

## **Polychlorinated dibenzothiophenes: Separation from polychlorinated dibenzodioxins and -furans and the prediction of their gas chromatographic retention indices**

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### **Introduction**

Polychlorinated dibenzothiophenes (PCDT) have been identified in a series of environmental samples [1]. Since their masses are nearly identical to those of the polychlorinated dibenzodioxins (PCDD), low resolution mass selective detection cannot be used to distinguish between these two classes of compounds. A method is presented which may allow this [2], involving the oxidation of the PCDTs to the corresponding sulfones (PCDTO<sub>2</sub>) which have a higher mass than the PCDDs. If desired the PCDTO<sub>2</sub>s can easily be separated from the PCDDs and the polychlorinated dibenzofurans (PCDFs) by simple chromatographic techniques.

Furthermore, a simple reaction is shown for the synthesis of PCDTs as reference compounds with a known substitution pattern. Several mono- to tri-chlorinated dibenzothiophenes and their corresponding sulfones have been synthesised and their gas chromatographic elution on the widely used DB-5ms column is discussed with a view to predict the gas chromatographic properties of higher chlorinated PCDTs, especially of the potentially toxic 2,3,7,8-substituted PCDTs. A first attempt to define the retention time windows for PCDTs and the corresponding sulfones is under investigation.

### **Material and Methods**

The standard mixtures of PCDTs, PCDDs and PCDFs used for the separation experiments and the spiking experiment were synthesised by direct chlorination of the parent compounds. The oxidation of the higher chlorinated PCDTs was done by refluxing the PCDTs dissolved in toluene with a mixture of equal amounts of acetic acid and hydrogen peroxide (30 %) and a few drops of conc. sulphuric acid. The separated organic layer was washed with saturated sodium hydrogen carbonate solution and water and then chromatographed on 5 g activated alumina (preheated at 155 °C for at least 12h). 20 ml of toluene was used for a pre-fraction (elutes the PCDDs and PCDFs) and the oxidised compounds were eluted with toluene/methanol (4:1 v/v, 20 ml). High resolution gas chromatography combined with mass spectrometric detection (HRGC/MS) was performed on a Finnigan MAT, GCQ-system [2]. The cleanup procedure was according to the EPA 8280 method [3].

The PCDTs with a definite substitution pattern were synthesised in the following way: A chloroaniline was diazotized and then reacted with a chlorothiophenol to a chlorodiphenylsulfide. The chlorodiphenylsulfide was dissolved in cyclohexane and irradiated for 4 to 6 h with a medium pressure UV lamp. The product was chromatographed on silica gel 60 with cyclohexane. <sup>1</sup>H-NMR and MS spectra were recorded for the pure products.

The gas chromatographic elution of some mono- to tri-chlorinated dibenzothiophenes and their corresponding sulfones was studied on a DB-5ms column 30 m x 0.25 mm i.d. coated with a 0.25 μm film. The retention indices were calculated according to a method described by Andersson [4].

### Results and Discussion

Due to the low concentration of PCDDs/Fs and PCDTs in real-world samples, it is necessary to use a fairly complex workup scheme in order to separate the analytes from different matrix components. The widely used EPA 8280 does not separate the PCDTs from the PCDDs and PCDFs. No PCDT congener is lost or discriminated during this cleanup. This is true not only for standard mixtures but it has also been demonstrated for a sediment spiked with PCDTs and PCDFs at a real-world concentration level (10-20 ppb per congener). This experiment also shows that in case PCDTs are present in a sample, they will definitely occur together with the oxygen heterocycles after workup and therefore possibly interfere with the quantification of PCDDs unless a high resolution mass spectrometer is used as detector. With the oxidation step added to established workup procedures, this problem can easily be solved, because the PCDDs and the PCDFs are not discriminated under these harsh conditions. If other detectors like an ECD is used the PCDT<sub>2</sub>s can be separated from the PCDDs/Fs by chromatography on activated alumina.

To identify the PCDTs in different environmental samples it is necessary to have reference compounds with a definite substitution pattern. A simple reaction pathway is described here. To get defined PCDTs, the corresponding polychlorinated diphenylsulfide (PCDPS) has to have at least one chlorine atom in the ortho-position to the sulphur atom which is eliminated in the subsequent photochemical ring closure (Fig. 1):

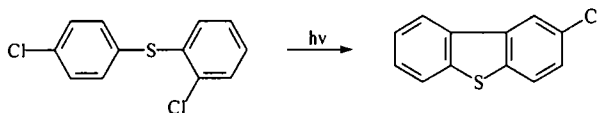


Fig. 1: Synthesis of 2-Chlorodibenzothiophene by photochemical ring closure of 2,4'-Dichlorodiphenylsulfide

Several mono- to tri-chlorinated dibenzothiophenes have been synthesised and characterised by <sup>1</sup>H-NMR and MS.

Besides developing a new synthesis for the PCDTs, we tried to find out if it is possible to predict the gas chromatographic properties of higher chlorinated PCDTs. We find that from known data in an attempt to avoid synthesising the potentially toxic in 2,3,7,8-chlorinated PCDTs it is not possible to predict the gas chromatographic retention indices of the PCDTs with the help of the published retention indices of the PCDFs. The elution of the PCDFs on a DB-5 column is totally different of that of the PCDTs. For example 4-Cl-dibenzothiophene elutes before all other mono-chlorinated dibenzothiophenes but 4-Cl-dibenzofurane elutes

after all other mono-chlorinated dibenzofuranes. Therefore we tried to calculate the retention indices of the higher chlorinated dibenzothiophenes from the retention indices of the lower chlorinated dibenzothiophenes. These investigations have been done for the corresponding sulfones, too. These results will be reported at the meeting.

Finally we tried to predict the retention time windows of the PCDTs based on the measured retention indices. This knowledge is important to when the single-ion monitoring mode of HRGC/MS is used for better detection limits. The retention time windows of the sulfones, however, overlap on nonpolar columns.

#### **Acknowledgements**

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#### **References**

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