DETERMINATION OF CHLORINATED AND BROMINATED LIPOPHILIC COMPOUNDS IN SPENT BLEACH LIQUORS FROM A SULPHITE PULP MILL

GLASS CAPILLARY COLUMN GAS CHROMATOGRAPHY–MASS SPECTROMETRY–COMPUTER ANALYSIS AND IDENTIFICATION

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SUMMARY

Effluents from the bleach plant of a sulphite pulp mill have been investigated for their contents of non-polar chlorinated and brominated compounds. The total amount of cyclohexane-extractable organic chlorine and bromine was first quantified by neutron-activation analysis of the effluent waters taken at different stages in the bleaching process. The nature of the low-molecular-weight constituents was studied in detail by means of gas chromatography–mass spectrometry. Special emphasis was placed on optimizing the separation of components prior to the ionization step in the mass spectrometer, for which a glass capillary column was employed in gas chromatography. Furthermore, the column was connected directly to the ion source by means of a deactivated glass coupling.

Nineteen halogenated compounds were identified. Monochlorocymenes, dichlorocymenes and monobromocymenes were quantified in different stages with a gas chromatograph equipped with a flame-ionization detector.

INTRODUCTION

Spent bleach liquors discharged into the environment from bleach plants are one of the remaining pollution problems of pulp mills. Owing to corrosion, the high content of chloride and organochlorine compounds in the waste effluents complicates recirculation. The effluents contain dissolved and polydispersed wood degradation products from reactions between bleaching chemicals and the pulp. Effluents from the chlorination stage have been shown to be toxic to fish but little is known of the chemical constituents that are responsible for these effects[1–4].

Some papers[3-6] have been published that show that chlorinated hydrophilic compounds are present. The compounds found are chlorinated phenols, guaiacols and catechols as well as chlorinated dehydroabietic and unsaturated carboxylic acids.

Only a few compounds of lipid character have been found, including chloroform[7]. Recently, the presence of some non-polar compounds in effluents from chlorine bleacheries in a sulphate and a sulphite plant has been demonstrated by gas chromatography–mass spectrometry (GC–MS) and neutron-activation analysis[8,9].

The analytical technique used when characterizing the chlorinated compounds was based on chromatographic separation followed by structure identification by NMR, IR and mass spectrometry. Leach and Thakore[4] enriched the compounds in bleachery effluents on Amberlite XAD-2 resin columns and extracted the adsorbed material with polar solvents. They continued with complicated fractionation procedures with extractions at different pH values, silica gel separations, thin-layer chromatography (TLC) and preparative gas–liquid chromatography (GLC) before achieving structure recognition. Different fractions were also analysed on a packed steel GLC column coupled to a mass spectrometer. Lindström and Nordin[5] extracted the spent liquor with diethyl ether and worked up the extract to establish the presence of chlorophenols from lignin decomposition products. The chlorophenols were finally characterized as their ethyl derivatives on a glass capillary GLC column coupled to a quadrupole mass spectrometer.

Our intention was to investigate the cyclohexane-extractable materials from different chlorination processes. The total amount of organohalogenated compounds were first determined in the extract by means of neutron-activation analysis[8,10,11], which gave information about the sources of these compounds, then the extracts were analysed directly on a glass capillary GLC column coupled to a mass spectrometer.

EXPERIMENTAL

Neutron activation on chlorine and bromine

A 4.5-l sample was adjusted to pH 11 with potassium hydroxide and the non-polar organic compounds were extracted twice with a total of 250 ml of cyclohexane using a magnetic stirrer. The cyclohexane phase was concentrated to 20 ml on a Rotavapor and then washed twice with distilled chloride-free water to remove chloride ions and dried with cyclohexane-washed sodium sulphate. The extract was finally concentrated to 5 ml in a heating block at 30° with a gentle stream of purified nitrogen.

The neutron-activation analysis of the extract was carried out at the Institute of Atomic Energy, Kjeller, Norway. Neutron activation was effected at a flux of about $1.5 \cdot 10^{13}$ n/cm²·sec. The induced radioactivity was registered immediately after irradiation with a multi-channel spectrometer equipped with a Ge (Li) detector. The isotopes ^{38}Cl and ^{80}Br were used for the determination of chlorine and bromine, respectively. The detailed experimental procedure has been described elsewhere[10].

Gas chromatography–mass spectrometry

A combination of a Carlo Erba Fractovap 2101 gas chromatograph and a Varian-MAT 112 mass spectrometer with a Spectrosystem 100 MS was used.

Gas chromatography. The gas chromatograph was equipped with a splitless

injector. The compounds were separated on a 50 m × 0.34 mm I.D. OV-1 glass capillary column. The column was obtained from H + J Jaeggi (Trogen, Switzerland). The following conditions were chosen: injector block, 270°; temperature programming from 25° to 260° at 3.5°/min, with an initial isothermal period of 8 min; carrier gas, helium at a flow-rate of 2 ml/min at ambient temperature.

Two microlitres of the concentrated extracts were injected without splitting with a splitless period of 60 sec[12].

Interface. The gas chromatograph and mass spectrometer were interfaced directly with a 20 cm × 0.2 mm I.D. glass-lined steel tube and a 20 cm × 1.6 mm I.D. quartz tube. The chromatographic column was butted to the glass-lined steel tube and connected with a 1/16-in. Swagelock union, using graphite ferrules (Graphlock; Scientific Glass Engineering, Melbourne, Australia). The total effluent from the capillary column entered the ion source of the mass spectrometer. The outlet of the column was operated at reduced pressure, and dead volumes in the Swagelock union and tube leading to the ion source were therefore of little importance for the chromatographic resolution. The construction is identical with that described by Rapp *et al.*[13], with the important modification that the interface consisted entirely of glass. As Grob[14] has pointed out, noble metals are not ideal materials for the interfaces in capillary column GLC. The glass surface in this interface was deactivated with 0.1 % Carbowax 20M solution to prevent adsorption of polar and labile components. The interface has a few drawbacks, however; column interchanges are not easily and rapidly performed and the connection of the glass capillary column to the glass-lined steel tube is delicate.

Mass spectrometer. The mass spectrometer was equipped with highly efficient turbomolecular pumps (200 l/sec) which give an oil-free background. The vacuum system was constructed to accomodate the carrier gas flow used in the glass capillary column separation. Mass spectra were recorded in the mass range *m/e* 25–500 at a scan rate of 1 sec/decade, with automatic repetetive scanning. There was a programmed delay of 1 sec after each scan and the spectrum was recorded approximately every 2 sec. The spectra were stored on a magnetic disc.

The following experimental conditions were chosen: ionization energy, 80 eV; emission current, 1.5 mA; acceleration voltage, 800 V; multiplier voltage, 2 kV; ion source temperature, 250°; interface temperature, 250°; resolution, 700. The total ion current (TIC) from a second ion source with an ionization energy of 20 eV was used as the signal for the gas chromatographic trace.

Quantitative analysis

For the quantitative determinations, a gas chromatograph with a flame-ionization detector (FID) was used. The peaks were integrated (Perkin-Elmer integrator). The carrier gas flow-rate was adjusted so as to give the same retention times as in the GC–MS analyses. Apart from this, the experimental conditions were identical. The amounts of halogenated cymenes were determined relative to a *p*-cymene standard. The molar response factors were quantified by assuming that the FID response factors for the halogenated cymene isomers were identical with that of cymene.

Control of extraction procedure

      .   To control the efficiency of the extraction procedure, 0.5 l of distilled water was spiked with 10 µl of a 2500 ppm solution of *p*-cymene in acetone. The pH of the water was adjusted to 11 and the water was extracted twice with 10 ml of cyclohexane. The combined extract was evaporated to 100 µl.

RESULTS

Neutron-activation analysis

      The results of the determination of non-polar chlorinated organic compounds, which are extractable with cyclohexane, are given in Table I. These results (expressed as parts per million of chlorine or bromine) relate to a plant that showed a discrepancy

TABLE I

TOTAL AMOUNT OF HALOGENATED ORGANIC COMPOUNDS EXTRACTABLE WITH CYCLOHEXANE IN DIFFERENT STAGES OF A PLANT FOR BLEACHING SULPHITE PULP

Stage	*Sample*	*Cl (ppm)*	*Br (ppm)*
1	First chlorination	0.3	0.08
2	Second chlorination	0.6	0.08
3	Alkaline extraction	0.8	0.06
4	First hypochlorite	0.8	0.09
5	Second hypochlorite	0.5	0.02
6	SO$_2$ treatment	1.0	0.03
	Blank	0.001	<0.0001
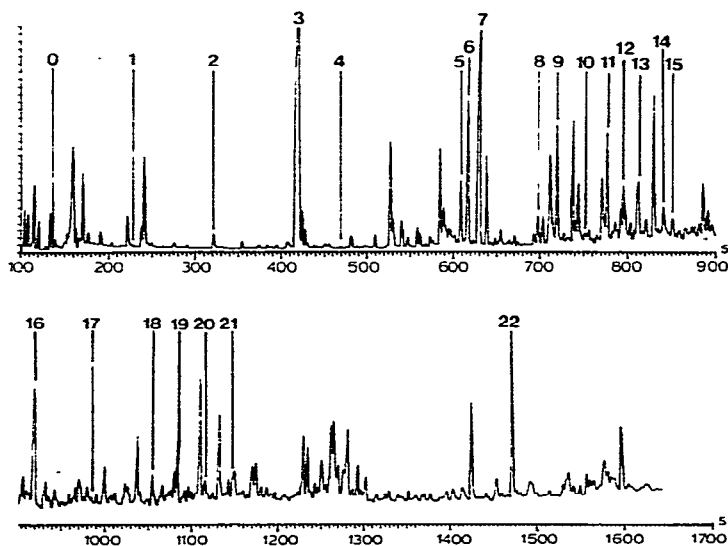
Fig. 1. Computer-reconstructed chromatogram, showing sum of the ion intensities *versus* the scan number. The halogenated compounds are listed in Table II. In addition, peak 3 is cymene, 5 is cymene-α-ol, 16 is calamenene and 22 is methyl dehydroabietate.

from other pulp mills in that, in addition to organochlorine compounds, organo-bromine compounds were also present. The effluents from this plant were selected for a GC–MS study.

Mass spectrometric identification

The computer-reconstructed chromatogram is shown in Fig. 1. There were several hundred components in the mixture and about 1600 mass spectra were registered and stored on a disc.

Visual searches for chlorinated and brominated compounds were carried out by plotting all of the mass spectra on a Tektronic 4010 display. Emphasis was placed on finding typical isotopic cluster patterns. To facilitate structure elucidation of halogenated compounds, a comparison with the plausible non-halogenated precursor

TABLE II

HALOGENATED COMPOUNDS FOUND IN SULPHITE BLEACHERY EFFLUENTS

Structure	Compound	Peak number
Br_2CHCl	Dibromochloromethane	0
Br_3CH	Bromoform	1
	Chlorotoluene	2
C_2Cl_6	Hexachloroethane	4
	Chlorocymene (2 isomers)	6, 7
	Dichlorocymene (3 isomers)	10, 11, 13
	Trichlorocymene	17
	Bromocymene (2 isomers)	8, 9
	Bromochlorocymene	15
	Chlorocymene-α-ol	12
	Bromocymene-α-ol	14
	Chlorocalamenene (2 isomers)	18, 19
	Bromocalamenene (2 isomers)	20, 21

was carried out. The fragmentation patterns of the halogenated compounds were very similar to those of the non-halogenated compounds. The non-halogenated precursors were all found in the mass spectral library[15] used. The halogenated compounds found are listed in Table II.

The positions of chlorine and bromine in the aromatic rings were not determined. The mass spectra of p-cymene (p-methylisopropylbenzene) with its different halogenated forms are shown in Fig. 2.
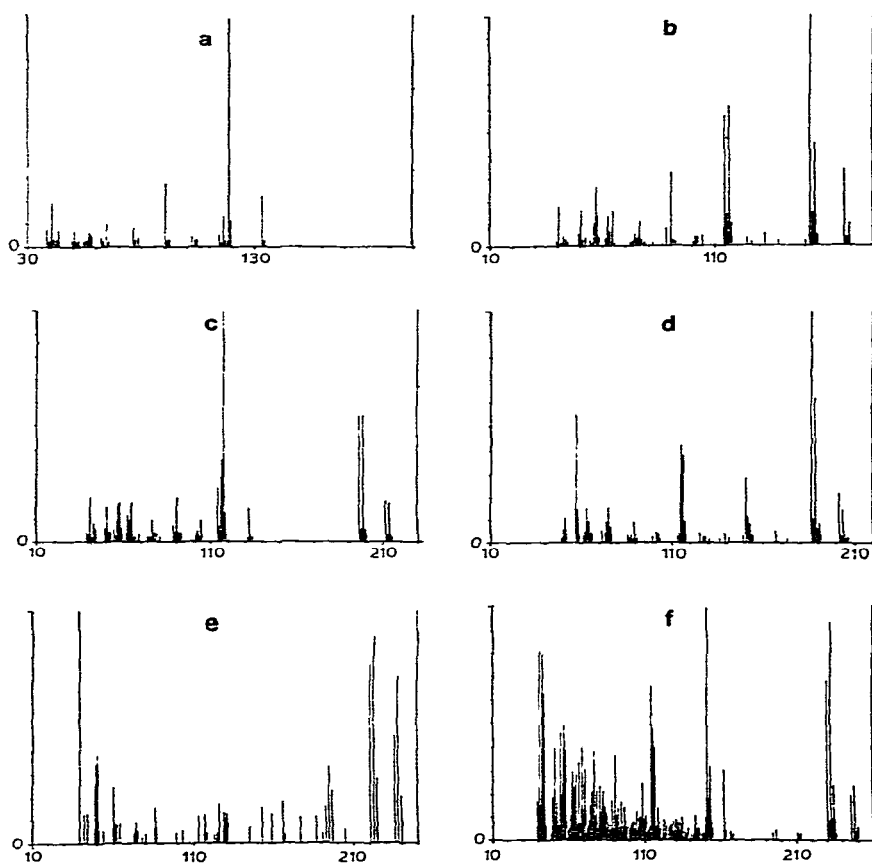

Fig. 2. Mass spectra of (a) cymene, (b) chlorocymene, (c) bromocymene, (d) dichlorocymene, (e) bromochlorocymene and (f) trichlorocymene.

Cymene-α-ol was found together with its chlorinated and brominated analogues (see Fig. 3A). A very rare compound was identified as calamene from a library search in the Registry of Mass Spectral Data[15] [Fig. 3B (a)]. The chlorinated and brominated calamenes were found, with two isomers of each [Fig. 3B (b) and (c)].

Quantitative determinations

The recovery of the extraction and concentration procedure was found to be 95%. The principal components were quantified in the four middle bleaching stages in Table I and are reported in Table III.
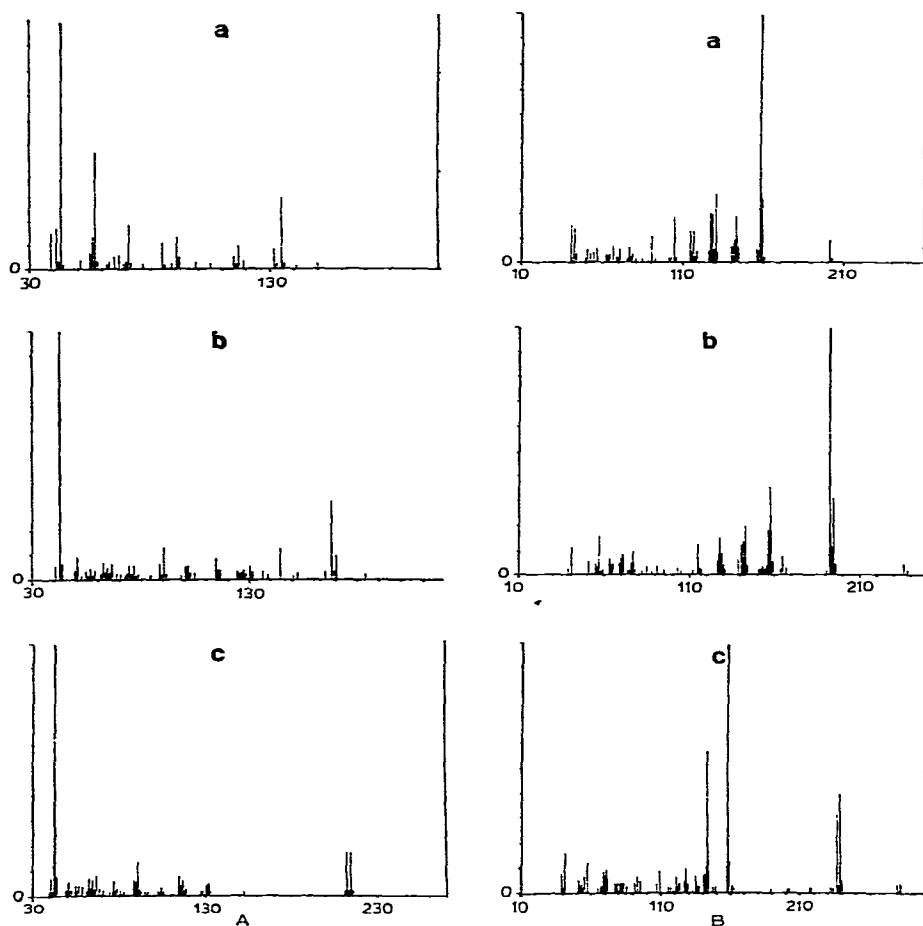
Fig. 3. (A) Mass spectra of (a) cymene-α-ol, (b) chlorocymene-α-ol and (c) bromocymene-α-ol. (B) Mass spectra of (a) calamenene, (b) chlorocalamenene and (c) bromocalamenene.

TABLE III

CONCENTRATION OF CYMENES (μg/l) IN BLEACHERY EFFLUENTS

Compound	Stage*			
	2	3	4	5
Cymene	180	n.a.**	n.a.	n.a.
Monochlorocymene	48	51	37	41
Dichlorocymene	6.5	5.8	4.1	5.0
Monobromocymene	6.5	6.9	3.7	5.3

* See Table I.
** Not analysed.

DISCUSSION

The bleaching of chemical pulp is accomplished in several stages, in some of which chlorine in different forms is added. The chlorine reacts with lignin in three different ways: substitution, addition and oxidation[16]. In addition, chlorine reacts with other organic compounds present in the pulp. The products are then extracted from the pulp with alkali. and the spent chlorination and alkali extraction liquors contain a very complex mixture of products that is difficult to analyse.

It has been found that the percentages by weight of organically bound chlorine in the organic material in spent chlorination and alkali extraction liquors were about 16 and 8%, respectively[17]. There is some concern that during bleaching processes chlorinated compounds might be produced that possess properties similar to those of polychlorinated biphenyls (PCBs)[18]. Hydrophobic chlorinated compounds may easily accumulate in lipid tissues. Hence even low concentrations may create an environmental problem with effects similar to those of DDT and PCBs.

Neutron-activation analysis specifically on chlorine and bromine after simple cyclohexane extraction is a very practical method for screening large numbers of samples. The effluents studied here show the presence of chlorinated compounds at a level of about 1 ppm, which corresponds to about 7 tons/year with a water consumption of 20,000 m^3/day. The GC–MS study demonstrated, however, that only approximately one tenth consisted of low-molecular-weight and volatile compounds. The ratio of total content of cyclohexane-extractable chlorine compounds to chlorinated cymenes remained constant in the different bleaching stages.

It is noteworthy that an appreciable fraction of halogenated compounds were brominated. The presence of brominated organic compounds could be explained by noting that in the plant studied sea water is used in the first chlorination stage. Bromide ions in sea water are oxidized by chlorine to give highly reactive bromine.

The simple procedure used to fractionate the lipid substances ensures good contamination control and little change or destruction of the chemicals present in the sample. However, when analysing such a complex mixture as bleach plant effluents, it is necessary to use a high-performance glass capillary column, the resolving power of which compensates the simple fractionation procedure. The column has to be coupled to the mass spectrometer in such a way that the resolution is retained. In our work the column is operated under low pressure because of the absence of a restrictor. We have not found any disadvantages with this coupling other than a slight effect on the retention times. The chromatographic peak patterns from an ordinary FID run and the GC–MS run with total ion current detection were similar, giving no problems in identifying the different compounds. The inert all-glass interface pathway was found to be ideal for giving mass spectra with very low background from memory effects.

The main component in sulphite bleach plant effluents is p-cymene, which appears in many halogenated forms. The cymenes originates from naturally present terpenes. It is known that during sulphite cooking processes, the oxidation of α-pinene and some monocyclic terpenes yields p-cymene as the principal product[19]. Evidently halogenated cymenes are formed by substitution reactions during the chlorination stage. The lipid character of the cymenes made it difficult to remove them completely from the pulp before the chlorination processes. The compound calamenene has, to

our knowledge, been reported only as a constituent in sweet flag oil[20]. The properties of this compound, especially in halogenated forms, are not known.

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