

Kovats and Lee Retention Indices for Characterization of PCBs, PCNs, and Dioxins

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Introduction:

Polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs), polychlorinated biphenyls (PCBs), and polychlorinated naphthalenes (PCNs) are persistent organic pollutants that are formed by combustion or as unintended by products from industrial processes. They have been important compounds to analytical chemists for decades, with the first publications appearing in the 1970s.¹⁻³ The mixture of these compounds in environmental samples can pose a daunting separation challenge for chromatographers. While there are historic studies that compare relative retention ratios for these compounds such as Frame's work with PCBs and Ryan's work with PCDD/Fs, a study that compares all of these compounds under similar conditions with columns in current use is lacking. Frame has compiled a comprehensive list of all 209 PCBs and their elution orders on 24 chromatographic columns; however a majority of this work was accomplished using now outdated columns, ECD detectors, and PCBs as relative retention markers.⁴ Modern analyses that rely on this work that use a different detector, such as a mass spectrometer, and want to use a more universal retention marker may find it difficult to utilize Frame or Ryan's data. Ryan's work with PCDD/Fs, like Frame's, used a relative retention system and now outdated columns.⁵

Modern chromatographic separations utilize columns with stationary phases similar to Frame and Ryan's work, however many of the columns used in the previous studies are no longer common and new columns like the Dioxin2 were not characterized. A retention index system that is compatible with mass spectrometer analysis and is easily identifiable from the target compounds would offer a great advantage over the previous works described. Herein, a retention index system utilizing Kovats and Lee retention indices⁶ is proposed for PCBs, PCNs, and PCDD/Fs as a means to identify individual congeners and coelutions on a variety of current, popular, GC columns as well as influence optimization of column choice to determine optimal orthogonality for confirmation analyses and GCxGC separations.

Materials and Methods:

The nine PCB mixes used in this analysis were obtained from AccuStandard (AccuStandard, Inc., New Haven CT) and are the same standards used by Frame in his evaluation of 24 stationary phases. 36 PCNs standards were provided by Restek (Restek, Bellefonte, PA) and purchased through Cambridge Isotope Laboratories Inc. (Cambridge Isotopes, Tewksbury, MA). PCDD/Fs as well as several polybrominated and mixed chloro/bromo dioxin and furan congeners were obtained from Wellington Laboratories (Wellington Laboratories, Guelph, Ontario, Canada). Five polyaromatic hydrocarbons, Naphthalene, Phenanthrene, Chrysene, and Picene were also purchased from AccuStandard for use as Lee retention index markers. MA aliphatic hydrocarbon standard was obtained from Restek and used for the Kovats retention index markers.

Retention index profiling was performed with a Waters Xevo TQ-S triple quadrupole mass spectrometer (Waters Corporation, Milford, MA) coupled to an Agilent 7890A gas chromatograph, and Agilent 7693 autosampler (Agilent Technologies, Santa Clara, CA). Helium carrier gas was used, and the GC was operated at a split ratio of 10:1 with a flow rate of 1.2 mL/min. The injector was maintained at a temperature of 290 °C and utilized a 4.0 mm Split/Splitless Skyliner with wool plug (Restek, Bellefonte, PA). Samples were injected under these conditions at a volume of 1.0 µL. Two oven programs were used for this analysis the first started with an

initial temperature of 50°C for 1min, 5°C/min to 300°C hold for 10mins. The second oven program started with an initial temperature of 100°C for 1min, 10°C/min to 315°C hold for 2mins.

Several columns were used for this work; however, this discussion will focus on the Rtx-Dioxin2, Rtx-1MS, Rtx-5MS, and Rtx-200. All dimensions were 60m x 0.18mm x 0.1µm except for the Rtx-200 which was 60m x 0.25mm x 0.25µm. All columns were obtained from Restek (Restek, Bellefonte, PA).

Results and Discussion:

Figures 1 and 2 are the comparison of retention indices on 60m x 0.18mm x 0.10µm Rtx-1MS and Rtx-Dioxin2 columns. Other columns are used in this work, but for clarity and brevity the Rtx-Dioxin2 and Rtx-1MS columns will be the only columns discussed here. Other examples will be provided in the presentation of this work. The line through the data points represents the best fit of the data, and as such data points on the line represent no effective selectivity difference between the two columns for that congener. Deviation from the line of best fit indicates a selectivity difference for one phase over the other for that particular congener.

Figures 3 and 4 are the specific deviation from this line of best fit for the most toxic congeners; 12 PCB's and 17 PCDD/Fs. The small differences in selectivity allow for the pronounced separations observed during GC separations as well as GCxGC separations. Quantifying the selectivity difference each congener has for a specific stationary phase will allow for greater column optimization and improved separation. A retention index database for these compounds is currently being finalized on eight modern columns. To the best of our knowledge, this is the first-time complete elution orders for all 209 PCBs and all commercially available PCNs have been established on the Rtx-Dioxin 2 and Rtx-200. This will provide a comprehensive list of all PCBs, PCNs, and PCDD/Fs elution orders and retention indices for anyone to use for alternative identification of these compounds.

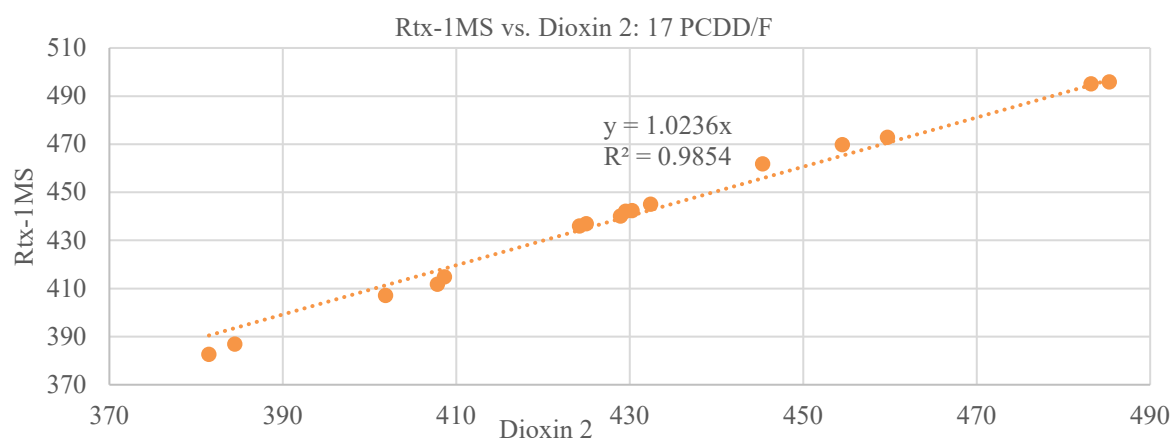


Figure 1: The 17 PCDD/Fs which are considered the most toxic congeners are plotted in figure 1. The deviation above or below the line indicates a difference in selectivity for that stationary phase. If the congener is above the line it favors the Rtx-1MS and below the line it favors the Rtx-Dioxin2.

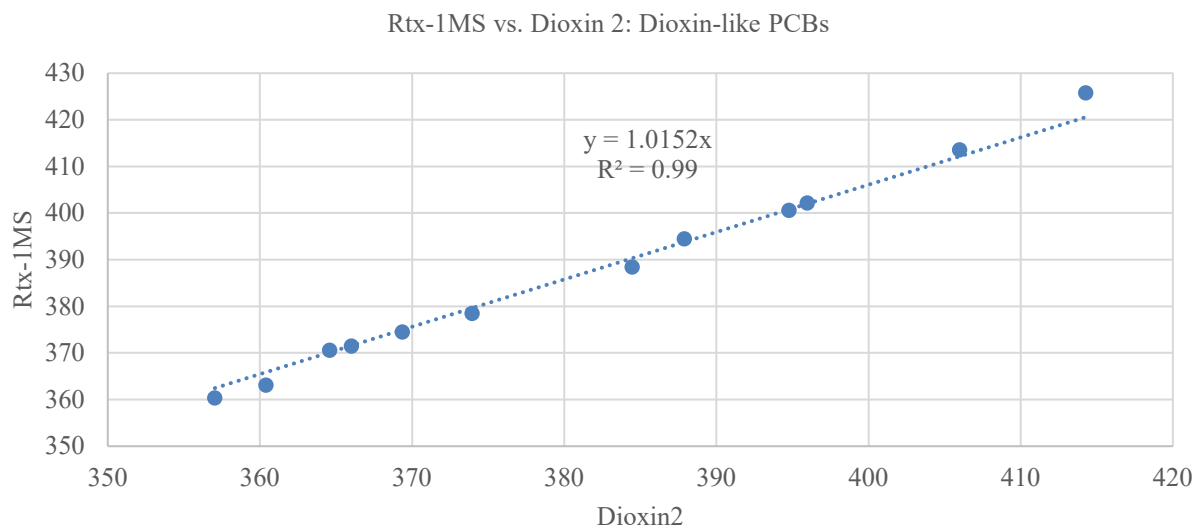


Figure 2: The dioxin-like PCBs, which are considered the most toxic congeners, are plotted in figure 2. The deviation above or below the line indicates a difference in selectivity for that stationary phase. If the congener is above the line it favors the Rtx-1MS and below the line it favors the Rtx-Dioxin2.

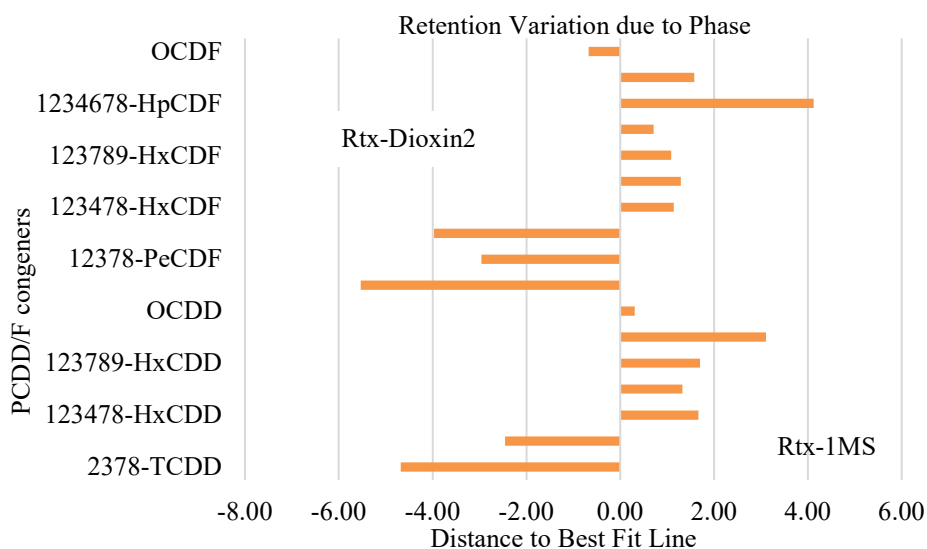


Figure 3: The distance from the best fit line for the 17 PCDD/F congeners. The small variations in phase affinity are responsible for the separation of similar congeners. These relatively small differences actually allow for optimizing column choices as these compounds are not significantly different in chemical properties.

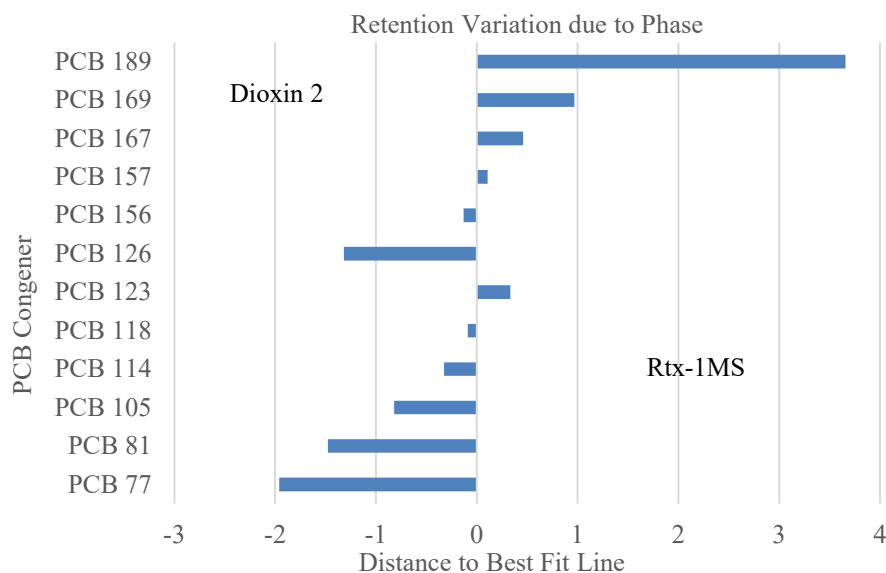


Figure 4: The distance from the best fit line for the 12 dioxin-like PCB congeners. The small variations in phase affinity are responsible for the separation of similar congeners. These relatively small differences allow for optimizing column choices as these compounds are not significantly different in chemical properties.

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