HRGC Determination of Toxic PCBs in Marine Organisms after SPE with Carbopack B

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Investigations carried out with multidimensional GC and mass spectrometry have shown that regulation-relevant PCBs and toxic PCBs may both be interfered with by other PCB congeners on an SE 54 column [1, 2, 3]. Difficulties arise mainly with the routine determination of the regulation-relevant PCBs 28, 101, 138 and 153 [4] and the toxic PCB congeners 77, 105, 118, 126, 156 and 157 [5] on an SE54 column.
Therefore, the parallel application of two dual-column GCs equipped with SE 54 and OV 1701 as stationary phases in the first GC-oven and CP SIL 8/C18 and the dioxin column SP2331 in the second GC-oven was proposed for unambiguous determination of PCBs in the presence of chlorinated pesticides in seafood [6].
The procedure of sample preparation consists of liquid extraction of organochlorines with n-hexane, clean up of the extracts with H_2SO_4 [7] followed by SPE on silicagel [8]. The highly purified extracts were injected into the chromatograph. The chromatograms from these initial runs then allowed preliminary assessment of the contamination of samples with chlorinated pesticides and PCBs (see fig 1).
For exact quantification of the toxic PCBs in the presence of higher concentrations of regulation-relevant PCBs an additional clean-up step to enrich the various PCBs is necessary [9]. Therefore, we developed a method based on the selective elution of the three groups of PCBs from a chromatographic column filled with Carbopack B / Celite 1:1. The purified extract obtained after SPE with silicagel [8] is transferred to the column packed with 4.0 g Carbopack B / Celite. Selective elution is then carried out in three steps, resulting in three PCB fractions (elution 1: 50ml n-hexan, fraction 1: di-ortho PCB; elution 2: n-hexane/ 5% toluene, fraction 2: mono-ortho PCB; elution 3: 50ml toluene, fraction 3: non-ortho PCB).

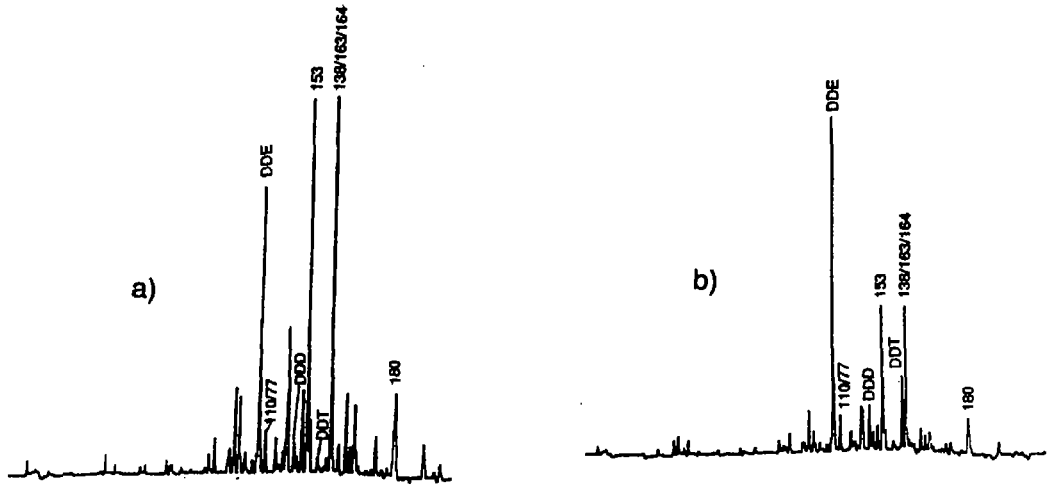

Fig. 1: HRGC chromatogram of cod liver extracts a) North Sea, b) Baltic after clean up with H_2SO_4 and SPE on silicagel (GC-column: SE 54 [7])

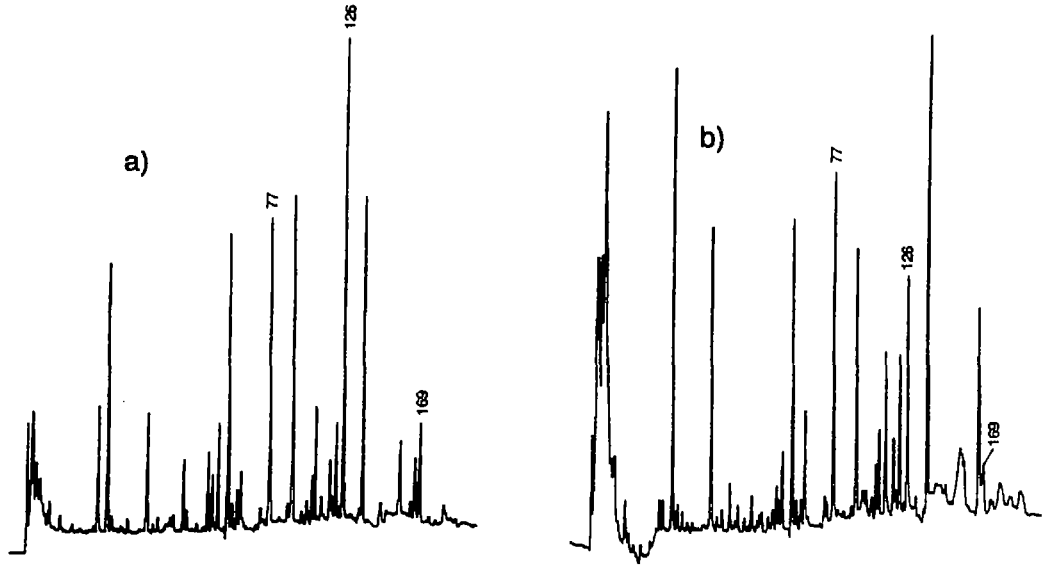

Fig. 2: HRGC - chromatogram of fraction 3 (non-ortho PCBs) of cod liver extracts a) North Sea, b) Baltic after selective elution from the Carbopack B / Celite column with toluene

Figure 2 demonstrates the distribution of the most important toxic PCBs (77, 126, 169) and reveals the presence of these non-ortho PCBs in the liver of cod from different marine regions. We succeeded in separating the co-planar PCBs by GC without interferences on any of the four capillary columns, because no PCBs, either mono-ortho or di-ortho, were present.

However, problems arose in the determination of the regulation-relevant PCB 138 when only an SE 54-column and a second capillary column were used in combination in a dual column GC-system [9,10].

Fraction 1 contains all di-ortho PCBs. Therefore, the unambiquous determination of PCB 110 (without co-elution with PCB 77 on an SE 54 column) is possible. More difficult is the separation of the di-ortho hexachlorobiphenyl PCBs 163, 164 and 138 [11].

By parallel application of a CP SIL 8/C18 column and a polar SP 2331 column the simultaneous quantification of the otherwise interfering PCB congeners could be achieved (Fig. 3).

Summarizing, it can be stated that the proposed approach represents an effective alternative to previous methods recommended for determination of chlorobiphenyls in food and fish [12,13].

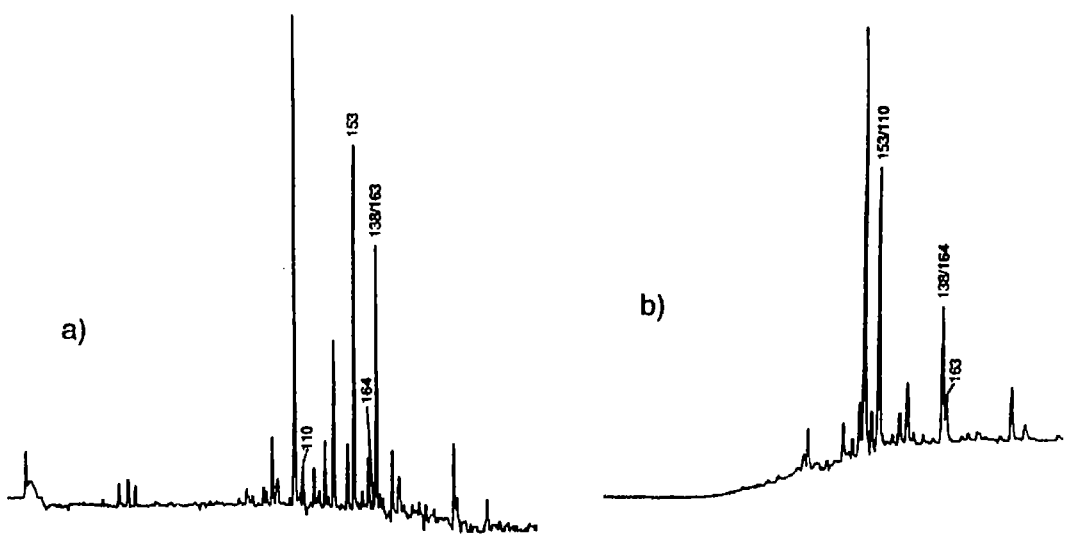

Fig. 3: Separation of the regulation-relevant PCB 138 from fraction 1 (di-ortho PCB) by combination of CP SIL 8/C18 (a) and SP 2331 (b) columns (sample: cod liver, Baltic)

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