CONGENER-SPECIFIC IDENTIFICATION OF PCB CONTAMINATION IN LABORATORY AIR, SOLVENTS AND ADSORBENTS

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INTRODUCTION

One source of the inter-laboratory variation observed with congener-specific PCB analysis may be background contamination. Identifying and preventing contamination of laboratory facilites, solvents, adsorbents, and air by PCBs is crucial for a reliable PCB analytical result. Due to their persistence and various uses, PCBs have been shown to be ubiquitous in the environment. Generally, the analysis of a laboratory method blank is sufficient to demonstrate that the samples are free from contaminants[1)]. Glassware must be scrupulously cleaned and high purity solvents and reagents should be used. Even so, the reagents should be checked for purity and adsorbents should be purified prior to use by solvent extraction or thermal desorption. Up to 160 ng PCBs/g silica gel were found in liquid-chromatographic grade silica gels from several manufacturers[2)]. In order to develop a cleanup method for congener specific determination of PCBs in human milk, we checked all relevant solvents, adsorbents, laboratory air and evaporation procedures for possible PCB contamination. This paper presents our findings.

EXPERIMENTAL

Solvents test: The hexane, petroleum ether, toluene and dichloromethane were from J.T Baker Inc., for organic residue analysis. The ethyl ether was from Mallinckrodt, for pesticide residue analysis. The ethanol was from Gold Shield Chemical Co. Each solvent was spiked with a mixture of ^{13}C-PCBs, concentrated with a rotary evaporator, transferred to a 1.2mL Reactivial and finally evaporated to 10 μL (tetradecane as solvent) under a gentle stream of nitrogen gas.

Adsorbents test: The ICN Alumina B-super I was from ICN Biomedicals GmbH. The Silica Gel 60 (70-230 mesh) Extra pure, for column chromatography, was from EM SCIENCE. The Florisil (60-100 mesh), PR, was from Floridin. 10 grams of each adsorbent were packed in a small glass column (ID 14 mm). The columns were first washed with 150 mL 1:1 hexane/dichloromethane. This wash fraction was collected and spiked with the ^{13}C-PCB standard and evaporated to a final volume of 10 μL. The washed column was then loaded with the ^{13}C-PCB standard with 5 mL hexane. Then, the Alumina and Florisil columns were eluted with 150 mL 98:2 hexane/dichloromethane. The Silica gel column was eluted with 150 mL hexane. The fractions were then evaporated as described above.

Air sampling test: Air samples were collected from several locations according to a modification of NIOSH Method 5503. Briefly, air was pumped through a glass fiber filter followed by a 110 mm x 8 mm glass tube containing two sections (400 and 200 mg) of Florisil. Approximately 1800 L were sampled over 60 hours at a flow rate of 500 mL/min. The filter and the front Florisil section were spiked with labeled PCB standards, extracted with 10 mL of hexane and evaporated to 10 µL of tetradecane.
All samples were injected onto a 60 meter DB-5 column and monitored with a high resolution MAT-90 mass spectrometer. The PCBs were quantitified under the assumption that all isomers with the same chlorination have the same response factor. About 80 congeners from tri- to decachlorinated biphenyls were quantitated.

RESULTS AND DISCUSSION

The PCB concentrations in ethyl ether, adsorbents' wash fractions, and laboratory air are shown in Table 1. Among all the solvents tested, ethyl ether showed the highest PCB contamination with the total PCB level approaching 400 pg/mL. The total concentration of tri-CBs was the highest of the chlorinated homologues. Since ethyl ether is used for fat and analyte extraction in many cases, any PCB contamination can directly contribute to the method blank.
Significant amounts of PCB 180 and a mixture of PCB 47 and 48 could be found in all tested solvents. It is hard to say whether the PCB 180, 47 and 48 were from the solvent manufacturer or from absorption of PCB contaminated laboratory air.
Among the adsorbents tested, Florisil showed the heaviest PCB contamination, followed by Silica gel and Alumina. Up to 13 ng PCBs/g Florisil were detected. However, the Florisil tested had been stored in the laboratory for a few years. It is not clear whether the PCBs in the adsorbents were from the manufacturing process or from adsorption of PCBs from ambient air during storage. After washing with 15 times the adsorbent volume of 1:1 hexane/dichloromethane, more than 90 percent of the PCB contaminants in the adsorbents could be removed.
The concentration of PCB contamination in the laboratory air was about 18 ng/m^3. The isomer pattern of the PCBs in the laboratory is shown in Fig. 1. The PCBs in the laboratory air are a mixed contamination from different Aroclors based on the percentage composition (not included in this paper) and isomer pattern. The major source of PCBs in the laboratory air appears to be the past use of fluorescent light fixtures with Aroclor containing ballasts. The effect of the quality of laboratory air on the method blank needs further assessment, especially since nitrogen evaporation appeared not to contribute to PCB contamination.
The most toxic and coplanar PCBs, 77, 126 and 169, were not detected in any solvents, adsorbents or air samples.
In summary, in order to get a satisfactory method blank, all solvents should be tested for PCB contamination, even the pesticide residue analysis grade solvents. Contaminant levels in the solvents from different manufacturers should be compared with each other. All adsorbents tested showed significant amounts of PCB contamination. Thus, the adsorbents should be thoroughly rinsed before use, which can be completed in a liquid-chromatographic column.

REFERENCES

1) Mitchell D. E., Analytical Chemistry of PCBs, Lewis Publishers, 1991
2) Bergman, Å., Jansson, B., and Reutegårdh, L., J. Chromatogr. Vol. 291, p392-397, 1984

Table 1 PCBs concentration in ethyl ether, florisil, Silica gel, alumina and Lab. air samples

Matrix Unit	Ether pg/mL	Florisil pg/g	Silica pg/g	Alumina pg/g	Lab. air ng/m^3	Matrix Unit	Ether pg/mL	Florisil pg/g	Silica pg/g	Alumina pg/g	Lab. air ng/m^3
19	1.66	33.09	ND	1.00	0.057	153/132	15.18	230	75.05	19.39	1.13
18	26.51	365	2.03	14.14	0.51	168	2.57	67.16	23.88	3.64	0.38
17	13.05	182	0.68	7.06	0.25	141	1.44	45.48	16.87	5.26	0.35
27	1.53	27.36	ND	9.88	0.047	138	11.41	156	97.63	15.41	1.13
16/32	15.04	130	1.22	10.31	0.34	158	ND	11.53	7.09	ND	0.087
26	3.70	138	0.52	1.50	0.084	129	ND	4.53	ND	ND	0.023
25	0.21	35.15	ND	0.87	0.028	159	ND	6.25	3.14	6.76	0.044
31	18.32	674	3.68	16.49	0.52	128/162	0.54	9.24	6.88	2.10	0.086
28	18.33	674	3.68	16.49	0.52	156	ND	ND	20.21	0.42	0.087
33/20	9.07	645	2.58	11.35	0.36	157	ND	ND	6.96	1.96	0.041
22	4.82	330	0.94	6.90	0.15	169	ND	ND	ND	ND	ND
Total triCB	112.3	3233	15.33	95.99	2.87	Total hexaCBs	69.65	1059	345	76.75	5.88
53	1.05	72.56	ND	ND	0.031	179	4.92	84.75	17.38	6.28	0.49
51	ND	24.97	ND	ND	0.013	176	1.03	22.61	3.27	1.76	0.12
45	1.25	52.66	ND	0.85	0.027	178	ND	16.18	5.27	2.72	0.12
52	13.17	500	9.44	4.97	0.28	175	ND	ND	ND	ND	ND
49	7.10	501	3.79	3.23	0.20	182/187	10.46	533	48.48	20.73	0.75
47/48	5.04	283	2.42	3.20	0.073	183	7.41	57.55	27.23	9.62	0.34
44	11.03	408	6.44	3.64	0.12	185	0.64	17.53	41.95	1.76	0.067
42	3.17	172	ND	1.22	0.041	177	4.22	ND	16.91	11.67	0.43
72/71/41	10.47	513	4.73	3.53	0.12	171	0.56	ND	ND	3.95	0.17
74	5.47	184	4.73	2.35	0.067	192/172	ND	ND	8.58	0.66	0.096
70/76	8.21	369	29.42	4.60	0.14	180	15.11	NA	183	9.85	1.64
66	1.87	580	8.71	4.14	0.092	193	ND	ND	ND	ND	0.076
60/56	2.09	420	5.65	2.21	0.071	191	ND	ND	ND	0.76	0.029
77	ND	ND	ND	ND	ND	170/190	9.06	184	72.86	69.75	0.62
Total tetraCBs	69.95	4080	75.33	33.94	1.28	Total heptaCBs	53.40	916	425	140	4.95
95/88	16.33	416	58.05	18.22	0.38	202	0.72	ND	12.20	2.89	0.087
91	1.06	96.00	7.66	ND	0.02	201	0.76	ND	4.6	2.20	0.064
84/89/92	1.59	89.43	19.04	1.49	0.046	197	ND	ND	ND	ND	0.024
101	15.72	693	146	23.32	0.50	200	0.30	ND	3.08	1.97	0.073
113/99	2.39	178	44.81	0.61	0.065	198	0.11	6.65	ND	0.85	0.018
97/83	2.30	197	32.26	2.09	0.049	199	1.72	101	75.66	31.17	0.32
87	6.12	304	48.49	5.56	0.10	196/203	2.62	134	81.04	42.70	0.42
111	ND	165	15.58	ND	0.018	195	0.35	30.92	22.90	15.27	0.11
110	25.45	716	130	23.66	0.34	194	0.62	52.04	66.82	48.88	0.20
123	ND	32.13	8.31	ND	ND	205	ND	5.08	ND	2.54	0.008
118	11.16	420.3	128	17.43	0.2	Total octaCBs	7.21	330	266	148	1.32
105/127	0.85	151	36.64	6.49	0.054	208	ND	7.82	7.30	1.76	0.019
126	ND	ND	ND	ND	ND	207	ND	3.75	2.20	1.47	0.014
Total pentaCBs	82.97	3458	675	98.87	1.77	206	ND	12.07	12.38	7.36	ND
154	4.56	80.37	13.99	1.99	0.32	Total nonaCBs	ND	23.64	21.88	10.59	0.033
151	6.36	107	13.40	2.99	0.43						
135/144	3.29	42.39	8.10	1.64	0.24	209	ND	7.3	0.79	0.85	0.003
149	21.66	266	40.06	13.39	1.39						
146/161	2.63	33.02	12.00	1.80	0.14	Total PCBs	395.4	13107	1825	605	18.11

ND-Not Detected; NA-Not Analyzed

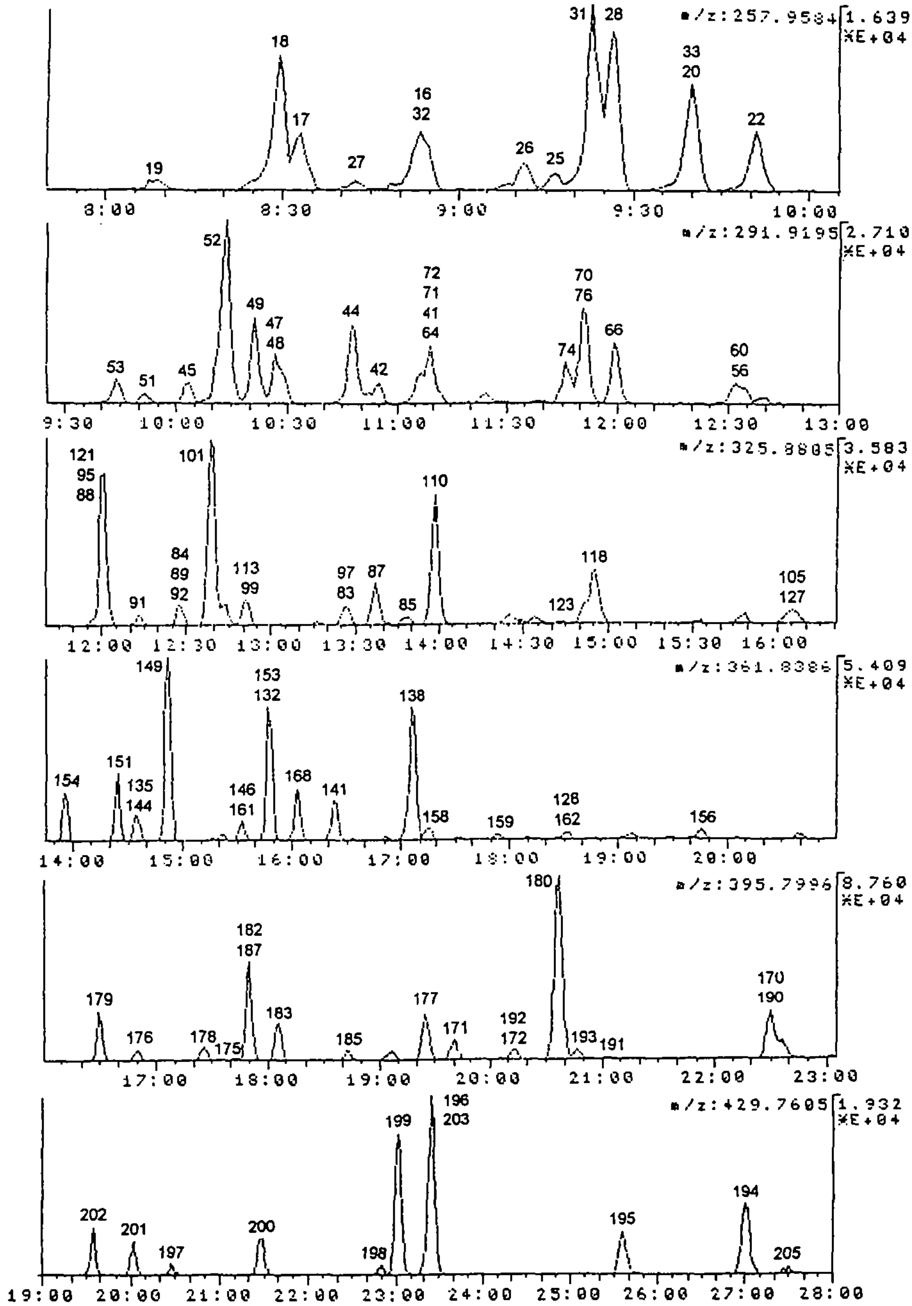

Fig. 1: Isomer pattern of tri- to octachlorinated biphenyls in the laboratory air sample