Rapid screening with a comprehensive two-dimensional gas chromatograph

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1. Introduction

Comprehenisve two-dimensional gas chromatography (C2D-GC) is a newly developed dual column technique formally equivalent to a planar bed gas chromatograph. [1] The C2D-GC technique increases pak capacity, analysis speed, and sensitivity of GC by factors of 10 to 30, typically. Even more importantly, the method provides the opportunity to use peak capacity efficiently through the generation of ordered chromatograms, which can reduce peak overlaps significantly, [2,3] This paper describes a C2D-GC instrument which generates a peak capacity of about 1,200 in 4.0 minutes, and can separate at least 135 peaks in that time. Such a system is potentially useful for rapid screening of dioxins and related substances.

2. Experimental

The construction of a C2D-GC consists of a fast second dimension column interfaced to a slower first dimension column through a structure known as a "multistage thermal modulator" [4] (Figure 1). The modulator "chops" effluent from the first column into a series of focussed "plugs", then transfers these onto the second column. Coeluents from the first column are found to separate rapidly on the second, resulting in a series of "secondary chromatograms." When a computer "stacks" these secondary chromatograms side by side and interpolates the surfaces formed by alignments between secondary peaks, an intensity surface appears over a retention plane bound by first and second retention time axes. Viewed from above, the peaks form a spot pattern on this plane.

In its commercial form, [5] the thermal modulator is a mechanically rotated heater added to a conventional GC oven. This heater is slotted, and slides over an arc of capillary column known as a "modulator tube." Stationary phase in the modulator tube is typically 10 times thicker than in the secondary column to provide hold-up time. The analytical columns and the modulator tube are housed in a cartridge structure that attaches to a shelf installed inside the oven. First and second column temperatures can be independently controlled.

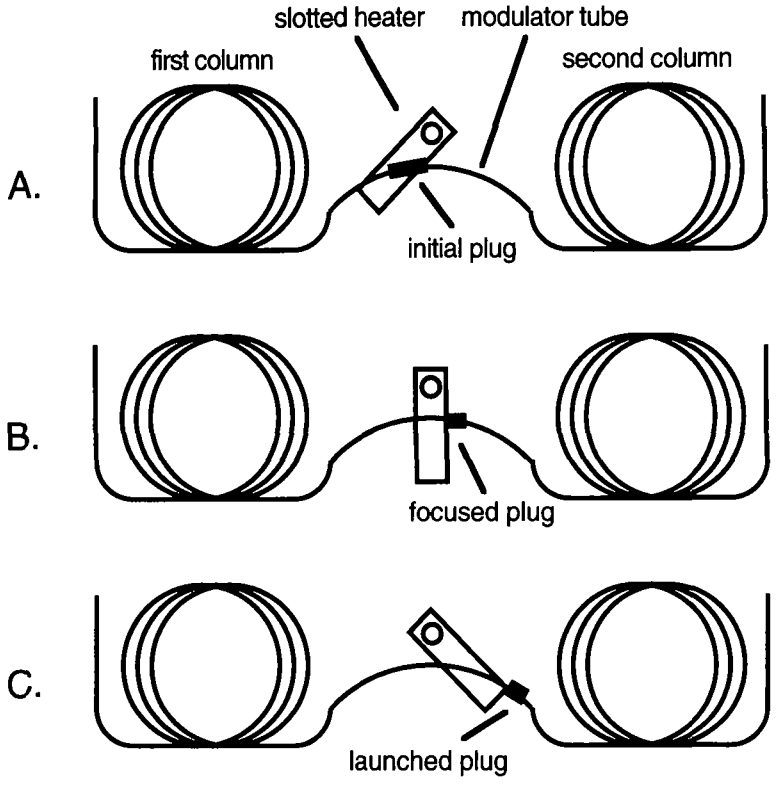

Figure 1. Operation of a multi-stage thermal modulator.

In operation, the modualtor heater raises the temperature of the upstream portion of the modulator tube to a value at which analytes are unretained (Figure 1A). Carrier gas rapidly removes this "inital plug" from the upstream heated zone and deposits it onto a donwstream, cooler zone just beyond. There it decelerates and becomes a "focussed plug" (Figure 1B). Finally, the heater sweeps over the downstream section of the moduator tube, which heats all at once (Figure 1C). The plug is "launched" onto the secondary column. This starts a secondary chromatogram. The sequence is repeated typically every few seconds by computer controlled rotation of the slotted heater. This repetition generates a comprehensive two-dimensional gas chromatogram, in which the separation mechanisms of the two dimensions operate independently. [6] As a consequence of this independence or orthogonality, the peak capacity of the C2D-GC system approaches the arithmetic product of the peak capacities of the individual columns. Because the second dimension column operates so fast (seconds per chromatogram), the increase in peak capacity over what would be available from the first column alone is obtained at no cost in analysis time. Moreover, focussing effects considerably increase sensitivity over that available from the first column alone.

In rapid screening mode, typical column dimensions and parameters would be: first dimension colum length 0.75 m, i.d. 100 μm, D_f 3.0 μm, stationary phase 007-1 (Quadrex Corporation, USA); modulator tube length 0.30 m, first 0.20 m coated, last 0.10 m uncoated deactivated fused silica capillary tubing, i.d. 100 μm,D_f 3.0 μm, stationary phase SE-30 (Quadrex); second dimension column length 0.5 m, i.d. 100 μm, D_f 0.14 μm, stationary phase 007-1701 (Quadrex).

3. Results

In a high speed screening mode, a volatility-by-polarity separation resolved 135 peaks from kerosene in 4.0 minutes (Figure 2).

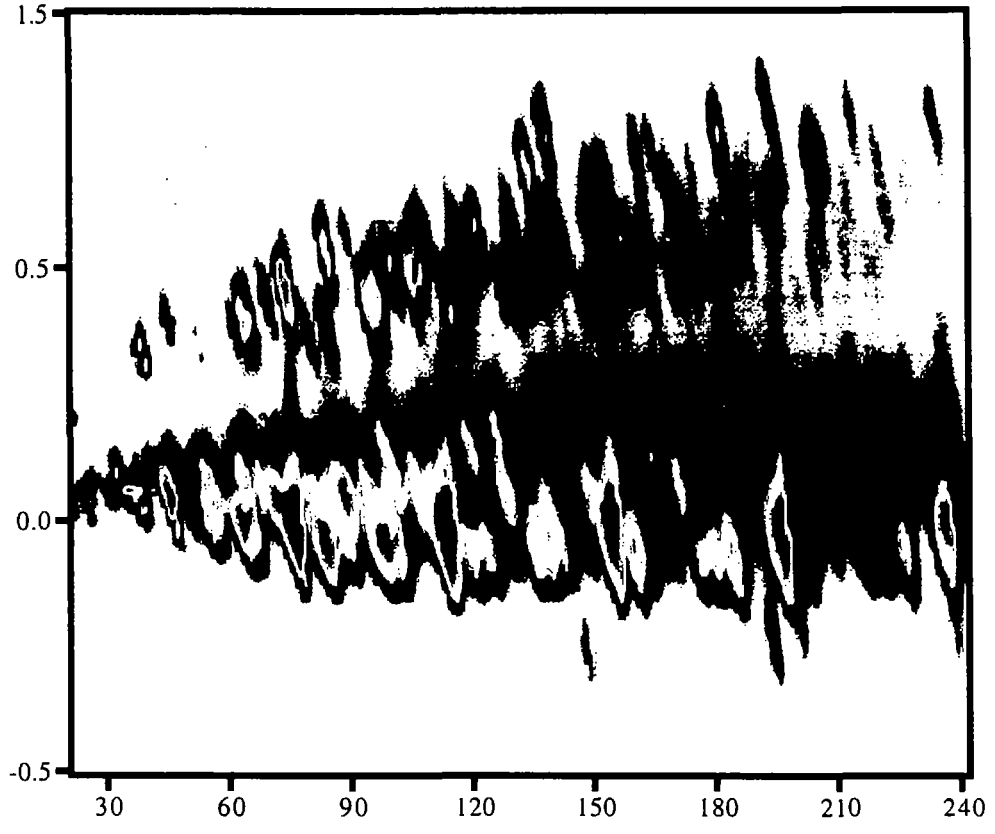

Figure 2. A comprehensive two-dimensional gas chromatogram of kerosene.

Preliminary trials indicate C2D-GC is quantitative. Linear calibrations with three-nines correlation coefficients are typical. This would be expected, since the thermal modulator is valveless. Sample is transferred quantitatively from the first dimension column to the second.

A multistage thermal modulator improves sensitivity by an order of magnitude or more by focussing (75 ms wide peaks), which increases sample concentration at the detector. Workers at the Centers for Disease Control, Atlanta, GA, have detected 335 x 10^{-18} g (335 attograms) of 2,3,7,8-TCDD with a signal-to-noise ratio of 15:1 using a mass spectrometer in single ion monitoring mode as the detector. [7] The same group developed a quantitative C2D-GC method for analysis of pesticeds extracted from human serum. [7]

4. Conclusion

Preliminary work indicates that a C2D-GC method for dioxin analysis should be developed in the form of a rapid screening analysis. The sensitivity improvement inherent in the C2D-GC technique should make it possible to analyse smaller samples, thus simplifying sample workup. The speed of the C2D-GC analysis should make it possible to rapidly detect positives, which could then be verified by established GC/MS methodologies.

5. References

[1] Giddings, J. C. (1990): in J. H. Cortes (Editor), *Multidimensional Chromatography: Techniques and Applications*, Marcel Dekker, New York, Ch. 1.
[2] Giddings, J. C. (1995): Sample dimensinality: a predictor of order-disorder in component peak distribution in multidimensional separation, *J. Chromatogr. A*, 703 3-15.
[3] Ledford, E. B., Jr., John B. Phillips, Richard B. Gaines, and Jan Blomberg (1996): Ordered chromatograms: a powerful methodolgy in gas chromatography. *American Laboratory* (June issue) in press.
[4] Phillips, J. B. and E. B. Ledford, Jr. (1996): Thermal Modulation: A Chemical Instrumentation Component of Potential Value in Improving Portability, *Field Analtyical Chemistry and Technology*, Wiley, in press.
[5] Zoex Corporation, Lincoln, NE, USA (402) 475-7640.
[6] Venkatramani, C. J. and John B. Phillips (1996): Separation Orthogonality in Temperature Programmed Comprehensive Two-Dimensional Gas Chromatography, *Anal. Chem.* 68 1486-1492.
[7] Patterson, Donald G., Z. Liu, J. Grainger, J. Barr, (1995): The Use of Gas Chromatography / High Resolution Mass Spectrometry for the Fast and Ultra-Sensitive Analysis for Environmental Toxicants in Human Exposure Assessment, FACSS, Cincinnati, Ohio USA, October 16, 1995.
[8] Liu, Zaiyou, Sarath R. Sirimanne, Donald G. Patterson, Jr., Larry L. Needham and John B. Phillips, (1994): High-Speed Comprehensive Two-Dimensional Gas Chromatography for the Fast Separation and Analysis of Non-Persistent Pesticides Extracted from Human Serum, *Anal. Chem.* 66 3086-3092.