

DETERMINATION OF POLYCHLORINATED DIBENZOTHIOPHENES IN STACK GASES AND IN BLEACHED PULP MILL EFFLUENTS

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INTRODUCTION. Polychlorinated dibenzothiophenes (PCDBTs) are environmentally interesting compounds due to their structural resemblance with polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs).^{1,2} The potential hazard of PCDBTs has been recently indicated by finding PCDBTs in emissions of waste incineration.³⁻⁵ The origin of the PCDBTs in different environmental samples is not known. It is possible that these compounds are formed from polychlorobiphenyls and sulfur quite generally found in raw materials and chemicals or from different polychlorinated thiophenols which are degradation products of certain pesticides and in part naturally occurring compounds through condensation reactions in a similar way as PCDFs are suggested to be formed from chlorophenols⁶.

In this study some PCDBTs have been prepared to serve as model compounds in environmental and toxicological analysis. The determination of PCDBTs from stack gas and bleached pulp mill effluent samples was done by HRGC/HRMS with a MS-resolution of 20 000 to obtain an unique separation of the PCDBTs from the PCDDs.

THE MODEL COMPOUNDS. The number of possible TeCDBTs is 38 and of PeCDBTs 28. Only a few of these have been synthesized. The compounds were prepared by Friedel-Crafts type reactions from PCBs and sulfur. Separation of the different isomers was done by HPLC and their structures verified by GC/MS and ¹H NMR spectroscopy.^{7,8} Three TeCDBTs were obtained as pure isomers: 2,3,7,8-TeCDBT, 3,4,6,7-TeCDBT and 1,2,7,8-TeCDBT. In extraction and chromatographic clean-up methods used to analyse PCDDs and PCDFs, the PCDBTs behave analogically to these. Consequently, PCDBTs can be analyzed by GC/MS from the so called dioxin-fraction.

PREPARATION OF THE SAMPLES. The samples were from two stack gases and from six bleached pulp mill effluents. One stack gas sample consisted of gas phase only and the other one of both gas phase and particles. The samples were

from different incinerators. The pulp mill effluents were acid and alkaline effluents from a softwood plant and from a hardwood plant (C/D-stage and E-stage), an input of activated sludge treatment of combined effluents and an output of activated sludge treatment plant. Both bleaching plants had a multi-stage bleaching, where chlorine, chlorine dioxide and oxygen were used in the bleaching.

Only particles in the effluent waters were studied, while it can be assumed that PCDBTs are in large part particle-bound. The water samples were filtered twice, first with Whatman Glass Microfibre Filters GF/D ($2.7\mu\text{m}$) and then with Microfibre Filters GF/F ($0.7\mu\text{m}$). The filters were let to dry and the dry weight was determined. The samples were Soxhlet-extracted with toluene for 48 hours. The $^{13}\text{C}_{12}$ -labeled 2,3,7,8-TeCDD used as an internal standard was added to the samples before extraction. Column chromatography with basic aluminium oxide and activated carbon was used to separate the dioxin fraction from the extracts.

HRGC/HRMS ANALYSIS OF THE SAMPLES The exact molecular weight of tetrachlorodibenzothiophenes (TeCDBTs) is $\text{MW} = 319.8788$ and that of tetrachlorinated dibenzodioxins (TeCDDs) is $\text{MW} = 319.8965$. Consequently, HRMS resolution of about 20 000 is needed for a unique distinction between these compounds. In the HRGC with unpolar SE-30 and SE-54 columns the retention times of the PCDBTs compared with the retention times of the corresponding PCDDs and PCDFs are obviously longer. However, in many environmental samples there are interfering peaks eluting in the same window as the PCDBTs if low resolution in MS is used.

A high resolution mass spectrometer VG 70-250 SE coupled to a HP 5890 gas chromatograph was used in the analysis of the stack gas samples and a VG AutoSpec high resolution mass spectrometer connected to a HP 5890 Series II gas chromatograph in the analysis of the bleached pulp mill effluent samples. The column was a 25 m HP-5 (0.2mm , $0.11\mu\text{m}$). Helium was used as carrier gas. The temperature program was $100^\circ\text{C}(1\text{min})-20^\circ\text{C}/\text{min}-180^\circ\text{C}-5^\circ\text{C}/\text{min}-280^\circ\text{C}(15\text{min})$. The temperature of injector was 260°C , transfer line 280°C and ion source 260°C . The electron ionization potential was 36 eV.

The selected ion monitoring was done with m/e values of M and $M + 2$ ions for the PCDBTs. TeCDBTs were monitored with values 319.8788 and 321.8758 and PeCDBTs with values 353.8398 and 355.8369. The $^{13}\text{C}_{12}$ -labeled 2,3,7,8-TeCDD used as a (tentative) internal standard was monitored with m/e values 331.9368 and 333.9339.

When a resolution of 20 000 was used in the GC/MS analysis it could be seen that the peaks of the ions of TeCDDs disappeared nearly completely when the exact values of the ions the TeCDBTs were used in the monitoring. Fig. 1. When the resolution of MS was decreased to 10 000 it was found that the sensitivity of the MS-detector increased about 4-5 fold, but PCDD peaks were visible by PCDBT ions. The resolution of 20 000 was further used in the analysis of the PCDBTs from the samples.

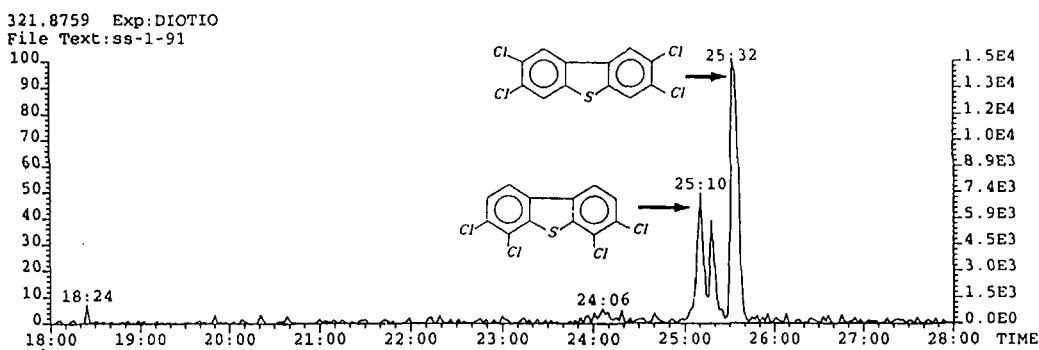
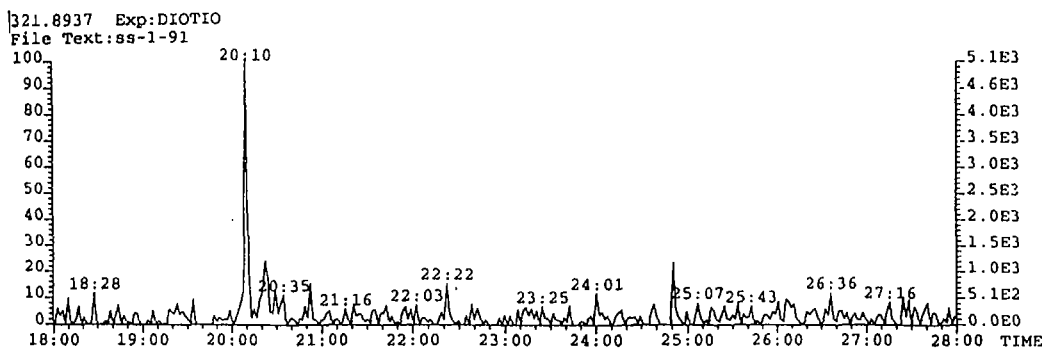


Figure 1. Selected ion monitoring chromatograms of a pulp mill effluent sample with M + 2 ions of a) TeCDDs = 321.8937 and b) TeCDBTs = 321.8759.⁹

RESULTS. Both stack gas samples were found to contain several tetra- and pentachlorinated dibenzothiophenes. From the pulp mill effluent samples were found only three TeCDBT isomers. The 2,3,7,8-TeCDBT was found to be the dominating TeCDBT isomer in all the pulp mill effluent samples which were found to contain TeCDBTs. Preliminary quantitative determination was done comparing the peak heights of the compounds under investigation with the height of the peak of the ¹³C₁₂-labeled 2,3,7,8-TeCDD. It was thus supposed that the MS-responses of these compounds are near the same. The contents per litre of particle-bound TeCDBTs in the samples were < 1 to 60pg/l. Also the contents of all particle-bound PCDDs and PCDFs studied from the effluent samples were low. Higher chlorinated DBTs tentatively monitored from the samples were not detected (< 1 pg/l). Even though exact quantitative determination were not done for the PCDBTs in the stack gas samples, because the stack emissions were unknown to us due to confidentiality, it was found that the amounts emitted from process per time unit of TeCDBTs and PeCDBTs were significantly higher in the stack than in the pulp mill.

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