CONGENER-SPECIFIC ANALYSIS OF PCBs IN HUMAN MILK

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INTRODUCTION

Coplanar PCBs are of interest to analytical chemists and toxicologists because of their structural and toxicological similarities to the 2,3,7,8-substituted PCDD/Fs. It is frequently possible to analyze coplanar PCBs together with PCDD/Fs without further separation, because of structural and concentration similarities. For exposure and risk assessment, however, it is also important to analyse the more abundant mono- and multi- ortho PCBs. We report here a further modification of our dioxin and co-planar PCB analytical method to include all tri- to decachloro-substituted PCBs. This method is compatible with analysis for PCDD/Fs and organochlorine pesticide residues. It has been applied to analyze PCBs and PCDD/Fs in human milk. We report here on the PCB analysis.

METHOD AND MATERIALS

Milk samples were kept frozen until analysis. About 100g of milk were transferred to a 500 mL narrow mouth Teflon bottle, and spiked with 17 $^{13}C_{12}$-2,3,7,8-substituted PCDD/Fs and 11 $^{13}C_{12}$-PCBs (77, 126, 169, 28, 47, 52, 101, 153, 180, 194 and 209). Sodium oxalate (1 gram) was added to the sample, followed by 100mL ethanol and 100mL 1:1 n-hexane/ethyl ether. After shaking on a mechnical shaker for 15 min, the aqueous phase was removed, and the organic phase was loaded on a AX-21 carbon column, eluted with 50 mL 6:4 dichloromethane/n-hexane in the forward direction, and collected as fraction 1. The column was eluted with 50 mL toluene in the reverse direction and collected as fraction 2. For the analysis of PCDD/Fs and PCBs 77, 126 and 169, fraction 2 was cleaned up on a silica column and a small alumina column according to HML method 880. Fraction 1 was split into two equal parts. One part was used for the fat determination. The other part was used for analysis of all PCBs, except congeners 77, 126, and 169. Fat was digested with concentrated H_2SO_4, and the organic layer was loaded onto a small silica gel column and eluted with 40mL hexane. The hexane fraction was cleaned on a small alumina B-super I

column, and eluted with 30 mL 98:2 hexane/dichloromethane. The eluate was further concentrated by evaporation under a gentle stream of nitrogen, and was then spiked with $^{13}C_{12}$-PCB 128 and 178 as recovery standards. The final volume was 20 μL. All samples were analysed by a HRGC/HRMS (Finnigan MAT 90). For quantitation, all isomers within one homolog group were assumed to have the same response factor.

RESULTS AND DISCUSSIONS

Traditionally, PCBs have been regulated as a class. This "class", however, includes a wide variety of manufactured complex mixtures that contains 20 - 60 congeners. Thus, quantitation of total PCBs continues to be a problem. One approach is to measure levels of representative PCB congeners, e.g. 6 or 7 predominant components found in technical mixtures[1]. However, widely differing toxicities of various congeners and the availability of $^{13}C_{12}$-labeled standards encourage the reporting of data as individual congeners. With the help of CLB-1 standards, individual $^{13}C_{12}$-labeled PCB standards, and retention data from the literature[2], we separated and identified about 80 PCB congeners on a DB-5 column[3]. For the human milk samples, **Table 1** lists a subset of 26 congeners, which are either major peaks or toxic members of the 80 congeners analyzed in our laboratory. For the three coplanar PCBs, the concentration order in human milk is 126>169>77, in agreement with data reported in the literature. Coplanar PCBs are minor constituents of the mixtures. The predominant congeners are 153 (15.5%), 138 (12.0%), 118 (10.2%), 74 (9.9%), 180 (8.8%), 99 (5.9%), 105 (4.6%), 170 (4.6%), 28 (3.5%), and 182/187 (3.4%). Each of PCB congeners 66, 183 and 156 contributes about 2%. PCBs 52, 101 and 110 are major peaks in many environmental samples, but, each of them contributes less than 1% of the total PCBs in the milk samples. Compared to other constituents, these congeners are either poorly taken up or are readily metabolised by the human body. Major homolog groups in the human milk samples are hexachlorobiphenyls > penta- > heptachlorobiphenyls.
The isomer patterns of tri- to hexachlorobiphenyls in human milk (Figure 1) illustrate that each homolog group contains only a few isomers.

REFERENCES

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3) Jianwen She, Patria Visita, Fred Sy, and Myrto Petreas, Proceedings of the 14th International Dioxin Conference, Kyoto, Japan, 1994

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Table 1: Major PCBs in human milk samples (pg/g, fat weight)

IUPAC No.	min n=12	max n=12	mean n=12	median n=12	% of Total
28	3680	39565	12920	7262	3.5
Total tri-CBs	3886	89445	19960	7655	5.4
52	358	13506	2818	1092	0.76
74	9662	129652	36647	23927	9.9
66	2723	31094	9344	4408	2.5
60/56	1054	9482	3390	2198	0.91
77	2	15	7	7	0.002
Total tetra-CBs	15675	192725	55490	32204	15.0
101	91	9348	2296	1244	0.62
99	3666	67543	22007	15715	5.9
97	51	2991	975	491	0.26
110	295	4026	1248	916	0.34
118	10492	87292	37901	26521	10.2
105	4655	36914	16887	10891	4.6
126	21	197	58	35	0.02
Total penta-CBs	28472	224252	85761	55704	23.1
151	96	1906	596	331	0.16
149	295	6361	1544	826	0.42
146	148	8198	2385	1226	0.64
153	20381	123286	57641	39025	15.5
141	181	6569	1574	692	0.42
138	13021	104314	44617	25280	12.0
128	808	4530	2144	1633	0.58
156	67	22934	5658	3359	1.5
169	7	35	15	13	0.004
Total hexa-CBs	37867	252238	116922	71073	31.5
178	255	10496	1956	861	0.53
182/187	1585	69909	12760	5512	3.4
183	255	41750	6656	2485	1.8
177	140	15494	4336	2412	1.2
180	9058	83973	32516	22437	8.8
170	2739	127733	17257	6091	4.6
Total hepta-CBs	17060	360952	79592	42836	21.5
Total octa-CBs	3601	32358	12463	9756	3.4
Total nona-CBs	110	2049	518	251	0.14
Deca-CBs	64	784	163	98	0.04
Total PCBs	124233	1004413	370864	241639	100

PCB

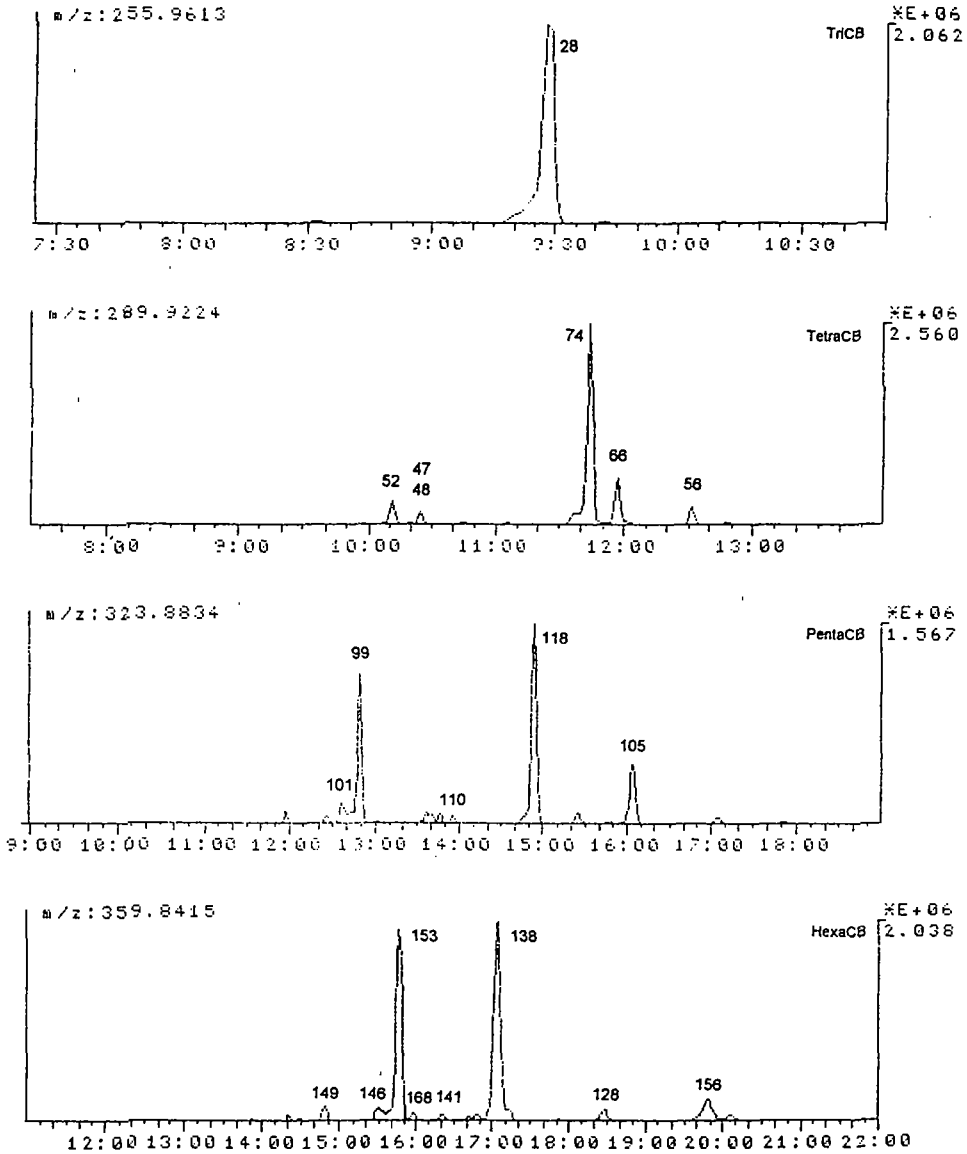

Fig. 1: Mass fragment chromatograms of tri- to hexa-chlorobiphenyls in human milk