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PHENOLIC CONSTITUENTS IN PULP MILL PROCESS STREAMS

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SUMMARY

Concentrations and identities of phenols in seven in-plant process streams at a bleached kraft pulp mill were determined. Phenols were analyzed by a method involving absorption on Amberlite XAD-2 resin at pH 2, liquid–liquid partitioning and electron capture gas chromatography of their heptafluorobutyrates. Results were compared with those obtained by the standard 4-aminoantipyrene method. Total concentrations of phenols ranged from a low of 0.05–0.45 mg/l in the acid sewer to a high of 5.1–11 mg/l in sewered condensates. Guaiacol was present in sewered condensates in concentrations up to 5 mg/l, the highest for any individual phenol. Guaiacol, vanillin and 4-hydroxy-3-methoxyacetophenone were major phenols in unbleached whitewater, and 3,4,5-trichloroguaiacol, tetrachloroguaiacol and 4,5-dichloroguaiacol were major phenols in the caustic sewer.

INTRODUCTION

A variety of methods are available for the analysis of phenols. The standard colorimetric analysis using 4-aminoantipyrene (4-AAP) is sensitive to levels of a few μg/l, however, most *para*-substituted phenols cannot be measured and the identity of the various phenols remains unknown[1]. Analysis by gas chromatography (GC) permits measurement of concentrations of individual phenols and a variety of derivatizing reagents have been employed for this purpose[2].

A number of recent publications concerning the analysis of phenols describe methods for chlorophenols. Detection of very low levels of chlorophenols is possible by electron capture GC of chlorophenol acetates[3], ethyl ethers[4] or other derivatives. Use of electron capture GC for the detection of low levels of non-chlorinated phenols requires derivatization with a halogen containing reagent. Non-halogenated phenols have been analyzed as the trifluoroacetate[5], heptafluorobutyrate[6] and pentafluorobenzyl ether[7] derivatives.

Lignin is partially degraded to a variety of monomeric phenols during the production of pulp and paper. Most of the phenols produced are substituted guaiacols or catechols whose formation may be rationalized by cleavage of bonds linking the basic propylguaiacol building blocks in lignin and by subsequent reactions such as chlorination during bleaching of the pulp. Process streams within the mill

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carry these phenols to effluent sewers and may result in some of these compounds being discharged into the environment. Some phenols can taint water at a level of 1 $\mu g/l$[8] and studies have demonstrated chlorinated guaiacols bioaccumulate in fish[8]. Sensitive methods are therefore required for the analysis of phenols resulting from pulp and paper processes.

The degradation of lignin during the production of pulp and paper results in the formations of both chlorinated and non-chlorinated monomeric phenols. This paper describes use of the heptafluorobutyrate derivative to measure phenols in seven process streams of a bleached kraft mill and compares results with those obtained by the 4-AAP method.

EXPERIMENTAL

Samples

4- to 8-h composite samples of seven mill streams were collected on two occasions and six streams were sampled on a third occasion from a kraft pulp mill in interior British Columbia. The three main sewers, namely, acid, caustic and general were sampled along with the clarifier influent which is a combination of the three. Process streams which contribute to the general sewer, namely unbleached white-water (UWW) or the pulp wash prior to bleaching, and sewered condensates from condensors were sampled. In addition, the general sewer was sampled above the point of introduction of the UWW or sewered condensates. Samples were adjusted to pH 4, preserved with copper sulfate and packed in coolers of ice at the time of collection. After shipment to B.C. Research the samples were stored at 2°C until analyzed.

Analyses

Samples were analyzed by the standard 4-AAP (chloroform extraction) method and in duplicate as follows: an amount of 10–25 g of sodium chloride was dissolved in 100–250 ml of the sample adjusted to pH 2. Samples were passed over 30 min through 50 ml columns packed with Amberlite XAD-2 resin prewashed with 250 ml diethyl ether, 250 ml methanol and 500 ml distilled water. Columns were eluted with 250 ml diethyl ether and the eluate was transferred to a separatory funnel. Excess aqueous layer was discarded and the ether extracted with 2 × 10 ml 0.5 *M* sodium bicarbonate, 1 × 10 ml water and 2 × 10 ml 0.5 *M* sodium hydroxide. The sodium hydroxide extracts were combined and acidified with 20 ml 1 *M* HCl and extracted with 2 × 20 ml diethyl ether. The ether extract was concentrated at room temperature to 1–2 ml on a rotary evaporator, 2–3 ml benzene added and the sample filtered by gravity through anhydrous magnesium sulphate into a 10-ml volumetric flask. The anhydrous magnesium sulphate was washed in portions with additional benzene (*ca.* 6 ml), 0.25 ml of 10–100 $\mu g/ml$ 2,3-dichlorophenol in benzene added as internal standard, and the solution made up to volume with benzene. A 1–2-ml portion of the benzene solution was transferred to a 15-ml centrifuge tube and washed with 2 × 0.5 ml water using a Vortex stirrer. The benzene was dried (anhydrous $MgSO_4$) and 0.5 ml derivatized with 200 μl 0.1 *M* trimethylamine in benzene and 20 μl heptafluorobutyric anhydride in a centrifuge tube using a Vortex stirrer to homogenize the mixture. After standing 15 min at room temperature the solution was washed with 3 × 0.5 ml phosphate buffer, pH 6, using a Vortex stirrer, diluted with benzene and 2 μl

analyzed by GC with an electron capture detector (ECD). The first two sets of samples were analyzed on a column 180 cm × 3 mm I.D., 10% OV-17 (Western Chromatography Supplies, Richmond, Canada) at 90°C for 8 min followed by programming to 180°C at 4°/min. The third set of samples was analyzed on a 12-m SP2100 (Western Chromatography Supplies) capillary column. After an initial hold at 50°C for 8 min the temperature was programmed to 140°C at 2°/min.

Concentrations of individual phenols were determined by reference to the internal standard 2,3-dichlorophenol and using appropriate response factors. Phenols were identified by mixed injections with authentic samples or by gas chromatography–mass spectrometry of the methyl ethers obtained by derivatization with diazomethane.

Recoveries of 2,4,6-trichlorophenol and 4,5-dichloroguaiacol from distilled water and a sample of whole mill effluent spiked with 10 μg/l of each phenol were determined in the same manner.

Standards

Guaiacol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, vanillin, 4-hydroxy-3-methoxyacetophenone and dihydroconiferyl alcohol were purchased from chemical suppliers. Chlorination of guaiacol according to methods described in the literature provided 4,5-dichloroguaiacol[9], 4,5,6-trichloroguaiacol[10] and tetrachloróguaiacol[10]. The isomeric 3,4,5-trichloroguaiacol was prepared by monomethylation of 3,4,5-trichlorocatechol with methyl iodide and anhydrous potassium carbonate followed by purification on polyamide. All standards were at least 95% pure as determined by GC of the heptafluorobutyrate derivatives.

RESULTS AND DISCUSSION

Recoveries of 2,4,6-trichlorophenol and 4,5-dichloroguaiacol from distilled water and whole mill effluent were 77–95% (see Table I). Blank determinations revealed no interfering peaks were present at levels higher than 1 μg/l in either sample at the retention times of either phenol or the standard. Similar recoveries were obtained with higher concentrations of standards, however, lower concentrations were not studied since analysis of process streams soon revealed concentrations of most phenols were substantially higher than 10 μg/l.

TABLE I
RECOVERIES OF 2,4,6-TRICHLOROPHENOL AND 4,5-DICHLOROGUAIACOL FROM DISTILLED WATER AND WHOLE MILL EFFLUENT

Compound	*Distilled water (%)*	*Whole mill effluent (%)*
2,4,6-Trichlorophenol	77	86
4,5-Dichloroguaiacol	95	83

The total concentration ranges of phenols in each process stream as determined by the 4-AAP method and by summation of peak areas of individual heptafluorobutyrates is shown in Table II. Phenols were highest in UWW and sewered condensates and lowest in the acid sewer by both methods. Generally 90% or more of

TABLE II
TOTAL CONCENTRATION RANGES (mg/l) OF PHENOLS IN MILL PROCESS STREAMS

Method	*Clarifier influent*	*General sewer*	*General sewer before UWW*	*UWW*	*Sewered condensates*	*Acid sewer*	*Caustic sewer*
GC	0 68–1 7	0.77–3.0	0.2 –1.0	2 7–7 4	5 1–11	0 05–0 45	0.55–2 2
4-AAP	1.1–1.2	1.5–2.0	0 37–0 89	4.0–4.9	6.6–16	0 15–0.32	0 50–1.1

the total peak area in GC chromatograms of phenol heptafluorobutyrates could be accounted for by known phenols.

Concentrations of individual phenols in the various process streams are shown in Table III. Guaiacol was found in sewered condensates in concentrations up to 5 mg/l, the highest for any individual phenol. Guaiacol, vanillin and 4-hydroxy-3-methoxyacetophenone (acetoguaiacone) were the major phenols in UWW (see Figs. 1 and 2). Concentrations ranged from 1.0–2.6 mg/l for guaiacol, 0.82–2.1 mg/l for vanillin and 0.66–1.7 mg/l for 4-hydroxy-3-methoxyacetophenone. These phenols were also present in clarifier influent and the general sewer as expected. The caustic

TABLE III
CONCENTRATION RANGES (mg/l) OF INDIVIDUAL PHENOLS IN MILL PROCESS STREAMS

	Clarifier influent	*General sewer*	*General sewer before UWW*	*UWW*	*Sewered condensates*	*Acid sewer*	*Caustic sewer*
Guaiacol	0 24–0.65	0 45–1 4	0.14–0.59	1.0 –2 6	4 0 –5 0	–	–
2,4-Dichloro-phenol	–	–	–	–	–	0–0 03	0–0 06
2,4,6-Tri-chlorophenol	–	–	–	–	–	0–0 03	0 03–0 11
4,5-Dichloro-guaiacol	0–0 04	–	–	–	–	–	0 10–0 97
3,4,5-Tri-chloro-guaiacol	0 23–0.49	–	–	–	–	–	0.51–1.0
Vanillin	0 23–0 49	0 14–0 62	0 01–0.16	0 82–2 1	0–1.5	–	–
4-Hydroxy-3-methoxy-acetophenone	0 09–0 32	0 15–0 57	0 02–0 12	0 66–1 7	0–1.4	–	–
4,5,6-Tri-chloro-guaiacol	0.03–0 10	–	–	–	–	–	0 11–0 37
Tetrachloro-guaiacol	0 06–0 12	–	–	–	–	–	0.31–0.95
4-Hydroxy-3-methoxy-propiophenone	0 06–0 12	0 02–0 08	0 02	0 15–0 20	0.04–0 21	–	–
Dihydro-coniferyl alcohol	–	0 13*	0 41*	0 41*	0 48*	–	–

* Single determination

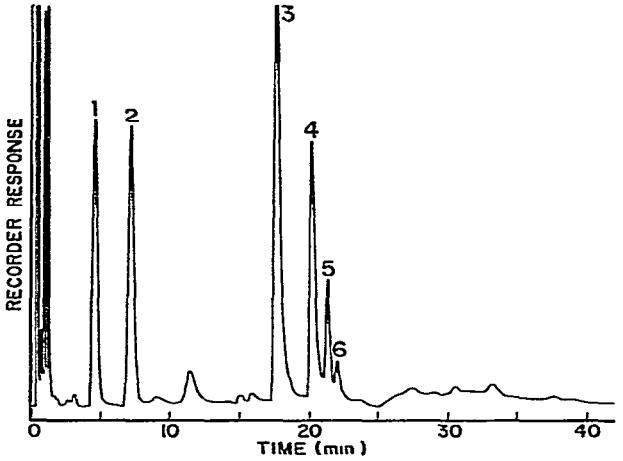

Fig 1. Chromatogram of phenol heptafluorobutyrates from a sample of UWW. GC on OV-17 using conditions described in Experimental. Peaks. 1 = guaiacol; 2 = 2,3-dichlorophenol standard; 3 = vanillin; 4 = 4-hydroxy-3-methoxyacetophenone; 5 = dihydroconiferyl alcohol; 6 = 4-hydroxy-3-methoxypropiophenone

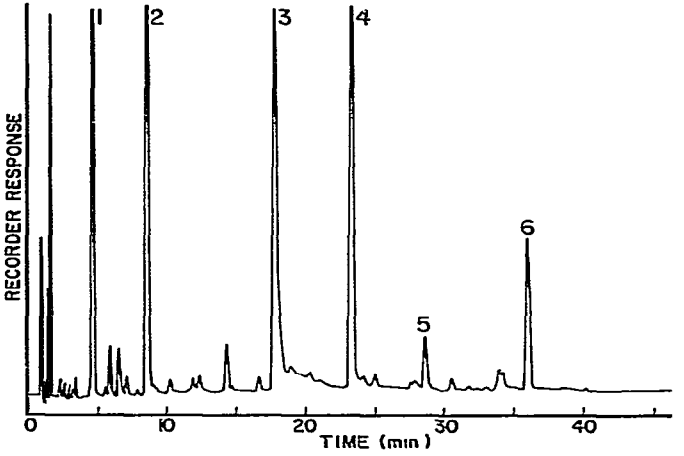

Fig. 2. Chromatogram of phenol heptafluorobutyrates from a sample of UWW. GC on SP2100 using conditions described in Experimental Peaks 1 = guaiacol; 2 = 2,3-dichlorophenol standard; 3 = vanillin, 4 =4-hydroxy-3-methoxyacetophenone; 5 = 4-hydroxy-3-methoxypropiophenone, 6 = dihydroconiferyl alcohol

sewer contained a variety of chlorinated phenols, major ones being 3,4,5-trichloroguaiacol (0.51–1.0 mg/l), tetrachloroguaiacol (0.3–0.95 mg/l) and 4,5-dichloroguaiacol (0.10–0.97 mg/l) as shown in Figs. 3 and 4.

Capillary column GC was required to separate all the phenol heptafluorobutyrates. The following pairs of phenol derivatives had the same retention times on the OV-17 packed column: vanillin and 3,4,5-trichloroguaiacol, dihydroconiferyl alcohol and 4,5,6-trichloroguaiacol, and 4-hydroxy-3-methoxypropiophenone and tetrachloroguaiacol (see Figs. 1 and 3). All phenol heptafluorobutyrates listed in Table III separated readily on the SP2100 capillary column.

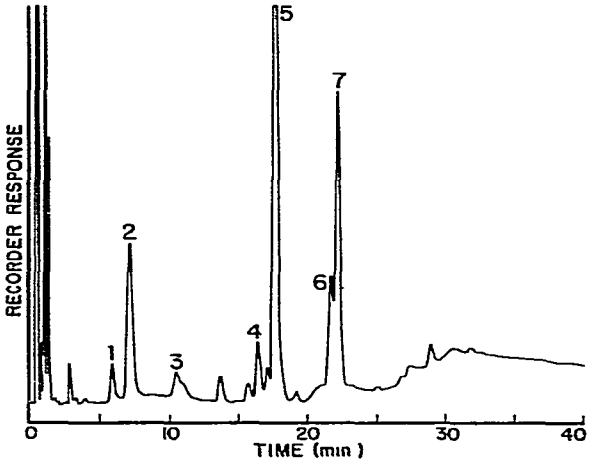

Fig 3. Chromatogram of phenol heptafluorobutyrates from a sample of caustic sewer. GC on OV-17 using conditions described in Experimental. Peaks. 1 = 2,4-dichlorophenol; 2 = 2,3-dichlorophenol standard; 3 = 2,4,6-trichlorophenol; 4 = 4,5-dichloroguaiacol; 5 = 3,4,5-trichloroguaiacol, 6 = 4,5,6-trichloroguaiacol; 7 = tetrachloroguaiacol.

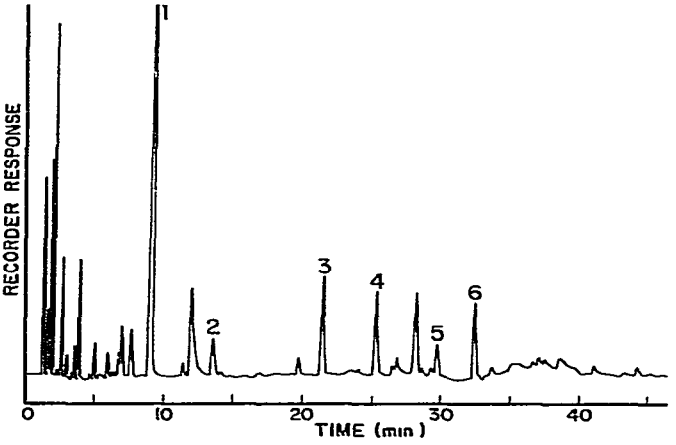

Fig. 4. Chromatograms of phenol heptafluorobutyrates from a sample of caustic sewer. GC on SP2100 using conditions described in Experimental Peaks· 1 = 2,3-dichlorophenol standard; 2 = 2,4,6-trichlorophenol; 3 = 4,5-dichloroguaiacol; 4 = 3,4,5-trichloroguaiacol; 5 = 4,5,6-trichloroguaiacol; 6 = tetrachloroguaiacol

The method described permits analysis of both chlorinated and non-chlorinated phenols. While our work was in process use of XAD-2 resin in the first step of the 4-AAP method was reported[11]. Attempts to employ extraction with ether instead of Amberlite XAD-2 resin in the first step were not successful with many of our samples because of the formation of emulsions. The separation of phenols from carboxylic acids and non-acidic compounds by liquid–liquid extraction has been used previously in a procedure to measure chlorophenols in bleach plant effluents[4]. Attempts to derivatize chlorinated catechols, known constituents of chlorination-

stage effluents[4,12] gave variable results. Derivatization was inconsistent and efforts are being made to determine the reasons for these variations. Derivatization of polyhydric phenols has been reported with heptafluorobutyrylimidazole, however, failure of trichlorophenols to react was attributed to increased acidity[13].

Concentrations of phenols reported in this paper refer to process streams within the mill only. Final mill discharges after biotreatment would be expected to contain substantially lower concentrations of phenols.

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REFERENCES

1 M C. Rand, A E. Greenberg and M. J. Taras (Editors), *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington, D.C , 14th ed , 1976
2 K. Blau and G. S. King (Editors), *Handbook of Derivative for Chromatography*, Heyden and Son, London, Bellmawr, Rheine, 1978
3 *R. C. C. Wegman and A. W M. Hofstel, Water Res* , 13 (1979) 651
4 K Lindström and J Nordin, *J. Chromatogr* , 128 (1976) 13
5 A. T. Shulgin, *Anal. Chem.*, 36 (1964) 920.
6 H. Ehrsson, T. Walle and H. Brotell, *Acta Pharm. Suecica*, 8 (1971) 319.
7 L. G. Johnson, *J. Ass. Offic. Anal. Chem.*, 56 (1973) 1503.
8 R. C. Pierce, *The Aqueous Chlorination of Organic Compounds Chemical Reactivity and Effects on Environmental Quality*, Environmental Secretariat, Ottawa, Publication No. NRCC 16450, 1978, and references cited therein.
9 M. Matell, *Acta Chem. Scand* , 9 (1955) 1017.
10 R. Fort, J. Sleziona and L Denivelle, *Bull. Soc. Chim. Fr* , (1955) 810
11 T Ramstad and D. N. Armentrout, *Anal. Chim. Acta*, 102 (1978) 229
12 A B. McKague and C C Walden, *Identification of the Toxic Constituents in Kraft Mill Bleach Plant Effluents*, Environmental Protection Service, Ottawa, Publication No. CPAR 245-6, 1979
13 L L. Lamparski and T J. Nestrick, *J Chromatogr* , 156 (1978) 143.