ANALYSIS OF POLYCHLORINATED BIPHENYLS (PCBs) IN COD LIVER OIL BY USING THE LIPOPHILIC GEL LIPIDEX

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ABSTRACT

A method has been developed for specific analysis of PCB congeners in cod liver oil. The lipophilic gel Lipidex was used for extraction and preliminary purification. Recoveries of di- and mono-ortho PCBs added to the oil were 80-90% and 64-102% for non-ortho PCBs.

INTRODUCTION

During the last years attention has been focused on the toxicity of PCB congeners that elicit toxical respones similar to those of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). According to a structure-activity relationship the non-ortho congeners 3,3',4,4'-tetrachloro-, 3,3',4,4',5-pentachloro- and 3,3',4,4',5,5'-hexachlorobiphenyl (IUPAC Nos. 77, 126, 169) are the most toxic ones[1]. Among the mono-ortho PCBs 2,3,3',4,4'-pentachloro-, 2,3',4,4',5-pentachloro- and 2,3,3',4,4',5-hexachlorobiphenyl (IUPAC Nos. 105, 118, 156) are considered the most potent.

PCBs are biomagnified in the food chain of aquatic organisms and are generally found in fish samples. Due to their solubility in fat they are accumulated in e.g. cod liver[2-3]. The knowledge of the occurrence and levels of the most toxic PCB congeners in commercial cod liver oil is therefore of importance.

Extraction with Lipidex has previously been used for analysis of organochlorine contaminants in aqueous samples[4-6]. In the present study solid phase extraction was used for specific analysis of PCB congeners in cod liver oil.

MATERIALS AND METHODS

Extraction and preliminary purification

Cod liver oil (Apoteksbolaget AB, Sweden) was dissolved in hexane and an aliquot was taken for analysis. After addition of internal standards, isopropanol and Lipidex 5000, the sample was extracted by shaking at 35 °C. During the extraction procedure water was continuously added to facilitate the transfer of fat-soluble compounds into the gel. The latter was then transferred to a glass column. The solvent was drained and the gel was eluted with solvents of different polarities, Fig. 1, to achieve separation of chlorinated compounds and most of the fat. Further clean-up and separations were made by column chromatography using aluminium oxide, silica gel and charcoal, Fig. 1.

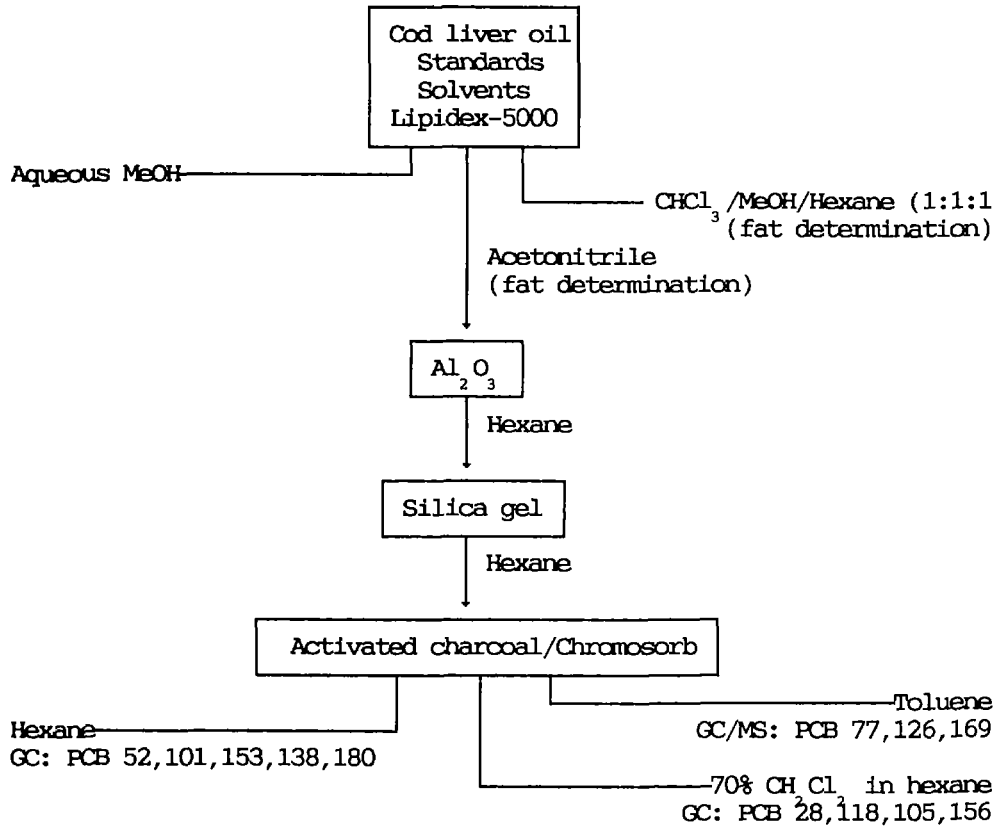

Fig. 1. Flow scheme of the method.

Gas chromathography (GC)

GC-analyses of di-ortho and mono-ortho PCB congeners were performed using a gas chromatograph equipped with an all-glass falling-needle injector with a heater at 220 °C, a fused silica capillary column coated with SE-54 (25m X 0.32mm; Quadrex Co., New Haven, CT, USA) and ^{63}Ni electron-capture detector. Nitrogen was used as carrier gas. The column temperature was kept at 190°C for 15 min., programmed to 260° at 5 °C/min and then isothermal for 30 min.

Gas chromatography-mass spectrometry (GC/MS)

GC/MS analyses of non-ortho PCB congeners were performed with a VG 7070 E mass spectrometer. Ionization was made by electron impact at 49 eV and the accelerating voltage was 6 kV. Compounds were monitored in groups. The resolution was 8000-9000 at m/z 293. An SE-30 fused silica capillary column (25m X 0.32mm; Quadrex Co., New Haven, CT, USA) was used with an all-glass falling-needle injector with a heater at 250-260 °C. The column temperature was 190° for 8 min., programmed to 270° at 5 °C/min and kept at this temperature for 8 min. Helium was used as carrier gas.

Solvents and standards

All solvents were of analytical reagent grade and were redistilled. Unlabelled standards (PCB 28, 52, 101, 105, 118, 138, 153, 156, 180) were from Ehrenstorfer, Augsburg, FRG or recieved from Dr. Åke Bergman Wallenberg Laboratory, Stockholm University, Sweden. ^{13}C-Labelled standards (PCB 77, 126, 169) were from Cambridge Isotope Laboratories Inc., USA.

RESULTS AND CONCLUSIONS

Lipidex 5000 proved to be an effective sorbent for fat-soluble compounds in cod liver oil. The continuous addition of water was essential for the complete transfer into the gel. About 60 % of the lipids were removed from the sample, by the elution system used for Lipidex. Complementary purification from lipids and separation from most of the pesticides were achieved on aluminium oxide and silica gel. The mono-ortho PCBs and non-ortho PCBs were separated from the other PCBs and eluted in three different fractions from a charcoal column. Analyses were performed for a number of di-, mono- and non-ortho PCBs. Structures of these are given in Table 1. The recoveries of di- and mono-ortho PCBs added to 0.2 g of oil were 80-100%, and the recoveries of added ^{13}C-labelled non-ortho PCB were 64-102%.

The present study suggests a method for congener specific analysis of PCBs in fish oil. The technique adopted is partly based on a non-destructive method for analysis of organochlorine pesticides, polychlorinated dibenso-p-dioxins, polychlorinated furans and PCBs in mother's milk[5-6]. Such compounds can also be included and analysed by the present method.

Table 1. PCB congeners determined.

IUPAC No.	Structure	Comments
28	2,4,4'-TrCB	Disturbed by No.31
52	2,2',5,5'-TeCB	
77	3,3',4,4'-TeCB	
101	2,2',4,5,5'-PeCB	Separation from No.90 not confirmed
105	2,3,3',4,4'-PeCB	
118	2,3',4,4',5-PeCB	
126	3,3',4,4',5-PeCB	
138	2,2',3,4,4',5-HxCB	Separation from Nos.163 & 164 not confirmed
153	2,2',4,4',5,5'-HxCB	
156	2,3,3',4,4',5-HxCB	
169	3,3',4,4',5,5'-HxCB	
180	2,2',3,4,4',5,5'-HpCB	

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