Use of a Gas Chromatographic Modeling Program to Identify Toxic PCB Isomers Detected in Aquatic Organisms

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Abstract

Two criteria are used to identify compounds by gas chromatography/mass spectrometry (GC/MS). First, the mass spectrum of the compound must match the spectrum of a standard or a spectrum from a mass spectral library. Second, the retention time of the compound must fall within a retention time window that is based on the retention time of a standard or surrogate compound.

Pro ezGC, a chromatographic modeling program, uses Thermodynamic Retention Indices (TRIs) to predict retention times and peak widths on capillary GC columns. This program has been used to model the retention times of the 209 polychlorinated biphenyl (PCB) isomers. The retention time predictions from the model have been used to confirm the identifications of individual PCB isomers detected in freshwater aquatic organisms.

Introduction

The ezGC model is based on the thermodynamic properties of each compound on a given stationary phase (1).

$$1 = \int_0^{t_r} \frac{1}{(t_m(1+k_i))} dt$$

Where:

$$\ln K_i = \frac{-\Delta H_{v,i}}{RT} + \Delta S_{v,i} - \ln \beta$$

ΔH_v = Enthalpy of vaporization
ΔS_v = Entropy of vaporization
t_m = column dead time
K_i = capacity factor
T = column temperature
β = column phase ratio

The TRIs for all 209 PCB isomers were calculated for the DB-5 column using retention times from two temperature programs. Published retention time data were used to confirm the identification of each PCB isomer (2 , 3). The TRIs were used to accurately predict the retention times of the PCBs for different column dimensions, carrier gas flows and temperature programs. The predicted retention times are within 0.1% of the measured retention times when a few PCB isomers are used to calibrate the modeling program.

Experimental Methods

The following samples were obtained from rivers and reservoirs in Tennessee.

River Otter - liver from otter autopsy
Turtle - composite without shell
Ebony Mussel - composite without shell
Channel Catfish - composite whole body

Aliquots of the samples (10-20 g) were mixed with sodium sulfate, spiked with $^{13}C_{12}$-labelled PCB internal standards and extracted in a Soxhlet extraction apparatus using 50% dichloromethane/hexane. Following extraction, the samples were partitioned with sulfuric acid and chromatographed on a multi-layer silica column (acidic, basic and neutral silica layers). Finally, the samples were chromatographed on an activated basic alumina column. The sample extracts were concentrated to 10 µL and then 3 µL of each sample extract was analyzed by GC/MS using the following chromatographic conditions.

Temperature Program: 100 °C, 6 °C/min to 300 °C
Column: 30 m x 0.25 mm x 1.0 µm - fish and mussel
Column: 60 m x 0.25 mm x 0.25 µm - otter and turtle

Calibration standards containing PCB isomers 77, 126 and 169 were analyzed on each of the columns and the retention times of the standards were used to calibrate the model. The following table shows the accuracy of the predicted retention times for five tetra-chlorinated PCBs. The average accuracy of the predictions for the 23 tetra-chlorinated PCBs was 0.1%.

Comparison of Measured and Calculated Retention Times for Tetra-Chlorinated PCBs

PCB Isomer	Measured Retention Time	Calculated Retention Time	% Error
53	16.47	16.45	0.1
51	16.61	16.61	0.0
66	18.77	18.79	-0.1
56	19.22	19.22	0.0
77	20.31	20.28	0.2

Results and Discussion

The calibrated model was used to predict the retention times of all 209 PCBs and the retention time predictions were used to identify individual PCB isomers in the sample extracts. The following tables list the PCB concentrations that were measured in fish, mussel, otter liver and turtle samples.

PCB Concentrations - Fish and Mussel

Isomer #	PCB Isomer	Concentrations (ppb) Fish	Mussel
77	3,3',4,4'-TetraCB	ND (0.005)	ND (0.001)
105	2,3,3',4,4'-PentaCB	6.2	0.10
118	2,3',4,4',5-PentaCB	20.6	0.32
126	3,3',4,4',5-PentaCB	ND (0.005)	0.024
153	2,2',4,4',5,5'-HexaCB	21.2	0.36
156	2,3,3',4,4',5-HexaCB	1.1	ND (0.002)
169	3,3',4,4',5,5'-HexaCB	ND (0.02)	ND (0.002)
180	2,2',3,4,4',5,5'-HeptaCB	3.1	0.21
195	2,2',3,3',4,4',5,6-OctaCB	0.41	0.042
206	2,2',3,3',4,4',5,5',6-Nona CB	0.32	0.095
209	DecaCB	0.48	0.26

PCB Concentrations - Otter Liver and Turtle

Isomer #	PCB Isomer	Concentrations (ppb) Otter Liver	Turtle
77	3,3',4,4'-TetraCB	ND (0.01)	0.24
105	2,3,3',4,4'-PentaCB	ND (0.002)	42.1
118	2,3',4,4',5-PentaCB	ND (0.1)	109
126	3,3',4,4',5-PentaCB	ND (0.001)	0.82
153	2,2',4,4',5,5'-HexaCB	248	290
156	2,3,3',4,4',5-HexaCB	ND (0.3)	51.2
169	3,3',4,4',5,5'-HexaCB	ND (0.07)	ND (0.27)
180	2,2',3,4,4',5,5'-HeptaCB	292	266
195	2,2',3,3',4,4',5,6-OctaCB	25.5	27.6
206	2,2',3,3',4,4',5,5',6-Nona CB	21.5	19.2
209	DecaCB	6.5	4.0

Modeling the retention times of compounds has several advantages. In the present study, the routine calibration of the GC/MS was performed with a small set of PCB isomers. The accurate retention times calculated by the model allowed the identification of individual PCB isomers in tissue extracts. Using the TRIs, the retention times of the PCBs were predicted when the column, carrier gas flow and temperature program were modified. In addition, routine calibrations performed with the subset of PCBs compensated for any changes that occurred as the columns aged.

The model can easily be used to optimize separations. This means procedures can be developed to identify selected PCB isomers in the presence of other PCB isomers and interfering peaks. Thus, the model can also be used to develop rapid screening procedures that resolve and identify selected isomers in the shortest analysis time.

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