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GAS CHROMATOGRAPHY–MASS SPECTROMETRY OF CHLOROPHENOLS IN SPENT BLEACH LIQUORS

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SUMMARY

Spent bleach liquors from the bleach plant of some kraft pulp mills have been investigated for their content of chlorophenols. The chlorophenols are determined as their ethyl derivatives by means of gas chromatography–mass spectrometry after extraction, fractionation and purification. Separation of the various components is performed by means of glass open-tubular columns connected to either a flame ionization detector or an electron capture detector.

INTRODUCTION

In recent years considerable efforts have been made to control effluents from the pulp and paper industry. Because chlorine is generally involved as a bleaching agent, the presence of chlorinated organic compounds in such effluents may be expected.

Das *et al.*[1] showed indirectly the presence of tetrachloro-*o*-benzoquinone in bleach kraft chlorination effluent. Rogers[2] isolated and identified some toxic substances from kraft mill waste and detected trichloroveratrole, derived from either trichloroguaiacol or trichlorocatechol, on methylation with diazomethane. Ota *et al.*[3] identified several low molecular weight constituents of pine kraft spent chlorination liquor, some of which were chlorinated aliphatic substances, by using thin-layer and gas chromatography. Dence and Ota[4] characterized residues in spent chlorination liquors, and by using various spectroscopic methods, identified functional groups present in the residual organic matter of the diethyl ether extracted liquors.

Little has been done to examine the chlorinated aromatic content of the spent bleach liquors. Initially, it appeared desirable to investigate the occurrence of chlorophenols. This paper describes the identification and quantitation of some chlorophenols in spent bleach liquors of pine kraft pulp.

EXPERIMENTAL

Extraction and removal of acidic substances

About 1 litre of spent liquor was continuously extracted with 250 ml of diethyl ether for 48 h. (At the extraction stage spent liquors were adjusted to pH 2.) The ether extract was then shaken with two 10-ml portions of 0.5 mole/l sodium hydrogen carbonate solution. After separation, the aqueous phase was acidified with 20 ml of 1 mole/l hydrochloric acid and extracted with two 10-ml volumes of pentane–diethyl ether (1:2). The combined organic phases were transferred to a 50 ml centrifuge tube with a screw-cap and PTFE packing, and anhydrous sodium sulphate (*ca.* 5 g) was added to it. After centrifugation, the solution was transferred, in portions, to a 15 ml test tube and evaporated to dryness. The sodium sulphate was rinsed with about 5 ml of diethyl ether, which was likewise transferred to the test tube and evaporated to dryness. The residue obtained was then dissolved in 0.5 ml of isooctane–ethanol (9:1) and transferred to a 1-ml calibrated flask, the test tube being rinsed with a small volume of the same solvent (not more than 0.5 ml), which was also added to the flask. After making it up to the mark, the solution was transferred to a 2-ml tube with a screw-cap and alumina foil packing, and stored in a refrigerator (4°) for further investigations.

Isolation and purification of phenolic substances

After separation of the above ether extract from the sodium hydrogen carbonate phase, the extract was washed with 10 ml of ether-saturated water and then shaken with two 10-ml portions of 0.5 mole/l sodium hydroxide solution. The aqueous phase was then acidified with 20 ml of aqueous hydrochloric acid (1 mole/l) and the procedure was repeated exactly as described under *Extraction and removal of acidic substances* after acidification of the aqueous phase. The phenols were likewise finally dissolved in isooctane–ethanol (9:1). For quantitative analysis, 25 μl of the isooctane–ethanol extract were subjected to purification by means of high-performance liquid chromatography on a Waters liquid chromatograph equipped with double pumps and a solvent programmer for gradient elution. The chromatographic conditions used were: column, 3.2 × 150 mm, Micropak-CN, 5 μm; flow-rate, 2 ml/min; mobile phase, isooctane–ethanol (9:1); detector, 8 μl UV cell, for measuring the absorption at 280 nm.

An elution volume of 2 ml was collected, starting from the solvent peak, internal standard (2,6-dibromophenol) added, and the eluate subjected to derivatization (see under *Derivatization* below). For combined gas chromatographic–mass spectrometric analysis the liquid chromatographic column was overloaded by injection of 250 μl of sample. An elution volume of 5 ml was collected, evaporated to dryness in a stream of nitrogen and the residue diluted with 100 μl of isooctane–ethanol (9:1) and derivatized.

Derivatization

The isooctane extract was treated with diazoethane generated in a modified apparatus according to the method of Schlenck and Gellerman[5]. When a pale yellow colour persisted (about 30 sec) the reaction vessel was closed and allowed to stand overnight. Diazoethane reagent, a mixture of 1 ml of N-nitroso-N-ethylurea (Fluka, Buchs, Switzerland), 5 ml of diethyl ether, 3 ml of aqueous potassium hydroxide (10 mole/l) and 10 ml of diethylene glycol monoethyl ether, was freshly prepared prior to each derivatization.

Gas chromatography

A Perkin-Elmer Model 900 gas chromatograph equipped with a flame ionization detector (FID) and electron capture detector (ECD) was used. The chromatograph was reconstructed so as to suit glass open-tubular columns with Grob-type injectors and purge gas systems used separately for FID and ECD. The column used was an SE-30 glass open-tubular column (25 m × 0.25 mm I.D.) manufactured by LKB (Stockholm, Sweden). The gas chromatograph was programmed so that the initial temperature was 150° for 10 min followed by an increase in temperature to 200° at 2°/min. The carrier gases used were nitrogen (FID) and argon–methane (95:5) (ECD). The injector gas flow-rate was 25 ml/min and carrier gas flow-rate 0.5 ml/min so that the split ratio was 1:50. Purge gases were used to speed up the flow of the eluates entering the detectors, which had flow-rates of 60 ml/min (FID) and 90 ml/min (ECD). The injector temperature was 250°, and the manifold and ECD temperatures were 200° throughout the experiment.

Gas chromatography–mass spectrometry

Mass-spectrometric investigations were carried out using a Finnigan gas chromatograph (9500)–mass spectrometer (3200 F) with an on-line computer system (6000). Gas chromatographic data were as described above except for carrier gas (helium) flow-rate (1.2 ml/min) and split ratio (1:25). The capillary interface and ion-source temperatures were 250° and 270°, respectively. Mass spectra were recorded every 1.5 sec with a speed of 225 a.m.u./sec up to 400 a.m.u. at an electron energy of 40 eV.

Quantitative analysis

The peaks in the electron capture detected chromatograms were evaluated by means of a Hewlett-Packard electronic integrator (Model 3770 A) and the amount of substance (m_x mole) injected was calculated according to the formula:

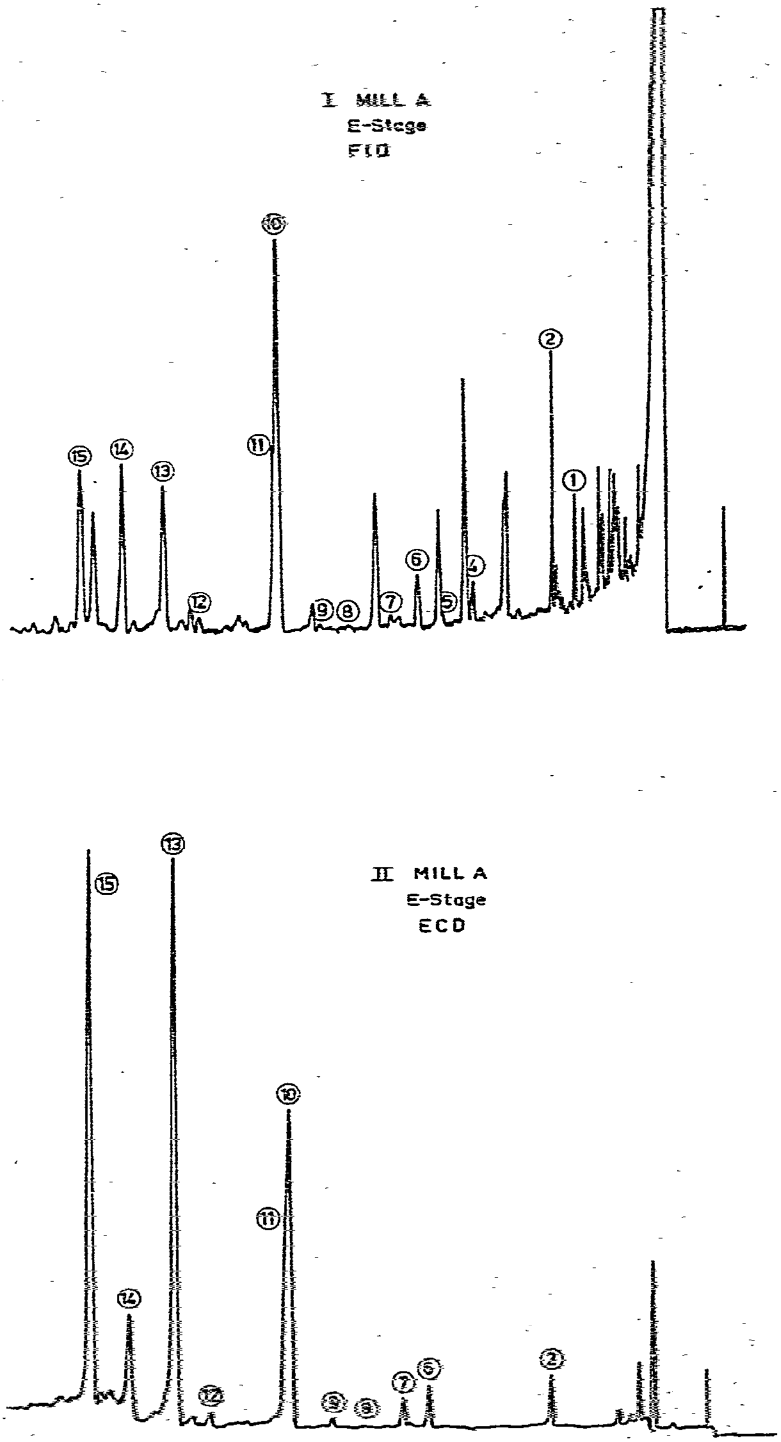
$$m_x = f_x \cdot m_i \cdot \frac{A_x}{A_i}$$

where f_x is the molar response factor, m_i mole the amount of internal standard, A_x the peak area for substance x and A_i the peak area for the internal standard.

RESULTS AND DISCUSSION

Gas chromatograms of the various extracts are shown in Fig. 1. Chromatogram I consists of substances in the extract containing the phenolic fraction and the sample was taken from the spent extraction liquor of a mill producing bleached pine kraft pulp (mill A). Detection was carried out by means of flame ionization. In the corresponding chromatograms with electron capture detection (II, Fig. 1), fewer peaks can be seen. This reduction in the number of peaks is due to the halogen specificity of the ECD, so that only chlorinated compounds are detected. The detector response increases with increasing number of chlorine atoms. The extracts giving chromatograms I and II (mill A) were analyzed qualitatively, which explains the absence of peak 3 (internal standard).

In order to relate the substances found to the amount of pulp, laboratory chlorination followed by alkali extraction was carried out on pine kraft pulp from mill C. Kappa numbers (a measure of residual lignin) of the pulp and pulp concentra-


I MILL A
E-Stage
FID
⑩
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⑭
⑬
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II MILL A
E-Stage
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Fig. 1.

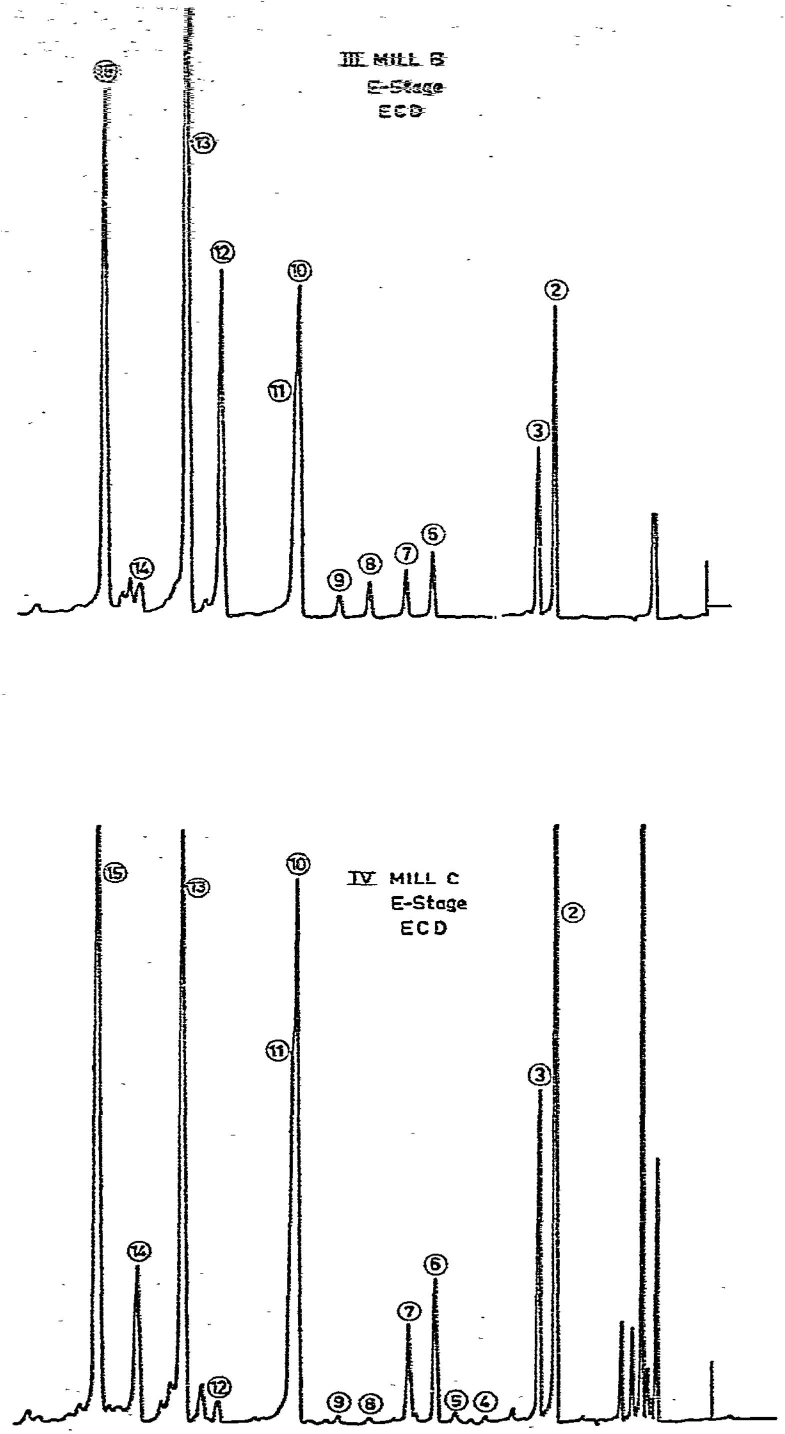

Fig. 1.

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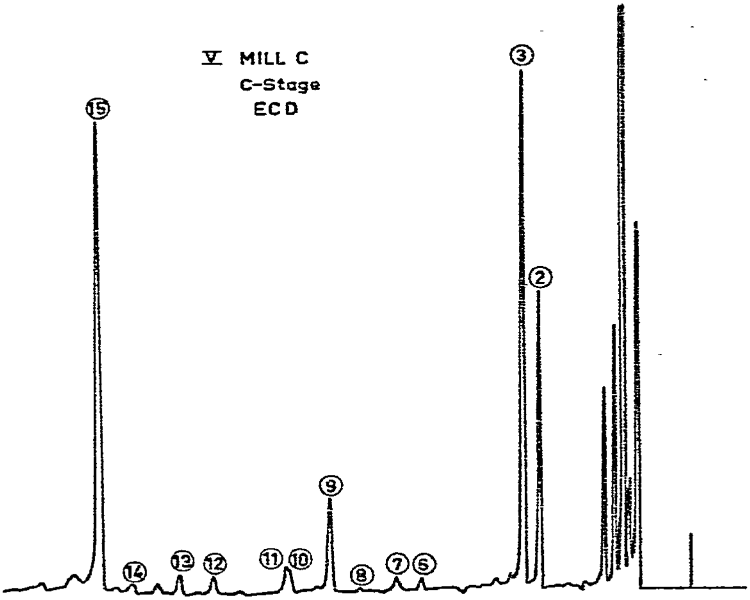


Fig. 1. Gas chromatograms of ethylated chlorophenols of ether-extracted spent bleach liquors from three different plants obtained with an open-tubular column. Recorder chart speed, 1 cm/min. For gas chromatographic conditions see under *Gas chromatography*.

tions were determined and the spent liquors were quantitatively analyzed for chlorophenols against an internal standard. Chromatogram IV (Fig. 1) shows the results of the chromatography. The phenolic content of spent bleach liquors from mills A, B and C are in fairly good agreement, taking into account that detection was performed in the picogram (10^{-12} g) range. Recoveries of substances found, together with bleach conditions of laboratory-bleached pulp, from mill C are listed in Table I.

Three main types of chlorinated phenols predominate: chloroguaiacols, chlorocatechols and chlorophenols (I, II and III, respectively, Fig. 2). The formation of catechols may be caused by cleavage of the methyl aryl ether bond by the nucleophilic components of the cooking liquor[6].

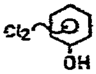
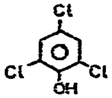
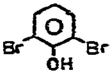
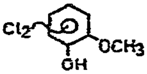
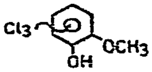
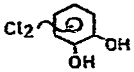
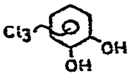
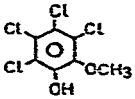
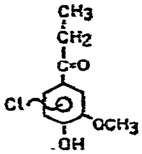
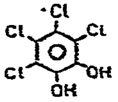
As expected, the concentrations of the chlorophenols were higher in the spent extraction liquors than in the spent chlorination liquors. Furthermore, Table I shows that the concentrations of chlorinated catechols are relatively higher in the latter while those of chlorinated guaiacols are relatively higher in the former. This is probably due to the specific solubility of the substances in water, being higher for catechols in spent chlorination liquors at low pH than for the more lipophilic guaiacols, which require alkaline conditions in order to form water-soluble salts.

A schematic presentation of the analytical procedure is illustrated in Fig. 3. In order to obtain quantitative results the recoveries of tetrachlorocatechol and 2,4,6-trichlorophenol in the various steps of the procedure were calculated. Each step was then quantitatively analyzed by gas chromatography. Table II shows the recoveries obtained from spiked acidified aqueous solutions of the two phenols at each step of the working-up procedure (*cf.* Fig. 3). It can be seen that the recovery of tetrachloro-

TABLE I

RECOVERY OF SUBSTANCES FOUND FROM MILL C (FIG. 1)

Bleach conditions: unbleached pine kraft pulp, kappa number 32.9 (unwashed), 31.6 (washed); chlorination: 3.5% unwashed pulp, 6.64% Cl_2, 20°. 60 min; extraction: 8% bleached pump, 2.8% NaOH, 50°, 120 min, final pH 10.4; washed, bleached and extracted pulp: kappa number 10.6, viscosity 1100 dm^3/kg. + indicates substances found but not quantified.

Peak No.	*Structure*	*Number of isomer found*	*Compound*	*Concentration*			
				Chlorination stage		*Extraction stage*	
				µg/l	*g/t pulp*	*µg/l*	*g/t pulp*
1		—	Dichlorophenol	+		+	
2		—	2,4,6-Trichlorophenol	25	0.9	115	1.8
3		—	2,6-Dibromophenol (internal standard)	+		+	
4		3	Dichloroguaiacol	+		+	
5	Isomer to 4	—	Dichloroguaiacol	+		+	
6	Isomer to 4	—	Dichloroguaiacol	+		+	
7		3	Trichloroguaiacol	+		35	0.5
8		—	Dichlorocatechol	+		+	
9		2	Trichlorocatechol	18	0.6	+	
10	Isomer to 7	—	Trichloroguaiacol	+		168	2.7
11	Isomer to 7	—	Trichloroguaiacol	+			
12	Isomer to 9	—	Trichlorocatechol	83	3.0	+	
13		—	Tetrachloroguaiacol	+		137	2.2
14		—	Monochloropropiovanillone	+		+	
15		—	Tetrachlorocatechol	32	1.6	42	0.9

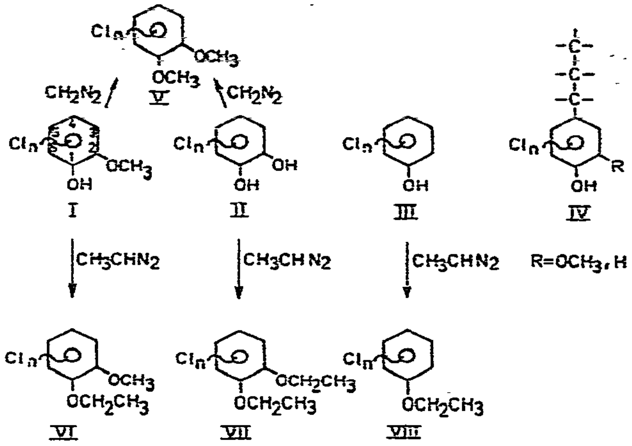


Fig. 2. Derivatization of various chlorophenols.

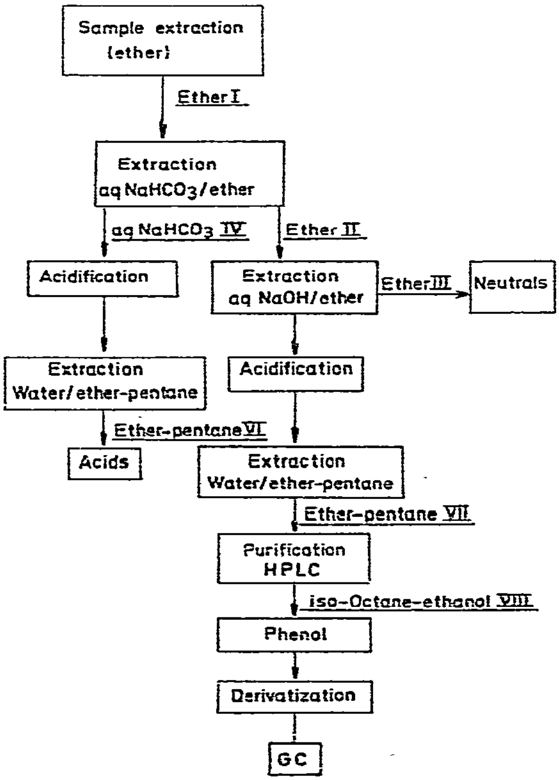


Fig. 3. A schematic presentation of the analytical procedure for the separation of the chlorophenols from acids and neutral substances.

TABLE II

RECOVERIES AT VARIOUS STEPS IN THE ANALYTICAL PROCEDURE ACCORDING TO FIG. 3

Substance	*Recovery (%)*				*Number of determinations*	*Coefficient of variation (%)*
	Extraction I (ether phase)	*Extraction II (ether phase)*	*Extraction VII (ether–pentane phase)*	*Total*		
2,4,6-Trichlorophenol	98	94	86	79	3	6
Tetrachlorocatechol	87	80	80	55	3	10

catechol is low compared with that of 2,4,6-trichlorophenol, which is in agreement with the more polar character of the former, which is more soluble in water; 20% of tetrachlorocatechol was lost when the ether phase (step I, Fig. 3) was extracted with sodium hydrogen carbonate (step IV, Fig. 3) compared with only 5% of 2,4,6-trichlorophenol. The overall recoveries were 55 and 79%, respectively.

The molar response factors were calculated for 2,4,6-trichloroethoxybenzene ($n = 3$, VIII, Fig. 2) and tetrachloro-1,2-diethoxybenzene ($n = 4$, VII, Fig. 2) relative to 2,6-dibromoethoxybenzene (ethylated 2,6-dibromophenol). To five separate solutions of equal concentration of these substances, the dibromophenol was added in varying amounts. The solutions were derivatized and the molar response factors calculated. The results are shown in Table III.

The quantitative results were based on the assumptions that the recoveries in the working-up procedure of various chlorocatechols were similar to that of tetrachlorocatechol and that those of chloroguaiacols were similar to that of 2,4,6-trichlorophenol according to Table II. Furthermore, the molar response factors of tri- and tetrachlorophenyl ethers (Table III) were assumed to be equal to those of 2,4,6-trichloroethoxybenzene and tetrachloro-1,2-diethoxybenzene, respectively. Quantitation of mono- and dichloro compounds was neglected.

The calculated values for the recoveries are approximate, but nevertheless they give an estimation of the contents of chlorophenols. Also, the response factors of the trichloro compounds may differ from that of 2,4,6-trichloroethoxybenzene.

Derivatization of the chlorophenols with diazoethane instead of diazomethane to form chlorophenyl ethyl ethers was carried out mainly to distinguish free phenolic

TABLE III

ELECTRON CAPTURE DETECTOR RESPONSE

Substance	*Concentration*		*Detected amount (g)*	*Electron capture response*	
	g/µl	*mole/µl*		*Molar response factor*	*Coeff. of variation (%)*
2,4,6-Trichloroethoxybenzene	$2.06 \cdot 10^{-9}$	$9.2 \cdot 10^{-12}$	$41 \cdot 10^{-12}$	0.69	2.6
Tetrachloro-1,2-diethoxybenzene	$2.02 \cdot 10^{-9}$	$6.7 \cdot 10^{-12}$	$41 \cdot 10^{-12}$	0.28	3.0

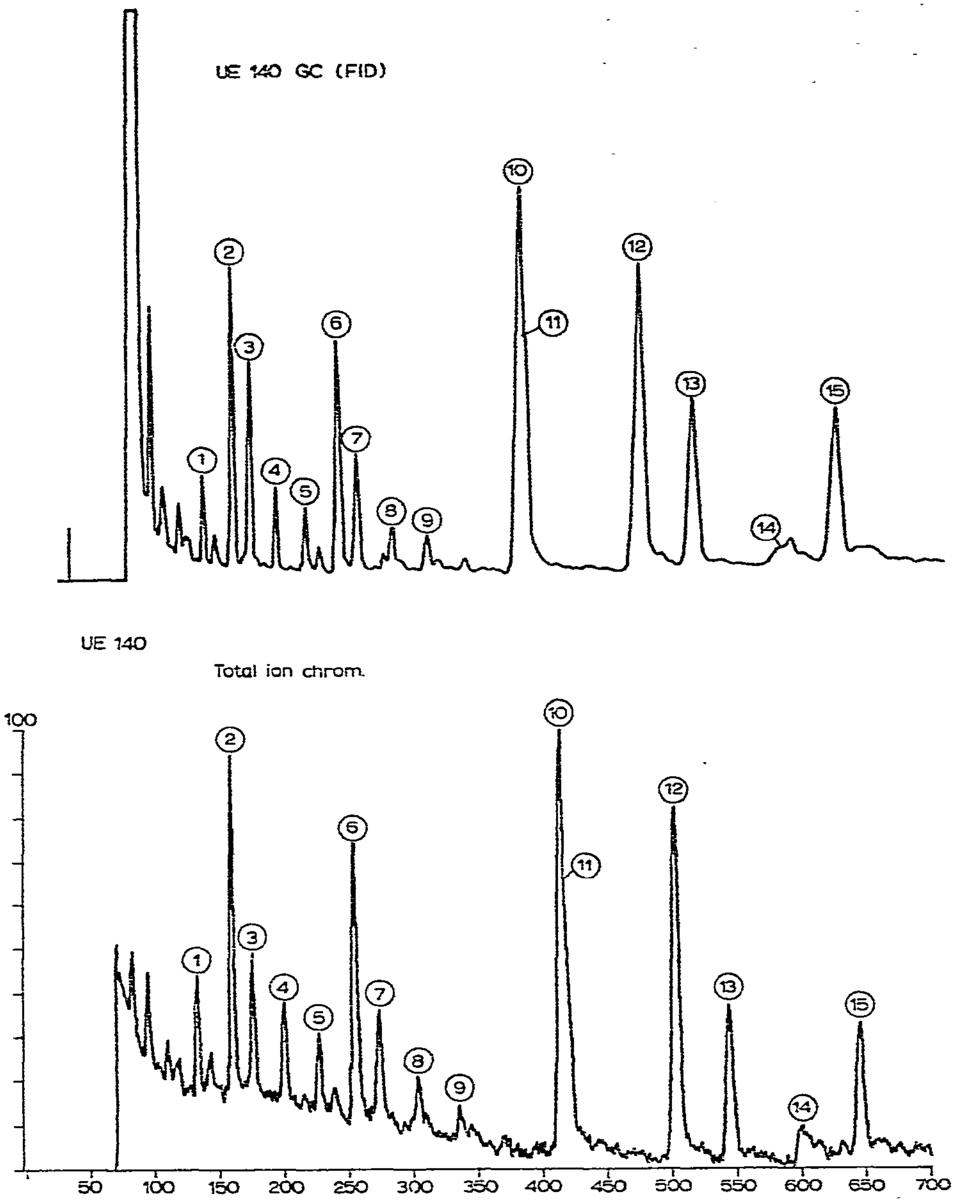


Fig. 4. Comparison of a GC (FID) chromatogram and a GC–MS total-ion chromatogram with identical column flow-rates (1.2 ml/min). The compounds are listed in Table I. Recorder chart speed, 2 cm/min. For GC and GC–MS conditions see under *Gas chromatography* and *Gas chromatography–mass spectrometry*.

groups from the naturally occurring methoxy groups. Derivatization with diazoethane was surprisingly reproducible in a solution of isooctane–ethanol (9:1) (ref. 5).

For the identification of peaks obtained in the electron capture detected chromatograms, combined gas chromatography–mass spectrometry was used. The capillary column (see under Experimental) was connected to a platinum-tube interface emerging directly into the ion source. Mass spectra were stored by means of an on-line computer. A computer-reconstructed total-ion chromatogram is shown in Fig. 4, in which scan numbers are plotted against the response.

Computer-stored mass spectra were plotted for peaks with typical chlorine clusters arising from the presence of isotopes ^{35}Cl and ^{37}Cl occurring naturally in the ratio 3:1. Thus, for ions containing n chlorine atoms, a cluster of $n + 1$ peaks should be obtained with an m/e difference of 2, the ratio of the relative intensities corresponding to the coefficients of the polynomial $(3x + 1)^n$ for $x = 1$.

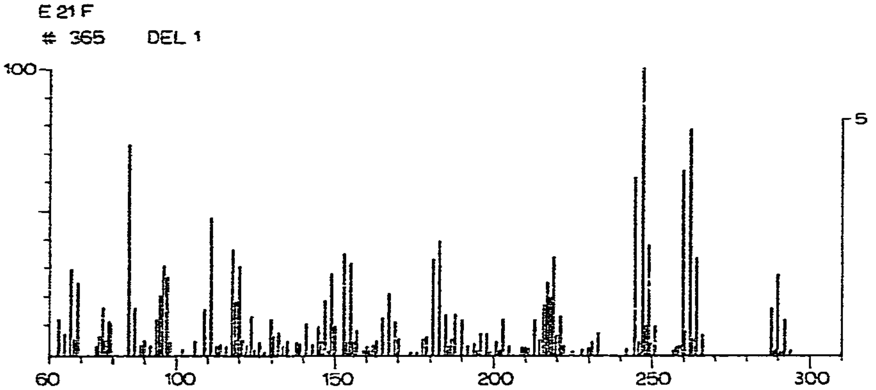


Fig. 5. Mass spectrum of ethylated tetrachloroguaiacol obtained from peak 13 (*cf.* Fig. 4).

For example, Fig. 5 illustrates a mass spectrum of a tetrachlorinated compound occurring in a sample from mill B with scan number 365, which is due to peak 13 (Fig. 4). The molecular ion (M^+) is 288, which may indicate ethylated tetrachloroguaiacol ($n = 4$, VII, Fig. 2). Peaks 6 and 10 show similar fragmentation patterns with two and three chlorine atoms, respectively, indicating the occurrence of di- and trichloroguaiacol in the extract. On methylating the sample from mill B, peaks 13 and 15 (chromatogram III, Fig. 1) were reduced to one peak having a retention time identical with tetrachloroveratrole ($n = 4$, V, Fig. 2), which is available at our laboratory. The mass spectrum of peak 15 was interpreted as being that of ethylated tetrachlorocatechol ($n = 4$, VII, Fig. 2) and was identical to that of an authentic specimen. Thus, peaks 13 and 15 correspond to tetrachloro-1-ethoxy-2-methoxybenzene and tetrachloro-1,2-diethoxycatechol. Similarly, peaks 10 and 12 were reduced to one peak on methylation, with the same retention time as that of 3,4,5-trichloroveratrole ($n = 3$, V, Fig. 2). This leads to the conclusion that peak 10 corresponds to 3,4,5-trichlorocatechol ($n = 3$, II, Fig. 2) and peak 8 to either 3,4,5-trichloroguaiacol ($n = 3$, I, Fig. 2) or the 4,5,6-isomer, the latter being the more plausible. The presence of a tri- and a tetrachloroguaiacol in spent bleach liquors has recently been verified by Rogers and Keith[7].

In a search for specific compounds, the selectivity can be increased by plotting mass chromatograms, *i.e.*, only those peaks of compounds with ions of a certain m/e number are plotted. As can be seen from Fig. 5, the most abundant fragment is m/e 247, which arises by the loss of ethylene and a methyl radical from the molecular ion.

Figs. 6a, b and c show mass chromatograms for ions with *m/e* 226, 212 and 192, which are among the most abundant fragments of the parent ethylated trichloroguaiacols, trichlorocatechols and dichloroguaiacols, respectively. Peaks 7, 10 and 11 are found to be derived from isomers (Fig. 6a). The mass spectra of peaks 10 and 11 are almost identical, but there are differences in the relative intensities of the chlorine clusters.

Peak 2 is 2,4,6-trichloroethoxybenzene. The mass spectrum is identical with that of the pure compound.

Only two isomeric trichlorocatechols are possible. The corresponding ethylated

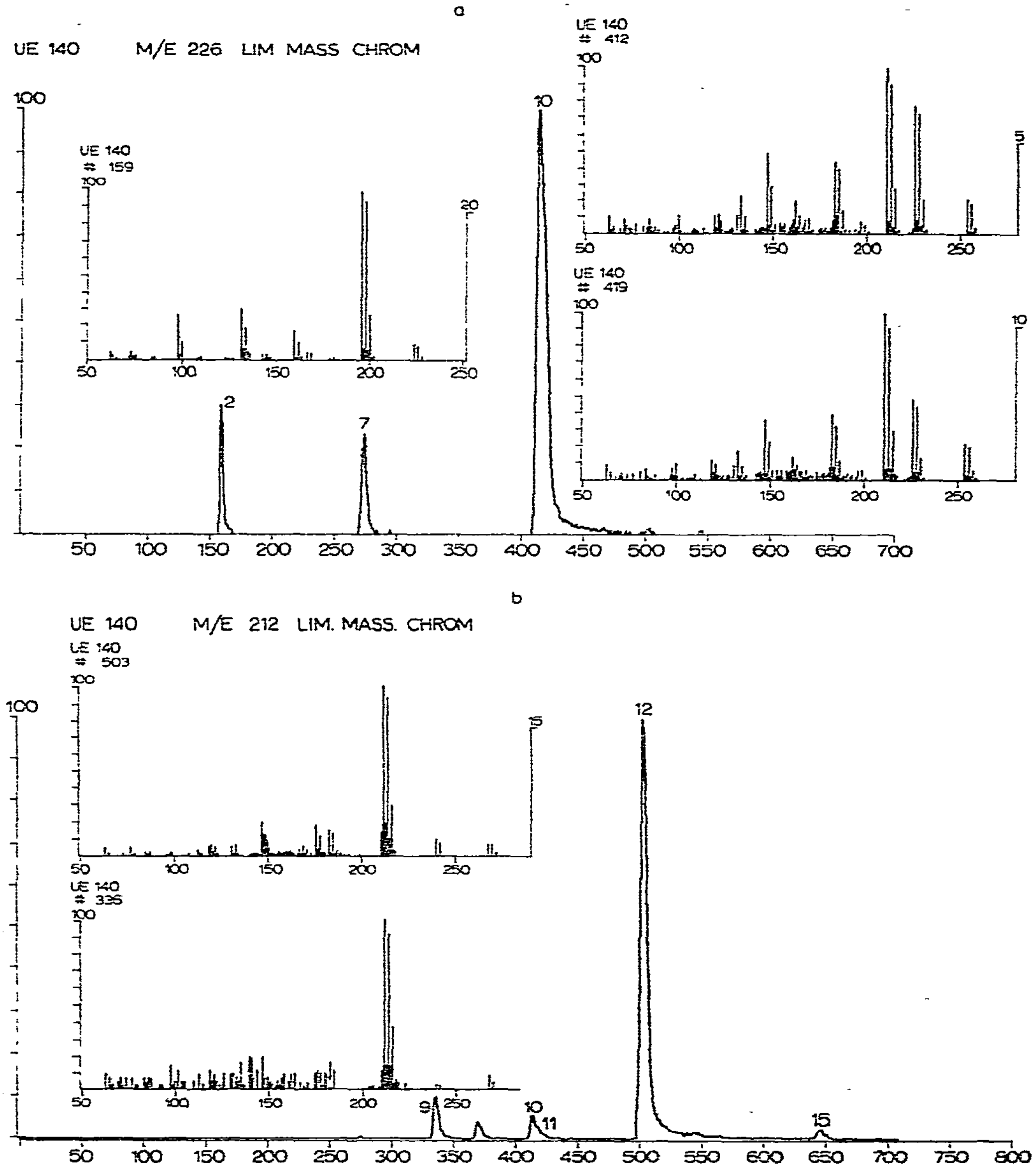


Fig. 6.

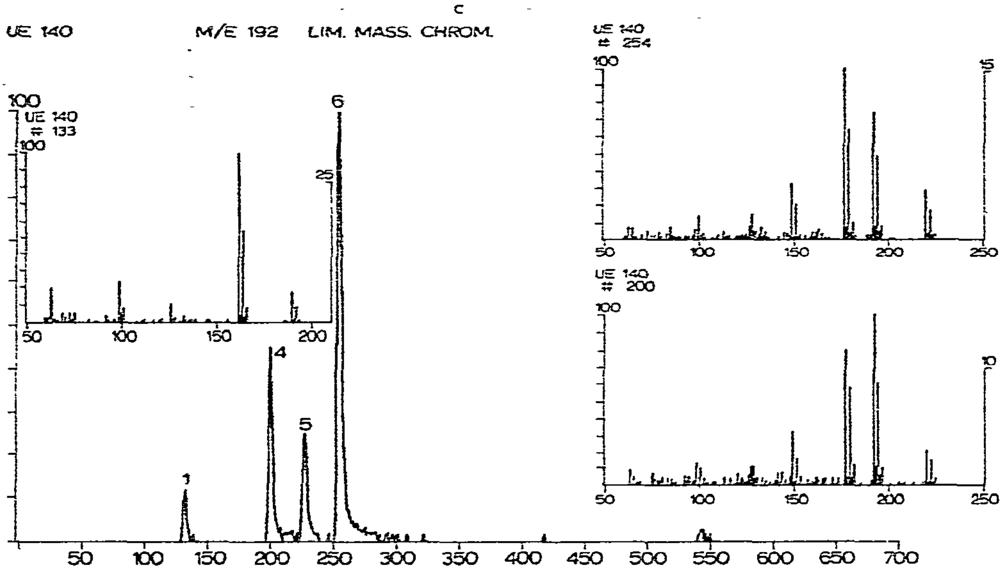


Fig. 6. Computer-reconstructed limited mass chromatograms obtained from the same run as in Fig. 4. (a) Peaks 7, 10 and 11 represent ethylated trichloroguaiacol isomers. (b) Peaks 9 and 12 represent ethylated trichlorocatechol isomers. (c) Peaks 4, 5 and 6 represent ethylated dichloroguaiacol isomers and peak 1 is an ethylated dichlorophenol. Scan numbers of the peaks are given at the top of each mass spectrum.

compounds proved to be represented by peaks 9 and 12 (Fig. 6b). The peak between peaks 9 and 10 is a trichloro compound but the mass spectrum was not distinct enough to permit interpretation.

Four sharp peaks were obtained in a search for ethylated dichloroguaiacols (*m/e* 192). Peaks 4, 5 and 6 are derived from isomers, but peak 1 shows a similar fragmentation pattern to peak 2. It was therefore interpreted as being due to an ethylated dichlorophenol.

The mass spectrum of peak 14 indicates a monochloro compound with M^+ at *m/e* 242. Peaks at $(M - 29)^+$ and $(M - 57)^+$ indicate loss of an ethyl radical followed by carbon monoxide. Further fragmentation showed certain similarities to ethylated chloroguaiacols although the spectrum is not clear. The compound is therefore assumed to be monochloro-4-ethoxy-3-methoxyphenyl ethyl ketone. Another monochloro compound was found between peaks 1 and 2 (scan 143, Fig. 4). Interpretation of the mass spectrum indicated a monochloroguaiacol.

Finally, the mass spectrum of peak 8 showed the presence of two chlorine atoms and M^+ at *m/e* 234. The fragmentation was similar to that of the chlorocatechols, thus indicating an ethylated dichlorocatechol.

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