IDENTIFICATION OF VOLATILE ORGANO-CHLORINE COMPOUNDS FORMED DURING PULP BLEACHING - OCCURRENCE IN WORK ENVIRONMENT AND GENOTOXIC EFFECTS

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ABSTRACT

More than 30 volatile organo-halogen compounds were monitored in the workplace air in a softwood bleaching plant. Chloroform, carbon tetrachloride, tetrachloroethane, 1,1,1-trichloroethane were detected in the low $\mu g/m^3$ level. Spent liquor from the first chlorination stage of bleached softwood pulp was positive in the Ames test and SOS chromotest without metabolic activation. The same sample induced also chromosome aberrations and sister chromatid exchanges in CHO cells in vitro.

INTRODUCTION

The nature and properties of organo-chlorine compounds, including polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), formed in kraft pulp mill bleaching operations, have been extensively studied since the 1970s (1). Research in this area has concentrated on spent pulp liquors and particularly their environmental effects. However, scanty data are available on the nature and occurrence of volatile compounds released into the workplace air (2,3). We studied the volatile or purgeable compounds in spent liquors from different bleaching stages of softwood and birch kraft pulp. The workplace air was monitored with regard to identified organo-chlorine compounds to evaluate the exposure profile of the workers. The spent liquors were also tested for their genotoxic effects.

EXPERIMENTAL

The spent liquors were sampled from different stages of a soft- and hardwood kraft process, where the bleaching was accomplished with a multistage treatment with chlorine (Cl_2), alkali and chlorine dioxide (ClO_2). A mixture of Cl_2 and ClO_2 or only ClO_2 was used in the first chlorination stage. The volatile compounds were isolated in laboratory experiments by heating the liquors to temperatures corresponding to

process conditions, purging with nitrogen and trapping in a cold-trap (-70 °C). The trap was eluted with n-pentane or ethyl acetate, and the eluates analysed by capillary gas chromatography/mass spectrometry. A Finnigan MAT 8200 mass spectrometer was used with both electron impact and chemical ionization. The air in a softwood bleaching plant was monitored with stationary and personal samplers. The sampling devices consisted of solid sorbents, e.g., activated charcoal, silica gel, XAD-2 and Tenax, and cold traps. The air samples were analysed by selective ion monitoring with a Hewlett-Packard gas-chromatograph - mass selective detector combination or additionally with flame ionization or electron capture detection.

The same process samples were tested in four genotoxicity tests. The testing battery consisted of the Ames test using Salmonella typhimurium strains TA98 and TA100, SOS chromotest in Escherichia coli PQ37, and assays for chromosome aberrations (CA) and sister chromatid exchanges (SCEs) in Chinese hamster ovary (CHO) cells in vitro.

RESULTS AND DISCUSSION

The purgeable compounds from spent bleaching liquors identified in the laboratory experiments included chlorinated and brominated methanes, chlorinated ethenes, ethanes, propenes, propanes, cyclopropenes, acetones, benzenes and some chlorinated sulfur compounds. The identification of compounds classified as A was based on mass spectral interpretation and comparison with a reference spectrum of the substance. Class B compounds denoted identification based on mass spectral interpretation and comparison with a reference spectrum of a library data base and with a purity > 50 %.

The purgeable fraction of the first chlorination stage of the softwood pulp comprised numerically most of the organo chlorine compounds detected. The Cl_2/ClO_2 ratio applied at this stage affected markedly the number of compounds formed. The compounds detected at the alkaline extraction stage were significantly fewer in number. E.g., 35 organo-halogen compounds were tentatively identified when the Cl_2/ClO_2 ratio was 9:1 in a softwood kraft pulp. Of these compounds 8 were identified with technique A and 12 with technique B. The 5 most abundant A and B class substances, were chloroform (class A), pentachloro-2-propanone (class A), pentachloropropene (class B), 1,1,1-trichloro-2-propanone (class B), and trichloromethanesulfonyl chloride (class A). Chloroform accounted for about 95 % of the relative abundance of these compounds, the remaining comprising about 4 %.

Based on the results for the purgeable compounds in the laboratory experiments, the workplace air in the softwood bleaching plant was monitored for more than 30 organo-chlorine compounds. Only few compounds were found in concentrations above the detection limit in the work environment. The

compounds detected included, chloroform, carbon tetrachloride, 1,1,1-trichloroethane, tetrachloroethene and methanesulfonyl chloride (Table 1). The concentrations of both the stationary and personal samples were in the low $\mu g/m^3$ range, corresponding to about 1/100 of the current Finnish permissible limit values. In general, no marked difference in the concentrations between the measurements during bleaching operations using Cl_2/ClO_2 ratios 9:1 or 1:1 was observed. It is noteworthy that pentachloro-2-propanone found in the laboratory studies was not detected in the workplace air samples, whereas methanesulfonyl chloride was found in samples taken from the workroom air but not in those from the laboratory experiments.

Table 1. Concentrations (mg/m^3) of volatile organo-halogen compounds in stationary and personal workroom air samples from a softwood bleaching plant.

Compound	Cl_2/ClO_2 ratio	Personal samples	Stationary samples	Permissible[1] limit value
chloroform	(9:1)	0.05 - 0.12	0.05 - 0.3	50
	(1:1)	nm[2]	0.14 - 1.7	
carbon tetrachloride	(9:1)	0.01 - 0.06	0.01 - 0.03	31
	(1:1)	nm	nd < dl[3]	
tetrachloroethane	(9:1)	0.10 - 0.13	0.02 - 0.07	335
	(1:1)	nm	nd < dl	
1,1,1-trichloroethane	(9:1)	nm	0.004 - 0.008	540
	(1:1)	nm	0.002 - 0.003	
methanesulfonyl chloride	(9:1)	nm	nd < dl	
	(1:1)	nm	0.002 - 0.02	

1 = National Board of Labour Protection in Finland, 1987
2 nm = not measured
3 nd < dl = not detected, below detection limit (0.005 mg/m^3)

The spent liquors from the first chlorination stage in softwood bleaching were positive, without metabolic activation (-S9 mix), both in the Ames test using S. typhimurium strain TA100 and the SOS chromotest. The mutagenic activity decreased when the Cl_2/ClO_2 ratio was changed from 9:1 to 1:1. Also, when the pH of the sample (Cl_2/ClO_2 = 9:1) was adjusted from 2 (initial) to 7, a decrease in mutagenic activity was observed. The neutralized sample was also much less toxic to the test bacteria than the original one. The spent liquors from the process of hardwood (mainly birch) bleaching, where only ClO_2 was used in the first chlori-

nation stage, showed negative results in both bacterial tests.

The softwood spent liquor (first chlorination stage, Cl_2/ClO_2 = 1:1) tested for the induction of CAs, showed a clear increase of aberrant cells (with mainly chromatid-type aberrations) only at a dose of 204 µl/ml without metabolic activation (-S9 mix). A slight elevation of cells with chromatid-type aberrations was observed with S9 mix at doses of 65 and 113 µl/ml. A lengthening of the treatment time from 4 h to 20 h (-S9 mix) did not affect the CA induction observed. The 20 h treatment time gave a stronger induction of CAs (-S9 mix) with doses of 63, 113 and 204 µl/ml in a sample where the Cl_2/ClO_2 ratio was 9:1 compared to the 1:1 sample, giving significantly greater numbers of aberrant cells.

Results from the SCE test on the first chlorination stage spent liquor (Cl_2/ClO_2 = 1:1) showed a dose-dependent increase in SCEs (65, 113 and 204 µl/ml) without S9 mix, while only the highest dose (204 µl/ml) was positive with S9 mix.

Volatile organo-chlorine compounds detected in the workroom air during bleaching operations were few in number and the concentrations were well below current Finnish permissible limit values. In the future we shall focus our interest on the possible occurrence of more complex organo halogen compounds in the work environment, i.e., polychlorinated dibenzo-p-dioxins and dibenzofurans, as well as chlorinated phenolic compounds. In addition, studies on in situ mutagenicity of workplace air, using a portable test system where the air is directly impinged through a suspension of bacteria, are in progress.

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