



Comprehensive two-dimensional gas chromatographic separations with a temperature programmed microfabricated thermal modulator



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ABSTRACT

Comprehensive two-dimensional gas chromatography (GC × GC) with a temperature-programmed microfabricated thermal modulator (μ TM) is demonstrated. The 0.78 cm², 2-stage μ TM chip with integrated heaters and a PDMS coated microchannel was placed in thermal contact with a solid-state thermoelectric cooler and mounted on top of a bench scale GC. It was fluidically coupled through heated interconnects to an upstream first-dimension (¹D) PDMS-coated capillary column and a downstream uncoated capillary or second-dimension (²D) PEG-coated capillary. A mixture of *n*-alkanes C₆–C₁₀ was separated isothermally and the full-width-at-half-maximum (*fwhm*) values of the modulated peaks were assessed as a function of the computer-controlled minimum and maximum stage temperatures of μ TM, T_{\min} and T_{\max} , respectively. With T_{\min} and T_{\max} fixed at –25 and 100 °C, respectively, modulated peaks of C₆ and C₇ had *fwhm* values <53 ms while the modulated peaks of C₁₀ had a *fwhm* value of 1.3 s, due to inefficient re-mobilization. With T_{\min} and T_{\max} fixed at 0 and 210 °C, respectively, the *fwhm* value for the modulated C₁₀ peaks decreased to 67 ms, but C₆ and C₇ exhibited massive breakthrough. By programming T_{\min} from –25 to 0 °C and T_{\max} from 100 to 220 °C, the C₆ and C₇ peaks had *fwhm* values ≤ 50 ms, and the *fwhm* for C₁₀ peaks remained < 95 ms. Using the latter conditions for the GC × GC separation of a sample of unleaded gasoline yielded resolution similar to that reported with a commercial thermal modulator. Replacing the PDMS phase in the μ TM with a trigonal-tricationic room temperature ionic liquid eliminated the bleed observed with the PDMS, but also reduced the capacity for several test compounds. Regardless, the demonstrated capability to independently temperature program this low resource μ TM enhances its versatility and its promise for use in bench-scale GC × GC systems.

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1. Introduction

Comprehensive two-dimensional gas chromatography (GC × GC) is often the most effective means of separating complex mixtures of volatile and/or semi-volatile organic compounds (S/VOCs). Examples include the congeners of polychlorinated biphenyls and other polyhalogenated aromatic compounds [1,2], pesticide residues [3,4], hydrocarbon fractions in crude oil [5,6], fatty-acid methyl esters in biodiesel blends [7], and trace-level VOC biomarkers of disease or metabolism in breath and urine [8,9].

In GC × GC a first-dimension (¹D) column is connected through a thermal or pneumatic modulator to a short second-dimension (²D) column with retention selectivity that differs from that of the ¹D column [10–12]. As peaks elute from the ¹D column they are parsed by the modulator into segments and injected in rapid succession into the ²D column such that no mass is lost. This requires very rapid ²D separations. If operated under the proper conditions then the total peak capacity approaches the product of the peak capacities afforded by each dimension [13], which should exceed that provided by a one-dimensional separation column of similar length. In any case, the reductions in peak widths achieved with modulation can improve both the resolution and detectability of the eluting peaks [12,13]. In addition, information about analyte functionality can often be inferred from the structure of the GC × GC contour plot

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of ^1D vs. ^2D retention times (t_R), because analytes within the same class usually occupy segregated bands within the plot [10–12].

Pneumatic GC \times GC modulators create peak segmentation by injecting pulses of carrier gas or by redirecting flow at regular intervals across peaks eluting from the ^1D column [14–18]. Values of full width at half maximum ($fwhm$) < 25 ms have been achieved for peaks separated by GC \times GC with state-of-the-art pneumatic modulation systems [15]. Thermal modulation (TM) entails alternately trapping ^1D peak segments by condensation, typically by bathing a short section of the (typically ^2D) capillary column in a fluid at cryogenic temperatures, and then remobilizing them by removing the fluid and/or applying a jet of hot air, which rapidly raises the temperature for passage of the segment to the ^2D column [19–25]. Values of $fwhm$ as low as 20 ms have been reported by use of TM [25].

With TM, the trapping efficiency depends critically on the minimum modulator temperature, T_{\min} , the rate at which T_{\min} is recovered after each heating cycle, and the analyte vapor pressure, p_v . The efficiency of remobilization, in turn, depends on T_{\max} and the rate at which T_{\max} is attained after each cooling cycle. For GC \times GC separations of analyte mixtures spanning a large p_v range, there is a tradeoff between maintaining T_{\min} low enough to avoid breakthrough of relatively high- p_v components and attaining a sufficiently high T_{\max} at a sufficiently high rate to minimize broadening of relatively low- p_v components upon re-injection into the ^2D column.

Several investigators have reported on ways to address this problem by gradually ramping the modulator temperature as a separation proceeds [19,26–28]. For example, the Marriott group addressed this problem effectively with their longitudinally modulated cryogenic system (LMCS), in which a moveable sleeve around a section of capillary column is cooled with a flow of cryogenic fluid [19]. As the sleeve is moved back and forth along a designated section of one of the columns, peak segments are first immobilized by virtue of the cooling and then remobilized by virtue of the column section returning to oven temperature. By modulating the flow of cryogenic fluid to the sleeve, they were able to gradually increase T_{\min} over the course of a temperature programmed separation so as to maintain the difference between T_{\min} and the oven temperature constant [21,23]. This resulted in narrower and more symmetric re-injected peaks and reduced consumption of cryogen, while also avoiding breakthrough of the more volatile components of the mixtures analyzed.

Inspired by this approach, we were interested in incorporating a similar feature into the microfabricated thermal modulator (μTM) on which we have reported recently [29–33]. First described in 2010 [29,30], this μTM is cryogen-free and requires much less power to operate than conventional TMs. It consists of a single, Pyrex-sealed Si microchannel with two thermally isolated spiral sections, or stages, each with independent thin-metal-film heaters. The μTM is mounted on a solid-state thermoelectric cooler (TEC) capable of maintaining T_{\min} as low as -35°C , and it can be heated rapidly to $> 250^\circ\text{C}$ and then cooled again with modulation periods, P_m , as short as 5 s. We have used this device in GC \times GC separations with conventional capillary columns [30,31], as well as in $\mu\text{GC} \times \mu\text{GC}$ separations with microfabricated columns [32] and, most recently, with a polymer-coated, microfabricated optofluidic ring resonator (μOFRR) as the detector [33].

Recognizing the constraint on the analyte volatility range over which effective $\mu\text{GC} \times \mu\text{GC}$ separations could be performed with fixed values of T_{\min} and T_{\max} , we first explored a passive approach to ramping these μTM temperatures by placing the device inside the GC oven during a temperature programmed separation [32]. As the oven temperature increased, T_{\min} increased because of the reduction in heat dissipation from the TEC heat sink and T_{\max}

also increased because of the improved efficiency of heating the stages at constant applied voltage. This was marginally effective at reducing peak widths for low p_v analytes as compared to isothermal operation, but the maximum oven temperature was limited to $< 100^\circ\text{C}$ by the temperature sensitivity of the printed circuit boards (PCB) on which the μTM was mounted. Furthermore, despite cross-linking the PDMS stationary phase lining the wall of the μTM channel, loss due to bleed (i.e., decomposition) of the PDMS became notably greater at $T_{\max} > 210^\circ\text{C}$, which placed an additional constraint on this operating parameter.

Several commercial stationary phases are now available that have been formulated to exhibit low bleed at temperatures exceeding 350°C [34–36]. Many of these are siloxane or silylene polymers, which also have low glass transition temperatures. The complexity or proprietary nature of required synthesis or deposition procedures, and/or the need for high-temperature surface pretreatments render the incorporation of such low-bleed stationary phases into microfabricated devices difficult. Recently, a relatively new class of stationary phase coatings, trigonal tricationic room temperature ionic liquids (RTILs), was shown to exhibit a combination of properties that make them attractive candidates for μTM stationary phases, including high decomposition temperatures, low melting temperatures, low bleed rates at high temperature, high viscosities, and reasonably good retention of non-polar compounds [37,38]. Synthesis is relatively straightforward and although the surface pretreatment is tricky it does not involve high temperatures [32,37]. RTILs of this type have been used in the ^2D column for GC \times GC separations [32,39], and they were, therefore, pursued in this study as phases for our μTM .

Here, we describe an extension of our previous studies in which we demonstrate the feasibility of incorporating active temperature programming of the μTM to gradually increase T_{\min} and T_{\max} values over the course of a GC \times GC separation. Toward this end, we used a bench scale GC, commercial ^1D (non-polar) and ^2D (polar) capillary columns, manual syringe injection, and flame ionization detection (FID). We mounted the μTM assembly on top of the GC oven and used heated interconnects to couple the μTM to the ^1D and ^2D columns. Although most experiments used a μTM with a PDMS wall coating, we also performed preliminary tests with an RTIL μTM wall coating, in an attempt to extend the value of T_{\max} . After describing the methodology, separations of a simple mixture of alkanes are presented in which the μTM was cycled between different fixed T_{\min} and T_{\max} values and then was temperature programmed such that T_{\min} and T_{\max} were increased over the course of the run. As a practical application, the GC \times GC separation of unleaded gasoline was then demonstrated. A trigonal tricationic RTIL coated μTM was then evaluated as a substituted for the PDMS stationary phase. The impact of the results on the design and function of a μTM as a simple replacement for more cumbersome and costly TMs in bench scale GC \times GC is assessed.

2. Experimental methods

2.1. Materials

Solvents and individual test compounds were purchased from either Sigma-Aldrich (St. Louis, MO) or Fisher Scientific (Pittsburgh, PA) in $> 98\%$ purity. Unleaded regular gasoline was obtained from a local filling station. PDMS was obtained from Ohio Valley Specialty Chemicals (OV-1, Marietta, OH). The RTIL used, tris[2-(6-aminopropylphosphonium-hexaamido)ethyl]amine tris[bis(trifluoromethylsulfonyl)imide], was taken from an existing supply, which was synthesized by a known method [32,37]. It showed a stable melting transition temperature of -27°C by

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