Congener Specific PCB Analysis by HRGC/HRMS: Reference Materials

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Abstract

As the requirement for congener specific PCB data increases, a need for PCB data for reference materials for various matrices has also emerged. PCB reference materials are needed to complement existing PCDD/PCDF reference materials. HRGC/HRMS calibration solutions containing 72 PCB congeners, 22 recovery surrogates and 5 injection surrogates have been developed. A number of reference materials such as sediments, Aroclors™ and fish tissue have been characterized to develop reference values. The calibration mixtures were also compared to PCB standard reference mixtures from the National Research Council of Canada (NRC-CLB).

Introduction

The 1994 EPA reassessment of dioxin also targeted "dioxin-like" PCBs[1]. Combined with this information and the fact that some PCBs have been assigned TEFs (toxic equivalency factors) in the same range or higher than some 2378-substituted PCDDs/PCDFs, it can be seen that the need for congener specific PCB data is increasing[2]. This requires method development, the development of a wider range of $^{13}C_{12}$-labelled surrogates and the development and certification of reference materials.

As with PCDDs/PCDFs, PCBs are found in a wide range of matrices and at varying levels. The conventional method of determining PCBs by total Aroclor PCB content is not really valid as it is known that the Aroclor mixtures change in the environment due to degradation and bioaccumulation.

Therefore, our laboratory has developed methods for the HRGC/HRMS analysis of PCB congeners, synthesized additional $^{13}C_{12}$-PCB surrogates, and undertaken the analysis of a variety of existing reference materials (certified for other parameters) for congener specific PCBs. The reference materials tested include sediments, tissue and Aroclor mixtures.

Experimental Methods

Sample Preparation

Sediment, tissue and Aroclor samples were spiked with a mixture of $^{13}C_{12}$-labelled PCB surrogates listed in Table 1 and processed as described previously[3]. Prior to HRGC/HRMS analysis, a mixture of five $^{13}C_{12}$-PCB internal standard surrogates were added (see Table 1).

Analysis

All sample extracts were analyzed using HRGC/HRMS on a VG70SE magnetic sector HRMS. The HRGC was equipped with a 60 m J&W DB5 column. 2 μL splitless injectors were made using a CTC 200 autosampler. The calibration mixtures contained first and last eluters for each homologue group. A four-point calibration was used with calibration standards ranging from 4 pg/μL to 200 pg/μL. The 7-function HRGC/HRMS experiment contained two quantitation ions for each native homologue group and 2 quantitation ions for each labelled PCB present. Loss of 2Cl was used to confirm the presence of a PCB congener. Each function also included ions to distinguish contributions from higher chlorinated PCBs. The Micromass quantitation package OPUSQUAN™ was used for data manipulation.

Results and Discussion

In recent years, a number of sediments and tissue samples have been characterized as reference materials for PCDDs/PCDFs. Some of these materials have been examined by our laboratory as candidates for reference materials for congener specific PCB analysis. A number of Aroclors have also been characterized for specific PCB congener concentration. Coplanar PCBs were analyzed separately. A between-laboratory comparison has also been carried out.

There is significant overlap of the ten homologue groups within the 7 acquisition functions of the GC/MS experiment. Therefore, in preparing our calibration solutions, an attempt was made to provide a surrogate PCB for each homologue group within a GC/MS function. This was in order to provide a more accurate result for all 209 PCB congeners. Due to lack of availability, 3 homologue groups do not have a surrogate within their GC/MS window, but do have a number of surrogates in the nearest functions. Currently, more $^{13}C_{12}$-PCB surrogates are being synthesized by our laboratory (Wellington Laboratories).

A number of reference sediments have been analyzed (Environment Canada's EC2, EC3 and EC8 and National Research Council of Canada's HS-1 and HS-2). For the Environment Canada sediments, greater than 80% of the total reference value for PCBs has been accounted for using our 72 individual isomers. Table 2 lists some non-coplanar "dioxin-like" PCB data for two Environment Canada sediments. There are also a large number of other major PCB congeners in these sediments. The HS1 and HS2 sediments have lower PCB levels.

Table 3 shows PCB data for three Aroclor mixtures. When more than 60 individual "named" PCBs were monitored, greater than 64% of the total PCB value for these mixtures was accounted for. When "named" PCBs and other congeners were taken into account, the values rose to 100% or slightly higher.

Fish tissue reference materials from Environment Canada have also been analyzed using the surrogate mixtures and calibration solutions used in this paper. These tissue samples have been well characterized for PCDD/PCDF levels.

The synthesis of further $^{13}C_{12}$-PCB surrogates and addition to the calibration mixture as well as addition of more individual native PCB congeners has improved the accuracy of the PCB HRGC/HRMS analysis. A number of the reference materials analyzed are good candidates for PCB reference materials. Further interlaboratory comparisons and stability tests are planned.

Table 1: Surrogate and Internal Standard Mixtures

GC/MS Function	# of Chlorines	Surrogate Standard*	Internal Standard*
1	1	3	--
2	2	15	--
3	3	28	37
	4	52	
	5	--	
4	4	70, 77	81
	5	101, 118	
	6	--	
5	5	105, 126	114
	6	153, 138, 167	
	7	178	
6	6	156, 169	157
	7	170, 180, 189	
	8	--	
7	8	194	208
	9	206	
	10	209	

* IUPAC Numbers

Table 2: Non-Coplanar Dioxin-Like PCB Data (ng/g)

	EC2	EC3	Detection Limits
PCBs*:			
PCB 81	1120	912	5
PCB 118	3650	24100	6
PCB 114	1150	980	7
PCB 105	22500	15300	6
PCB 167	7950	5580	2
PCB 156	4160	2460	1
PCB 157	1010	729	1
PCB 189	413	357	1

* IUPAC Numbers

Table 3: Aroclors versus Targeted PCBs

	% of Totals Identified using Targeted PCBs*	% of Totals Identified using Targeted PCBs and Other Congeners Detected
Aroclor 1242	64.0%	113%
Aroclor 1254	90.3%	113%
Aroclor 1260	77.2%	100%

* >60 PCBs monitored

References

(1) U.S. Environmental Protection Agency. *Health Assessment Document for 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD) and Related Compounds,* Vol. III; external review draft; Office of Health and Environmental Assessment. Office of Research and Development. U.S. Government Printing Office: Washington, D.C., **August 1994;** EPA/600/BP-92/001C.

(2) Safe S.: Polychlorinated biphenyls (PCBs), dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), and related compounds: Environmental and mechanistic considerations which support the development of toxic equivalency factors (TEFs). *Critical Reviews in Toxicology* **1990**, 21: 51-88.

(3) Tashiro C., Potter D.W., Sharratt B.J., Yeo B.R., Chittim B.G., Stokker Y., *Organohalogen Compounds,* Vol. 23, **1995,** 273-278.