Enantioselective determination of persistent toxaphene compounds: possibilities on and alternatives to *tert.*-butyldimethylsilylated ß-cyclodextrin

Walter Vetter[1], Ulrike Klobes[1], Bernd Luckas[1], and Georg Hottinger[2]

[1] Friedrich-Schiller-Universität Jena, Institut für Ernährung und Umwelt, Dornburger Str. 25, D-07743 Jena, Germany
[2] BGB Analytik KG, Lettenstr. 97, CH-8134 Adliswil, Switzerland

Introduction

The first successful enantioseparations of compounds of technical toxaphene (CTTs) were published in 1994 [1][2]. However, enantioselective determination of chiral CTTs is still a challenge for analytical chemists. For a long time it was thought that enantioseparations of CTTs are restricted to *tert.*-butyldimethylsilylated ß-cyclodextrins [1-6]. This CSP was used in several studies to determine the enantioratios (ER) of the two major abundant CTTs in biota, B8-1413 and B9-1679 [1][2][5][6]. In all reports, ER close to one were reported for B8-1413 and B9-1679 [1][2][5][6].

Recently, enantioresolution of B8-2229 in seal blubber was described [7]. In contrast to the first mentioned CTTs, B8-2229 showed a significantly enantioenriched first eluted enantiomer on ß-BSCD [7]. The accuracy of the results was confirmed by isolation of the respective compounds from seal blubber [8][9] and injection of the pure extracts. By this, artifacts due to coeluents [10] were excluded.

Due to the significant alteration of the ER of B8-2229 in the seal blubber samples, it was concluded that enantioselective breakdown of higher chlorinated CTTs might explain the change in the enantioratio [11][12].

However, enantioseparation of CTTs other than B8-1413 and B9-1679 is cumbersome. While eight persistent CTT standards were enantioseparated on ß-BSCD, determination of ER in environmental samples was restriced to B8-1413, B9-1679, and B8-2229 [6][7]. Therefore, application of alternative CSPs was tested to confirm the results. Recently, enantioseparation of eight CTTs was obtained on ß-TBDM phase [13][14][15]. These CTTs included a persistent CTT in different biological samples, B8-1412, which was not enantioresolved on ß-BSCD. Enantioseparation of B8-1412 in marine organisms also showed a more pronounced enantioenrichment of one of the enantiomers [16]. Furthermore, a high ER of B8-2229 which was determined with ß-BSCD was confirmed with ß-TBDM [15].

Here, we present a third chiral stationary phase, ß-PMCD, which enantioseparated four CTTs. Enantioseparation of CTTs was never before obtained on ß-PMCD. Furthermore, advantages and disavantages of the respective CSPs are discussed.

Experimental Methods

Enantioseparations were performed on HP 5890 (Hewlett-Packard) gas chromatographs equipped with either ^{63}Ni electron capture detector (ECD) or electron capture negative ionization mass spectrometry (ECNI-MS). The following three chiral stationary phases were used:

(i) ß-BSCD column consisted of 25% randomly *tert.*-butyldimethylsilylated ß-cyclodextrin diluted in PS086 (BGB Analytik, Adliswil, Switzerland). The column parameters were: 30 m length, 0.25 µm i. d., and 0.20 µm film thickness.

(ii) ß-PMCD consisted of 10% immobilized permethylated ß-cyclodextrin (Chirasil-Dex, Chrompack, Middelburg).

(iii) The two ß-TBDM columns consisted of 35% heptakis(6-O-*tert.*-butyldimethylsilyl-2,3-di-O-methyl)-ß-cyclodextrin diluted in OV1701, respectively. Two different qualities of the CSP were at our disposal: The first one contained randomly silylated ß-TBDM. The CSP was a gift from M. D. Müller (Swiss Federal Research Station Wädenswil, Switzerland) and the column was prepared by G. Hottinger. This phase was used in our earlier presentations [14][15].

The second ß-TBDM phase consisted of purified silylation product (saturation degree approx. 99%). This column is commercially available from BGB Analytik (Switzerland). To distinguish the two phases, the purified CSP is labelled with the suffix P (ß-TBDM$_P$).

Results and Discussion

Table 1 lists structure and enantioseparation results obtained on three CSPs. All CTTs except B8-1412 were enantioseparated on ß-BSCD [7]. On the other hand, alternative CSPs were available for all CTTs except B8-1413, the major octachlorobornane in biological samples.

Table 1: Enantioresolution of CTTs on different chiral stationary phases

CTT	substitution pattern	ß-BSCD	ß-TBDM	ß-TBDM$_P$	ß-PMCD
B6-923 (-)	2-*exo*,3-*endo*,6-*exo*,8,9,10	+*[17]	-*[17]	n.t.*	- [17]
B7-1001 (-)	2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,9,10	+ [17]	+ [17]	n.t.	+[17]
B7-1453 (-)	2-*exo*,3-*endo*,5-*exo*,9,9,10,10	+ [7]	+ [15]	-	-
B8-1412 (-)	2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,9,10	- [7]	+ [16]	-	+
B8-1413 (#26)	2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,10,10	+ [1-6]	- [15]	-	-
B8-1414 (#40)	2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,9,10,10	+ [7]	+ [15]	+	+
B8-1945 (#41)	2-*exo*,3-*endo*,5-*exo*,8,9,9,10,10	+ [7]	+ [15]	+	+
B8-2229 (#44)	2-*exo*,5,5,8,9,9,10,10	+ [7]	+ [15]	-	-
B9-1025 (#62)	2,2,5,5,8,9,9,10,10	+ [7]	+ [15]	-	n. t.
B9-1679 (#50)	2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,9,10,10	+ [1-6]	+ [15]	-	-

* + = enantioseparated; - = not enantioseparated; n. t. = not tested;

ß-PMCD separated the enantiomers of four CTTs. These CTTs include the major heptachloro compound in sediment samples, Hp-Sed or B7-1001 [17] and B8-1412 which was not enantioresolved on ß-BSCD. The enantiomers of B7-515, B8-2229, and B7-1453 were partly resolved on ß-PMCD. Unfortunately, the major CTTs in biota, B8-1413 and B9-1679, were not enantioseparated on this chiral stationary phase. At the moment, enantioseparation of B8-1413 is restricted to ß-BSCD. On this CSP, all CTTs mentioned hitherto except B8-1412

were enantioseparated. However, the enantioseparation of B8-1414, B8-1945, and particularly B8-1412 on ß-PMCD is a promissing addition to the other discussed CSPs on the way to establish enantioratios of persistent CTTs in addition to B8-1413 and B9-1679.

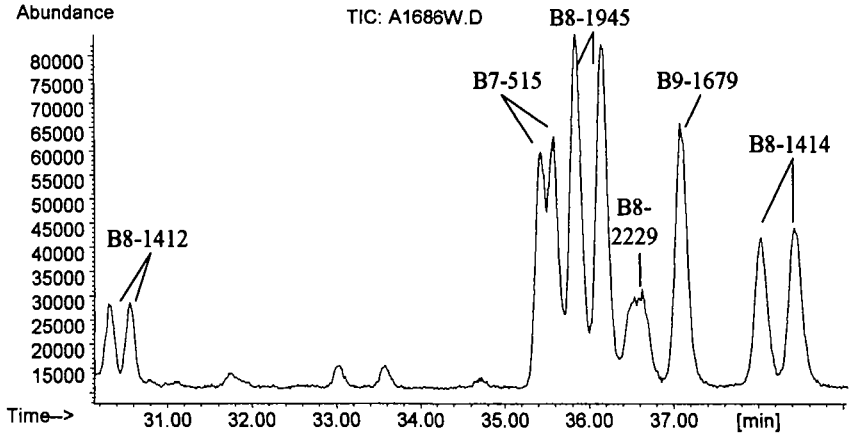

Figure 1: Enantioseparation of CTTs on ß-PMCD. This chiral stationary phase has not been successfully applied to CTTs before [3]. Not shown: B7-1453 and B8-1413

Another advantage of the ß-PMCD (Chirasil-Dex) phase is the good reproducibility of the CSP. Therefore, data obtained on this CSP seem to be reliable and most likely easy to reproduce on other CSPs of the same type.
This is not the case with ß-BSCD and ß-TBDM. While this effect has been described for ß-BSCD [6][18][19], the phenomenon is less known on ß-TBDM [20]. Two types of ß-TBDM were available for this study: randomly silylated ß-TBDM and purified ß-TBDM (see above). While the purified ß-TBDM$_P$ only enantioseparated 2 CTTS, the randomly silylated ß-TBDM phase enantioseparated 8 or the 9 tested CTTs. The results confirm that the purification of ß-TBDM decreased the efficiency of the chiral resolution of CTTs on ß-TBDM.

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