which it was held for 4 sec. The rapid heating of the wire caused pyrolysis of the sample, and the volatile products were swept by a carrier gas flow of 3 ml/min of Helium without splitting onto the capillary column.

Py-(GC)-(MS) was performed with a Packard 438-S gas chromatograph, a JEOL DX303 [E/B] double focussing mass spectrometer and a DA-5000 data system. Pyrolysis products were separated on a 50 m. CP-SIL-5 column (I.D. 0.32 mm, film thickness 1 µm) by temperature programming (40 °C to 320 °C, 4 °/min). The capillary column was directly introduced into the ion source. Mass spectrometric parameters used were ionisation mode EI, ionisation energy 70 eV, acceleration voltage 3 kV, mass range 20–500 a.m.u. and cycle time 1 sec.

## RESULTS AND DISCUSSION

### *Ultrafiltration*

Ultrafiltration was used to separate the water samples into three molecular weight fractions, and to concentrate the higher molecular weight fractions M and H. An important aspect of ultrafiltration is the removal of inorganic salts, which is a necessary prerequisite to prevent catalytic degradation of pyrolysis products during the pyrolysis process.<sup>17</sup> Effective removal of salts is ensured by introducing washing steps in the ultrafiltration procedure.

### *DOC and AOX-Values of Pulp Mill Effluent and Reference Water*

The DOC and AOX-values of the pulp mill effluent and reference water ultrafiltrates are given in Table 1. The ratio of the number of carbon atoms per chlorine-atom has been calculated. A low carbon/chloride ratio means a high

**Table 2** Aromatic pyrolysis products of spruce milled wood lignin. Scan numbers refer to peaks in the total ion current chromatogram in Figure 1.

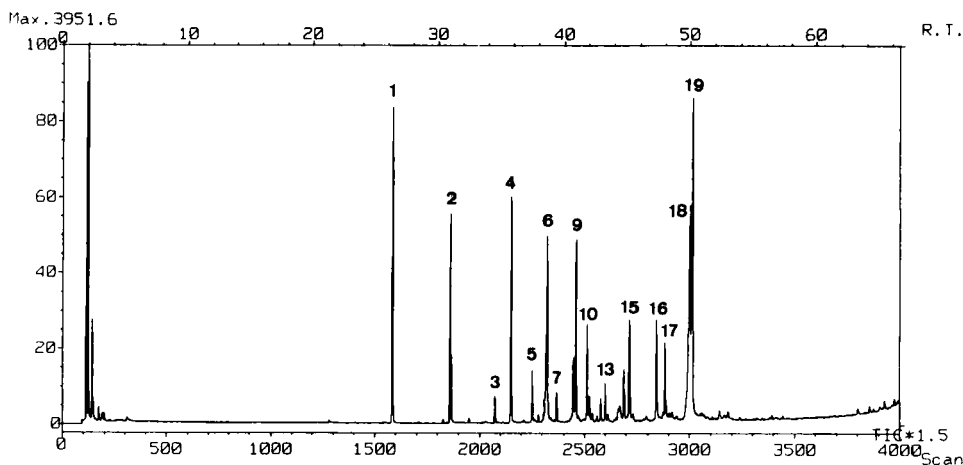
No.	M <sup>+</sup>	Scan	Compound name	Structure
1	124	1583	2-methoxyphenol	G-H
2	138	1861	2-methoxy-4-methylphenol	G-C
3	152	2073	2-methoxy-4-ethylphenol	G-C-C
4	150	2150	2-methoxy-4-vinylphenol	G-C=C
5	164	2253	2-methoxy-4-(prop-2-enyl)phenol	G-C-C=C
6	152	2321	2-methoxy-4-formylphenol	G-CHO
7	164	2366	2-methoxy-4-(prop-1-enyl)phenol (c)	G-C=C-C
8	166	2447	2-methoxy-4-ethanalphenol	G-C-COH
9	164	2458	2-methoxy-4-(prop-1-enyl)phenol (tr)	G-C=C-C
10	166	2513	2-methoxy-4-acetylphenol	G-CO-C
11	162	2524	2-methoxy-4-(prop-1-enyn)phenol	G-C≡C-C
12	182	2578	2-methoxy-4-(carboxymethyl)phenol	G-COO-C
13	180	2600	2-methoxy-4-(propan-2-one)phenol	G-C-CO-C
14	180	2689	2-methoxy-4-(prop-1-en-3-ol)phenol	G-C=C-C-OH
15	178	2716	2-methoxy-4-(prop-2-en-1-one)phenol	G-CO-C=C
16	182	2841	2-methoxy-4-(methylcarboxy)phenol	G-C-COOH
17	180	2883	2-methoxy-4-(prop-1-en-3-ol)phenol (c)	G-C=C-C-OH
18	178	2994	2-methoxy-4-(prop-1-en-3-al)phenol	G-C=C-CHO
19	180	3013	2-methoxy-4-(prop-1-en-3-ol)phenol (tr)	G-C=C-C-OH

degree of chlorination. The DOC-value of the pulp mill effluent is 18 times higher than in the reference water and there is a significant difference in molecular weight distribution between the samples; with a much higher proportion of material in the highest molecular weight fraction in the effluent sample. The proportion of chlorinated material in the higher molecular weight fractions (M + H) is also much greater for the effluent sample and the overall AOX-value of pulp mill effluent is 140 times higher than the reference water, indicating a highly chlorinated waste water.

The molecular weight distribution of organochlorine compounds in this effluent is consistent with values obtained by Lindstrom, Nordin and Osterberg<sup>2</sup> for spent chlorination liquors. The carbon/chlorine ratio is very low for fraction M of pulp mill effluent (19), indicating a highly chlorinated organic material. Similar ratios have been reported for this molecular weight fraction obtained from alkaline (14) and acidic (9) spent chlorination stage liquors.<sup>4,5</sup>

### *Pyrolysis of MWL*

The pyrolysis (GC)-(MS) total ion current (TIC) chromatogram of MWL is given in Figure 1. The absence of carbohydrate-markers in the retention time range from 2 to 25 minutes indicates a relatively pure milled wood lignin. The lignin markers which have been found are given in Table 2. These characteristic pyrolysis products all consist of a 2-methoxyphenol core, with various side-chains at the 4-position.<sup>18</sup> Due to differences in GC-conditions the retention times in this



**Figure 1** Total ion current chromatogram of Spruce Milled Wood Lignin, 25  $\mu\text{g}$ . Peak numbers refer to compounds listed in Table 2.

TIC-chromatogram are not directly comparable with TIC-chromatograms of pulp mill effluent.

#### *Pyrolysis of Reference Water Concentrates*

Concentrated reference water samples gave very weak TIC-chromatograms. Small amounts of carbohydrate markers were observed, but the concentration levels of humic acids were too low to be detected.

#### *Pyrolysis of Pulp Mill Effluent Fraction H*

The TIC-chromatogram of this fraction is given in Figure 2. Many 2-methoxyphenols and chloro-2-methoxyphenols were identified in this fraction, as listed in Table 3. The diversity of 2-methoxyphenols, with a wide range of side chains which have not been removed by chlorine oxidation, indicate a relatively intact lignin; this is supported by the similarity of the TIC-chromatogram of this fraction to that of MWL (Figure 1). 2-Methoxyphenols (guaiacols) are the dominant pyrolysis products, only small amounts of 2,6-dimethoxyphenols (syringols) were detected. This indicates that the lignin originates from soft wood. Most of the detected chloromethoxyphenols are monochloro-2-methoxyphenols; relatively small amounts of dichloro-2-methoxyphenols and trichloro-2-methoxyphenols were found.

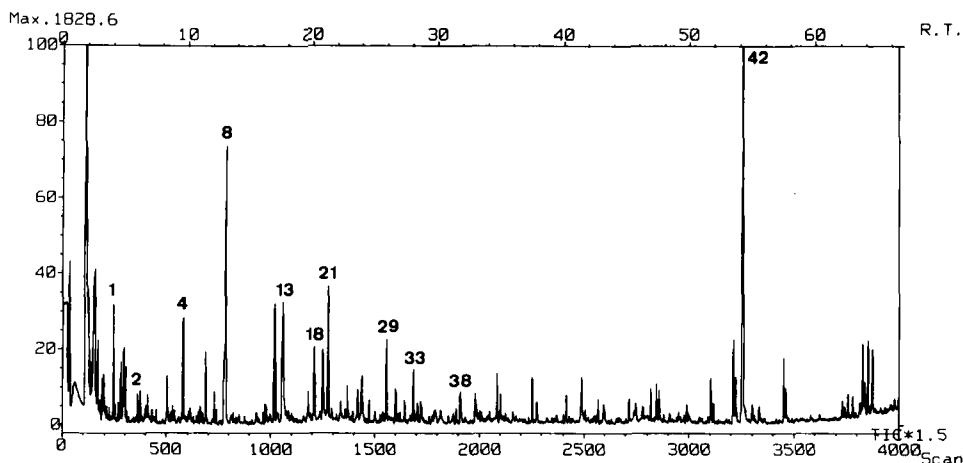
In model studies of alkaline and acidic spent bleach liquors by Lindstrom and Osterberg,<sup>2,4,5</sup> oxidative degradation revealed many chlorinated 2-methoxy-4-carboxyphenols and 2-hydroxy-4-carboxyphenols, in which the carboxy-group derives from the oxidized propane-type side chain. Our results indicate the

**Table 3** Aromatic pyrolysis products of pulp mill effluent Fraction H. Scan numbers refer to peaks in the total ion current chromatogram in Figure 2.

No.	$M^+$	Scan	Compound name	Structure
1	92	242	Toluene	
2	106	359	Ethylbenzene	
3	106	373	Dimethylbenzene	
4	94	577	Phenol	
5	108	728	2-methylphenol	
6	134	738	Isobutylbenzene	
7	108	775	4-methylphenol	
8	124	782	2-methoxyphenol (guaiacol,G)	G
9	148	965	Pentylbenzene	
10	122	973	Ethylphenol	
11	122	980	Dimethylphenol	
12	138	1017	2-methoxy-4-methylphenol	G-C
13	110	1056	1,2-dihydroxybenzene	
14	120	1084	4-vinylphenol	
15	140	1158	2-methoxy-4-hydroxyphenol	G-OH
16	124	1180	2-hydroxy-3-methylbenzene	
17	152	1208	2-methoxy-4-ethylphenol	G-C-C
18	158	1212	2-methoxy-6-chlorophenol	G-Cl
20	124	1250	1,2-dihydroxy-4-methylbenzene	
21	150	1275	2-methoxy-4-vinylphenol	G-C=C
22	154	1337	2,6-dimethoxyphenol (syringol,S)	S
23	164	1369	2-methoxy-4-(prop-2-enyl)phenol	G-C-C=C
24	166	1394	2-methoxy-4-propylphenol	G-C-C-C
25	152	1419	2-methoxy-4-formylphenol	G-COH
26	172	1435	2-methoxy-4-methyl-6-chlorophenol	Cl-G-C
27	164	1471	2-methoxy-4-(prop-1-enyl)phenol (c)	G-C=C-C
28	156	1538	2-6-dimethoxy-4-methylphenol	S-C
29	164	1555	2-methoxy-4-(prop-1-enyl)phenol (tr)	G-C=C-C
30	166	1599	2-methoxy-4-acetylphenol	G-CO-C
31	192	1599	2-methoxy-dichlorophenol	G-(Cl) <sub>2</sub>
32	184	1643	2-methoxy-4-vinyl-6-chlorophenol	Cl-G-C=C
33	180	1685	2-methoxy-4-(propan-2-on)phenol	G-C-CO-C
34	180	1787	2-methoxy-4-propanal-phenol	G-C-C-COH
35	194	1791	2-methoxy-4-(propane-1,2-dione)phenol	G-CO-CO-C
36	200	1878	2-methoxy-4-(chloropropyl)phenol (T)	G-C-C-C-Cl
37	198	1891	2-methoxy-4-(prop-2-enyl)-6-chlorophenol	Cl-G-C-C=C
38	182	1909	2-methoxy-4-methylcarboxy-phenol	G-C-COOH
39	214	1980	2-methoxy-4-(propan-2-one)-6-chlorophenol	Cl-G-C-CO-C
40	226	2000	2-methoxy-3,5,6-trichlorophenol	G-(Cl) <sub>3</sub>
41	218	2050	2-methoxy-4-vinyl-3,5,6-trichlorophenol	(Cl) <sub>3</sub> -G-C=C
42		2438	Phtalate	

presence of similar chlorinated phenolic substructures, but significant additional information is gained from the presence of more differentiated side chains in the lignin pyrolysis products. Only minor amounts of catecholic products are formed on pyrolysis, suggesting that the identification of significant amounts of catechols on permanganate oxidation may be a result of oxidation of methoxy-groups in the guaiacol core.





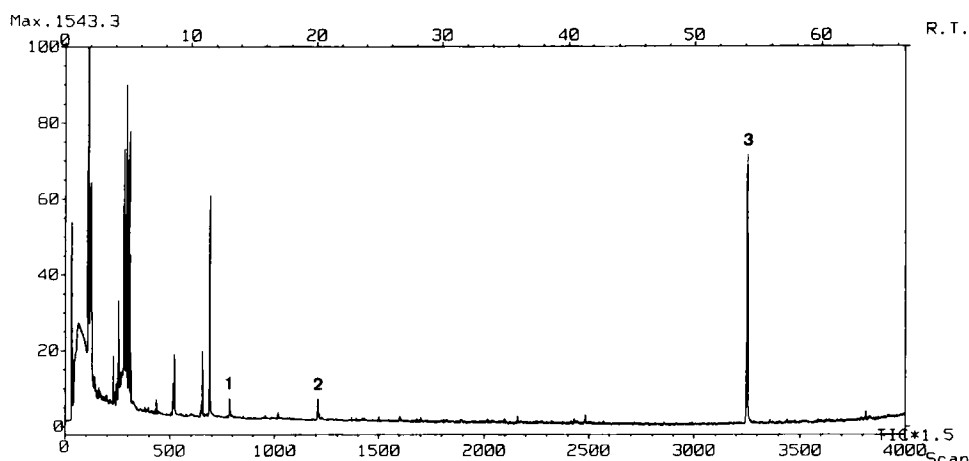
**Figure 2** Total ion current chromatogram of pulp mill effluent, Fraction H, 25 µg. Peak numbers refer to compounds listed in Table 3.

**Table 4** Aromatic pyrolysis products of pulp mill effluent Fraction M. Scan numbers refer to peaks in the total ion current chromatogram in Figure 3.

No.	$M^+$	Scan	Compound name	Structure
1	124	786	2-methoxyphenol (guaiacol,G)	G
2	158	1214	2-methoxy-6-chlorophenol	G-Cl
3		3252	Phtalate	

### *Pyrolysis of Pulp Mill Effluent Fraction M*

The TIC-chromatogram of this molecular weight fraction is given in Figure 3. The detected phenolic compounds have been listed in Table 4. 2-methoxyphenol and 2-methoxy-6-chlorophenol are the only significant phenolic peaks, and probably originate from chlorinated residual lignin. Relatively large amounts of carbohydrate markers were detected, mainly in two early eluting unresolved complex peaks. The limited number of peaks in the TIC-chromatogram of this fraction suggests a smaller amount of pyrolysed material than in the case of fraction H; integration of the two TIC-chromatograms however indicates that the amounts of pyrolysed material are comparable. It appears that this fraction has a relatively low lignin content and a high carbohydrate content. The high AOX-value of this fraction is accounted for only by 2-methoxy-6-chlorophenol, which has approximately the same peak height as 2-methoxyphenol. The absence of wide variety of lignin markers may be explained by the highly oxidized and chlorinated nature of the lignin in this fraction and by the effective removal of propane side-chains by chlorine-oxidation.<sup>19</sup> It is likely that ether bonds and the alkyl-aryl carbon bonds (propane side chain links) between the guaiacyl-monomers are oxidized/cleaved



**Figure 3** Total ion current chromatogram of pulp mill effluent, Fraction M, 25 µg. Peak numbers refer to compounds listed in Table 4.

more easily than aryl-aryl carbon bonds, carbon-chloride bonds, and carbon-methoxy group bonds.<sup>1</sup> Such degradation would lead to chlorinated guaiacyl oligomers linked by aryl-aryl carbon bonds. It is therefore not unexpected that the molecular weight fraction with the lowest carbon/chlorine ratio correlates with the oxidatively most degraded lignin.

## CONCLUSIONS

A range of chlorinated 2-methoxyphenols have been identified as pyrolysis products of macromolecular material in pulp mill effluent, probably originating from chlorinated lignin or liginosulfonic acid. The combination of ultrafiltration and pyrolysis gas chromatography mass spectrometry has been demonstrated to be an effective and rapid method for the analysis of chlorolignins in pulp mill effluent. A more detailed comparative study of oxidative degradation techniques and pyrolysis gas chromatography mass spectrometry of high molecular weight material in pulp mill effluent is in progress.

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