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GCxGC-TOFMS OF POLYCHLORINATED BIPHENYLS

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Introduction

The separation of all 209 polychlorinated biphenyls (PCBs) in one gas chromatographic run with one detector could be considered a Holy Grail for separation science. Practically speaking though, it may be only an interesting lab exercise, as the environmental, health effects, and regulatory communities generally monitor for only those PCBs on "short lists" when doing congener specific PCB work (1). Often these lists are based on a congener's potential for toxicity, its frequency in the environment, and/or its abundance in animal tissues.

Even when only a limited number of congeners are targeted for analysis, separating those select congeners from other congeners present in a sample can be a challenge. One way to achieve the desired separation is to choose a selective stationary phase (2). Employing dual columns of differing phases, which end in separate electron capture detectors (ECDs), is another method (3). To determine the most toxic congeners (non- and mono-*ortho*-chlorinated), sorbent column cleanup methods may be employed to separate them from the bulk of the other PCBs prior to GC analysis. Mass spectrometry (MS) sometimes allows individual determination of coeluting congeners when they differ in chlorination level.

Some analysts are using comprehensive two-dimensional GC (GCxGC) to solve their PCB separation problems (4-6). GCxGC is a way to increase resolution by applying two independent separations to a sample in one analysis. Typically GCxGC involves a serial column configuration (differing phases) separated by a thermal modulator. A separation is performed on the first column, and then effluent from the first column is continually (and quickly) focused and injected onto the second column. By keeping the second column short, a series of high speed chromatograms are generated, and the first column separation can be maintained. Separation results are plotted as a retention plane (column 1 time x column 2 time).

Due to modulation, GCxGC peaks are on the order of 50 to 500 ms wide, requiring a fast detector. When MS is used, only time-of-flight (TOF) has the necessary acquisition rates (hundreds of spectra/sec). A study was conducted to evaluate GCxGC-TOFMS potential to individually determine significant PCB congeners. A column shown to be selective for PCBs was used as the secondary column (7). To make the study complete, retention times for all 209 PCBs were recorded. An Aroclor mix was analyzed to demonstrate the results.

Materials and Methods
PCB standard solutions and dilutions of Aroclors were obtained from AccuStandard (New Haven, CT, USA). Separations were carried out using a LECO Pegasus 4D GCxGC-TOFMS that has a dual jet modulator (St. Joseph, MI, USA). The GCxGC column configuration was from Restek Corporation (Bellefonte, PA, USA). The integral column, a 50m x 0.18mm x 0.18µm Rtx-1 x 10m x 0.10mm x 0.1µm Rtx-PCB, was installed so that 4m of the Rtx-PCB resided in a secondary oven past the modulator. No press fit connection is necessary for this type of column.

A splitless injection at 250°C, with a purge time of 60 sec, was used for each analysis. The primary oven was programmed as follows: 70°C (1 min), 50°/min to 120°, 8°/min to 340° (0.5 min). The modulator temperature offset was 40°C. The second dimension separation time (modulation time) was set to 2 sec, with hot pulse time and cool time between stages at 0.5 sec each. The secondary oven program was: 90°C (1 min), 50°/min to 120°, 8°/min to 340° (3 min). Helium carrier gas was a constant 1.5 mL/min. Total run time was 30 min.

Electron ionization at 70eV was used for TOFMS with a source temperature of 225°C, a data acquisition rate of 100 spectra/sec, and a stored mass range of 120 to 520u.

Results and Discussion
The limited space here prevents listing of all of the PCB retention times so a graphic example will be used to demonstrate the potential utility of GCxGC for separating significant PCBs. PCBs 153, 132, and 105 can coelute on some methyl- and phenylmethylsilicone columns. The individual determination of PCB 153 is important because it is one of the European indicator congeners. While 105 can be distinguished through MS since it is a pentachlorobiphenyl, 153 and 132 are both hexachlorobiphenyls, making chromatographic separation mandatory if they are to be quantified individually. When operated under one dimensional conditions, using the same primary and secondary oven conditions described in **Materials and Methods** but without modulation, 153, 132, and 105 coelute on the Rtx-1/Rtx-PCB column (**Figure 1**).

GCxGC allows the separation of PCBs 153, 132, and 105 by taking advantage of the secondary column's selectivity. In **Figure 2**, a contour plot is shown that consists of the first dimension retention time (sec) as the x-axis and the second dimension retention time (sec) as the y-axis. In the x-axis plane the three PCBs are almost aligned, detailing again how they would coelute if only a one-dimensional analysis was used. But, these PCBs are separated in space in the y-plane; all three PCBs could be quantified individually.

It should be noted that the modulation time for this work was very short (2 sec) for a relatively long secondary column (4m). The goal was to try and maintain as much of the primary column separation as possible under the relatively fast primary oven programming (8°C/min). PCB congeners 138, 163, and 164, which were previously resolved in a long run on a 60m x 0.18mm x0.18mm Rtx-PCB (7), coeluted under the GCxGC conditions used here. These congeners are difficult to impossible to resolve on methyl- and phenylmethylsilicone columns. Different GCxGC conditions must be explored to increase the efficiency of the system.

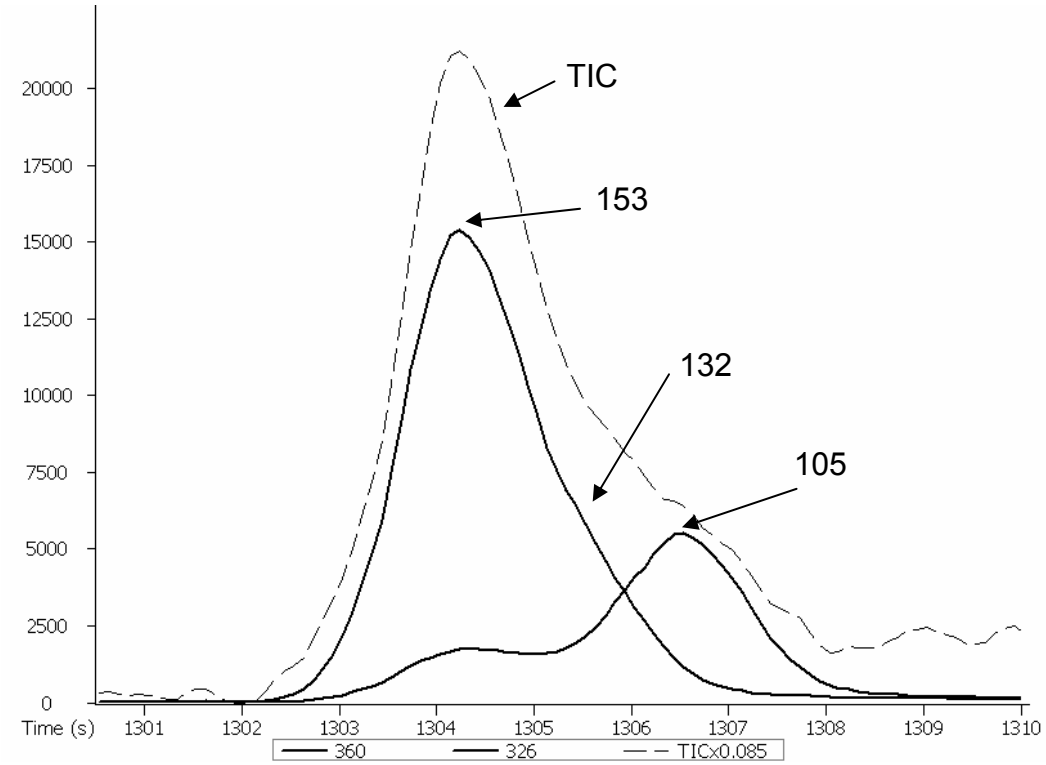

Figure 1. Coelution of PCBs 153, 132, and 105 in an Aroclor mix on the Rtx-1/Rtx-PCB column operated in one-dimensional mode.

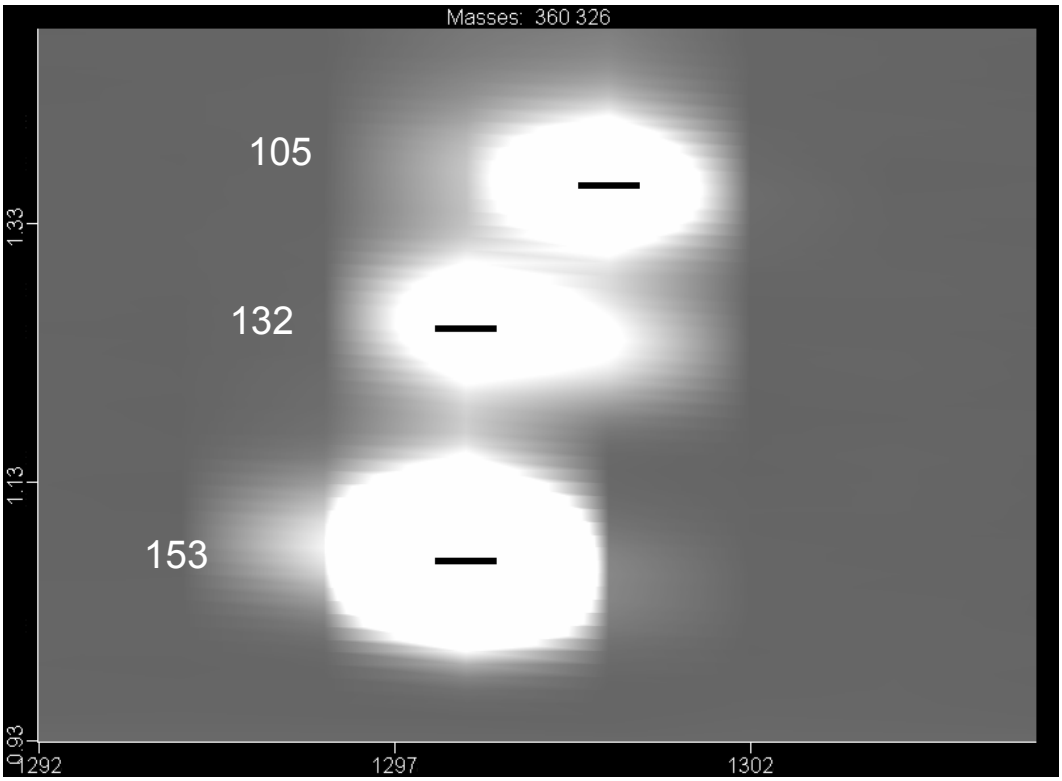

Figure 2. Resolution of PCBs 153, 132, and 105 in an Aroclor mix on the Rtx-1/Rtx-PCB column operated as GCxGC. The x-axis is the first dimension retention time (sec) and the y-axis is the second dimension retention time (sec).

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