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Congener specific analysis of polychlorinated terphenyls

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ABSTRACT

In order to identify and to quantify polychlorinated terphenyls (PCT) in environmental matrices, the chromatographic behavior of coplanar and non-coplanar congeners was evaluated. A mixture of 16 single PCT congeners was used for method development. Four of these compounds were synthesized for the first time by SUZUKI-coupling reaction. These were *p*-PCT (2,2″,6,6″-tetrachloro-, 2′,3,3″,4,4″,5′,-hexachloro-, 2′,3,3″,5,5′,5″-hexachloro-) and *m*-PCT (2,2″,3,3″,5,5″-hexachloro-). They were characterized by NMR (^{1}H, ^{13}C) spectroscopy. By means of the new column chromatographic clean-up reported here, a good matrix removal and the separation of the coplanar PCT congeners from the non-coplanar ones was obtained. The recovery rates for all congeners were good for the PCT in different test matrices like fat, charcoal, and soil. The quality of the clean-up, the separation and the recovery rates were determined by GC/MS analysis. The method was applied for the first time to a real sample from a fire accident, where different PCT, obviously formed during the combustion process, were found. The conclusion is drawn that this method is suitable for the analysis of PCT in different environmental samples.

1. Introduction

In the past, about 60 000 tons of PCT were produced worldwide. The application patterns of PCT were similar to those of PCB due to similar chemical and physical properties of both substance groups (Birn and Jung, 1993; de Boer, 2000). From the former application fields, disposal sites like landfills as well as from combustion processes (new formation) PCT are emitted into the environment as low volatile, persistent, and bioaccumulating substances. In spite of comparably limited knowledge about this substance group, its environmental and toxicological relevance should not be neglected. The main reason for this lack of knowledge is that the 8557 possible PCT congeners (Remberg et al., 1998) could not be handled sufficiently by common gas chromatographic techniques so far. Furthermore, with a few exceptions, single reference substances are not available, which are necessary for the development of suitable analytical methods. In consequence, published data on the occurrence of PCT should be dealt with utmost care, due to strongly varying analytical procedures and calculation methods used (Gallagher et al., 1993; Wester et al., 1996; Fernandez et al., 1998).

Some approaches were undertaken in the past in order to synthesize particular PCT congeners as authentic standards for analytical investigations. First works in this area were done by Chittim et al. (1977), they synthesized 22 PCT congeners. At the beginning of the new millennium the next approach in the synthesis of PCT was successfully started (Bahadir et al., 2003; Hopf et al., 2007). The syntheses are based on the SUZUKI-coupling (Miyaura et al., 1981; Lehmler and Robertson, 2001). Within the work, introduced here, the number of single PCT congeners was extended. Four new congeners were synthesized: *p*-PCT (2,2″,6,6″-tetrachloro-, 2′,3,3″,4,4″,5′,-hexachloro-, 2′,3,3″,5,5′,5″-hexachloro-) and *m*-PCT (2,2″,3,3″,5,5″-hexachloro-). These compounds were characterized by NMR (^{1}H, ^{13}C). In addition, the NMR data of earlier synthesized congeners are introduced, as well (s. Appendix A). As a result, 38 single congeners with different degrees of chlorination (1–6 and 14) are now available, including coplanar and non-coplanar species. Most of all PCT are of non-coplanar structure. These are all compounds with at least one substitute (a chlorine atom or a phenyl-ring) in *ortho*-position. The amount of compounds with no such *ortho*-substitution is quite low, only 61 congeners as shown in Table 1 (Remberg et al., 1998).

As already mentioned, no standardized and generally accepted method for PCT quantification is known, yet. As can be seen from Table 1, there are 20 para- and 41 meta-terphenyls among the 8557 congeners with no *ortho* chlorine atom. This substitution pattern easily allows molecular planarity. On the one hand, derived from PCB, PCDD and PCDF, those congeners are suspected of being most toxic among the PCT. On the other hand, this special property of planarity can be used to separate these interesting PCT congeners by an additional column chromatographic step integrated into a regular clean-up procedure. Thus, gas chromatographic separation of the selected PCT now becomes possible and some of those

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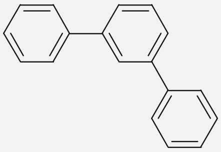
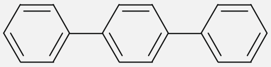
Table 1
Number of all non-ortho substituted terphenyls.

Basic structure of terphenyl congeners (meta, para)	Degree of chlorination							Sum of species
	Cl_1	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	
	3	7	10	10	7	3	1	41
	2	5	5	5	2	1	–	20

planar congeners can be chosen and analyzed as indicator substances with GC/MS, following the well established strategy of e.g. PCDD/PCDF-, PCB-, or PAH-analyses. Besides the synthesis of reference standards, the development and a first application of this procedure is described in the following.

2. Materials and methods

2,6-Dichlorobromobenzene, 1,3-dibromobenzene, benzene-1,4-diboronic acid, 2,3,5-trichlorobenzeneboronic acid, 3,4-dichlorobenzeneboronic acid, 3,5-dichlorobenzeneboronic acid and tetrakis-(triphenylphosphine)palladium(0) were commercially available with a purity of 97–98% (Lancaster Synthesis GmbH, Acros Organics). 1,4-Dibromo-2,5-dichlorobenzene was synthesized by Sandmeyer reaction. Solvents were purchased in p.a. quality (Merck AG). The sorbents Alumina B-Super I and silicagel (63–200 mesh) were purchased from ICN Biomedicals GmbH, and florisil for residue analysis (0.150–0.250 mm) was purchased from Merck AG.

The congeners PCT 1, 8 and 16 (numbering according to Table 2) were purchased from Promochem GmbH, PCT 2, 3, 5, 6 and 7 were synthesized in the Institute of Organic Chemistry, TU Braunschweig, PCT 9, 10, 13 and 15 were synthesized earlier in the own institute (Bahadir et al., 2003; Hopf et al., 2007).

Four new PCT congeners were synthesized according to the SUZUKI-coupling: *p*-PCT (2,2″,6,6″-tetrachloro-, 2′,3,3″,4,4″,5′,-hexachloro-, 2′,3,3″,5,5′,5″-hexachloro-) and *m*-PCT (2,2″,3,3″,5,5″-hexachloro-). The 2,2″,6,6″-tetrachloro-*p*-terphenyl was synthesized by reaction of one equivalent benzenediboronic acid with two equivalents bromobenzene, the other terphenyls were synthesized by the reaction of one equivalent dibromobenzene with two equivalents of benzenemonoboronic acid. The recrystallized terphenyls were characterized by NMR (^1H and ^{13}C) and GC/MS analysis.

NMR-spectra were obtained using a Bruker AM 400 at 400.1 MHz (^1H) and at 100.6 MHz (^{13}C), applying $CDCl_3$ as solvent and TMS as internal standard.

GC/MS analyses for PCT quantification were performed with an Agilent GC 6890 Series/Agilent MSD 5975C equipped with a DB5-MS column, 30 × 0.25 mm, film thickness 0.25 μm, single ion mode. Temperature program: 90 °C (2 min) – 17 °C min^{-1} to 200 °C – 3.5 °C min^{-1} to 300 °C (26 min). The following masses (m/z) were used for SIM-measurements of the PCT: monochloro: 264.0/266.0; dichloro: 298.0/300.0; trichloro: 332.0/334.0; tetrachloro: 365.9/367.9/369.9; pentachloro: 399.9/401.9/403.9; hexachloro: 433.9/435.9/437.9; tetradecachloro: 709.7/711.7/713.7. As internal standard for quality control, 1,2,3,4-tetrachlorodibenzo-*p*-dioxin was used.

For the clean-up procedure in general, column chromatography was conducted with self-prepared glass columns with 30 cm length and 1.6 cm inner diameter. The clean-up consists of four steps including alumina column, mixed silicagel column, again alumina column and florisil column.

The alumina columns were filled in with 30 g aluminium oxide (basic, activity I, 0% water), 10 g Na_2SO_4 and conditioned with 80 mL hexane. Three fractions were gained from elution with 80 mL hexane, 150 mL hexane/dichloromethane (99:1), and 250 mL hexane/dichloromethane (1:1).

The mixed silicagel column was filled in with 2 g silicagel neutral, 5 g silicagel 33% 1 M NaOH, 2 g silicagel neutral, 10 g silicagel 44% conc. H_2SO_4, 2 g silicagel neutral, and 10 g Na_2SO_4 on top. It was conditioned with 80 mL hexane. The elution was done with 250 mL hexane/dichloromethane (99:1).

The florisil column contained 23 g florisil (conditioning: 2 h at 180 °C, deactivation with 2% water) and 10 g Na_2SO_4. It was rinsed with 80 mL cyclohexane/dichloromethane (99:1) before use. The elution was done with 500 mL cyclohexane/dichloromethane (99:1) and with 250 mL dichloromethane. Both fractions were reduced to 1 mL and analyzed by GC/MS as described before.

For the sample preparation the matrix materials (1 g vegetable oil, 10 g homogenized dry soil (type: Cambisol) and 5 g fine powdered wood charcoal) were spiked with 100 μL of PCT standard solution with a concentration of 20 μg mL^{-1} for each of the 16 PCT as listed in Table 2.

The spiked oil sample was shaken for 2 min, diluted with 2 mL hexane and directly introduced to the column. Na_2SO_4 (3 and 1 g) was added to the spiked soil and charcoal samples, before they were extracted with 80 mL toluene in a soxhlet extractor for 16 h. The volume of the extracts was reduced to approximately 2 mL before column chromatography.

3. Results and discussion

For the development of the clean-up procedure a mixture of 16 PCT with different chlorination degrees, mono- to hexa as well as tetradecachlorinated congeners, was used. This mixture contained four coplanar and 12 non-coplanar PCT (Table 2).

The clean-up procedure for PCT, as introduced here, is based on the classical method for the analysis of polychlorinated dibenzo-*p*-dioxins and dibenzofurans, using alumina columns and a mixed silicagel column (Dettmer et al., 1998). The first approach in this work was the optimization of that column chromatography (absorbents, solvents) for PCT analysis. The second, more important step was the introduction of an additional florisil column. This one is responsible for the separation of the PCT mixture into coplanar and non-planar constituents. The idea goes back to Ebert et al. (1999), who successfully separated non-planar polybrominated diphenylethers from planar polybrominated dibenzo-*p*-dioxins and dibenzofurans with florisil adsorbent.

In the first step of the clean-up, basic alumina was used for removing lipids and other fatty compounds of the matrix. Also