A MICROFABRICATED COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY SYSTEM Shaelah Reidy, Sung-Jin Kim, Katharine Beach, Bruce Block, Edward T. Zellers, Katsuo Kurabayashi, and Kensall D. Wise Engineering Research Center for Wireless Integrated MicroSystems The University of Michigan, Ann Arbor, MI 48105

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ABSTRACT

This paper reports a thermally-modulated comprehensive twodimensional chromatography system. A static stationary-phase coating process using non-polar polydimethlsiloxane (PDMS) and polar polytriluoropropylmethylsiloxane (PTFPMS) produced a resolution of 14,425 and 5,800 theoretical plates, respectively, using an air carrier in 3m columns. With a meso-scale thermal modulator between a 3m-long PDMS-coated first-column and a 0.25m-long PTFPMS-coated second column and working from -25°C to 200°C with 100ms peak widths, a 10-component mixture of alkanes and ketones was separated. Replacing the meso-scale modulator with a microfabricated device operating between -30°C and 250°C (with heating/cooling rates of 3000°C/s and -570°C/s), heptane and 2-hexanone were separated with a 7s modulation period. They would co-elute from a one-dimensional system,.

INTRODUCTION

Gas chromatography (GC) is the most widely-used technique for separating, identifying, and quantifying volatile and semivolatile organic compounds (VOCs and SVOCs), which are of concern in areas such as indoor and ambient air quality, climate change (global warming), industrial emissions control, and breath analysis. Measurements of these pollutants are essential to assessing the sources, sinks, and transport pathways of these compounds as well as their effects on the environment and its inhabitants.

The Engineering Research Center for Wireless Integrated MicroSystems (WIMS) at the University of Michigan is working to develop a completely microfabricated gas chromatograph for environmental monitoring. The microsystem uses preconcentration, separation, and gas sensing technologies that were developed by members of the WIMS μGC team. The system is designed for autonomous operation using ambient air as the carrier gas and a microfabricated pump to drive the separation. This microsystem is shown in Fig. 1. All of the system components have been achieved [1-4] and are capable of separating complex mixtures of VOCs with sub-ppb detection limits [5,6]. The separation of air-phase petroleum hydrocarbons utilizing a 3mlong microcolumn operating into a flame ionization detector is also shown in Fig. 1. Temperature programming is effective in these microfabricated components because of their very low mass and can speed up separations by more than an order of magnitude.

When analyzing highly-complex mixtures of 30-50 volatile organic compounds, achieving the required resolving power and avoiding co-elutions is a continuing challenge for one-dimensional separation systems. Since its invention over a decade ago, comprehensive two-dimensional gas chromatography (2D-GC, GCxGC) has been developed to separate and analyze complex mixtures (e.g., petroleum, flavors, environmental pollutants, breath biomarkers, and, in this case, extraterrestrial atmospheres). GCxGC employs two coupled columns of different selectivity, as in Fig. 1, but adds a modulator between the columns and subjects the entire sample to a two-dimensional separation. As effluent emerges from the primary column, it is collected and then rapidly re-injected to produce sharp chemical pulses that are rapidly separated by the second column. The results can be displayed using the two orthogonal retention-time axes of the columns. The horizontal separation plane displays the time output of the firstdimension column, and the vertical plane shows the much faster elutions from the second. Usually, the first column is coated with a non-polar stationary phase and the second with a polar phase. This



Fig. 1: Block diagram of a microfabricated chromatography-based gas analyzer (above), and a chromatogram showing the separation of air-petroleum hydrocarbons which utilizes the microcolumns.

combination allows components to be independently separated, first according to their volatility and then according to their polarity. In comparison to conventional one-dimensional gas chromatography, GCxGC has a much higher peak capacity because the available peak capacity is the product of the peak capacity of both dimensions. Other advantages of GCxGC include enhanced detectability due to analyte refocusing, true background around resolved peaks, and more reliable identification due to the use of two retention times and well-ordered bands of compound groups. The most important instrumental component in GCxGC is the modulator. Modulation is required to transfer the sample from the first (primary) column to the second column. The modulator continuously traps, focuses, and then re-mobilizes components eluting from the primary column, acting as a continuous injector for the secondary column. There are two classifications of modulators: pneumatic and thermal.

GCxGC SYSTEM DESIGN

The GCxGC system consisted of a 3m-long nonpolar (PDMS-coated) first-dimension column, a thermal modulator, and a 0.50m-long polar (PTFPMS or polyethylene glycol (PEG)) second-dimension column. The first-dimension column provides

the primary separation of the sampled mixture based on volatility. This column is connected to the modulator, which is a two-stage device that traps and releases the compounds as it cycles repeatedly from low to high temperature. Two modulators have been used. The first was a meso-scale device formed from a 10cm-long 0.18mm-id PDMS-coated section of stainless-steel tubing and divided into two separately-heated sections, cycling between -25°C and 200°C. The second was a microfabricated modulator (µTM) [7,8] cycling from -35°C to 250°C. The first and second stages of the µTM consisted of meander-line boron-doped-Si microchannels 4.2cm and 2.8cm long, respectively, with crosssectional dimensions of 250µm (w) x 140µm (h) and having a wall thickness of 30 µm. Both modulators were coated with PDMS and were heated from a resting temperature provided by a cold chamber or thermoelectric cooler. Since movement of the analytes through the system is strongly dependent on temperature, decreasing the temperature essentially stops the movement of analyte while increasing the temperature rapidly increases it.

Modeling was done to determine the optimum column dimensions. Using Spangler's equation [9] for the height equivalent to a theoretical plate (H), which is a measure of column efficiency, the expected column performance was explored as a function of the linear column velocity. The resulting Golay plots are shown in Fig. 3 for 3m-long first-dimension column crosssections of 150µm (w) x 240µm (d) and for 158µm (w) x 310µm The latter dimensions for used for the final µGC reported (d). here. The minimum H defines the optimum operating point for the column. The second-dimension columns were fabricated in 10cm and 25cm lengths (46µm wide and 170µm deep). By chamfering the corners of columns there is about a 20% improvement in column performance. Fig. 3 illustrates this improvement by the decrease in plate height (H).



Fig. 2: Theoretical Golay plot of the improvement in column performance by increasing the column dimensions.

FABRICATION

The separation columns have a square spiral geometry to minimize surface area (Fig. 4). The 3m-long primary column has a die size of $3.2 \text{ cm} \times 3.2 \text{ cm}$; the 25cm-long second column is 1.5cm x 1.5cm in size. Both are fabricated on 100mm silicon wafers using DRIE. A 4mm silicon rim around the column allows attachment of the fluidic connection lines and electrical connections to on-chip heaters and temperature sensors formed using $250\text{\AA}/500\text{\AA}$ Ti/Pt on the back of the silicon wafer. Two large heaters are patterned on the back side of the column to suppress any temperature gradients. The high thermal conductivity of silicon helps to ensure temperature uniformity over the surface area of the column. After the channel etch, the wafer is capped with an anodically-bonded Pyrex 7740 wafer at 400°C with



Fig. 3: Column performance versus linear velocity for rounded and square corner geometries.

a force of ~200N. A two-step DRIE process is used to etch the column inlet/outlet ports 380 μ m deep x 380 μ m wide to accommodate 250 μ m (i.d.) connection capillaries and reduce pressure restrictions. Fig. 4 shows the columns along with an SEM crosssection. Fig. 5 shows the center portion of a 3m column.



Fig. 4: 2D-GC columns (3m, 25cm, and 10cm) having optimized dimensions on a U.S. quarter, with heaters and sensors to allow closed-loop temperature program on their back surfaces.

The μ TM [7,8] had a similar structure. Its channels were sealed with anodically-bonded Pyrex, 40 or 100 μ m thick. Microheaters and temperature sensors made of Ti/Pt were patterned on the Pyrex. Microfabricated Si spacers were used to



Fig. 5: Top view of the center portion of a 3m-long microcolumn.

create a 22-63 μ m air gap between the μ TM and the top of the thermoelectric cooler and were precisely aligned with a microscope and bonded with an epoxy adhesive onto the Pyrex membrane. Then the μ TM was mounted on a printed circuit board with ultrasonically-bonded wire used for electrical connections. A thin layer of thermally conductive paste was used to ensure good thermal contact between the spacers and the thermoelectric cooler. With a height gauge, the μ TM with spacers was manually aligned and bonded to the cooling unit. Finally, a custom-made chamber was used to seal the μ TM. Further details on modulator performance and design considerations have been discussed in detail. [7,8]

The complete GC x GC microsystem consists of the two microcolumns, the thermal modulator, a commercial thermoelectric cooler, four transfer-line heaters, and associated electronics; it is assembled on a custom printed circuit board measuring 5 cm x 12.5 cm x 7.5 cm and shown in Fig. 6.



Fig. 6: The GCxGC system, with insets of the first-dimension column (bottom right) and the second-dimension column (top left).

TEST RESULTS

The columns were coated in a static process producing a stationary-phase thickness of about 0.15μ m. Polydimethlsiloxane and either polytriluoropropylmethylsiloxane (PTFPMS) or polyethylene glycol (PEG) were used for the non-polar and polar phases, respectively, producing a resolution of 14,425 and 5,800 theoretical plates, respectively, using an air carrier in 3m columns.

Using 3m- and 0.25m- long PDMS and PTFPMS microcolumns, a GCxGC microsystem was first implemented using the



Fig. 7: A two-dimensional contour plot of a 10-component GCxGC separation using 3m- and 0.25m-long microcolumns and a twostage thermal modulator. Alkanes are separated primarily by the first column (x-axis) and the ketones are separated primarily by the second column (y-axis). Color reflects peak height on the FID.



Fig. 8: Separation of hexane and heptane with the modulator off (a) and on (b) with fused silica capillaries as separation columns and the microfabricated thermal modulator.

meso-scale modulator described above. Modulation was between -25°C and 200°C within a few hundred milliseconds. Fig. 7 shows a two-dimensional separation of a 10-component mixture of alkanes (C_6 - C_{10}) and ketones (C_3 - C_7).

The μ TM was first tested using fused silica capillaries with the same cross-sectional areas as the microcolumns. Fig. 8a shows the separation of hexane and heptane with the modulator in the flow path but not operating, while Fig. 8b shows a modulated separation of the same two compounds. The modulation period was 10s with a 1s offset between the two stages. The microcolumns were then integrated into the system and additional separations were performed. Fig. 9a shows the modulation of a single peak. The modulation period was 10s and the modulated peak width is 217ms. Fig. 9b shows the separation of heptane and 2-hexanone, with a modulation period of 7s. These two peaks coelute from a one-dimensional separation but are clearly separated in the two-dimensional plane.

Since the modulator obtains more slices with a wider analyte band, an additional 3m non-polar column was coated and used as a first dimension column. This allowed an increase in the inlet pressure while utilizing the same volumetric flow rate. The increase in pressure increased the linear velocity in the second dimension column, reducing the second-dimension analysis time. The separation of three normal alkanes (C_7 , C_8 , and C_9) from two alcohols that co-elute was obtained as shown in Fig. 10.



Fig. 9: a) Modulated peak with microfabricated first- and second-dimension columns and a microfabricated thermal modulator. b) Separation of heptanes and 2-hexanone on micro-fabricated GCxGC system. The peaks would co-elute in a one-dimensional separation.

This separation shows the many benefits of GCxGC separations. The nonpolar alkanes align toward the bottom and the more polar alcohols separate more on the second dimension column. The alcohols are also at much lower concentration than the alkanes but are easily distinguished from the other peaks as well as the baseline.

CONCLUSIONS

There are many benefits to GCxGC separations compared to one-dimensional systems, including increased detection, structured chromatograms to aid in peak identification, and an increase in peak capacity. All of these benefits are critical for the development of field-portable systems. This is the first reported thermally-modulated microfabricated GCxGC system. With continued development such systems will be key in identifying complex VOC mixtures outside of the laboratory environment.

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Fig. 10: Separation of five compounds, three normal alkanes, and two alcohols, using a 6m-long first-dimension column and 0.25m-long second-dimension column.

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