POLYCHLORINATED DIBENZOTHIOPHENES, THIANTHRENES AND DIPHENYLSULFIDES FORMED IN METAL RECLAMATION

S. Sinkkonen[a], A. Vattulainen[b], J.-P. Aittola[c], J. Paasivirta[a] and M. Lahtiperä[a]
a) Department of Chemistry, University of Jyväskylä, Finland
b)Kuusakoski Ltd, Heinola, Finland
c)Viatek Tapiola Ltd., Environmental Technology, Jyväskylä, Finland

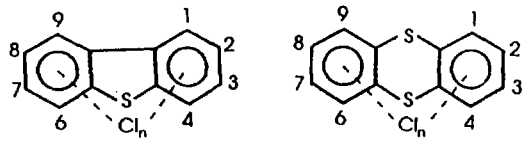
ABSTRACT

Polychlorinated dibenzothiophenes (PCDBTs), polychlorinated thianthrenes (PCTAs) and polychlorinated diphenylsulfides (PCDPSs) which are sulfur analogues for polychlorinated dibenzofurans (PCDFs), polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated diphenylethers (PCDEs), respectively, were analyzed by HRGC/HRMS in different samples from a metal reclamation plant. The samples were waste from processes where different temperatures (300-850 °C) were used. Tri-, tetra-and pentachlorodibenzothiophenes, tri-and tetrachlorothianthrenes and some chlorinated diphenylsulfide congeners were found in the samples. The concentrations of specific congeners were at the ng/g level.

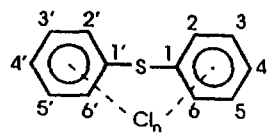
INTRODUCTION

PCDBTs, PCTAs and PCDPSs have previously been prepared to be used as model compounds in analytical work /1-4/. There exist some earlier reports about analyses of these compounds in environmental samples /3-8/. The structures of the compounds analyzed in this study are presented in Fig. 1. Some congeners of these compounds have been found in stack gas, fly ash and bleached pulp mill effluent samples. Recent investigations have shown that these compounds are AHH inducers, though not as potent as the corresponding oxygen compounds /9/. In the GC/MS analyses a high resolution is needed for the separation of many of these compounds. A resolution of about 20 000 is enough for the separation of TeCDDs and TeCDBTs. But, for example, for the MS separation between the $(M+2)^+$ ions of TeCDDs and M^+ ions of TeCDPSs a resolution of about 460 000,

which by normal techniques nowadays is not reached, would be needed. Fortunately, separation of PCDDs and PCDPSs could be readily done with LC clean up.



PCDBTs PCTAs



PCDPSs

Figure 1. The structures of the compounds analyzed.

EXPERMENTAL

The samples (5 g each) were soxhlet extracted with toluene for 48 hours. Before extraction 2.45 ng of $^{13}C_{12}$-2378TeCDD was added as internal standard. Toluene was evaporated, 0.5 ml of hexane added and activated carbon and basic aluminium oxide column chromatography were applied. A VG AutoSpec high resolution mass spectrometer connected to a HP 5890 Series II gas chromatograph was used in the mass spectrometric analyses of the samples. The column was a 25 m HP-5 (0.2 mm, 0.11 μm). The temperature program was 100°C (1min)-20°C/min-180°C-5°C/min-280°C (15min). The temperature of the injector was 260°C, transfer line 280°C and ion source 260°C. The electron ionization potential was 36 eV. In the HRGC/HRMS analyses a resolution of 20 000 was used in selected ion monitoring with the exact values of the $(M+2)^+$ and M^+ ions of PCDBTs, PCTAs and PCDPSs. Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) were determined for comparison.

RESULTS AND DISCUSSION

Tri-, tetra and pentaCDBTs and tri- and tetraCTAs were found in considerably high concentrations. The concentrations of pentaCTAs and PCDPS were lower. In the determination of PCDPSs there was a lot of interference by PCDDs and possibly also from some unknown compounds. Because many of these compounds

chromatographed in GC/MS in the same retention window very near each other the relative abundance ratios of the M^+ and $(M+2)^+$ ions as such could not in all cases be used to ascertain the identification of the compounds, even when the resolution was as high as 20 000.The total concentrations (sum of all isomers) of TeCDBTs in the samples were 5-20 ng/g and the concentrations of TriCTAs and TeCTAs in the range of 2-5 ng/g. Fig.2. presents the SIM chromatograms for TeCDBTs [$(M+2)^+$, 321.8758] in two samples, and for TeCTAs (M^+, 351.8509) and PeCDBTs (M^+, 353.8398) in one sample. The biggest peak in the chromatogram for PeCDBTs is supposed to be interference from $(M+2)^+$ for TeCTAs (353.8479). A resolution of about 44 000 would be needed for a complete separation of these.

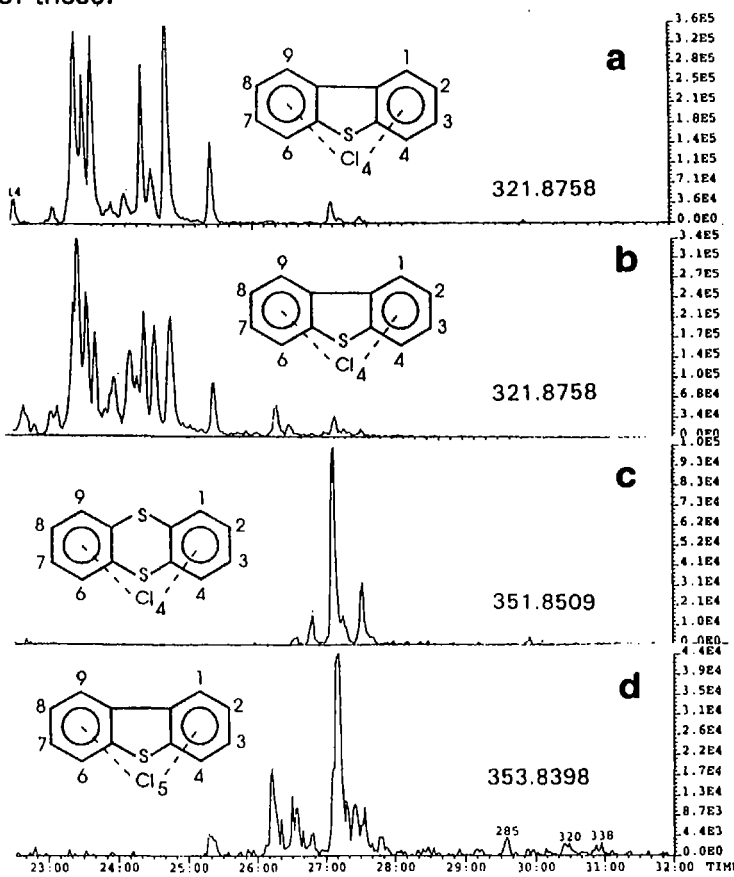


Fig.2. SIM chromatograms for TeCDBTs (a,b), TeCTAs (c) and PeCDBTs (d) in some samples.

Because PCDPSs were found in dioxin fraction, it is concluded that additional LC clean up to the applied carbon column and basic alumina treatments is needed to remove their interferences in analyses of PCDDs.

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