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ANALYSIS OF CHLORINATED GUAIACOLS IN SPENT BLEACH LIQUOR FROM A PULP MILL

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SUMMARY

Extraction stage spent bleach liquor from a pine kraft pulp mill was studied for its content of chlorinated guaiacols. The compounds were analysed by a method involving extraction with diethyl ether and glass capillary gas chromatography of their acetyl derivatives using a flame ionization detector and SE-30 and OV-351 quartz capillary columns. The structures of the components were confirmed by glass capillary gas chromatography–mass spectrometry. In quantitations both external and internal standard methods were used. All possible chlorinated guaiacols were used as reference substances. The guaiacol concentrations varied from *ca.* 0.004 to 1.57 ppm, the total concentration being about 4 ppm. 3,4,5-Trichloroguaiacol was present in the highest concentration (1.57 ppm). Other major components were tetrachloroguaiacol (1.21 ppm), 4,5-dichloroguaiacol (0.42 ppm) and 4,5,6-trichloroguaiacol (0.32 ppm). The identities and quantities of 4-chloro-, 5-chloro-, 3,4-dichloro-, 4,6-dichloro- and 3,4,6-trichloroguaiacol were also determined.

INTRODUCTION

In recent years chlorinated phenolic compounds have been the object of many intensive gas chromatographic (GC) and mass spectrometric (MS) studies. Of special interest have been chlorinated guaiacols which are formed during the production of pulp and paper^{1–10}. As chlorinated catechols are the main components of the chlorination (C-stage) effluents^{2,3,9}, chloroguaiacols dominate the E-stage effluents.

Several chlorinated guaiacols have been identified by MS in the effluents as their ethyl², acetyl³ and silyl⁴ derivatives. However, only five chlorinated guaiacols (5-chloro-, 4,5-dichloro-, 3,4,5-trichloro-, 4,5,6-trichloro- and tetrachloroguaiacol) have been previously used as reference substances. In addition, little work on the quantitation of those compounds has been reported^{2,3,8,10}. Recently we have carried out the syntheses¹¹ and the GC study¹² of all possible chlorinated guaiacols. The purpose of the present study was to identify and determine all possible chlorinated guaiacols occurring in more than 1 µg/l quantities in an E-stage spent bleach liquor from a Finnish pine kraft pulp mill.

EXPERIMENTAL

Preparation of samples

External standard. A 0.2% (w/v) solution in ethanol (99.5%) of each guaiacol (for the syntheses see refs. 11 and 12) was prepared as follows. A 200- μg amount of each compound was added to 0.5 l of distilled water. The mixture was acidified with 2 *N* sulphuric acid solution to pH 2 and extracted twice with 200 ml of diethyl ether. The combined ether extracts were concentrated to 10 ml by distillation and then transferred to separatory funnel. The solvent was evaporated to dryness with a nitrogen gas stream and the residue was dissolved in 20 ml of 0.1 *M* K_2CO_3 solution. Redistilled acetic anhydride (1 ml) was added and the mixture was shaken vigorously for 5 min. The mixture was then extracted with 10 ml of *n*-hexane and after concentration to 1 ml the organic layer was used as the external standard solution in quantitative as well as MS determinations.

Spent bleach liquor (SBL) sample. A mixture of 60 μg of 3,5-dichlorophenol (internal standard) and 0.5 l of E-stage spent bleach liquor from a Finnish pine kraft pulp mill was acidified to pH 2 with 2 *N* sulphuric acid solution and extracted twice with 200 ml of diethyl ether. The emulsions (precipitates) formed were filtered off with suction and washed with diethyl ether. The combined ether layers were concentrated to 1 ml and then treated further as described above.

GC analysis

A Perkin-Elmer Model Sigma 3 gas chromatograph equipped with a flame ionization detector (FID) was used in quantitations. An OV-351 (25 m \times 0.32 mm I.D.) quartz capillary column was employed. The carrier gas was nitrogen at a flow-rate of *ca.* 1 ml/min. The splitting ratio was 1:20 and the injector and detector temperatures were 275°C. The column temperature was raised from 80°C to 230°C at a rate of 6°C/min and then held for 10 min.

GC-MS analysis

MS investigations were carried out using a Varian MAT-212 mass spectrometer equipped with a Varian Series 3700 gas chromatograph. The quartz capillary columns contained OV-351 (same as in GC measurements) or SE-30 (25 m \times 0.22 mm I.D.). The capillary interface and ion source temperatures were 230°C and 300°C, respectively. The scan time was 1.5 sec per mass decade. The mass spectra were recorded at 70 eV from mass number 40 up to 400.

Quantitative analysis

Quantitative analyses were performed using both the internal standard (IS) and external standard (ES) methods. In the IS method, the amounts of the compounds were calculated as described by Lindström and Nordin². In the ES method, the amount of the substance, m_x , was calculated according to

$$m_x = m_s \cdot \frac{I_x}{I_s}$$

where m_s is the amount ($\mu\text{g/l}$) of compound *x* in the external standard solution, I_x the peak height (mm) of compound *x* in the external standard solution (1 μl of the

standard injected) and I_x the peak height (mm) of compound x in the SBL sample (1 μ l of the SBL sample injected). Before analysis the external standard mixture and the SBL sample were diluted accurately to the same volume (1 ml).

RESULTS AND DISCUSSION

Absolute retention times of acetyl derivatives of guaiacol, chlorinated guaiacols and internal standard (3,5-dichlorophenol) in GC-MS experiments are presented in Table I. Examples of real intensity chromatograms (RIC) and mass chromatograms are shown in Fig. 1. As reported previously¹², acetyl derivatives of chlorinated guaiacols can be successfully analysed using both the SE-30 and OV-351 quartz capillary columns. On the polar column, the 3,5- and 3,6-dichloro derivatives exhibit the same retention behaviour, but these substances can be separated on the non-polar SE-30 column (see Table I). The OV-351 stationary phase is, however, very suitable for the analysis of other polychloro derivatives and thus that column was used in the present study for quantitations.

The structures of nine acetylated chlorinated guaiacols 5, 6, 9, 10, 12, 13 and 15-17 (see Fig. 1) found to be present in the SBL extract were confirmed by recording the mass spectra, and in some cases by plotting mass chromatograms of certain characteristic ions. The fragmentation of some acetylated guaiacol derivatives have recently been published by Voss *et al.*¹³. However, in the present investigation, the mass spectra of all the structural isomers were found to be very similar, except for

TABLE I
RETENTION TIMES OF GUAIACOL DERIVATIVES IN GC-MS EXPERIMENTS

For GC-MS conditions see Experimental. S = Standard.

| No. | Acetylated compound | Retention time (min) | | | |
|-----|-------------------------|----------------------|-------|-------|-------|
| | | OV-351 | | SE-30 | |
| | | S | SBL | S | SBL |
| 1 | Guaiacol | 13.03 | — | 8.16 | — |
| 2 | 3,5-Dichlorophenol | 13.31 | 13.39 | — | — |
| 3 | 3-Chloroguaiacol | 15.07 | — | 10.43 | — |
| 4 | 6-Chloroguaiacol | 16.46 | — | 11.19 | — |
| 5 | 4-Chloroguaiacol | 17.01 | 17.08 | 11.38 | 11.38 |
| 6 | 5-Chloroguaiacol | 17.13 | 17.19 | 11.49 | 11.52 |
| 7 | 3,5-Dichloroguaiacol | 17.22 | — | 13.45 | — |
| 8 | 3,6-Dichloroguaiacol | 17.22 | — | 13.20 | — |
| 9 | 4,6-Dichloroguaiacol | 19.03 | 19.02 | 14.18 | 14.15 |
| 10 | 3,4-Dichloroguaiacol | 19.20 | 19.20 | 14.38 | 14.36 |
| 11 | 3,5,6-Trichloroguaiacol | 19.51 | — | 16.38 | — |
| 12 | 3,4,6-Trichloroguaiacol | 20.03 | 20.05 | 16.38 | 16.35 |
| 13 | 4,5-Dichloroguaiacol | 20.47 | 20.45 | 15.27 | 15.25 |
| 14 | 5,6-Dichloroguaiacol | 20.59 | — | 15.13 | — |
| 15 | 3,4,5-Trichloroguaiacol | 22.00 | 22.01 | 17.57 | 17.52 |
| 16 | 4,5,6-Trichloroguaiacol | 23.46 | 23.44 | 18.28 | 18.23 |
| 17 | Tetrachloroguaiacol | 24.02 | 24.00 | 20.28 | 20.28 |

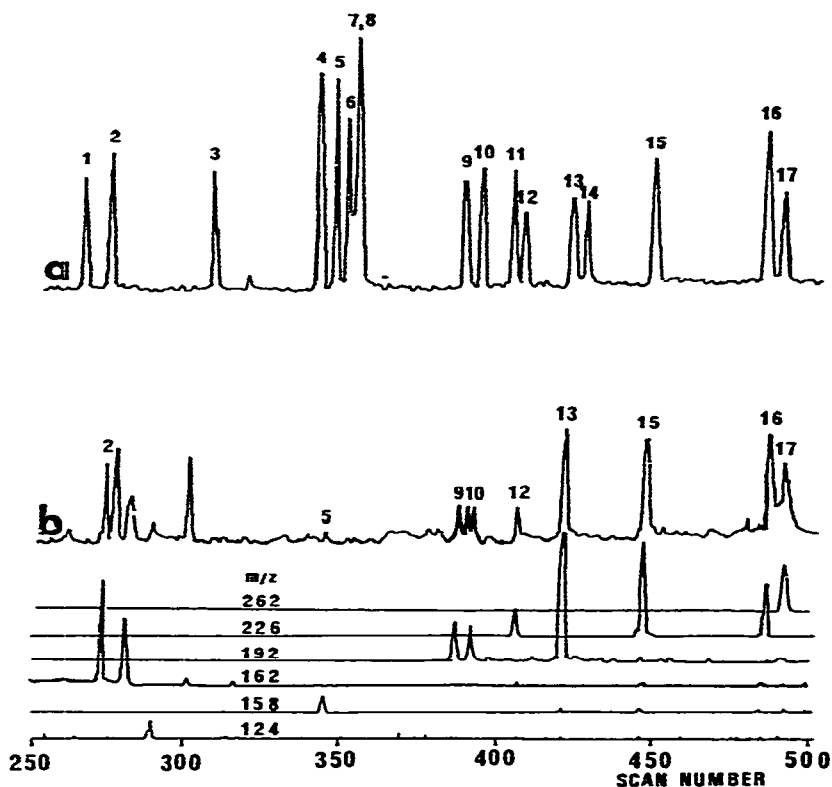


Fig. 1. Comparison of a GC-MS real intensity chromatogram of the mixture of acetylated guaiacols (a) and of the SBL extract (b). Mass chromatograms with certain ions are also given. The compounds are numbered as in Table I. For GC-MS conditions see Experimental.

small differences between the peak intensities. Thus, in future investigations, authentic reference substances must be available for the determination of the identities and quantities of all possible chloroguaiacols.

A gas chromatogram of the acetylated SBL extract is presented in Fig. 2. The concentrations of the individual guaiacols in SBL are given in Table II. Recently, three dichloroguaiacols, three trichloroguaiacols and tetrachloroguaiacol have been found to be present in different spent bleach liquors^{2,4}. However, few studies with model guaiacol reference substances have been published^{2,3,8,10}. According to those studies the main chloroguaiacols in E-stage SBL are tetrachloroguaiacol, 3,4,5- and 4,5,6-trichloroguaiacol and 4,5-dichloroguaiacol. For example, McKague⁸ found those substances in caustic sewer mill process streams in quantities of 0.31–0.95, 0.51–1.0, 0.11–0.37 and 0.10–0.97 ppm, respectively. As can be seen from Table II, the corresponding amounts in a Finnish effluent range from *ca.* 0.42 to 1.57 ppm. 3,4,5-Trichloroguaiacol was present in the highest concentration (*ca.* 1.57 ppm). This value is clearly higher than that reported previously¹⁰, which may be due to the different analysis procedures but also to the different spent bleach liquors used.

Of special interest are chlorinated guaiacols which have not been previously identified in SBL using authentic model substances. Lindström and Nordin² and later

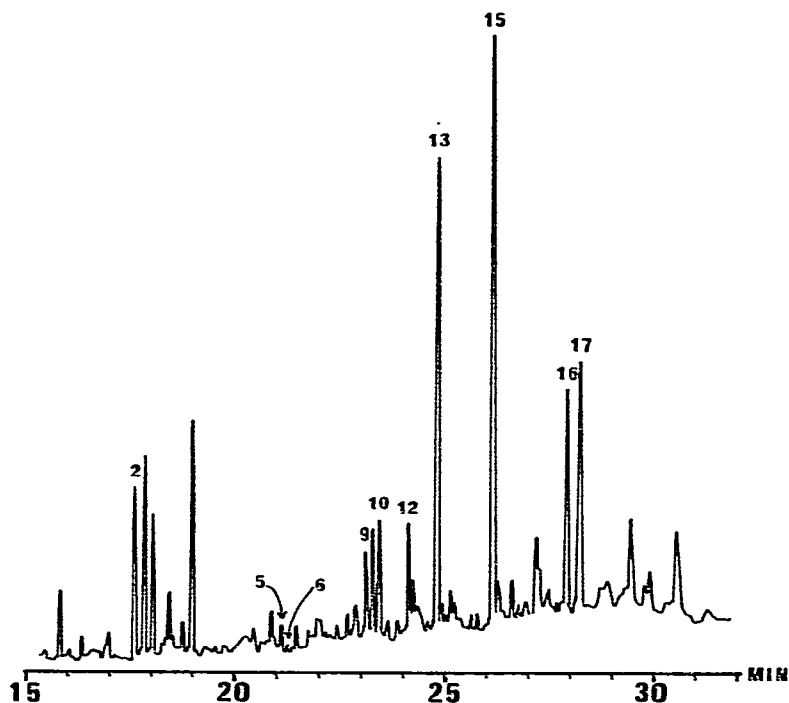


Fig. 2. GC-FID trace of acetylated guaiacols in the SBL extract. The compounds are numbered as in Table I. Column: OV-351. For GC conditions see Experimental.

TABLE II

CONCENTRATIONS OF CHLORINATED GUAIACOLS IN E-STAGE SPENT BLEACH LIQUOR

FID response factors (referred to internal standard, 3,5-dichlorophenol derivative) are also given. The detection limit was 1 $\mu\text{g/l}$ and the reproducibility of the results using ES and IS methods was *ca.* 10 and 5%, respectively. Amounts presented are mean values from four measurements. The compounds are numbered as in Table I.

| Acetylated compound | Amounts ($\mu\text{g/l}$) | | | Response factor |
|---------------------|-----------------------------|------|---------------|-----------------|
| | ES | IS | $(ES + IS)/2$ | |
| 2 | 60 | — | — | 1.00 |
| 5 | 26 | 13 | 20 | 0.85 |
| 6 | 5 | 3 | 4 | 1.15 |
| 9 | 73 | 66 | 70 | 1.15 |
| 10 | 97 | 88 | 93 | 1.15 |
| 12 | 150 | 145 | 148 | 1.98 |
| 13 | 470 | 370 | 420 | 1.18 |
| 15 | 1560 | 1580 | 1570 | 3.93 |
| 16 | 315 | 314 | 315 | 2.19 |
| 17 | 1200 | 1226 | 1213 | 7.40 |

Holmbom⁴ identified two previously unknown dichloroguaiacol isomers in E-stage effluents as ethyl and silyl derivatives, respectively. These dichloro derivatives are the 4,6- and 3,4-dichloro isomers (9 and 10) which have different retention times as the ethyl derivatives on non-polar columns such as SE-30² and SP-2100¹². The total amount of compounds 9 and 10, found in our study is slightly more than 150 $\mu\text{g/l}$ which agrees well with the results presented by Holmbom and Lehtinen¹⁰.

Some speculations have also been made regarding the two compounds 3,5,6-tri- and 3,4,6-trichloroguaiacol (11 and 12)^{6,13}, one of which has been proposed to be formed in pulp bleaching. The synthesis of isomer 11 has been described by Koopman¹⁴, whereas isomer 12 has, until now, remained unknown. In the present study, however, a mixture (*ca.* 1:1) of compounds 11 and 12 has been used as a reference mixture in the analysis. As can be seen, in Fig. 1 the structural isomer eluting more slowly on the OV-351 column is also present in SBL. The mass spectra of the two isomers are similar but, as previously proposed¹², the isomer in SBL should be the 3,4,6-trichloro derivative. This assignment was also based upon a consideration of reactions that occur between guaiacyl propane units in lignin and chlorine at the chlorination stage of the bleaching process. A verification of the structure of compound 12 (see Fig. 2) can be made after having synthesized the authentic reference substance 11 or 12 (or both of them) and after determining the retention times of the acetyl derivatives of these substances.

Finally, Lindström and Nordin² have reported one of four possible monochloroguaiacols to be present in E-stage effluents. The present study shows that this compound is, as expected, 4-chloroguaiacol (amount *ca.* 20 $\mu\text{g/l}$). Its isomer, 5-chloroguaiacol (6), was also found in small amounts by plotting mass chromatograms of the most abundant *m/z* values in the mass spectra of monochloro derivatives (see Fig. 3).

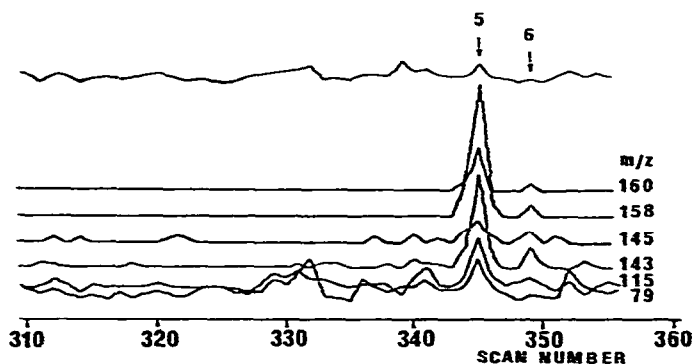


Fig. 3. Computer reconstructed limited mass chromatogram obtained from the sample in Fig. 2. Peaks 5 and 6 represent acetylated monochloroguaiacol isomers. Column: OV-351. For GC-MS conditions see Experimental.

CONCLUSION

The identities and concentrations of nine chlorinated guaiacols in a Finnish pine kraft pulp mill have been determined. In quantitations, internal and external standard methods have yielded similar results. The present analysis method is ap-

plicable to the determination of chloroguaiacols in concentrations greater than 1 $\mu\text{g/l}$. When smaller amounts must be analysed, their determination as trichloroacetyl or heptafluorobutyryl derivatives with electron-capture detection and both SE-30 and OV-351 quartz capillary columns is recommended.

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