FAST GAS CHROMATOGRAPHY/HIGH RESOLUTION MASS SPECTROMETRY AND COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY/HIGH RESOLUTION MASS SPECTROMETRY ANALYSIS OF CHLORINATED PCDDs, PCBs AND PCDFs AS MULTIGROUP ANALYTES

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INTRODUCTION

Comprehensive two-dimensional separations [1-3] are distinguished from conventional two-dimensional separations by transport of the total analyte mass through both dimensions. The theoretical peak capacity generated by an orthogonal two-dimensional separation process is the product of the peak capacities obtained in each dimension. Comprehensive two-dimensional separations - in contrast to conventional heart cutting techniques - do not sacrifice analytical range for a given sample. The critical design factor for a thermally modulated [4], comprehensive two-dimensional system is the interface. three critical functions necessary for highly resolved, comprehensive separations are; (1.) concentration of analytes eluted from the first dimension for a short time as the first dimension separation proceeds, (2.) transfer of very narrow sample plugs from the interface to the head of the second column which induces second column injection, and (3.) the reproducibility and nondiscrimination of solute concentration and reinjection operations. In this work, parameters were optimized for fast gas chromatography/high resolution mass spectrometry (FGC/HRMS) and for comprehensive two-dimensional gas chromatography (C2DGC) mass spectrometry analysis of a 22 component standard mixture from environmental toxicant groups [polychlorinated biphenyls(PCBs), chlorinated dibenzo-p-dioxins (CDDs), and chlorinated dibenzofurans (CDFs). These laterally tetrachlorinated congeners from each toxicant group, collectively referred to as multigroup analytes, are normally found in general population human tissue.

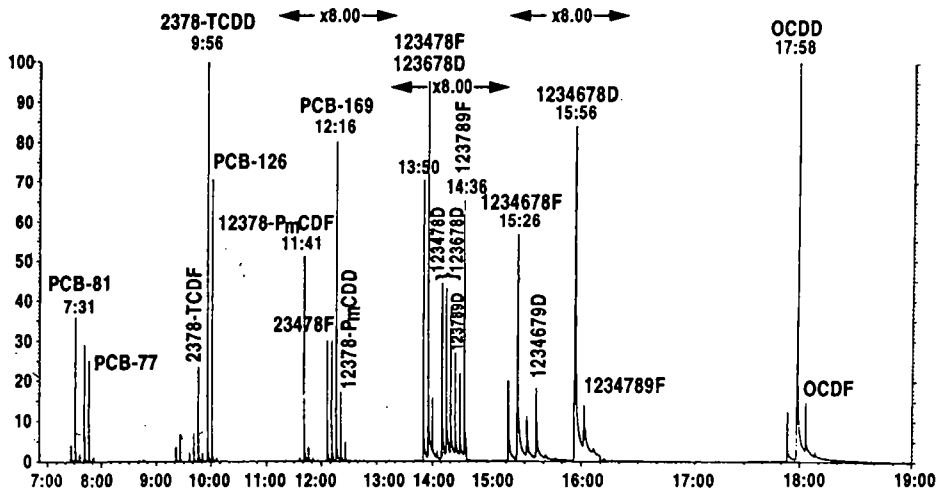
EXPERIMENTAL

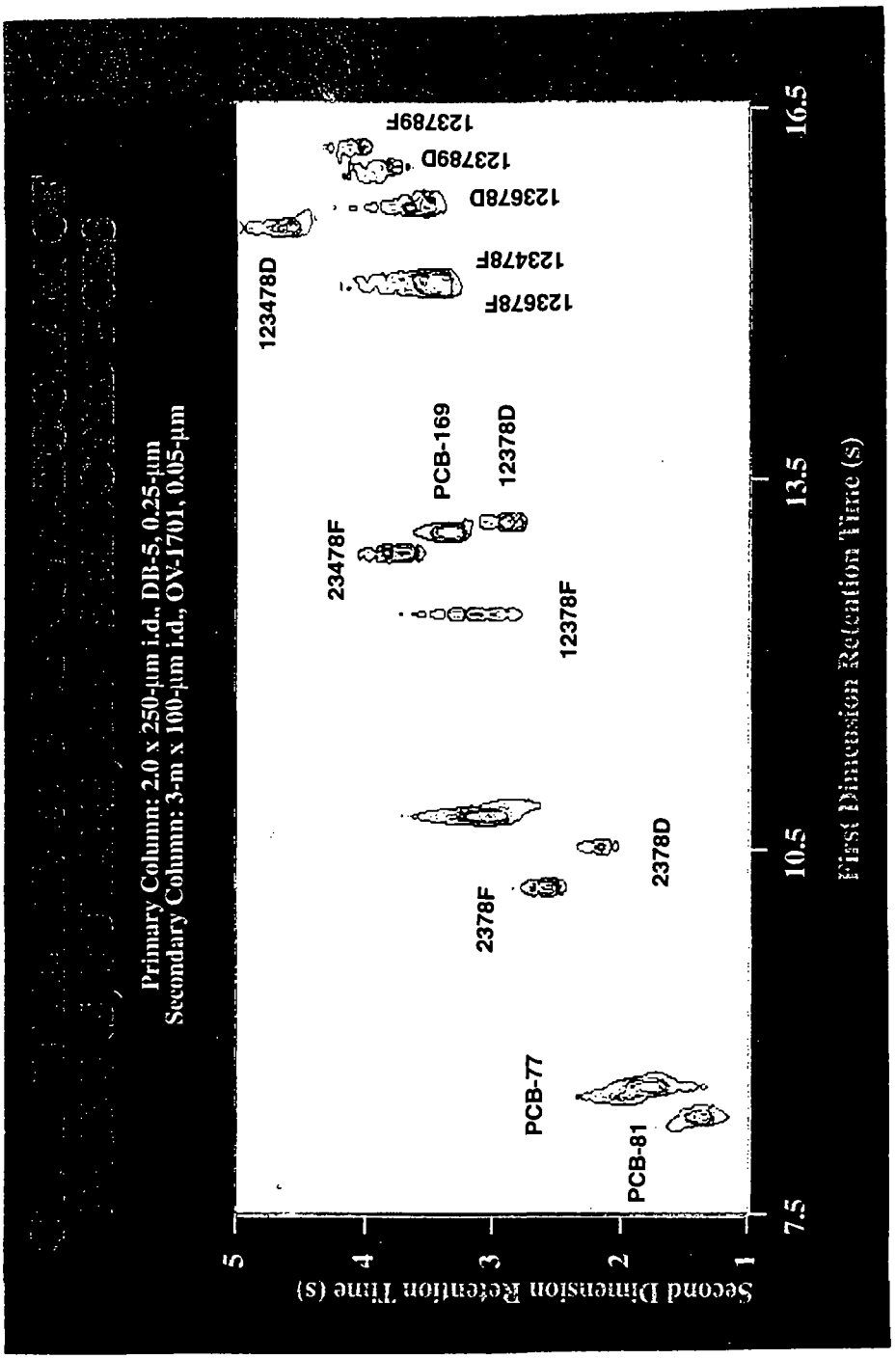
Comprehensive two-dimensional fast chromatography separations were accomplished with a commercial (ZOEX, Lincoln, NE) prototype thermally modulated comprehensive two-dimensional gas chromatography (C2DGC) system. Mass spectrometry was accomplished with a Fisons/VG Analytical Autospec.

RESULTS AND DISCUSSION

Analyte group mixture separations by comprehensive two-dimensional gas chromatography (C2DGC) were initially accomplished in significantly shorter analysis times (relative to GC/HRMS) using a computer controlled component system with a thermal modulator external to the GC oven and a flame ionization detector (FID). Comprehensive 2DGC is defined by the criteria that in orthogonal separations, the total quantity of sample introduced passes through both linearly connected capillary columns and that the first dimension chromatogram can be reproduced with fidelity from 2DGC data. Compounds from a 13 component phenol mixture were separated in two dimensions in 5 minutes using a linear combination of two columns of variable polarity (DB-1 and OV-1701) connected at the thermal modulator. Two stage thermal modulation compresses analyte peaks into narrower bands with a resulting S/N increase of approximately two orders of magnitude. Thermal modulations for two-dimensional analyte group separations were also examined using a commercial computer controlled vertically mounted heating element where thermal modulation occurs inside the oven. Variable parameters include oven temperature programs, flow rates, capillary column lengths, film type and thickness and modulation rates and temperatures where applicable. Thermal modulation of 2,3,7,8-TCDD (the most toxic CDD congener) by C2DGC/HRMS resulted in a sensitivity increase to 335 attograms at a S/N value of 9:1. A two-dimensional plot of a 24 component mixture of multigroup analytes (PCBs, CDDs, and CDFs) from C2DGC/HRMS analysis showed component separation in less than 7 minutes. The corresponding analysis run time for GC/HRMS was 56 minutes.

Comprehensive 2D/GC-HRMS (3000RP) of PCDDs, PCDFs, CPCBs




Primary Column: 2.0 x 250-µm i.d., DB-5, 0.25-µm
Secondary Column: 3-m x 100-µm i.d., OV-1701, 0.05-µm
Second Dimension Retention Time (s)
First Dimension Retention Time (s)
7.5
10.5
13.5
16.5
1
2
3
4
5
PCB-81
PCB-77
2378F
2378D
23478F
PCB-169
12378D
12378F
123478D
123678F
123478F
123678D
123789D
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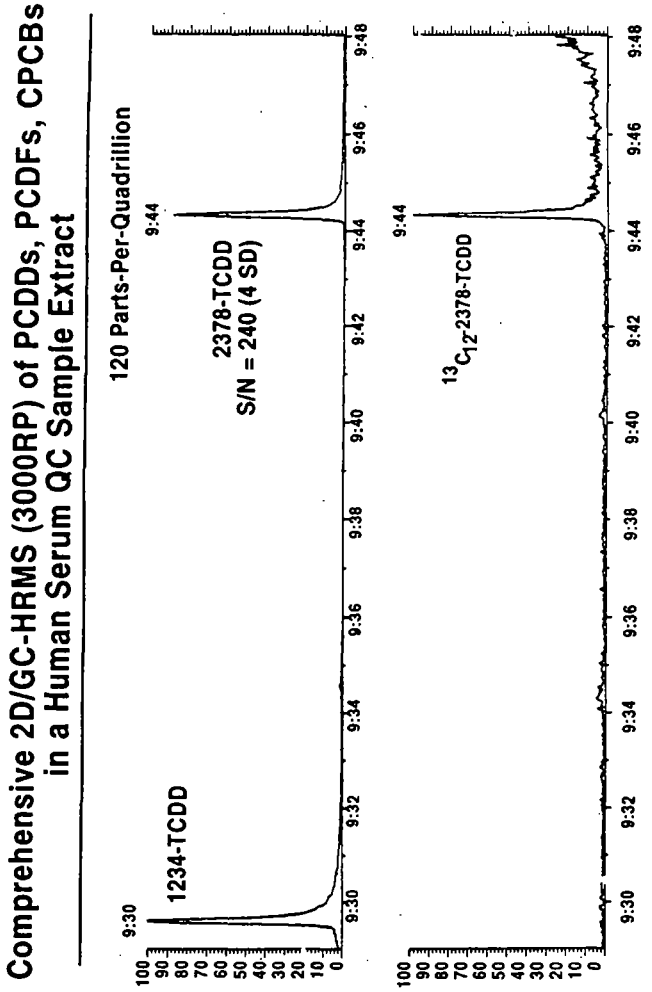

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