ANALYSIS OF ENVIRONMENTAL TOXICANT GROUP COMPONENTS BY TIME-COMPRESSED GAS CHROMATOGRAPHY AND COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY COUPLED WITH HIGH RESOLUTION MASS SPECTROMETRY AND TIME OF FLIGHT MASS SPECTROMETRY

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INTRODUCTION

As analytical chemistry incrementally evolves toward the ideal of instantaneous analysis, a great deal of effort has been expended toward developing methods and technologies that generate high sample throughput in time compressed separation[1-4] and detection domains[5] while maintaining or improving resolution and sensitivity. Environmental samples generally contain mixtures of analyte groups, and although one or several selected analytes may be of greater importance, the capability for generating an unequivocal determination for any mixture component in the shortest time (including cleanup steps for biological matrices) is always a high priority for analytical laboratories. Fast gas chromatography (FGC) has dramatically improved sample throughput by utilization of shorter columns and greater linear flow rates. Comprehensive two-dimensional gas chromatography[4] (C2DGC) is a more complex time compression separation method that also utilizes short columns while subjecting the entire sample mixture to two orthogonal separation dimensions with an increased peak capacity (the product of the peak capacities of the individual dimensions). C2DGC also generates a substantial (two orders of magnitude) sensitivity increase resulting from narrower peak widths. As more chromatographic data is generated in a shorter time, the limiting factor for a full range scanning mass detector becomes the scan rate limit of 1 to 10 scans per second.[5] Spectral skewing also becomes a problem as analyte concentration rapidly changes during the scan.

Time-of-flight mass spectrometry (TOFMS) with time array detection[5] (TAD) has been introduced as a technology that transcends the temporal detector limits of scanning instruments by total transient detection and temporal focusing of all ions from low to high m/z values. This generates a capability for very rapid analysis of time-compressed sample mixture components with normal acquisition rates of hundreds of spectra per second. Resolution enhancement is generated by deconvolution routines that when applied to data generated at 40 spectra per second, can discriminate a component separation of 100 ms. In this work, preliminary experiments in coupling the high throughput separation capabilities of FGC and thermally modulated C2DGC with TOFMS/TAD for the analysis of environmental toxicant mixtures and threat assessment analytes are evaluated with results from FGC/HRMS and 2DGC/FID and with GC/HRMS results where time compressed chromatography was not

utilized.

EXPERIMENTAL

FGC and C2DGC Equipment. Initial 2DGC separations were performed on a Perkin-Elmer 8500 gas chromatograph equipped with a flame ionization detector. A McIntosh Quadra 800 computer equipped with an NB-MIO 16X interface card and Labview Software were used for instrument control and data acquisition. A constant voltage DC power supply (60V) was used to supply current to the thermal desorption modulator. First generation C2DGC experiments were conducted with the modulator oven external to the GC oven. Second generation C2DGC experiments were conducted with a commercial ZOEX Thermal Modulation system with a verically mounted rotating heating element installed inside the oven of a a Hewlett-Packard 5890 gas chromatograph. Orthogonal 2D separations were accomplished using linear combinations of columns with divergent polarities. The ZOEX system without thermal modulation applications was also used for FGC experiments.

HRMS Instrumentation. HRMS data was acquired with a Fisons Autospec high resolution magnetic sector mass spectrometer utilizing tri-sector EBE double focusing geometry with a dynamic range ratio of 10^6:1.

TOFMS Instrumentation. TOFMS data was acquired wth a LECO FCD650 time-of-flight mass spectrometer equipped with an integrating transient recorder (ITR) and a time array detection (TAD) system to generate the high spectral acquisition rate (optimum rate of 200 spectra per second required for maximum deconvolution) required for FGC and 2DGC separation of complex mixtures. The ion source was extracted at 5000 Hz, and the mass range for environmental toxicant groups examined was 35-400.

RESULTS

Time-compressed and comprehensive 2DGC chromatograms are presented in Figures 1-6. GC/HRMS run times (56 minutes) for a 24 component multigroup analyte mixture (CDDs, CDFs and PCBs were reduced to less than 8 minutes by FGC/HRMS (2M, 0.1mm ID, 0.1μ film DB-1 column) with mass analysis distinguishing each mixture component except the two HxCDD isomers that coelute under time-compressed conditions. A time-compressed chromatogram for multigroup analytes is presented in Figure 1. Although peak tailing was observed for components at the back end of the chromatogram [higher flow rates from a larger diameter (7m, 0.25mm ID, 0.25μ DB-5 film) column], the run time is reduced to 5 minutes with only the two HxCDD isomers not identified by mass analysis. A 22 component mixture of coplanar PCBs (Figure 2) was separated in 7 minutes by FGC/HRMS with two cocluting analytes identified by mass analysis.

Analyte group mixture separations by comprehensive two-dimensional gas chromatography (C2DGC) were initially accomplished in significantly shorter times relative to GC/HRMS using a computer controlled component system with a thermal modulator external to the GC oven and an FID detector. 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. Components of a 13 component phenol mixture (Figure 3) were separated in two dimensions in 5 minutes using a linear combination of two columns of variable polarity (DB-1 and OV1701) connected at the thermal modulator. Two stage thermal modulation compressed analyte peaks into narrower bands with a resulting S/N increase of approximately

two orders of magnitude. Thermal modulations for C2DGC analyte group separations were also examined using a commercial computer controlled vertically mounted heating element where thermal modulation occurs inside the GC oven. Variable parameters include oven temperature programs, flow rates, capillary column lengths film type and thickness and modulation rates and temperatures where applicable. A three dimensional plot (including analyte concentration) of a 24 component mixture of multigroup analytes (PCBs, CDDs and CDFs) from C2DGC/HRMS analysis (Figure 4) showed component separation in less than 7 minutes with a sensitivity increase of approximately two orders of magnitude.

The FGC/TOFMS analysis run time for a 23 component mixture of PAHs and phenols (Figure 5) was less than 4 minutes, a substantially shorter time than was observed for GC/HRMS. A time-compressed chromatogram for FGC/TOFMS analysis of threat assessment analytes (Figure 6) showed separation of the analytes in ~6 minutes. Of the 13 components in the explosives mixture, 11 components were identified by a spectral library search. The non-appearance of RDX and Tetryl in this first run may possibly be attributed to errors in sample preparation or to difficulties with transfer line temperature programming optimization for less volatile analytes.

Figure 1. FGC/HRMS(10,000 RP) CHROMATOGRAM FOR CHLORINATED DIBENZODIOXINS, CHLORINATED DIBENZOFURANS AND POLYCHLORINATED BIPHENYLS

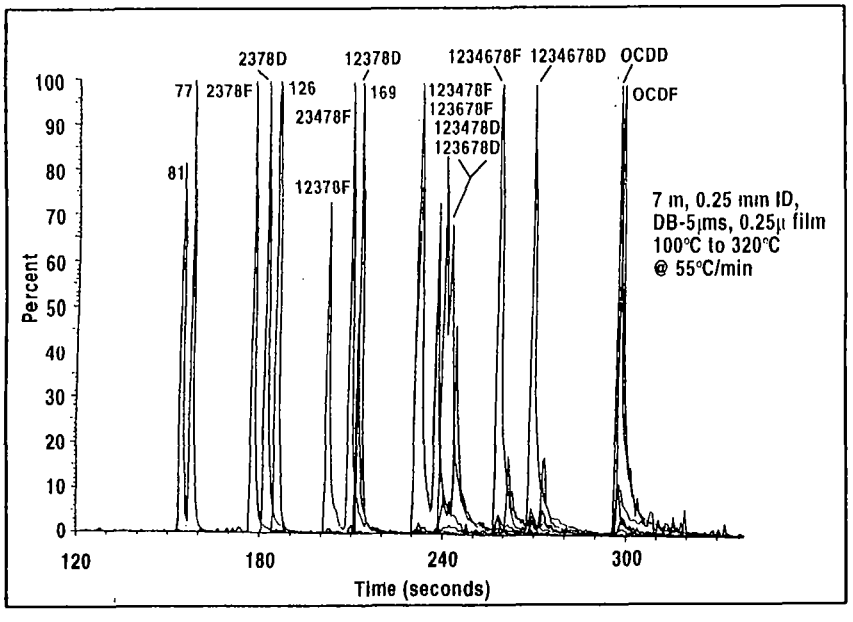


Figure 2. FGC/HRMS CHROMATOGRAM FOR COPLANAR POLYCHLORINATED BIPHENYLS

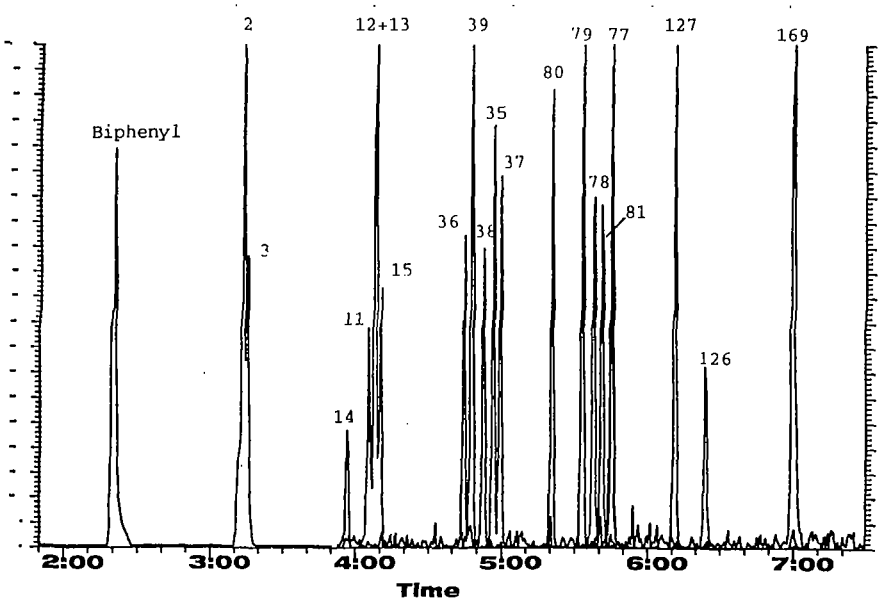
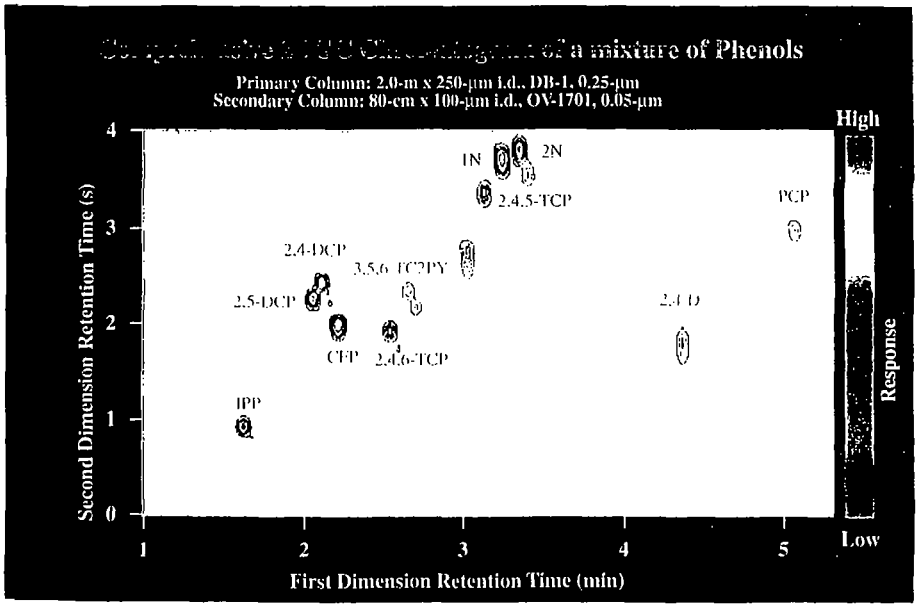


Figure 3.



ANA (po)

Figure 4.

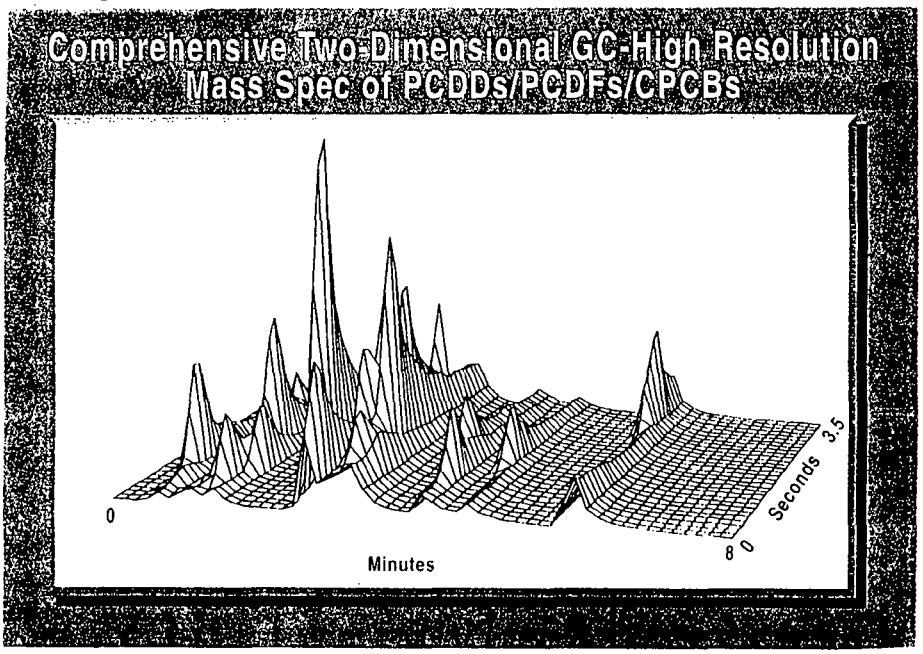


Figure 5.

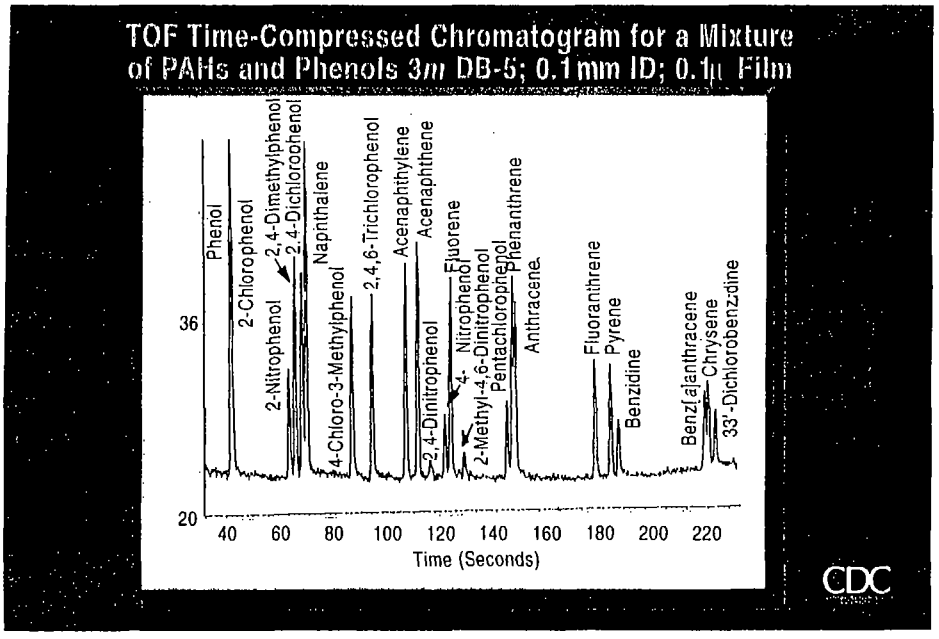
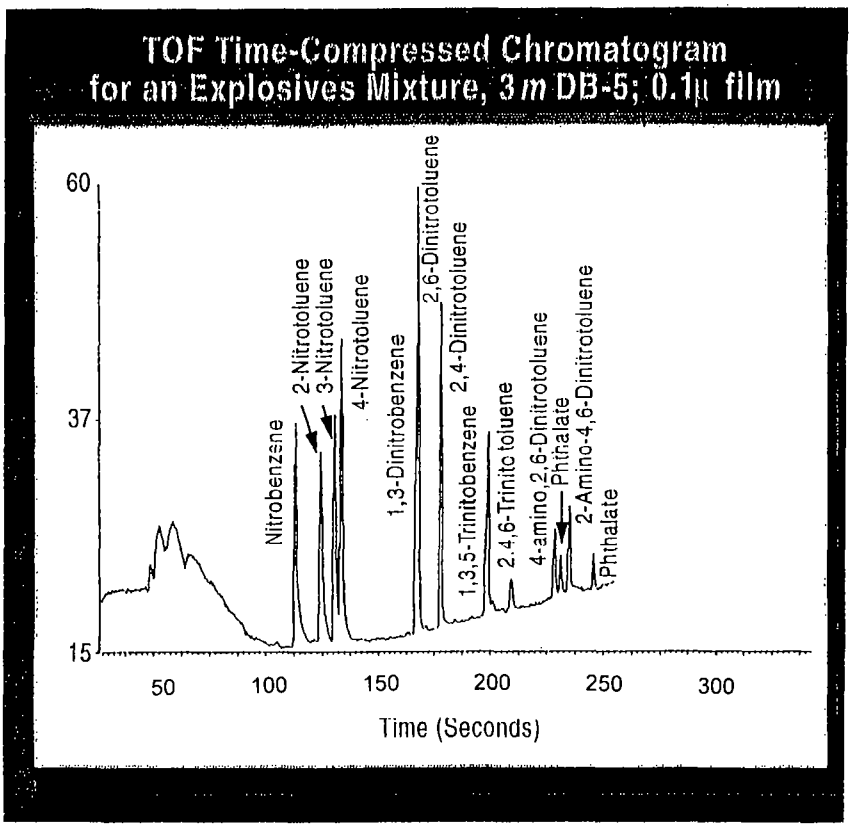


Figure 6.



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