Supporting Information for

Comprehensive Two-Dimensional Gas Chromatographic Separations with a Microfabricated Thermal Modulator

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µTM Mounting. The µTM chip was mounted with epoxy (EE129-4, Epoxy Technology, Billerica, MA) and wirebonded to a custom printed circuit board having a central rectangular cut out that allowed access to the underside of the chip. Two microfabricated Si spacer structures $(7.5 \times 4.5 \text{ mm}, \text{ and } 7.5 \times 3.5 \text{ mm}, \text{ for the first and second stage, respectively})$ were affixed to the Pyrex beneath each stage using thermally conductive paste (Silicon Heat Sink 340, Dow Corning, Midland, MI). Each spacer has a central mesa structure the cross section of which matches that of the overlying stage. The air gap between the mesa and the device substrate (Pyrex) was 19 μ m. In addition, a pair of 3×3 mm, 450- μ m thick Si slabs was inserted between each Si spacer and the TEC surface to localize the cooling to the regions beneath the stages. A thin layer of thermally conductive paste was spread on both surfaces of the Si slabs to ensure good thermal contact between the TEC and the device. This assembly was inverted and manually mounted and aligned on the top surface of the four-stage TEC (SP2394, Marlow Industries, Dallas, TX). A small axial fan (E1U-N7BCC-03, Sundial Micro, Ontario, CA) was placed below the TEC to facilitate heat dissipation. Finally, a shallow, rectangular glass shroud with a thick frame was bolted to the top side of the PCB on which the µTM was mounted. A barbed fitting in one wall of the frame permitted a tube to be connected for purging the μ TM and TEC surfaces with dried house air to prevent ice formation.

compound	$t_{R2}(s)$	Peak area $(pA \cdot s)^b$			
		mod 1	mod 2	mod 3	A _t
benzene	1.31 (3.6)	0.08 (4.5)	0.70 (5.9)	n/a	0.78 (4.9)
hexanal	1.52 (4.7)	0.09 (5.7)	0.51 (0.8)	0.06 (6.7)	0.66 (2.6)
isoamyl alcohol	1.87 (2.9)	0.07 (5.9)	0.13 (5.4)	0.23 (6.0)	0.43 (5.0)
n-octane	2.57 (2.8)	0.41 (2.8)	0.17 (5.4)	0.08 (4.9)	0.66 (1.0)
2-heptanone	2.76 (2.2)	0.21 (5.5)	0.23 (4.7)	0.07 (3.6)	0.51 (1.3)

Table S1. Reproducibility of the t_R values and areas of modulated peaks eluting from the ²D column.^a

^a From replicate sample-loop injections of test atmospheres containing 16-18 ng of each vapor (n = 4). Values in parentheses are RSDs (%). Conditions: ¹D column temp.: 33 °C, ²D column temp. = 80 °C, F = 0.9 mL/min, $T_{min}/T_{max} = -20/210$ °C, $P_M = 6$ s, $O_s = 600$ ms, FID. ^b mod 1, 2, and 3 refer to the series of modulated peaks for a given compound; A_t = total area of all modulated peaks.