STRATEGY FOR THE IDENTIFICATION OF UNKNOWN POP

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Introduction

POP as persistent organic pollutants consist of a priority subgroup called PBT. PBT are defined as "Organic substances that are persistent, bioaccumulative and possess toxic characteristics likely to cause adverse human health or environmental effects".
These persistent bioaccumulating toxicants accumulate in biological systems according to their lipophilicity and they exhibit long-term or chronic toxicological properties. Based on this properties novel test strategies have been developed and applied to investigate samples of environmental and technical origin.[1,2]

Materials and Methods

The methodology has been described elsewhere[3]. In brief, PBT are extracted with toluene as a lipophilic solvent, reflecting the properties of the compounds of interest. After extraction the extract is treated on an acidified silica column, where non-persistent compounds are quantitatively hydrolysed and oxidized.
Cleanup of samples and quantification of PCDD/F using high resolution gas chromatography and high resolution mass spectrometry (HRGC/HRMS) were carried out as described elsewhere[4,5]. MS measurements were conducted employing a Finnigan MAT 95 (resolution=10000) instrument for isomer specific measurement.
The final extract has been further investigated by a test system, which determines toxicity in terms of dioxin like response and which is solvent compatible to ensure bioavailability quantitatively.
Parallel to that the final extract was investigated by HRGC-LRMS and HRGC-HRMS employing a finnigan MAT SSQ7000 and MAT95 in full scan mode, respectively. Chromatography has been performed using a fused silica capillary column (DB-5ms, 60 m × 0.25 mm i.d. × 0.1 µm ,J&W Scientific Inc., Folson, CA). Unknown Peaks were identified with the help of mass spectrum libraries (WILEY, NIST).

Results and Discussion

The procedure employed for the identification of unknown PBT resulted –besides the information about dioxin like toxicity- in some libary matches which are depicted for an environmental sample (soil) in figure 1 and samples of technical origin (flue-gas, fly ash) in figure 2.
In Scan-mode in a flue gas sample and in a fly-ash sample substances with a molecular mass of 485.7 ($C_{25}H_{10}Cl_5$), retention: 22:25 min; 511.7 ($C_{27}H_{11}Cl_5$) retention: 25:17 min and 519.7 g/mol ($C_{25}H_9Cl_6$), retention: 23:42 min and with five or six chlorine atoms could be characterized. Corresponding structures could be proposed (Fig. 2).

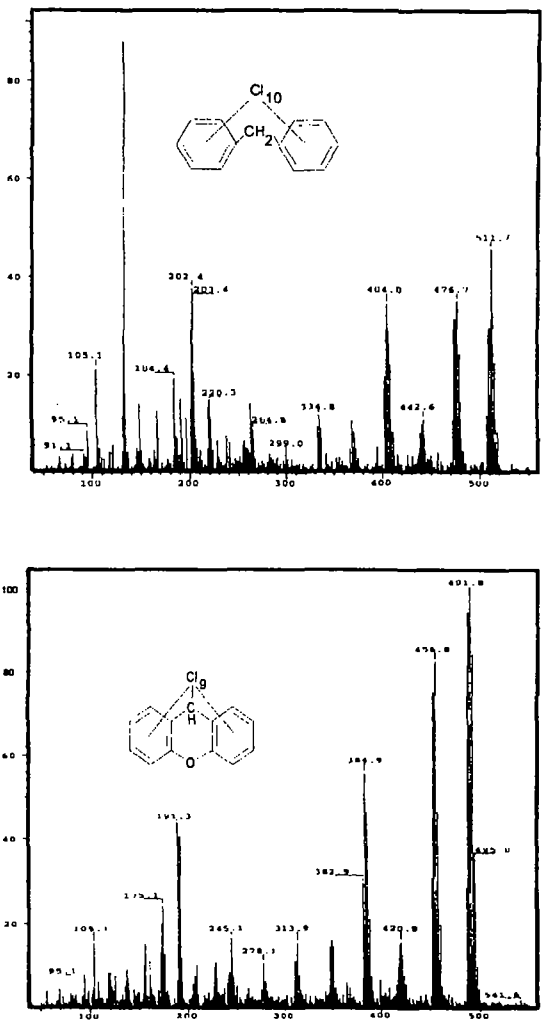
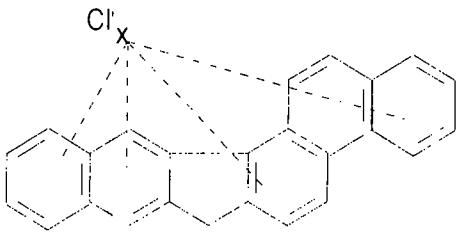
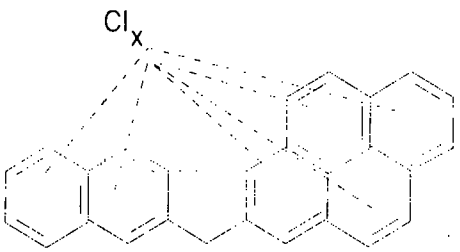


Figure 1: Library matches for polychlorinated diphenylmethanes and dibenzopyranes in final extracts of a soil.



$C_{25}H_{10}Cl_5$ and $C_{25}H_9Cl_6$;Penta- and Hexachloro-benzo(a,1,2-f)fluorene



$C_{27}H_{11}Cl_5$;Pentachloro-benzo(a,1,2-f,g)fluorine

Figure 2: Proposed PBT-like structures of compounds in residues of secondary aluminium smelting.

In the flue gas sample a pentachlorinated compound was found in relatively high amounts. In this sample the I-$TE_{Bioassay}$ was 14 ng/m^3, and the I-TE of chemical analysis was only 1.7 ng/m^3. The ratio of 8.2 could possibly be explained by pentachloro-benzo(a,1,2-f)fluorine. Confirmation of toxic potency has been not possible due to the lack of pure compound.

Conlusions

A simple pretreatment of lipophilic extracts with acidified silica can serve as a first easily performed attempt to identify unknown PBT. Further toxicological investigations of the pure compounds found and characterized will identify those as PBT.

References

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