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Short Communication

Determination of chlorinated benzaldehydes and acetophenones in pulp bleaching effluents by gas chromatography

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ABSTRACT

Application of modern sequences involving chlorine, chlorine dioxide and oxygen–alkali to the bleaching of hardwood pulps has led to the formation of chlorinated benzaldehydes and acetophenones as the major chlorinated phenols in the bleaching filtrates. Compounds identified in the filtrates include the chloro derivatives of vanillin, acetoguaiacone, syringaldehyde and acetosyringone. Thirteen of these compounds were converted to their acetates by *in situ* acetylation and were analysed by GC on a J&W DB5 capillary column. Chlorovanillins (2-chlorovanillin, 2,5- and 2,6-dichlorovanillin), chloroacetoguaiacones (2-, 5- and 6-chloroacetoguaiacone) and chloroacetosyringones (2-chloroacetosyringone and 2,6-dichloroacetosyringone) were positively identified as components of filtrates from bleaching of kraft pulps for the first time, along with the five other compounds tested. Satisfactory separation for all analytes was achieved except for 5-chloroacetoguaiacone and 2,5-dichlorovanillin, which co-eluted. Analysis of the latter compounds could be accomplished by mass detection with target ion monitoring. The DB5 column is thus useful for the analysis of the chlorinated benzaldehydes and acetophenones.

INTRODUCTION

The bleaching of wood pulps with molecular chlorine or reagents containing chlorine (chlorine dioxide, hypochlorite) leads to the formation of chlorinated phenols which as components of the effluents have known environmental effects [1]. The chlorinated phenols derive from the residual lignin in the pulps; the major analytes in effluents from bleaching of softwood pulps are chlorophenols, chlorocatechols, chloroguaiacols and chlorovanillins [2], whereas hardwood pulps give, in addition, chlorosyringols and chloro syringaldehydes [3]. Knowledge of the types and amounts of chlorinated phenols in bleaching effluents is an important factor in assessing the environmental quality of the effluents.

In response to the drive to minimise the formation of chlorinated organic compounds in bleaching effluents, continual changes in bleaching technology are taking place. Some of these modifications are oxygen delignification prior to bleaching, the use of chlorine dioxide instead of molecular chlorine in the first bleaching stage, and the reinforcement of the alkali extraction stage with oxygen [4]. These modifications have led to the preponderance of chlorovanillins in

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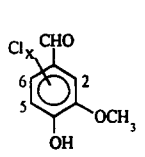
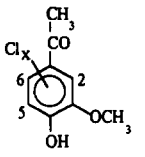
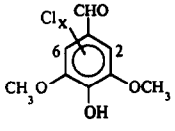


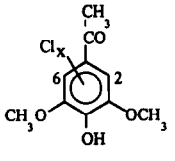
Chlorovanillins



Chloroacetoguaiacones



Chlorosyringaldehydes



Chloroacetosyringones

the effluents from bleaching of softwood pulps [5,6] and chlorovanillins, chlorosyringaldehydes and chloroacetosyringones with lesser amounts of chloroacetoguaiacones from bleaching of hardwood pulps [7]. Thus the composition of chlorinated phenols in the effluents is changing as the new technology is adopted, and the analytical techniques must be appropriate to accommodate these changes.

The chlorinated phenols in bleaching effluents are usually estimated by the procedure of Voss *et al.* [8] involving *in situ* acetylation GC with electron-capture detection (ECD). The method was assessed in an intercalibration study involving 11 laboratories in Scandinavia [9], and while it was found to be satisfactory for chlorophenols and chloroguaiacols, the precision obtained in the analysis of the chlorocatechols was poor. Lee *et al.* [10] applied a modified *in situ* acetylation procedure to the analysis of a total of 31 chlorinated phenols, and found good recoveries for all compounds including chlorocatechols, with the exception of 4-chlorocatechol. A recent study of the analysis of chlorinated phenols in pulp mill effluents has described a procedure in which acetylation is carried out after extraction [11].

Knuutinen and co-workers have reported the GC separation of the acetates of chlorinated phenols [12], catechols [13] and guaiacols [14], and the three classes of compounds in admixture [15]. In this paper, we describe the GC separation of ring-chlorinated derivatives of vanillin, syringaldehyde, acetoguaiacone and acetosyringone as their acetates after subjecting them to the *in situ* acetylation procedure, and the application of the method to the analysis of pulp bleaching filtrates.

EXPERIMENTAL

Chemicals

1,3-Dichlorobenzene, 2,3,6-trichlorophenol, 2-bromophenol, vanillin, syringaldehyde, acetoguaiacone and acetosyringone were purchased from Aldrich. The remaining compounds were prepared by established techniques. Satisfactory spectral and analytical data were obtained for new compounds.

2-Chlorovanillin was prepared from vanillin via the 2-nitro derivative by the method of Raiford and Lichty [16] as modified by Ross *et al.* [17]. 5-Chlorovanillin was the product of direct chlorination of vanillin [18], and 6-chlorovanillin was prepared by chlorination of benzalvanillin triacetate [16]. Chlorination of 2-chlorovanillin and 6-chlorovanillin yielded 2,5-dichlorovanillin and 5,6-dichlorovanillin respectively, and 2,6-dichlorovanillin was obtained from 6-chlorovanillin through the 2-nitro intermediate [16].

The ring-chlorinated acetoguaiacones, 5-chloroacetoguaiacone and 6-chloroacetoguaiacone, were prepared from the acetates of 5-chlorovanillin and 6-chlorovanillin respectively by reaction with diazomethane and subsequent hydrolysis [19]. Similarly, the hitherto-unknown 2-chloroacetoguaiacone, m.p. 97–98°C, was prepared from the acetate of 2-chlorovanillin.

Chlorination of syringaldehyde and acetosyringone in dioxane with 1 mol.equiv. chlorine in acetic acid gave 2-chlorosyringaldehyde, m.p. 108–109°C, and 2-chloroacetosyringone, m.p. 93–94°C, respectively. Analogously, reaction with 2 mol.equiv. chlorine afforded 2,6-dichloroacetosyringone, m.p. 114–115°C. 2,6-Dichlorosyringaldehyde, m.p. 195–196°C, was obtained by chlorination of syringaldehyde acetate in acetic acid, and subsequent alkaline hydrolysis. These four compounds have not been previously described.

Bleaching of wood pulp

An oxygen-delignified eucalypt kraft pulp was treated with an aqueous solution of chlorine at pH ≈ 2, washed, and was subsequently extracted in a steel autoclave with a sodium hydroxide solution in the presence of oxygen [7]. The filtrate from the alkaline extraction was acidifed to pH 2 with 18 *M* sulphuric acid and stored at −12°C until required for analysis.

Acetylation and extraction of the phenols

Analysis with ECD. To a well-mixed solution of the bleach filtrate (10 ml) in a test tube, an aliquot of 2,3,6-trichlorophenol (25 μl of 25 μg/ml solution in methanol) was added as the internal standard, and 2-bromophenol (25 μl of a 5.0 μl/ml solution in methanol) was added as the surrogate standard. Potassium carbonate solution (72%, 1.0 ml) was added with swirling, followed by acetic anhydride (1.0 ml). The contents of the test tube were mixed on a vortex mixer for 1.0 min, distilled hexane (5 ml) was added, and mixing was continued for a further 0.5 min. Part of the hexane solution which separated (1 ml) was transferred to a sample vial, and 1,3-dichlorobenzene (25 μl of 130 μg/ml solution in methanol) was added as check on the injection prior to the GC analysis.

Analysis with the mass-selective detector (MS). A solution of the bleach filtrate (50 ml) was placed in a 100 ml separating funnel, and an aliquot of 2,3,6-trichlorophenol (250 μl of 25 μg/ml solution in methanol) was added as the internal standard. Potassium carbonate solution (72%, 1.0 ml) was added with swirling, followed by acetic anhydride (1.0 ml), and the mixture was shaken with frequent venting for 1.0 min. Distilled hexane (5 ml) was added, and mixing was continued for a further 0.5 min. The hexane solution was removed, and was concentrated to *ca.* 1 ml by passing a stream of nitrogen over the solution, and was transferred to a sample vial for GC analysis.

Gas chromatography

GC was carried out on a Hewlett-Packard HP5890 series II chromatograph fitted with an autoinjector, an electron-capture detector and an HP5971 mass-selective detector. The column used for the analyses was a J&W bonded phase DB5 fused-silica column (30 m × 0.25 mm I.D.) with a phase thickness 0.25 μm. Additional data were obtained on an SGE bonded phase BP20 fused-silica column (12 m × 0.25 mm I.D.). Purified helium was used as the carrier gas with a linear flow velocity 30 cm/s. Injector and detector temperatures were 300°C. The column temperature was kept at 50°C for 1 min, then programmed at 5°C/min to 250°C, and 20°C/min to 280°C. Injections were splitless, 2.0 μl for analyses using ECD and 4.0 μl for analyses with MS, and a purge delay of 0.75 min was used. For MS, electron impact (70 eV) spectra were obtained for masses 40 to 450 u.

RESULTS AND DISCUSSION

The GC behaviour of a mixture of 46 acetylated chlorinated phenols, catechols and guaiacols on an SE-30 quartz capillary column was studied by Knuutinen and Korhonen [15]. Lee *et al.* [10] tested four capillary columns of different manufacture and polarity, and concluded that the columns with a bonded phase containing 5% phenyl silicone gave the best resolution of their 31 acetylated chlorinated phenols. The column with the same bonded phase, a 30 m J&W DB-5 fused-silica column, was used in the present work.

The *in situ* acetylation technique is satisfactory for the analysis of chlorinated phenols in effluents from pulp bleaching, providing care is taken to ensure the precision of the chlorocatechol analyses. We found that after rendering the solution to be analysed alkaline with sodium carbonate, the recoveries of chlorocatechols were poor unless the extraction with hexane was carried out immediately. As well as the internal standard, 2,3,6-trichlorophenol, a surrogate standard, 2-bromophenol, was added to the solutions before the derivatisation–extraction procedure. An aliquot of 1,3-dichlorobenzene was added to the final hexane solution to check the amount of solution injected into the GC system.

The chromatogram of the mixed acetylated phenols with mass detection is presented in Fig. 1A, and the retention times of the phenols are given in Table I. It can be seen that the

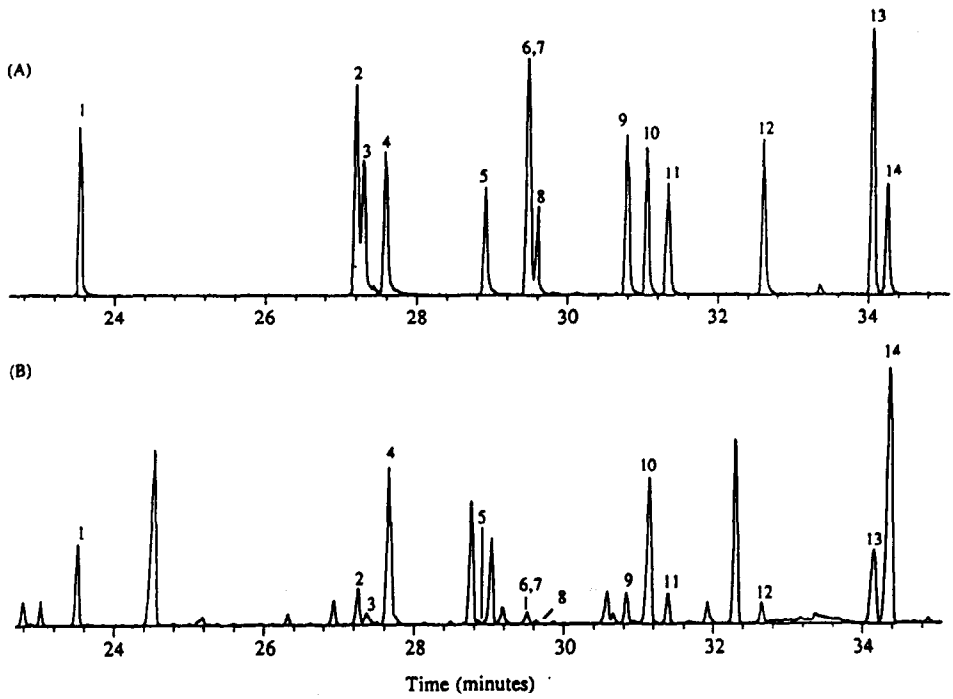


Fig. 1. Gas chromatogram with MS detection of (A) a standard mixture of acetylated phenols (numbers refer to compounds listed in Table I) and (B) a mixture of acetylated chlorinated phenols obtained by *in situ* acetylation of a filtrate from treatment of a chlorinated eucalypt kraft pulp with oxygen-alkali.

TABLE I

GC RETENTION TIMES OF ACETYLATED CHLORINATED PHENOLS

GC conditions as outlined in the Experimental section.

Peak No.	Phenol	Retention time (min)	Relative retention time
1	2,3,6-Trichlorophenol	23.50	1.00
2	2-Chlorovanillin	27.23	1.159
3	5-Chlorovanillin	27.35	1.164
4	6-Chlorovanillin	27.65	1.177
5	2-Chloroacetoguaiacone	28.91	1.230
6	5-Chloroacetoguaiacone	29.48	1.254
7	2,5-Dichlorovanillin	29.51	1.256
8	6-Chloroacetoguaiacone	29.61	1.260
9	5,6-Dichlorovanillin	30.81	1.311
10	2-Chlorosyringaldehyde	31.08	1.323
11	2,6-Dichlorovanillin	31.39	1.336
12	2-Chloroacetosyringone	32.62	1.388
13	2,6-Dichloroacetosyringone	34.11	1.451
14	2,6-Dichlorosyringaldehyde	34.32	1.460

13 acetylated benzaldehydes and acetophenones are separated well, with the exception of 5-chloroacetoguaiacone and 2,5-dichlorovanillin. Attempted separation of these components on a polar SGE BP20 column was not successful, as the analytes were retained on the column. In general, the J&W DB5 column is able to separate most of the chlorinated phenols in the bleaching effluents [10], and its continued use is recommended.

A GC trace with MS detection of an acetylated extract from a typical oxygen-reinforced alkali extraction of chlorinated eucalypt kraft pulp is given in Fig. 1B. The presence of 2,5-dichlorovanillin and 5-chloroacetoguaiacone in the peak at *ca.* 29.5 min may be ascertained by inspection of the mass spectra, and their quantification may be achieved by monitoring the m/z $220^{+\cdot}$ and $185^{+\cdot}$ ions respectively. The chlorovanillins, 2-chlorovanillin, 2,5- and 2,6-dichlorovanillin, the chloroacetoguaiacones, 2-, 5- and 6-chloroacetoguaiacone, and the chloroacetosyringones, 2-chloroacetosyringone and 2,6-dichloroacetosyringone, have not previously been positively identified in the effluents from pulp bleaching [20]. Both 5-chlorovanillin and 6-chlorovanillin have been reported as components of bleach effluents. However, 2-chlorovanillin is present in greater amounts than 5-chlorovanillin in an alkaline extraction filtrate following chlorination (Fig. 1B), and as the retention time of 2-chlorovanillin and 5-chlorovanillin are similar, it is possible that the compound analysed in the earlier studies was the 2-chloro isomer. An additional peak occurring in the acetylated bleaching filtrate at 33.42 min (Fig. 1B) is probably the acetate of 2,5,6-trichlorovanillin. The mass spectrum of the peak was consistent with the acetate of 2,5,6-trichlorovanillin (m/z $[M]^+$ 296).

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