IDENTIFICATION AND SEMI-QUANTIFICATION OF MONOBROMO-PCB IN RINGED SEAL AND TECHNICAL PCB

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1. INTRODUCTION

Polychlorinated biphenyls (PCB) have for quite a long time been regarded as a class of ubiquitous environmental pollutants. Large production volumes in combination with chemical and biological stability have resulted in high environmental levels (ppm range) of PCB. During a mass spectrometric screening of a ringed seal sample we found a number of signals that tentatively was identified as monobromopolychlorobiphenyls (Br-PCB). This class of PCB related compounds has earlier been reported as a trace contaminant in a technical PCB, viz. Aroclor 1254[1], but has to our knowledge never been found in biological samples. The aim of the present study has therefore been to perform an unambiguous identification, and a semi-quantification, of the Br-PCB in seal and technical PCB.

2. EXPERIMENTAL

Extraction and clean-up of ringed seal samples: A composite (pooled) sample of juvenile ringed seal (*Phoca hispida*) collected from the Baltic Sea along the Swedish south-eastern coast line was examined in duplicate. The seal samples were blended with Na_2SO_4 and were column extracted with acetone/ n-hexane 2.5:1 and n-hexane/ diethyl ether 9:1[2,3]. The solvent was evaporated, the residues were taken up into n-hexane, and lipids and other hydrolysable organic compounds were removed by sulphuric acid treatment. After evaporation into an appropriate volume of tetradecane (40 µl) the samples were ready for analysis by gas chromatography/ mass spectrometry (GC/MS).

Low-resolution GC/MS analysis: The analyses were carried out on a 5% phenyl-methyl silicone fused silica capillary column (60m, 0.32 mm I.D., 0.25 mm film) coupled on-line to an Finnigan 4500 MS. Helium was used as carrier gas at a head pressure of 16 p.s.i. Injections of 1µl aliquots were made in the split-less mode. The GC oven was temperature programmed: 200°C(6min)-5°C/min-300(hold). Methane negative ion chemical ionisation (NICI) full scan mass spectra were recorded by an INCOS data system.

High-resolution GC/MS analysis: High-resolution GC/MS were used both for accurate mass analysis and semi-quantification. The chromatographic parameters were the same

as for the low-resolution analysis. The MS, a VG 250-S, was operated in electron impact mode at a resolution of 9000, and the instrument was tuned in the selected ion recording (SIR) mode. 4'-Bromo-2,5-dichlorobiphenyl was used as an external standard in the semi-quantification. All Br-PCB congeners were assumed to have equal molar response.

3. RESULTS

Identification: The NICI mass spectra of the Br-PCB contained the following ions (from high to low mass): M^- of medium intensity, intense $(M-Br)^-$, a series of fragments originating from consecutive losses of chlorine, and finally very intense Br^- (m/z 79 and 81) and weak Cl^- ions (m/z 35 and 37). This fragmentation is in agreement with published NICI spectra[1]. The isotopic patterns of the Br-PCB were within 5% of the theoretical values. The accurate mass determination indicated a molecular weight of 367.830 g/mol for the monobromotetrachlorobiphenyls ($BrCl_4$-biphenyls) and 401.795 g/mol for the monobromopentachlorobiphenyls ($BrCl_5$-biphenyls). These values are close to the theoretical values, which are 367.833 g/mol and 401.794 g/mol, respectively. A computer program was used to find elemental compositions with molecular weights close to the experimentally determined. The elemental compositions of $BrCl_4$- and $BrCl_5$-biphenyls were ranked as the second and first candidate, respectively (when allowing for a maximum of 40 C, 90 H, 3 O, 1 N, and 2 S atoms). Since both the mass spectra, the isotope clusters, and the accurate mass determination were in agreement with the tentative structure it was concluded that the compounds studied were Br-PCBs.

Semi-quantification: The results of the semi-quantification are summarised in Table 1. As can be seen, the total concentrations of Br-PCB are about 20 ng/g in seal blubber and 0.24% in Clophen A50 (a technical PCB product). The $BrCl_4$ and $BrCl_5$ homologues accounted for the highest percentage of the total Br-PCB. Some of the peaks had improper isotopic ratio and were therefore not included in the quantification. The amount of Br-PCB found in Clophen A50 are in reasonable close agreement with the amounts that has been found in Aroclor 1254[1], viz. 0.5%.

Substance group	Levels in ng/g*			
	Seal A	Seal B	Seal x	A50
ΣCl_2Br-biphenyls	nd	nd	-	-
ΣCl_3Br-biphenyls	0.56	0.72	0.64	-
ΣCl_4Br-biphenyls	4.4	5.3	4.8	170000
ΣCl_5Br-biphenyls	12	14	13	66000
ΣCl_6Br-biphenyls	0.72	0.64	0.68	-
ΣCl_7Br-biphenyls	Traces	Traces	-	-
ΣCl_8Br-biphenyls	nd	nd	-	-
Total Σ Br-PCB	18	21	19	240000

Table 1: Levels of monobromopolychlorobiphenyls in ringed seal blubber and Clophen A50. * Based on fresh weight (seal) or total product weight (Clophen A50).

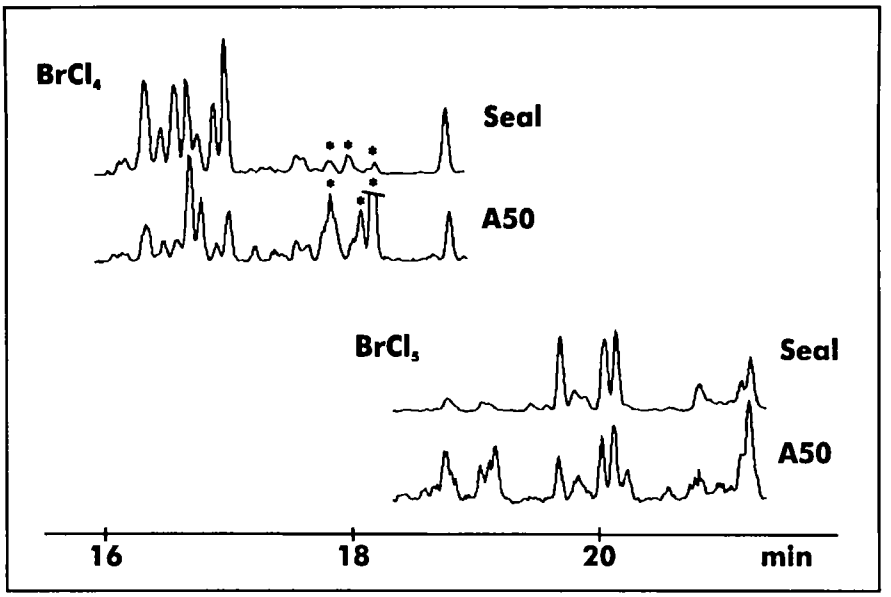

Figure 1: Mass fragmentograms of Br-PCB found in ringed seal blubber and a technical PCB, viz. Clophen A50. The peaks denoted with an * have an improper isotopic ratio. The chromatographic and mass spectrometric conditions are discussed further in the experimental section.

In Figure 1 and 2 mass fragmentograms from the GC/MS analysis are shown. A number of $BrCl_4$ and $BrCl_5$ peaks are found in both the ringed seal blubber and Clophen A50, c.f. Figure 1. It is therefore possible that technical PCB products are a source of Br-PCB found in the environment.

4. ACKNOWLEDGEMENTS

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5. REFERENCES

1 Buser, H.R. (1986): Selective Detection of Brominated Aromatic Compounds using Gas Chromatography/ Negative Chemical Ionisation Mass Spectrometry. Anal. Chem. 58, 2913-2919.

2 Jensen, S., Reutergårdh, L. and Jansson, B. (1983): Analysis Methods for Measuring Organochlorines and Methyl Mercury by Gas Chromatography. FAO Fish Tech. Pap. 212, 21-33.

3 Smith, L.H., Stalling, D.L. and Johnson, J.L. (1984): A Method for the Determination of Part-per-Trillion Levels of Polychlorinated Dibenzofurans, Dioxins and Ortho-unsubstituted Biphenyls in Environmental Samples. Anal. Chem. 56, 1830-1842

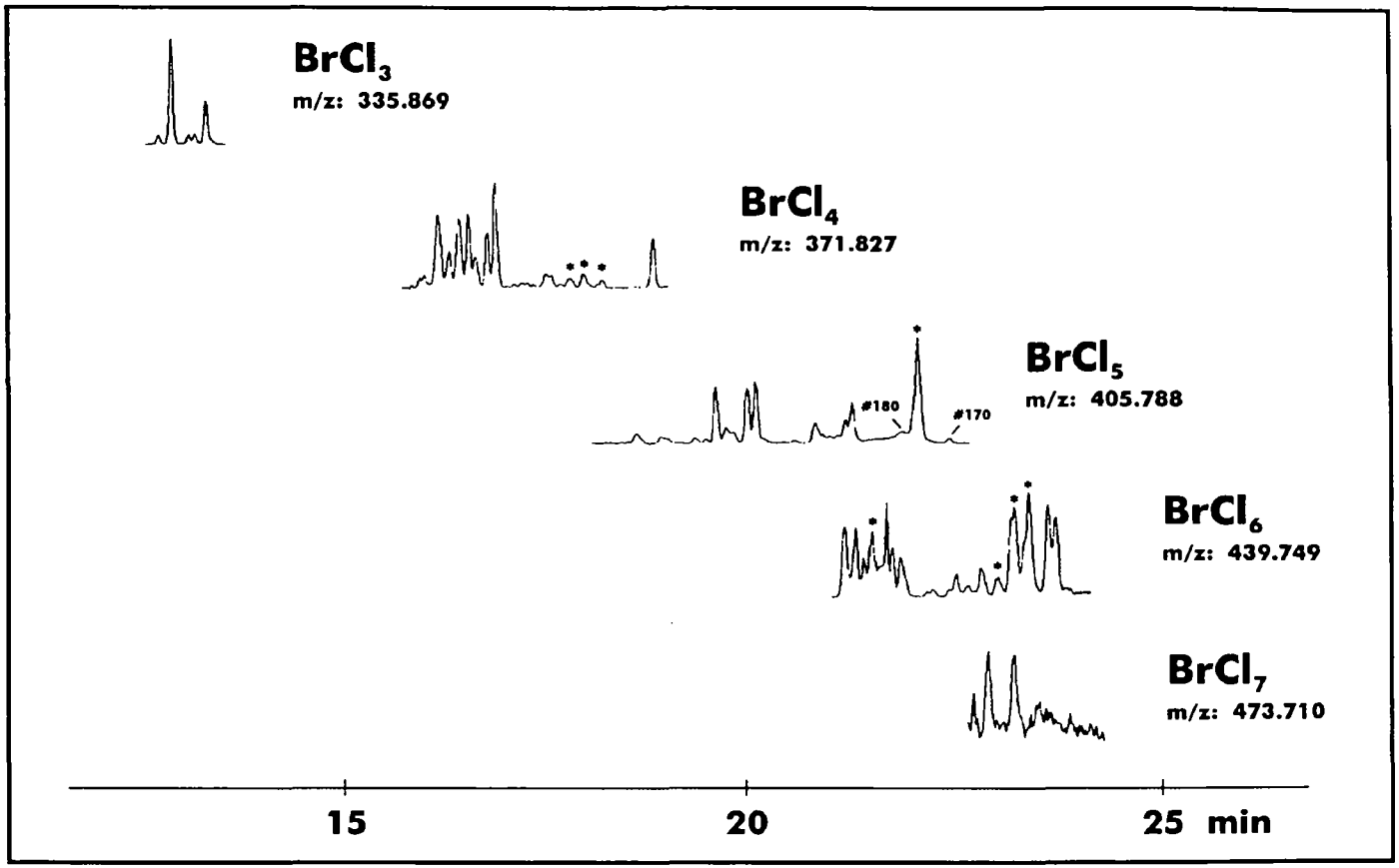

Figure 2: Mass fragmentograms of Br-PCB found in ringed seal blubber. The peaks denoted with an * have an improper isotopic ratio. The peaks marked with #170 and #180 are interfering signals from PCB #170 and PCB #180, respectively. The chromatographic and mass spectrometric conditions are discussed further in the experimental section.