GAS CHROMATOGRAPHIC RETENTION INDEX MODELLING FOR ENVIRONMENTAL MONITORING OF HALOGENATED DIOXINS

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ABSTRACT:

A gas chromatographic retention index (RI) model has been developed and tested for brominated, chlorinated, and bromochlorinated dioxins. The model is based upon the concept of expressing molecular RI as the sum of the RI of the two halves of the molecule plus the RI value of interactive effects. This model allows tentative identification of congeners found during environmental monitoring, and permits the establishment of preliminary retention time windows when seeking target analytes, such as 2,3,7,8-substituted isomers.

INTRODUCTION:

Brominated dioxins (PBDD) have been found in flame-retarded thermoplastic resin pyrolysates,[1] brominated phenols,[2] brominated diphenylether pyrolysates,[1,3] and vehicular exhaust.[4] Bromochlorinated dioxins (PBCDD) have been detected in municipal and hazardous waste incinerator fly ash.[5-10] Toxicological data suggest that the toxicities of these brominated and bromochlorinated dioxins are similar to the levels found for the PCDD analogs.[11,12]

A gas chromatographic retention index (RI) model was recently reported for the chlorinated dioxins (PCDD).[13] This model successfully estimated the molecular RI of PCDD by summing the RI contributions of the two "single rings" comprising the molecule, plus the readily-estimated magnitude of an interactive effect named the "ring-ring interaction" or "1,9-effect" which was observed in cases where both the 1 and 9 positions were chlorinated. In the event the 1,4,6, and 9 positions all were chlorinated, the total effect was experimentally observed to be approximately 1.5 times the magnitude of a single 1,9 effect.

Because of the apparent toxicity of the halogenated dioxins (HDD), the large number of congeners (75 PCDD, 75 PBDD, 1550 PBCDD), and the scarcity of analytical standards, environmental monitoring for these analytes is performed with a few standards augmented by

a predictive tool for choosing retention time windows within which the analytes should elute. This report describes the successful extension and modification of the PCDD RI model to allow treatment of the other HDD.

EXPERIMENTAL:

Commercially-available standards were purchased from Cambridge Isotope Laboratories (Woburn, MA, U.S.A.), or from Chemsyn Science Laboratories (Lenexa, KS, U.S.A.). The self-condensation of halogenated phenolates[14] and the coupling of halogenated catechols with halobenzenes or halonitrobenzenes under basic conditions were used to prepare selected PBDD and PBCDD; all 26 bromochloro single rings were accessed through synthesis. Six of the nine possible bromo single rings were accessed through commercial standards, and three were synthesized.

Retention indices for HDD were determined against the normal hydrocarbons, using a Hewlett-Packard 5880A gas chromatograph (GC) with splitless injection, a Restek 30 m x 0.25 mm, 0.25 μm film RT_{α}-5 column, helium carrier gas at 25 psi, and flame ionization detection. The column was temperature programmed with 1 min at 170°C followed by 2°C/min to 320°C.

DISCUSSION:

Retention indices for the PBDD and PBCDD were successfully calculated and effectively applied by expressing the molecular RI as the sum of five contributors: (1) the index of single-ring A; (2) the index of single-ring B; (3) the index of a "ring interaction" effect, or "1,9-effect"; (4) the index increment from "buttressing" the 1,9-effect with additional substitution at the 2 and 8 positions; and (5) the index of a "phase interaction" effect.

The single-ring RI values are listed in Table 1. In general, each additional bromine substitution incremented the molecular RI about 1.5 times as much as a chlorine substitution did. The 1,9-chloro ring interaction was found to average 12 RI units; when two 1,9-effects were present (i.e. all four 1,4,6,9 positions were occupied by chlorine atoms), the total ring-ring effect was approximately 18 units.

The 1,9-dibromo ring-ring interaction was also found to increase the RI by approximately 12 RI units. Buttressing at the 2,8-positions with chlorines increased the magnitude of the effect to 18 RI units. "Buttressing" the 1,9 positions with 2,3,7,8-tetrabromo substitution increased the 1,9- ring-ring interaction effect to 34 RI units; 2,8-dibromo-3,7-dichloro buttressing gave the ring-ring interaction effect a magnitude of 22 RI units.

In those molecules containing two or more bromines on one ring, it appeared that the ability of the second ring, if unsubstituted, chlorinated only, or monobromo-monochlorinated, to interact with the column phase was diminished, resulting in a reduction of RI. It is suggested that the reduction in RI was related to the molecule assuming a distance from the phase greater than the optimum distance for interaction with the phase by the second ring. The experimental magnitude of the RI decrease, suggested to be caused by a "phase interaction" (PI) effect, was found to be dependent upon the number of bromines and upon whether the second was unsubstituted, chlorinated, or monobromo-monochlorinated. These findings have been summarized in Table 2.

Table 1. Single Ring Retention Indices for HDD.

Br positions	Cl positions	RI
		806
2		1074
1		1079
1,3		1354
1,4		1376
2,3		1411
1,2		1438
1,2,4		1705
1,2,3		1767
1,2,3,4		2123
	1	981
	2	986
	1,3	1130
	1,4	1145
	2,3	1174
	1,2	1186
	1,2,4	1319
	1,2,3	1359
	1,2,3,4	1534
1	3	1237
3	1	1244
1	4	1246
2	3	1291
1	2	1292
2	1	1292
1	2,4	1435
1	3,4	1436
2	1,4	1444
1	2,3	1488
3	1,2	1495
2	1,3	1496
1,4	2	1562
1,3	4	1567
1,2	4	1570
1,3	2	1621
1,2	3	1626
2,3	1	1633
1	2,3,4	1678
2	1,3,4	1691
1,4	2,3	1809
1,3	2,4	1823
1,2	3,4	1824
2,3	1,4	1836
1,2,4	3	1946
1,2,3	4	1965

Table 2. Phase Interaction Effect Values in RI Units

Single Ring Under Evaluation	Other Ring	PI Effect, RI Units
unsubstituted	Br_4	118
Cl	Br_2	22
Cl_2	Br_3	31
Cl_2	Br_4	53
BrCl	Br_2Cl	11
Cl_2 (1,3 or 1,4)	$BrCl_2$	11

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