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Uniform-temperature, microscale thermal modulator with area-adjusted air-gap isolation for comprehensive two-dimensional gas chromatography

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ABSTRACT

In comprehensive two-dimensional gas chromatography (GC × GC), thermal modulation is an important process to enhance the detectability of a volatile organic compound analyte and compound separation capacity. For increased detectability, we explore a method to enhance the temperature uniformity of a microfabricated thermal modulator with an area-adjusted air-gap spacer. The area-adjusted spacer controls the spatial distribution of heat transfer to increase the temperature uniformity of the analyte passing through the device's channel. This enables higher analyte peak-amplitude enhancement (PAE) during thermal modulation, thereby increasing detectability of the analyte. The influence of varying spacer area on temperature uniformity was characterized by simulation, and its effect on PAE was experimentally estimated. With an optimized spacer design, we achieved a 25% increase in PAE (34–42) for 10 ppm *n*-octane vapor.

1. Introduction

Analysis of volatile and semivolatile organic compounds, including breath biomarkers, explosive chemicals, and air pollutants, has gained increasing importance [1–8]. A highly effective method for such analysis is comprehensive two-dimensional gas chromatography (GC × GC), which has high resolution and detectability of each compound [9–11]. GC × GC uses a junction-point modulator to connect two columns having retention properties that are complementary to each other.

The modulator (Fig. 1a) couples the two columns by focusing vapor compounds separated on the first-dimension (^{1}D) column and reinjecting as a series of narrow peaks into the second-dimension (^{2}D) column. The profile of a vapor peak passing through the modulator is sliced into multiple bands. The modulation period is adjusted to be shorter than the difference in the retention time between two adjacent peaks from the ^{1}D column to preserve the peaks' original elution order upon the injection of the sliced bands into the ^{2}D column. Pneumatic [12,13] and thermal [14–22] modulators are common devices used for the modulation process. Pneumatic modulators require no consumables and less electric power. Thermal modulators (TMs) trap and focus the vapor compounds eluted from the ^{1}D column at low temperature. Then, TMs periodically heat up to rapidly reintroduce the compounds to the ^{2}D column. Importantly, detectability of vapors greatly increases by a TM because peak amplitude enhancements (PAE, defined as the modulated/unmodulated peak-height-maximum ratio) happen owing to the focusing and rapid reinjecting process of vapors [23]. The low-temperature focusing process of TMs increases the detectability enhancement relative to pneumatic modulation methods. However, the operation of TMs typically requires consumable coolants and high electric power, which prohibits their portable use.

As an effort to develop microfabricated GC × GC systems with microfabricated columns [24,25] for field-deployable vapor compound analysis, we recently reported on our development of a microfabricated TM (μTM) [21,22]. The μTM enables the heating operation at ~10 W, which is two orders of magnitude lower power consumption than that of conventional TMs [14–20], while replacing a conventional resource-intensive cooling unit using cryogenic fluids with a solid-state thermoelectric (TE) cooler operated at a continuous power input of 21 W. The relatively low power consumption of our μTM system could potentially allow for powering a portable GC × GC system with a high capacity battery. In our previous studies, we focused on the thermal analysis for rapid thermal cycling at low power and demonstrated chromatographic separations of compound mixtures with high PAE. These studies, however, did not explore the influence of the μTM's internal temperature distribution on PAE. The uniformity of the μTM's internal temperature is important because temperature greatly affects the mobility of the vapor compounds. To trap and release the compounds efficiently, the μTM swings over a wide range of temperature (−20 to 210 °C). During the process if the local temperature of the μTM

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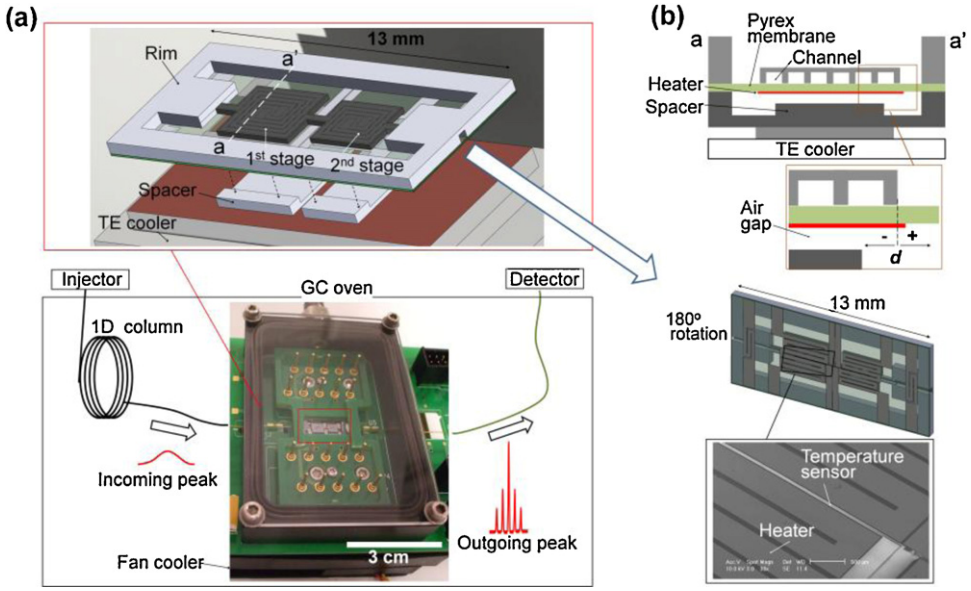

Fig. 1. Microfabricated thermal modulator (μTM). (a) Diagrams and photographs of the dual-stage μTM and its peripheral setup. The lengths of the first and second stage microchannels are 4.2 and 2.8 cm, respectively, and that of the interconnection is 1 mm. The microchannel cross section is 140 (h) × 250 μm (w), and the wall thickness is 30 μm. Temperature sensors measure the spatially averaged temperatures of the two stages. (b) Schematic showing cross section of the μTM system. A Si-spacer maintains the 19-μm air-gap between the μTM and the thermoelectric cooler. *d* is defined as the lateral distance between the edges of the μTM and the spacer.

is non-uniform, the elution peak becomes broad thereby reducing PAE. Thus, establishing uniform internal temperature is crucial to enable high-PAE analysis.

Here, we explore a method to improve internal temperature uniformity of the μTM for enhancing detectability of vapor compounds. First, we show that the μTM temperature affects the modulation peak profile, and discus how non-uniform temperature affects peak broadening. Then, to enhance temperature uniformity, we quantify the main path of heat dissipation through a heat transfer model, and show a spacer that makes an air gap between the device and the TE cooler is a main component for heat dissipation (Fig. 1b). Importantly, we show that regulating the spacer's lateral distance from the μTM stage's edge (*d*) greatly affects the μTM stage's temperature distribution. Finally, we demonstrate that an optimized value of *d* achieves the enhanced PAE of vapor peaks.

2. Materials and methods

2.1. Device fabrication

The device was fabricated by bulk and surface micromachining [22], and consists of a Si rim and two sequential serpentine Si microchannels (stages) on a 100 μm-thick Pyrex membrane (Fig. 1). The spacer made by deep reactive-ion-etching (DRIE) process formed a 19-μm air gap between the μTM stages and the TE cooler. Several spacers of different lateral lengths ranging from 3.44 to 4.6 mm were fabricated. These spacers were changed in the test fixture to vary the effective area of the air-gap between the μTM stages and the thermoelectric cooler in the device assembly. Resistive-type heaters and temperature-sensors made of thin-film Pt were on the Pyrex surface to independently heat the two stages and the rim and to measure their temperatures, respectively. The sensors individually measured the spatially averaged temperatures of each stage and the rim. The interior walls of the microchannels were coated with a 300 nm-thick polydimethylsiloxane stationary phase (PDMS, OV-1, Ohio Valley), using a static coating and thermal cross-linking method described previously [26]. The result of the stationary phase coating process could vary from device to device. To limit the focus of our study to understanding the temperature effect on the device performance, we repeatedly used the same μTM device across all the experiments only with the spacer design changed. This eliminated the influence of the device-to-device fabrication error from our experiments.

2.2. Experimental setup

Helium carrier-gas flew in the channel at a rate of 0.38 mL/min forming a mobile phase with an injected vapor. A 3-m section of commercial PDMS-coated capillary (250 μm i.d., 0.25 μm thickness, Restek) was used as the ^{1}D column, and the outlet of the device was connected directly to a flame ionization detector (FID) via a 10-cm segment of narrow-bore deactivated fused silica capillary (100 μm i.d.). A commercial GC oven (HP7890, Agilent), which contained the fully assembled μTM testing platform and capillaries, was maintained at 33 °C.

3. Results and discussion

3.1. Basic operating features

As shown in Fig. 2a, the two stages of the μTM were operated in the temperature range of −20 to 210 °C at heating and cooling rates of up to 2400 and −168 °C/s, respectively. The two stages were successively thermal-cycled to reduce sample loss due to incomplete trapping by the first stage during the heating-to-cooling transitions. Fig. 2b shows a chromatogram of unmodulated and modulated peaks for the injections of 10 ppm *n*-octane vapor. The unmodulated *n*-octane peak was first obtained by flowing the vapor through μTM channels while deactivating the TE cooler and the μTM heaters. With the μTM and the TE cooler activated, the modulated peak was then acquired by applying a modulation period of 6 s and a square-wave voltage-pulse input of 0.1 s duration to the both stages with an offset of 0.6 s taken between the two voltage-pulses. Also, the timing of an initial heating event was adjusted so that the heating events symmetrically bracket the apex of the unmodulated peak (in-phase modulation), or one of the heating events coincides with the apex (180° out-of-phase modulation). The in-phase modulation produces the largest PAE and a