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# Analysis of Organochlorine Compounds in Effluents from Bleacheries by Neutron Activation Analysis and Gas Chromatography/Mass Spectrometry

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Effluents from chlorine bleacheries in a sulfite and a sulfate paper plant have been investigated. The total amounts of nonpolar and phenolic organohalogenated compounds have been determined by neutron activation analysis. In the sulfate plant nonpolar (cyclohexane extractable) and phenolic (butyl acetate extractable) chlorinated compounds are present in concentrations of 0.36 and 1.7 ppm, respectively. In the sulfite plant both chlorinated and brominated compounds are present in average concentrations of 0.67 ppm Cl and 0.06 ppm Br for nonpolar compounds and 1.1 ppm Cl and 0.1 ppm Br for phenolic compounds. The occurrence of organobromine compounds in the sulfite plant is due to the use of seawater in the first chlorination step.

The effluents have also been analysed by gas chromatography/mass spectrometry, and a number of halogenated aromatic hydrocarbons have been identified. These include chloro-*p*-methylisopropylbenzene (2 isomers), dichloro-*p*-methylisopropylbenzene (2 isomers), bromo-*p*-methylisopropylbenzene, chloro-*p*-methylisopropenylbenzene (2 isomers) and dichloro-*p*-methylisopropenylbenzene (2 isomers). These compounds are presumably formed by substitution reactions of the parent molecules which are formed by the cooking of the terpenes naturally present in wood.

Production of paper often involves bleaching of the pulp to remove lignin and other organic material which is left in the pulp after the cooking. The most commonly used bleaching agent is chlorine. Acidic chlorination will usually degrade lignin to water or alkali soluble compounds which in turn are extracted by the subsequent alkali treatment.

Several bioassay studies have demonstrated that effluents from chlorine bleach plants contain materials with acute toxic and sublethal effects on different marine species,[1–4] and considerable efforts have been made to identify these compounds. Dence and Ota [5] characterized residues in spent chlorination liquor by spectroscopic titrimetric methods. Collins *et al.*[6] investigated the lignin and carbohydrate residues in bleach effluents by gel chromatography and spectroscopy. More recently, 15 chlorinated phenols, guaiacols and catechols were identified in the effluents from the bleaching and extraction steps utilizing gas chromatography/mass spectrometry (GLC/MS).[7]

Little attention has, however, been paid to the occurrence of nonpolar chlorinated hydrocarbons in the effluent. Harris *et al.*[8] identified chloroform, and more recently Keith [9] identified hexachloroethane (in unbleached kraft paper mill wastewaters). The aim of the present study was to investigate the formation and occurrence of nonpolar, halogenated organic compounds in chlorine bleaching plants. Batch samples from different steps in the bleaching process in plants using the sulfate and the sulfite method were studied. The samples were analysed by neutron activation to determine the total amount of organically bound halogen and by GLC/MS to identify the individual compounds.

## EXPERIMENTAL

*Sampling.* Approximately 5 l batch samples were taken from different steps in the chlorine bleaching plants (see Tables 1 and 2). The samples were stored in glass flasks at 4 °C until analysed. Samples were taken at 5 different steps in the sulfate plant and 6 different steps in the sulfite plant.

*Analysis.* The sample volume was adjusted to 4.5 l and KOH was added until pH = 11. Nonpolar organic compounds were extracted twice with 250 ml of cyclohexane using a magnetic stirrer. The samples were acidified to pH 2 – 3 with concentrated HCl and phenolic compounds extracted twice with butyl acetate. Both the cyclohexane and the butyl acetate extracts were concentrated to about 20 ml in a rotating evaporator. The extracts were washed twice with distilled water and dried with magnesium sulfate. The extracts were further concentrated to about 5 ml in a heating block at 30 °C with a slow stream of highly purified nitrogen.

Analysis of the total amount of organic chloro-, bromo- and iodo-compounds, both in the cyclohexane and the butyl acetate extracts, was performed by neutron activation analysis. Neutron irradiation and registration of induced radioactivity was done at the Institute for Atomic Energy, Kjeller, Norway. A complete description of the method used on environmental samples is given elsewhere.[10]

The nonpolar organic compounds in the extracts were further characterized by means of GLC/MS. The instrument used was a Hitachi-Perkin Elmer RMU 6L mass spectrometer equipped with a Perkin Elmer Model 990 gas chromatograph and connected to an AEI stereo DS-50 data system. A 2 m × 3 mm glass column packed with 3 % Dexsil 300 on Gasch-rom. Q was used, and the temperature ranged from 70 to 300 °C with a programming rate of 8 °C/min. The carrier gas was He and the flow-rate 17 ml/min. The mass spectra were recorded with 70 eV electron energy and an ion chamber temperature of 250 °C.

For the interpretation of some of the main components comparison was made with a reference compound of *p*-methylisopropylbenzene and its chlorinated and brominated analogs.[11,12]

## RESULTS

*Neutron activation analysis.* The results of the determination of nonpolar (cyclohexane soluble) organohalogenated compounds are given in Tables 1 and 2. Nonpolar organochlorine compounds are present in all samples, organobromine compounds are present in samples from one plant only, and organoiodine compounds are not detected. Assuming that

*Table 1.* Concentration of organohalogenated compounds (ppm) in the effluent of a sulfate plant chlorine bleachery.

| Sample | Cyclohexane extracts | | | Butyl acetate extracts | | |
|---|---|---|---|---|---|---|
| | Cl | Br | I | Cl | Br | I |
| 1. Chlorination | 0.5 | 0.002 | 0.0002 | 2.6 | <0.003 | <0.0003 |
| 1. Alkaline extraction | 0.9 | 0.003 | 0.0002 | 3.2 | <0.004 | <0.0006 |
| 2. Chlorination | 0.3 | 0.0009 | 0.0002 | 0.4 | 0.003 | 0.0004 |
| 2. Alkaline extraction | 0.01 | 0.0004 | 0.0001 | 1.5 | 0.002 | <0.0004 |
| Hypochlorite | 0.1 | 0.0009 | 0.0006 | 1.0 | 0.007 | 0.00007 |
| Average | 0.36 | – | – | 1.7 | – | – |
| Blank | 0.001 | <0.0001 | <0.0001 | 0.002 | <0.003 | <0.00001 |

*Table 2.* Concentration of organohalogenated compounds (ppm) in the effluent of a sulfite plant chlorine bleachery.

| Sample | Cyclohexane extracts | | | Butyl acetate extracts | | |
|---|---|---|---|---|---|---|
| | Cl | Br | I | Cl | Br | I |
| 1. Chlorination | 0.3 | 0.08 | <0.0002 | 0.6 | 0.2 | <0.0002 |
| 2. Chlorination | 0.6 | 0.08 | <0.0001 | 0.02 | 0.05 | <0.0001 |
| Alkaline extraction | 0.8 | 0.06 | <0.0002 | 5.0 | 0.3 | <0.002 |
| 1. Hypochlorite | 0.8 | 0.09 | <0.0002 | 0.04 | 0.003 | <0.001 |
| 2. Hypochlorite | 0.5 | 0.02 | <0.0002 | 0.5 | 0.04 | 0.005 |
| SO$_2$-treatment | 1.0 | 0.03 | <0.0002 | 0.5 | 0.02 | <0.0001 |
| Average | 0.67 | 0.06 | – | 1.1 | 0.1 | – |
| Blank | 0.001 | <0.0001 | <0.0001 | 0.002 | <0.0003 | <0.00001 |

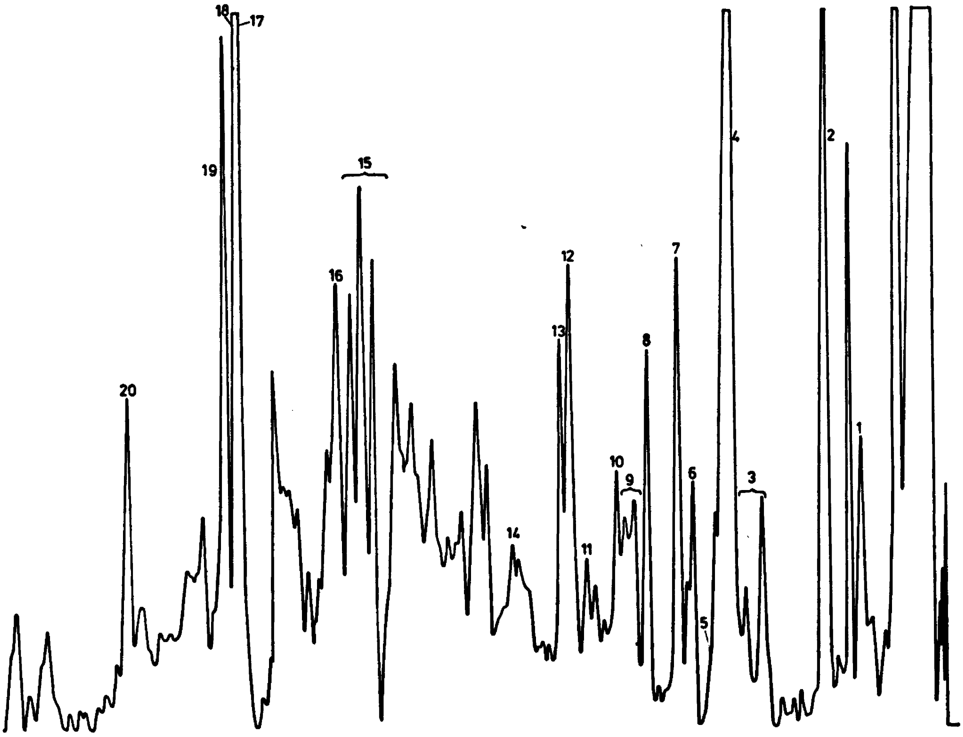

*Fig. 1.* Gas chromatogram (total ion current) of the cyclohexane extract of the effluent from a sulfite plant chlorine bleachery. The peaks 1 – 20 are interpreted as (1) M = 136 $C_{10}H_{16}$, (2) M = 134 methylisopropylbenzene, (3) M = 152 $C_{10}H_{16}O$, (4) M = 168 chloro-methylisopropylbenzene (2 isomers), (5) M = 134 alkyl(C4)-benzene, (6) M = 166, (7) M = 212 bromo-methylisopropylbenzene, (8) M = 202 dichloro-methylisopropylbenzene, (9) M = 204 sesquiterpene $C_{15}H_{24}$, (10) M = 202 dichloro-methylisopropylbenzene, (11) M = 204 sesquiterpene $C_{15}H_{24}$, (12) M = 202 dimethylpropyltetralin, (13) M = 200, (14) M = 218, (15) M = 272 diterpene $C_{20}H_{32}$, (16) M = 268, (17) M = 282 diterpene, (18) M = 284 diterpene, (19) M = 314 methyldehydroabietate, (20) M = 328 diterpene.

each step contributes approximately the same amount of process water, an average value is estimated.

In addition, the total amount of organohalogenated phenolic (butyl acetate soluble) compounds is also determined, and the results are given in Tables 1 and 2 for the sulfate and the sulfite plant, respectively.

*GC/MS-analysis.* The GC/MS technique was used to characterize the individual compounds in the cyclohexane extracts. The GC traces of the samples showed the same compounds to be present in all samples, and only extracts from the first chlorination and alkali-extraction steps were studied by MS. Chromatograms of the two extracts are shown in Figs. 1 and 2, and the identified compounds are listed in the pertinent captions. The molecular structures of the different nonpolar halogenated hydrocarbons are given in Fig. 3.

## DISCUSSION

Neutron activation analysis (NAA) is well suited for investigating organohalogenated compounds in the environment. The method is specific and sensitive, and provided that suitable solvents and extraction conditions are chosen, the nonpolar as well as phenolic compounds from the bleacheries may be characterized. The results demonstrate the presence of nonpolar organochlorine compounds in

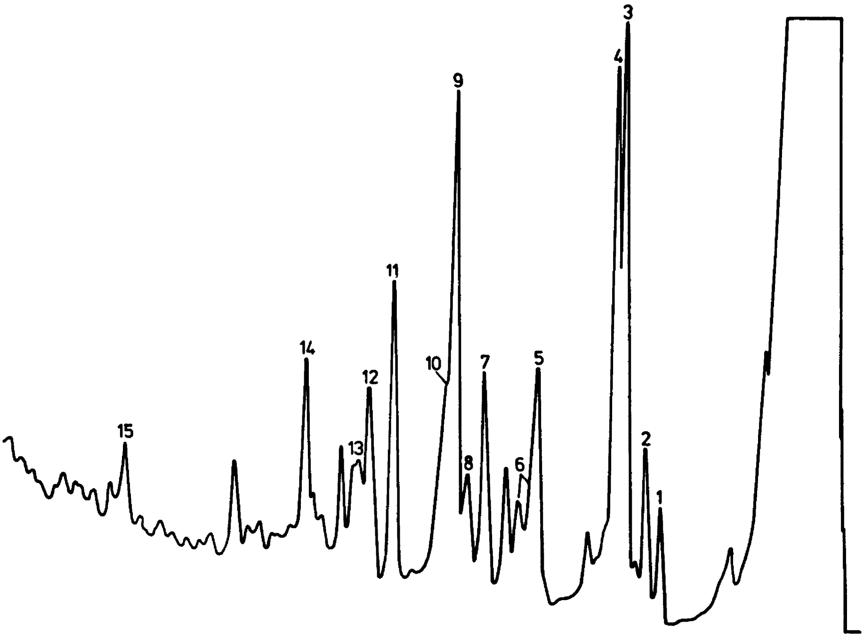

*Fig. 2.* Gas chromatogram (total ion current) of the cyclohexane extract of the effluent from a sulfate plant chlorine bleachery. The peaks 1 – 15 are interpreted as (1) and (2) M = 152 monoterpene, (3) M = 153 monoterpene, (4) M = 152 camphor, (5) M = 146, (6) terpene, (7) M = 202 dichloro-methylisopropylbenzene, (8) M = 166 chloro-methylpropenylbenzene, (9) M = 146 4-phenyl-3-buten-2-one, (10) M = 202 dichloro-methylisopropylbenzene, (11) M = 170 terpene, (12) M = 200 dichloro-methylisopropenylbenzene, (13) M = 200 dichloro-methylisopropenylbenzene, (14) M = 220 terpene, (15) phthalate.

bleachery effluents from both a sulfate and a sulfite plant. On the average, the concentration of the phenolic compounds is about two to three times the concentration of the nonpolar compounds.

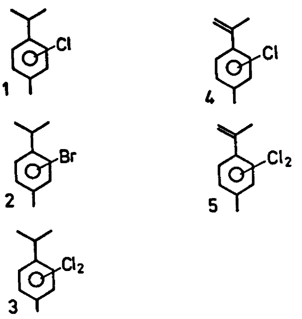

*Fig. 3.* Halogenated aromatic hydrocarbons identified in effluents from chlorine bleacheries. (1) chloro-methylisopropylbenzene (2 isomers identified), (2) bromo-methylisopropylbenzene, (3) dichloro-methylisopropylbenzene (2 isomers), (4) chloro-methylisopropenylbenzene (2 isomers) and (5) dichloro-methylisopropenylbenzene (2 isomers).

In the sulfite plant, brominated organic compounds are also present. In this plant the first chlorination step takes place in sea water. Presumably, chlorine will react with the bromide naturally present in sea water (usually about 65 ppm) to give bromine, which in turn may brominate the organic material.

From the data given, the discharge of nonpolar organochlorine compounds may be estimated. A concentration of 1 ppm organically bound chlorine in the effluent from a bleach plant with a water consumption of 20 000 $m^3$/day will result in a daily discharge of 20 kg (measured as chlorine). This corresponds to about 7 t/year.

The nonpolar halogenated compounds identified in this work are all substituted aromatic hydrocarbons. To the best of our knowledge, no such compounds have been previously identified in bleachery effluents. In general, halogenated aromatic compounds are of great environmental concern.[13–15] However, little is known about the chemical and biological persistence and the biological effects in the recipient of the specific compounds identified in this work.

As revealed by the GLC/MS-data (Fig. 1), one of the main components in the extracts is unsubstituted methylisopropylbenzene (cymene). This compound is assumed to be the *para* isomer (*p*-cymene) determined by comparison with a reference compound of *p*-methylisopropylbenzene. However, as the mass spectra data given in the literature are quite similar for the three cymene isomers, we could not exclude the *ortho* or *meta* isomer to be present. *p*-Cymene is known to be formed during the cooking process from the terpenes naturally present in the wood and the reaction is catalysed by lignin radicals.[16] It is therefore reasonable to assume that the halogenated *p*-cymenes are formed by substitution reactions on the parent molecule.

It is also interesting to note that chlorinated derivatives of *p*-methylisopropenylbenzene (structure based on the mass spectra and analogy with the methylisopropylbenzenes) are identified only in effluents from the sulfate plant. This suggests that the *p*-methylisopropenylbenzene is formed mainly under the conditions in the sulfate plant and by analogy with *p*-methylisopropylbenzene, that the chlorinated derivatives are formed by substitution reactions on the parent molecule.

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