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Identification by capillary gas chromatography–mass spectrometry of volatile organohalogen compounds formed during bleaching of kraft pulp

CHRISTINA ROSENBERG*, TIINA AALTO, JARKKO TORNAEUS and ANTTI HESSO

Institute of Occupational Health, Topeliuksenkatu 41 aA, SF-00250 Helsinki (Finland)

PAAVO JÄPPINEN

Enso-Gutzeit Oy, SF-55800 Imatra (Finland)

and

HARRI VAINIO

International Agency for Research on Cancer, F-69372 Lyon (France)

ABSTRACT

   The occurrence of volatile halogenated compounds in spent liquors from kraft softwood and hardwood pulp bleaching processes was studied. The identity of the low-molecular-mass constituents was verified by capillary gas chromatography–mass spectrometry using an NBS/Wiley reference database and mass spectra of reference compounds. The purgeable fraction of the first chlorination stage of the softwood pulp contained numerically most of the organohalogen compounds detected. The ratio of chlorine to chlorine dioxide applied at this stage greatly affected the formation of the compounds. Identity was confirmed for fourteen components, of which two, dichloroacetonitrile and trichloromethanesulphonyl chloride, have not been previously identified in, *e.g.*, bleach kraft effluents. The most abundant volatile compounds were chloroform, 1,1,1-trichloropropanone, trichloromethanesulphonyl chloride, 1,1,2,3,3-pentachloro-1-propene and pentachloropropanone. Several of these volatile compounds are known mutagens or suspected carcinogens.

INTRODUCTION

   Organochlorine compounds found in effluents from kraft mill bleaching processes are derived from the use of chlorine-containing bleaching agents. The chemical composition of these chlorinated compounds has been extensively studied since the 1970s [1]. It has been established that most of the chlorine is bound to high-molecular-mass material, and that only *ca.* 30% occurs in the low-molecular-mass ($M < 1000$) fraction in the spent liquor of the first chlorination step and only 5% in the first alkaline extraction liquor of softwood kraft pulp [1].
   Research in this field has concentrated especially on environmental effects of the effluents. The chlorinated compounds found in effluents are often resistant to chemical and biological degradation. Many of these compounds are toxic to aquatic organisms and several of them are genotoxic. The identified compounds include

chlorinated acids [2], phenolics [3,4], and neutral compounds such as chlorinated acetones and aldehydes [5,6] and furanones [7,8]. The lipophilic properties of some chlorinated compounds have received special attention because of the possibility of bioaccumulation in aquatic systems [9–11]. Suntio et al. [12] reviewed the properties of ca. 250 chemicals identified in bleached pulp mill effluents.

However, scant data are available on volatile organochlorine compounds formed during the bleaching operation. Chloroform has been reported to be the most abundant halogenated compound in the volatile fraction of bleached kraft mill effluents [13,14]. Further investigation is required concerning the nature and occurrence of volatile organohalogens formed and potentially released into the work environment during the bleaching process.

This paper describes the identification of low-molecular-mass purgeable organohalogen compounds in spent liquors from different bleaching stages of softwood and hardwood kraft pulp.

EXPERIMENTAL

The bleaching process and sample collection

Single samples of spent liquors were taken at a kraft pulp mill from one softwood and one hardwood line with production capacities of about 300 and 1100 t/d, respectively. The bleaching was accomplished by multi-stage treatment with chlorine (C), alkali (E) and chlorine dioxide (D). The liquors were sampled at the wash filters after each bleaching stage.

The reagent in the first bleaching stage of the softwood kraft process consisted of a mixture of chlorine and chlorine dioxide (either 90:10 or 50:50). The complete bleaching sequence was C_{90}/D_{10} (or C_{50}/D_{50})–E_1–D_1–E_2–D_2. The E_1 stage was combined with hypochlorite treatment. The total charge of chlorine compounds was 50 kg/t of pulp in the first chlorination stage, expressed as active chlorine. The kappa number of the unbleached pulp was ca. 25.

The hardwood kraft process utilized chlorine dioxide alone in the first chlorination stage (D_0). The first alkaline extraction stage consisted of hypochlorite treatment followed by alkaline plus oxygen treatment (E/O). The complete bleaching sequence was thus D_0–E_1–E/O–D_1–E_2–D_2. The hardwood pulp had a kappa number of ca. 20, and the consumption of bleaching agent, expressed as active chlorine, in the D_0 step was 36 kg/t of pulp.

Isolation of volatile compounds

About 1.5 l of spent liquor was purged with nitrogen at a rate of 50 ml/min for 1 h and concurrently heated at the process temperature, i.e., 45–55°C. The reaction vessel was equipped with a magnetic stirrer and any volatilized compounds were trapped in a glass coil, immersed in a mixture of ethanol and dry-ice, or in an activated charcoal tube connected in series with the coil. The temperature of the cold-trap was about −70°C. The purged liquor was then discarded and replaced with a new 1.5-l sample of liquor, and the collection of volatile compounds was continued using the same trapping equipment. This procedure was repeated a third time. The coil and the charcoal tube were then eluted with ethyl acetate and n-pentane, respectively. The ethyl acetate eluate was concentrated to one twentieth of its original volume prior to analysis.

Gas chromatography–mass spectrometry

All eluates were analysed by capillary gas chromatography with mass spectrometric detection (GC–MS). The mass spectrometric system consisted of a Hewlett-Packard quadrupole mass spectrometer (HP 5990A) operating in the electron impact (EI) mode (70 eV) and equipped with a merged NBS/Wiley database (HP 59983K). The mass spectra were confirmed using a Finnigan MAT 8200 mass spectrometer with an on-line computer system and an NBS database (MAT INCOS 5.6E). The system was operated in the EI mode at 70 eV at a resolution of 3000.

The EI mass spectra were recorded in the range m/z 35–550. A fused-silica column (50 m × 0.3 mm I.D.) coated (0.17 μm) with 95% dimethyl–5% diphenylpolysiloxane (Hewlett-Packard) was used, coupled directly to the ion source.

The temperature of the transfer line was 250°C in both mass spectrometers. The ion source temperature and emission current were 180° and 0.3 mA, respectively, in the Hewlett-Packard system and 150°C and 1 mA, respectively, in the Finnigan MAT 8200 system. Helium was used as carrier gas (24 cm/s at 100°C) and samples of 1 μl were injected using an on-column technique at 35°C. Chloroform was analysed using split injection in a Grob-type split–splitless injector operating at 220°C and with a 1:10 splitting ratio. The column temperature program was as follows: 6 min at 35°C, increased from 35 to 100°C at 5°C/min and from 100 to 250°C at 10°C/min, and held for 15 min at 250°C.

RESULTS AND DISCUSSION

The purgeable organohalogen compounds identified in the spent bleaching liquors included chlorinated and brominated alkanes, alkenes, esters, ketones, benzenes and some chlorinated sulphur compounds (Tables I and II).

A reconstructed ion chromatogram of the cold-trap eluate from the C_{90}/D_{10} first chlorination stage spent liquor is given in Fig. 1. Emphasis was placed on peaks with isotopic cluster patterns typical of chlorine and bromine compounds. Some of the compounds were identified using mass spectral interpretation confirmed by comparison with the mass spectrum of a reference compound (technique A). Others were identified by mass spectral interpretation and comparison with reference spectra from the NBS and Wiley databases (technique B).

In the C_{90}/D_{10} first chlorination stage sample fourteen volatile organohalogen compounds were encountered, eleven of which were identified using technique A and three using technique B (Table I). In addition, six peaks with a typical chlorine isotope cluster pattern were registered, but their identity was not solved accurately enough (Fig. 1, peaks I–VI). Of the eleven category A compounds, two have not been reported previously to be present in spent bleach effluents, *viz.*, dichloroacetonitrile [Chemical Abstracts Service (CAS) No. 3018-12-0] (Fig. 2a) and trichloromethanesulphonyl chloride (CAS No. 2547-61-7) (Fig. 2b) [5,12].

Dichloroacetonitrile has been reported as a component formed in the chlorination of humic acid, a precursor of halogenated compounds formed during chlorination of drinking water [15].

In this study, the source of trichloromethanesulphonyl chloride remained obscure. Chlorinated dimethylsulphones have been reported in biologically treated bleached kraft effluents [16]. The latter compounds were suggested to be derived from dimethyl thioether residues from the cooking process prior to bleaching [1].

TABLE I

PURGEABLE ORGANOHALOGEN COMPOUNDS IDENTIFIED IN THE SPENT LIQUOR FROM THE FIRST CHLORINATION (C_{90}/D_{10}) STAGE OF SOFTWOOD PULP

Peak No. [a]	Compound identified	Retention time (min)[b]	C_{90}/D_{10}	
			Identification technique	Peak area
—	Chloroform[c]	—	A[d]	—
1	Trichloroethene	6.95	A	★★[e]
2	Bromodichloromethane	7.09	A	★
3	Dichloroacetonitrile	7.38	A	★★
4	Tetrachloroethene	10.25	A	★
5	1,1,1-Trichloropropanone	11.61	B[f]	★★★★
6	Methyl 2,2-dichloropropanoate	12.65	B	★
7	Pentachloroethane	16.89	A	★
8	1,4-Dichlorobenzene	18.28	A	★
9	Trichloromethanesulphonyl chloride	18.88	A	★★★
10	1,2-Dichlorobenzene	19.12	A	★
11	1,1,2,2-Tetrachloropropane	19.48	B	★★
12	1,1,2,3,3-pentachloro-1-propene	20.79	A	★★★★
13	Pentachloropropanone	21.02	A	★★★★

[a] Peak number refer to Fig. 1 (reconstructed ion chromatogram from the C_{90}/D_{10} stage cold-trap eluate in ethyl acetate).

[b] The retention times are reported in minutes as absolute retention time. The relative standard deviation for the retention times was 0.01 within the elution range ($n = 12$).

[c] Chloroform was analysed in the n-pentane eluate from the activated charcoal tube connected in series with the cold trap and is therefore not recorded in Fig. 1.

[d] A = identification based on mass spectral interpretation and comparison with the spectrum of a reference substance.

[e] ★ → ★★★★ = Increasing peak area.

[f] B = identification based on mass spectral interpretation and comparison with a reference spectrum from the library database.

TABLE II

PURGEABLE ORGANOHALOGEN COMPOUNDS IDENTIFIED IN THE SPENT LIQUORS FROM THE FIRST (C_{50}/D_{50}) AND SECOND (D_1) CHLORINATION STAGES OF SOFTWOOOD PULP AND THE FIRST CHLORINATION STAGE (D_0) OF HARDWOOD PULP

Compound identified	C_{50}/D_{50} (softwood)	D_1[a] (softwood)	D_0 (hardwood)
Chloroform	A	A	A[b]
Dichloroacetonitrile	—[c]	—	A
Methyl chloroacetate	B[d]	—	—
1,1,1-Trichloropropanone	B	B	B
Tribromomethane	A	A	—
2,5-Dichlorothiophene	—	—	A
Trichloromethanesulphonyl chloride	A	—	
Pentachloropropanone	A	A	—
Tetrachlorothiophene	A	A	—

[a] Belongs to the bleaching sequence beginning with the C_{90}/D_{10} stage.

[b] A = identification based on mass spectral interpretation and comparison with the spectrum from a reference substance.

[c] Not present.

[d] B = identification based on mass spectral interpretation and comparison with a reference spectrum from the library database.
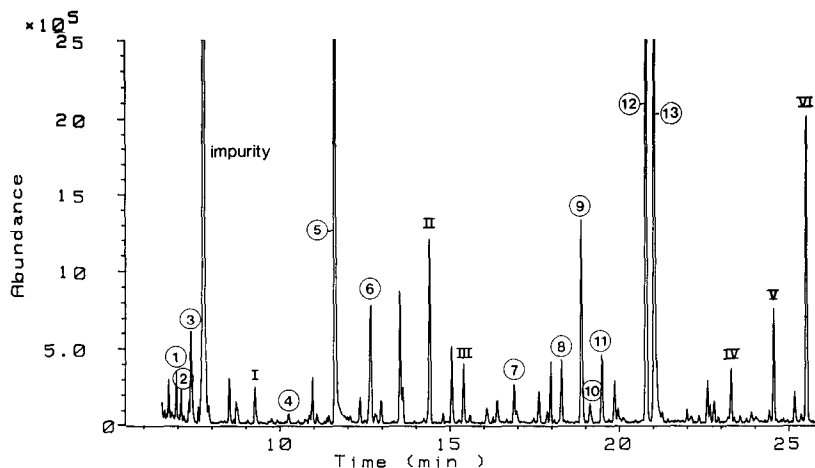
Fig. 1. A reconstructed ion chromatogram of the cold-trap eluate in ethyl acetate from the C_{90}/D_{10} first chlorination stage of softwood. Peaks 1–13 are listed in Table I. Compounds I–VI exhibited a chlorine isotope cluster pattern, but their identification was not unequivocal.

The category B compounds have also been found in bleached kraft effluents as such (peak 5), as a precursor (peak 6) or as a related compound (peak 11) [6, 17, 18].

Chloroform was found and confirmed with complete identification (category A) in the n-pentane eluates from the activated charcoal tubes connected in series with the cold trap. Traces of tetrachloroethene, 1,1,1-trichloroethane and carbon tetrachloride were also detected. The identity of the latter was verified by the selected ion monitoring technique with the Hewlett-Packard quadrupole mass spectrometer. The ions monitored were m/z 164, 166, 97, 99 and 117, 119 with intensities of 75/100%, 100/66% and 100/99%, respectively.

Quantification of the peaks was not done. However, on comparing the relative abundances of the GC–MS peaks, it was evident that the five most abundant compounds were chloroform, 1,1,1-trichloropropanone, trichloromethanesulphonyl chloride, 1,1,2,3,3-pentachloro-1-propene and pentachloropropanone. Chloroform accounted for about 80% of the relative abundance of the aforementioned compounds. The high proportion of chloroform in the volatile fraction is consistent with effluent studies [14,19].

The purgeable fraction from the softwood C_{90}/D_{10} first bleaching stage contained most of the organohalogen compounds identified. Considerably fewer compounds were detected in the cold-trap eluate when chlorine–chlorine dioxide (50:50) was used (C_{50}/D_{50}) in the softwood bleaching process. This was to be expected, as previous studied had showed that the formation organohalogens decreases with decreasing chlorine consumption [20,21]. Only seven compounds were detected (Table II, C_{50}/D_{50} column), five of which were identified by technique A and two by technique B. The overall pattern was similar to that for the C_{90}/D_{10} sample, in that chloroform, pentachloropropanone and trichloromethanesulphonyl chloride were the most abundant compounds. Even fewer volatile organohalogen compounds were detected in the spent liquor of the D_1 second chlorination stage (preceded by the
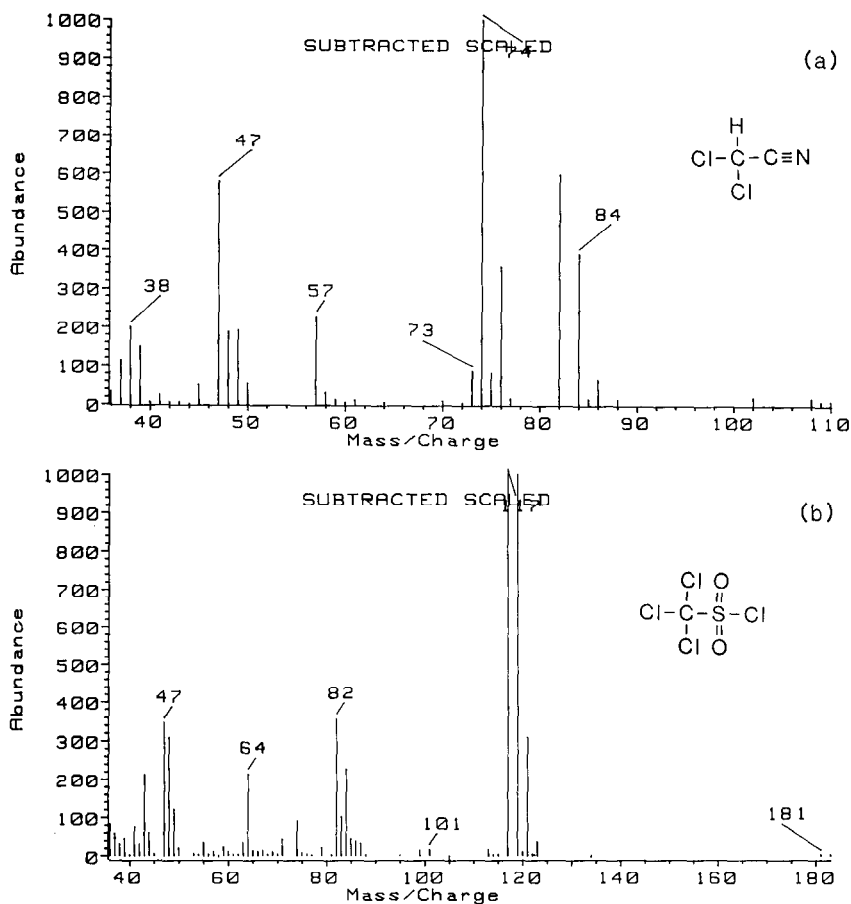
Fig. 2. Electron impact mass spectra obtained from peaks 3 and 9 in Fig. 1 (C_{90}/D_{10} first chlorination stage of softwood). (a) Dichloroacetonitrile; (b) trichloromethanesulphonyl chloride.

C_{90}/D_{10} stage). Of the total of five compounds classified (Table II, D_1 column), four belonged to the identification category A and one to category B. Trichloromethane-sulphonyl chloride was not detected at this stage; instead, another chlorinated sulphur compound, tetrachlorothiophene, was encountered. This compounds has also been previously identified in spent pulp bleach liquors [11].

Bleaching of hardwood usually produces less organohalogens [22], which was also evident in this study for volatile compounds. In the first chlorination stage of hardwood pulp (D_0), only three compounds were identified by technique A and one by technique B (Table II, D_0 column). On the other hand, the use of chlorine dioxide alone in this stage may account for the small number of compounds identified.

Virtually no volatile organohalogen compounds were detected in the cold-trap eluates from the softwood or hardwood third chlorination stage (D_2) or the alkali stages. However, chloroform and traces of 1,1,1-trichloroethane were found in the activated charcoal eluates from every stage of the two bleaching processes. Similarly,

traces of tetrachloroethene, carbon tetrachloride and bromodichloromethane were found in all but the alkaline stages of the hardwood bleaching process. It is noteworthy that whereas the relative abundance of chloroform and carbon tetrachloride decreased with decreasing chlorine use, that of 1,1,1-trichloroethane and bromodichloromethame remained more or less constant. This seems to indicate that they are present as impurities rather than as bleaching-derived compounds. The concentration of chloroform in the second chlorination stage of softwood (D_1) was about one quarter of that detected in the first chlorination stages (C_{90}/D_{10} and C_{50}/D_{50}). The corresponding figure was one fifteenth in the first chlorination stage with hardwood (D_0). The enhancement of chloroform formation by hypochlorite treatment [1,22] was evident in the E/O stage of the hardwood process. In this stage, which followed the first alkaline extraction stage combined with hypochlorite, the relative abundance of chloroform approached that found in the C_{90}/D_{10} stage of the softwood process.

CONCLUSIONS

The laboratory analysis of liquors from different bleaching stages of softwood and hardwood kraft pulp revealed numerous volatile low-molecular-mass organohalogen compounds. Most of the compounds were derived from the first bleaching stage. It is probable that these volatile compounds may be released into the workplace air during the process. Of the fourteen halogenated purgeable compounds identified, two have not been found previously in bleach kraft effluents, *viz.*, dichloroacetonitrile and trichloromethanesulphonyl chloride. Some of the most abundant compounds identified are known mutagens, *e.g.*, 1,1,2,3,3-pentachloro-1-propene and pentachloropropanone [23], or suspected carcinogens, *e.g.*, chloroform and carbon tetrachloride [24]. Further investigation is required to estimate the exposure of workers to these potentially harmful organohalogen compounds formed during bleaching of kraft pulp with chlorine-containing agents.

ACKNOWLEDGEMENTS

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