High-speed, temperature programmable gas chromatography utilizing a microfabricated chip with an improved carbon nanotube stationary phase

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ABSTRACT

A new growth recipe for producing carbon nanotubes (CNTs) combined with a new bonding technique was implemented in a microfabricated gas chromatography (micro-GC) chip. Specifically, the micro-GC chip contained a 30-cm (length) microfabricated channel with a 50 μm × 50 μm square cross-section. A CNT stationary phase "mat" was grown on the bottom of the separation channel prior to the chip bonding. Injections onto the micro-GC chip were made using a previously reported high-speed diaphragm valve technique. A FID was used for detection with a high-speed electrometer board. All together, the result was a highly efficiency, temperature programmable (via low thermal mass, rapid on-chip resistive heating) micro-GC chip. In general, the newly designed micro-GC chip can be operated at significantly lower temperature and pressure than our previously reported micro-GC chip, while producing excellent chemical separations. Scanning electron microscopy (SEM) images show a relatively thin and uniform mat of nanotubes with a thickness of ~800 nm inside the channel. The stationary phase was further characterized using Raman spectroscopy. The uniformity of the stationary phase resulted in better separation efficiency and peak symmetry (as compared to our previous report) in the separation of a mixture of five n-alkanes (n-hexane, n-octane, n-nonane, n-decane and n-undecane). The on-chip resistive heater employing a temperature programming rate of 26 °C/s produced a peak capacity of eight within a 1.5-s time window.

1. Introduction

Single and multi-wall carbon nanotube stationary phases for use in gas chromatography (GC) have been the subject of several recent reports [1–6]. The majority of these reports utilized carbon nanotubes within a silica capillary. Multi-wall carbon nanotubes (MWCNTs) utilized as a GC stationary phase have faster mass transfer properties than graphitic carbon stationary phases and result in more symmetrical peaks for both polar and non-polar compounds [3]. Carbon nanotubes utilized within open tubular capillaries have proven to be a robust stationary phase stable to high temperatures and capable of separating mixtures of compounds with good resolution [2]. Previously, we reported a microfabricated GC (micro-GC) chip implementing a single-wall carbon nanotube (SWCNT) stationary phase [1], whereby the SWCNTs were deposited through the lithographic patterning of the growth catalyst on a silicon wafer [7]. Stationary phases that can be grown within a microfabricated channel eliminate the potentially problematic coating methods that are used with polymer-based stationary phases [8,9].

While our previous report demonstrated that a SWCNT stationary phase could be readily incorporated in a on-chip resistively heated micro-GC chip, providing fast temperature programmed separations on the order of a few seconds [1], there was an observable shortcoming in the uniformity of the SWCNT phase that appeared to limit the separation efficiency, N, and hence limit device performance. In order to address this shortcoming, a new growth recipe for producing a highly uniform CNT phase material has been implemented. This new growth recipe has been combined with a more effective bonding technique in order to prevent damage to the nanotubes during the bonding technique and deactivate the glass surface. The channel structure is 30 cm in length, with a 50-μm by 50 μm cross-section that in principle should be able to provide rapid and efficient GC separations [10,11]. Only one of the four walls is coated with the CNT stationary phase, a coating procedure that greatly simplifies the separation channel design. However, analyte mass transfer should be extremely rapid across the narrow channel, which should minimize the potential source of band broadening due to coating only one channel wall. The CNT stationary phase was characterized via SEM and Raman

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spectroscopy in order to verify the presence and quality of the CNTs in the channel and to determine the diameter of the nanotubes. The separations obtained with this micro-GC chip contain peaks with more Gaussian-like peak profiles, as will be demonstrated via peak symmetry measurements [12]. The on-chip resistive heater that incorporated a thin serpentine film of metal (5 nm of Ti and 100 nm of Pt) will also shown to be significantly more efficient (improved relative to our initial report [1]). In this report, we will use a simple mixture of relatively volatile hydrocarbons to test the separation performance. However, it is envisaged that the micro-GC chip can, in principle, be more widely applicable to situations in which high-speed separations are needed, e.g., field monitoring, on-line process control, and as the second dimension of comprehensive two-dimensional gas chromatography (GC × GC).

2. Experimental

2.1. Column fabrication

In brief, the separation channel and connecting ports were etched in a silicon wafer and the nanotubes were grown in the separation channel; the channel was then sealed with SU8 2005, thus producing the GC column. The serpentine resistive heating element was fabricated on the opposite side of the wafer.

Specifically, the fabrication process began with PR4640 photoresist (Shipley Company, Marlborough, MA, USA) spun on the back side of a 500-μm thick Si wafer with native oxide. Ports 380 μm in circumference were patterned lithographically on the back of the wafer, then the photoresist was used as an etch mask for a 460 ± 10 μm deep reactive ion etch (DRIE). After the etching process, the photoresist was removed from the back of the wafer. Next, PR4640 was again spun on the back side of the wafer and resistive heaters (metal film) were patterned onto the wafer, i.e., a 5-nm of Ti and 100 nm of Pt metal film was evaporated onto the wafer before the photoresist was removed again. Then, the front side of the wafer was coated with PR4620, and a 30-cm long and 50 μm wide channel was patterned onto the wafer. The front channel was etched with DRIE to a depth of nominally 50 μm, again using the photoresist as an etch mask. The resulting separation channel was 30 cm long with a 50 μm × 50 μm square cross-section. A rectangular cross-section keeping the 50-μm depth constant could also be used, and in principle provide essentially the same separation efficiency but a higher sample capacity. The catalyst metals (100 Å Al, 1 Å Pt, 5 Å Fe) were deposited with an electron-beam evaporator, and lift-off was performed by soaking the wafer in acetone for 10 min, followed by brief (1–5 s) sonication and rinsing with acetone, ethanol and water.

The CNTs were grown onto one of the four walls of the separation channel via chemical vapor deposition; the CNT stationary phase was grown only in the bottom of the channel to simplify the microfabrication [1]. The 2 in.diameter furnace was heated to 500 °C before the wafer was introduced. The wafer was heated at a rate of 40 °C/min to 850 °C while flowing Ar gas at 240 ml/min combined with H$_2$ at 160 ml/min. Once 850 °C was reached, the temperature was held constant until the end of the growth. After 10 min of heating, water was added to the reaction mixture by mixing argon that was bubbled through a water bubbler into the gas stream, maintaining the total flow of argon at 240 ml/min. The water content was regulated to be constant at 1000 ppm at the feed end. After 20 min of heating, 40 ml/min of ethylene was added for 10 min (all gases in this process were from Matheson Tri-Gas, Newark, NJ, USA). During the growth, the pressure at the exhaust was maintained at 14 psi (99,300 Pa). The CNT coverage (i.e., on

one wall of the separation channel) was analyzed with scanning electron microscopy (SEM).

After the growth of the CNT phase, the channel structure was sealed by spin-coating the glass cover slide with SU8 2005 (Micro Chem, Newton, MA, USA) at 500 rpm for 5 s, then 2000 rpm for 30 s. The glass slide was desiccated for 5 min at 200 °C then cooled by blowing nitrogen over it before the SU8 was added. The silicon column was firmly pressed on top of the coated glass slide, making sure there were no voids between the glass and the silicon. With the glass facing down, the wafer was baked in an oven by ramping to 65 °C at a rate of 5 °C/min and baking for 10 min, then ramping to 95 °C at 5 °C/min, baking for another 5 min, and finally ramping to 200 °C at 5 °C/min and baking for an additional 5 min. Bare silicon micro-GC chips were manufactured in the same manner described above, omitting the steps relating to the growth of the CNT stationary phase.

2.2. Chromatographic instrumentation

All chromatographic experiments were completed using a Agilent 6890 GC (Agilent Technologies, Santa Clara, CA, USA) modified with a single diaphragm valve (VICI Valco, Houston, TX, USA) for high-speed sample injections onto the micro-GC chip, as previously reported [13–16]. The Agilent 6890 GC serves as a platform to study the separation performance of the micro-GC chip. Briefly, a sample is injected using the standard 6890 autoinjector, and a small portion of the autoinjected pulse is subsequently injected using the high-speed diaphragm valve (set to inject a 15-ms sample pulse for this study). This 15 ms sample pulse is then separated by the micro-GC chip either with or without the CNT stationary phase (and either with or without on-chip resistive heating), followed by a high-speed FID. Note that the GC oven was used for the initial temperature setting, i.e., for isothermal separations as well. The timing and actuation of the diaphragm valve was controlled using an in-house written LabVIEW (National Instruments, Austin, TX) program [11] and the FID was modified with an in-house built electrometer for high-speed detection of the narrow chromatographic peaks (20,000 Hz sampling rate). All temperature programming was completed using the on-chip resistive heating element (discussed in more detail in Section 2.1). The timing for the resistive heating was controlled via an in-house written LabVIEW program as previously reported [1,17]. A variable autotransformer (Stace Energy Products Co., Dayton, OH, USA) supplied a variable AC voltage (0–120 V) in order to resistively heat the micro-GC chip, as previously reported [1].
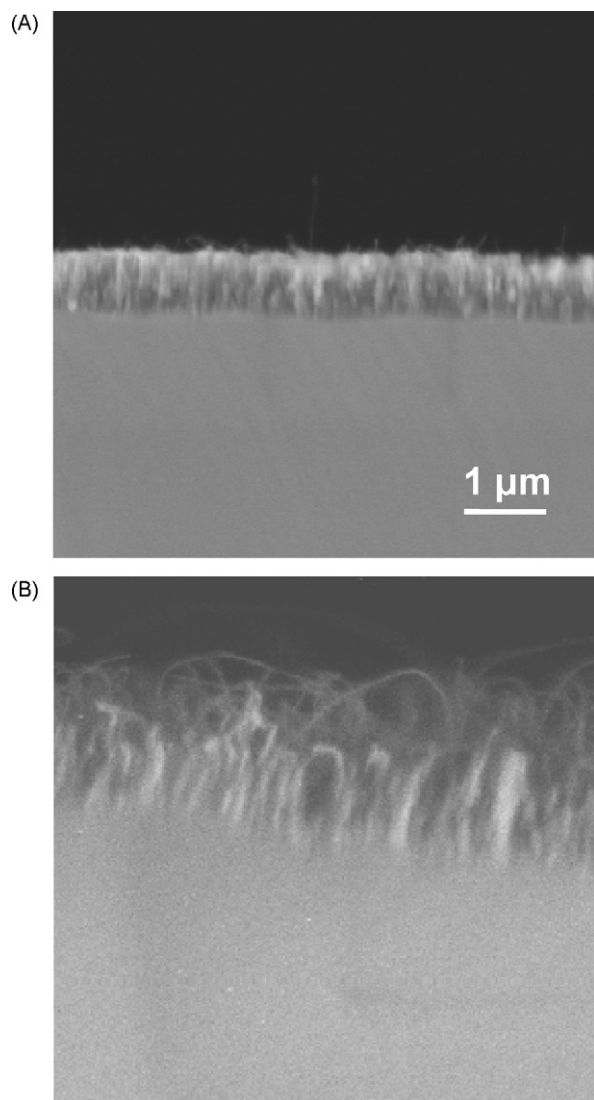
2.3. Chromatographic experiments

All chromatograms were collected with the 6890 GC inlet and FID temperature of 250 °C. The inlet was set for a splitless injection with a pressure of 10 psi (69,000 Pa) of hydrogen carrier gas, resulting in a carrier gas velocity of 95 cm/s at 50 °C. The transfer line from the 6890 GC autoinjector to the diaphragm valve was a 12-cm length of methyl deactivated capillary with an internal diameter of 100 μm. The auxiliary pressure (for the hydrogen carrier gas through the chip) was also set at 10 psi (69,000 Pa). The micro-GC chip was interfaced to the diaphragm valve and FID with 13 and 16 cm lengths of methyl deactivated capillary, respectively, both with an internal diameter of 100 μm. The capillary leads were attached to the micro-GC chip with high temperature epoxy (J-B Weld, Sulfur Springs, TX, USA) as previously reported [1]. The capillary leads were isothermal during all separations; they were not resistively heated. All chromatograms were obtained using a 15-ms injection pulse from the diaphragm valve.
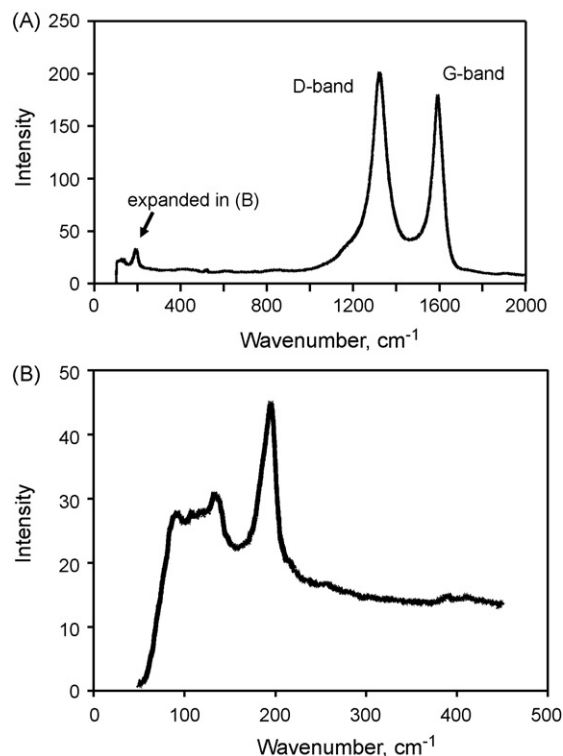
3. Results and discussion

3.1. Characterization of the CNT stationary phase

The CNT stationary phase on one wall of the separation channel was characterized via both SEM and Raman spectroscopy. The SEM images are shown in Fig. 1. Note that while this characterization is described first for clarity, the experiments themselves were done last, after all the chromatographic experiments were completed, since the chip needed to be carefully sliced open orthogonal to the channel to facilitate SEM and Raman characterization. Several channel locations were examined, and the results presented are representative and consistent.

The image in Fig. 1A is a SEM image and shows that the nanotubes have formed a relatively uniform mat in the microfabricated channel. This is different than the tangles (with voids) of SWCNTs that were previously reported [1]. The image in Fig. 1A shows that the CNTs are ~800 nm tall within the channel. A detailed SEM image of the CNT stationary phase is shown in Fig. 1B. Since only the bottom of the channel is coated with the CNT phase, there is no build up in the corners. The CNT stationary phase was further characterized

Fig. 1. (A) SEM image of the stationary phase composed of a "mat" of CNTs within a micro-GC separation channel. (B) Detailed SEM image to more readily observe individual CNTs within the separation channel.
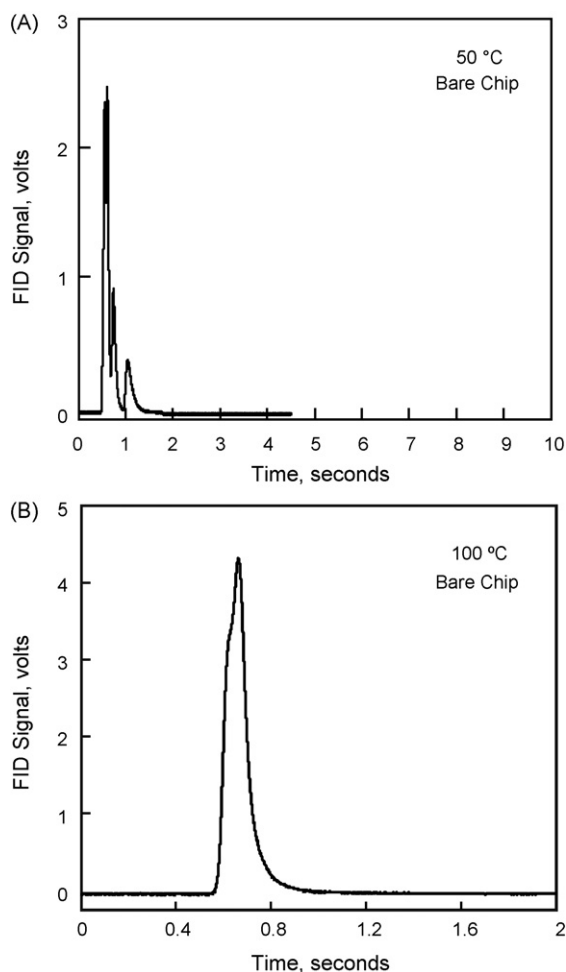

Fig. 2. Raman spectra of the CNT stationary phase grown in the separation channel. (A) Raman spectrum showing both the D-Band (~1350 cm^{-1}) and G-Band (~1600 cm^{-1}). (B) Detail of the radial breathing modes (<500 cm^{-1}) of the spectrum shown in (A).

utilizing Raman spectroscopy (with a laser excitation wavelength of 633 nm). The full spectrum is shown in Fig. 2A; the large intensity of the broad D-band (1250–1400 cm^{-1}) suggests the presence of multi-wall carbon nanotubes (MWCNTs) [18]. The presence of the narrow G-band (1500–1700 cm^{-1}), however, also suggests the presence of SWCNTs, possibly with defects such as shortened tubes and vacancies, within the channel. The radial breathing modes (<500 cm^{-1}), shown in Fig. 2B, suggest the presence of SWCNTs with a diameter of ~2 nm [18]. From high-resolution SEM images, not shown for brevity, the diameter of the MWCNTs was found to be ~40 nm. Overall, the CNT stationary phase appears reasonably uniform in size and distribution on the one wall within the micro-GC channel. Other channel locations analyzed provided similar results, not shown for brevity.

3.2. Evaluation of bare silicon micro-GC chips

In order to fully characterize the CNT stationary phase, chromatograms were collected utilizing bare silicon micro-GC chips. These bare silicon chips do not contain a CNT stationary phase. A five-compound n-alkane mixture was injected onto a representative bare micro-GC chip. Iosthermal separations of the n-alkane mixture are shown in Fig. 3. The sample was prepared neat, so there is no solvent peak. The isothermal separation of the mixture at 50 °C is shown in Fig. 3A. The separation is complete in less than 1.5 s with minimal separation of the first four compounds. The last eluting compound, n-undecane, is slightly retained most likely due to the differential between the boiling point of the compound and the separation temperature. The isothermal separation of the mixture at 100 °C is shown in Fig. 3B. There is no visible separation of the five-compound mixture at this high temperature. Due to the lack of separation at both isothermal separations (relative to the micro-GC

Fig. 3. Isothermal separations of a five-compound n-alkane mixture (retention order: n-hexane (C_6), n-octane (C_8), n-nonane (C_9), n-decane (C_{10}), n-undecane (C_{11})) utilizing a bare silica micro-GC chip. All data collected using H_2 carrier gas at an absolute head pressure of 10 psi (69,000 Pa). Separations were obtained using the 30 cm micro-GC chip with a 50 μm × 50 μm channel cross-section. (A) Separation obtained at an isothermal temperature of 50 °C. (B) Separation obtained at an isothermal temperature of 100 °C.

chip separations with the CNT stationary phase shown next), the conclusion that the bare silicon chip does not contribute significantly to the separation of the compounds in the n-alkane mixture can be reached.

3.3. On-chip resistive heating as a means of temperature programming

The micro-GC chip with CNT stationary phase was utilized to separate a mixture of five n-alkanes (n-hexane, n-octane, n-nonane, n-decane and n-undecane). The isothermal separation of the mixture at 50 °C is shown in Fig. 4A. The separation is complete in less than 10 s with the earlier peaks eluting with good signal-to-noise and adequate resolution. The later eluting peaks (n-decane and n-undecane) have significantly larger peak widths, and n-undecane is barely visible above the baseline. An increase of the isothermal temperature to 100 °C resulted in the separation shown in Fig. 4B. The separation is complete in less than 2 s, which is fivefold faster than the isothermal separation at 50 °C (Fig. 4A); however, the earlier eluting peaks are overlapped significantly. The decreased peak widths of the later eluting peaks and the increased signal-to-noise for n-undecane demonstrate the benefit of the higher isothermal

temperature (100 °C). This is commonly referred to as the general elution problem, where for GC no single isothermal temperature provides optimal resolution with consistently narrow peaks for a mixture of compounds with a sufficiently wide boiling point range.

A common solution to the general elution problem is the use of temperature programming. To address this issue, this micro-GC chip was equipped with an on-chip resistive heating element. Applying a voltage across the heating element results in a rapid and reproducible temperature program [1]. The five-compound n-alkane mixture separated isothermally in Fig. 4A and B was temperature programmed by applying 36 V to the heating element, producing a temperature program of 26 °C/s (with the calibration of the programming rate described below). The resulting temperature programmed separation is shown in Fig. 4C. The separation is complete in less than 2.5 s with sufficient resolution between all of the analytes and an improved signal-to-noise ratio for n-undecane, when compared to the separation obtained at an isothermal temperature of 50 °C. A peak capacity of eight within a 1.5-s time window can be computed from the data in Fig. 4C.

The new micro-GC chip was characterized isothermally using a single analyte to determine the linearity of analyte retention as a function of temperature, and ultimately to calibrate the temperature programming rate as a function of applied voltage. The test analyte, n-decane, was injected neat at four isothermal temperatures in order to create a van't Hoff plot (a plot of $\ln k$ vs. $1/T$), where k is the analyte retention factor and T is the separation temperature in Kelvin. This plot along with the best fit line and equation are shown in Fig. 4D. The equation of the line shown was used, as previously reported [1,17], to determine the rate of temperature programming in Fig. 4C. The rates of temperature programming resulting from several different voltages are tabulated in Table 1. The linearity of the van't Hoff plot suggests that the low temperatures do not adversely affect the retention of the analyte; the retention of n-decane is linear over the temperature range reported. Also, the on-chip resistive heater employed appears to be slightly more efficient than the previously reported model [1]. The previously reported temperature program of 60 °C/s was produced by applying 96 V to the heating element. The new micro-GC chip would require one third less voltage (63 V as extrapolated from the data in Table 1) to produce the same temperature programming rate.

3.4. Comparison of the new CNT micro-GC chip to previous study
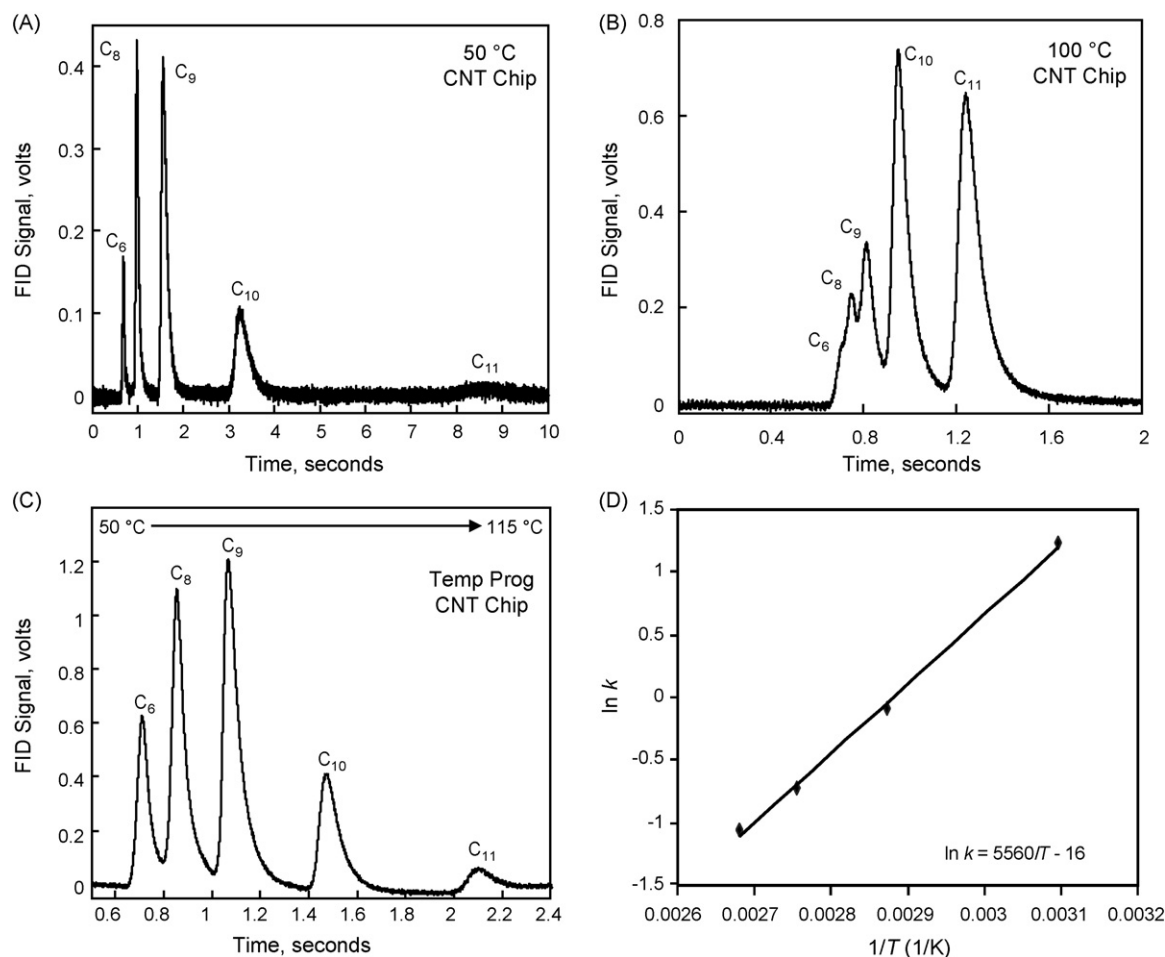
The CNT micro-GC chip reported herein is a redesign and improvement over our previous report [1] (see p. 5642, Figs. 3B and 4C and p. 5643, Table 1 of that reference), consequently a comparison of the two chips is presented. The new growth recipe for the CNT stationary phase results in a very uniform stationary phase (see Fig. 1 in the report herein). The old growth recipe resulted in a stationary phase consisting of nanotube "tangles" with spaces up to 500 nm between them (see p. 5642, Fig. 3B). The spaces between the nanotube "tangles" contributed to significant band broadening, and a uniform mat of stationary phase is preferred.

Table 1
Temperature programming rates for the on-chip resistive heater (T_i = 50 °C) for various applied voltages.

Voltage applied (V)	Temperature programming rate (°C/s)
24	10
30	18
36	26
42	33

Fig. 4. Isothermal and temperature programmed separations of a five-compound n-alkane mixture (retention order: n-hexane (C_6), n-octane (C_8), n-nonane (C_9), n-decane (C_{10}), n-undecane (C_{11})) utilizing a silica micro-GC chip with CNT stationary phase. All data collected using H_2 carrier gas at an absolute head pressure of 10 psi (69,000 Pa). Separations were obtained using the 30-cm micro-GC chip with a 50 μm × 50 μm channel cross-section. (A) Separation obtained at an isothermal temperature of 50 °C. (B) Separation obtained at an isothermal temperature of 100 °C. (C) Temperature programmed separation obtained by applying 36 V across the on-chip resistive heating element resulting in a temperature programming rate of 26 °C/s (initial column temperature was 50 °C). (D) van't Hoff plot ($\ln k$ vs. $1/T$) of n-decane for the micro-GC chip with the CNT stationary phase used for the calibration of the temperature programming rates. The best fit line and equation are displayed on the graph. All data obtained using H_2 carrier gas at an absolute head pressure of 10 psi (69,000 Pa). Methane was used as a dead time marker for k calculations, t_M = 632 ms.
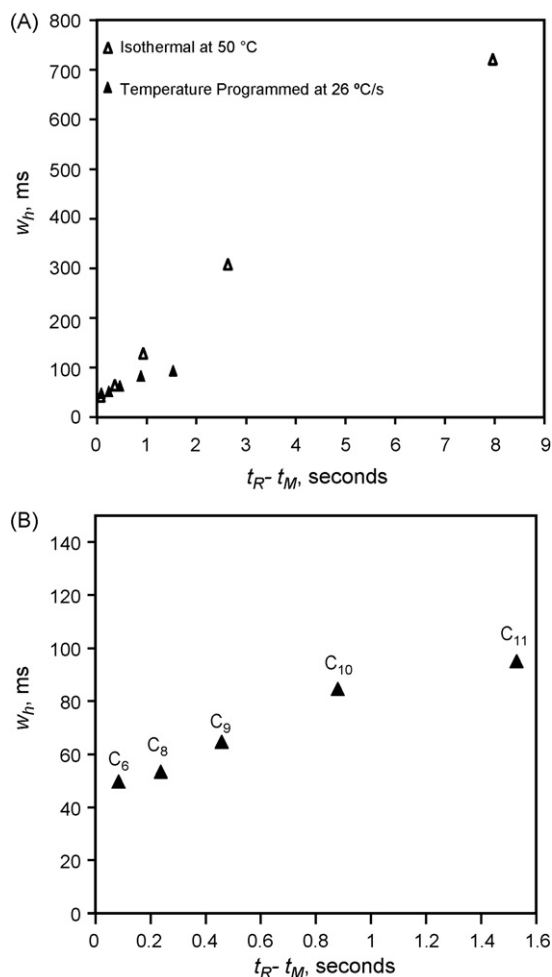
The previously reported chips resulted in chromatograms with highly tailed peaks, even when temperature programmed (see p. 5642, Fig. 4C). Chromatograms obtained with the chips reported herein contain peaks that are significantly more Gaussian-like in nature. The peak tailing, even in the isothermal chromatogram at 50 °C, is minimal when compared to the previously reported chips. The separations using the new chips resulted in a 66% reduction in the skew of the isothermal n-hexane peaks. For n-octane, which was slightly more retained, a reduction in the skew of 98% was observed. Since there was minimal retention for the bare chips (Fig. 3A and B), adsorption to the bare walls was not a significant contributor to peak tailing. More likely, the observed peak tailing in the present study was due to the difficulty in minimizing sources of extra-column band broadening such as dead volumes.

A plot of the peak width-at-half-height, w_h, as a function of the adjusted retention time, $t_R - t_M$ (the retention time minus the dead time), for both the isothermal (at 50 °C) and temperature programmed separations is shown in Fig. 5A (data from separations shown in Fig. 4A and C). For isothermal GC, band broadening is essentially linear with adjusted retention time (as well as k) [11]. Temperature programming significantly reduces the width and retention time of the more retained compounds, which leads to a larger S/N ratio. For example, at a common adjusted retention

time of ∼0.9 s, the temperature programmed peak width is approximately two thirds of the isothermal peak width. A detailed view of the temperature programmed data from the plot in Fig. 5A is shown in Fig. 5B. Since the w_h values increase only moderately as a function of $t_R - t_M$ suggests that the temperature programming rate has been nearly optimized in the context of the slow velocity utilized for the separation in Fig. 4C. The same statement cannot be applied to the previously reported devices, where the w_h values increase dramatically as a function of $t_R - t_M$ (see p. 5642 Fig. 4C).

Moreover, the analyte n-hexane, with the smallest adjusted retention time on the previously reported micro-GC chip, has a peak width that is actually fourfold narrower than obtained with the new chip, ∼12 ms versus ∼50 ms. This is predominately due to the difference in the carrier gas velocities for the two chips. The previous micro-GC chip was operated at an average linear flow velocity, $\bar{u}$, of ∼1100 cm/s while the new micro-GC chip was operated at a $\bar{u}$ of ∼95 cm/s. Meanwhile, as for the more retained analytes, the peak widths on the new chip are significantly narrower, suggesting that the temperature programming rate for the new chip was essentially optimized.

The new micro-GC chip also results in a higher peak capacity for a temperature programmed separation. The peak capacity for the new micro-GC device is approximately 8 for a time window of 1.5 s

Fig. 5. Plots of width-at-half-height, w_h, as a function of adjusted retention time, $t_R - t_M$ for the five compound n-alkane mixture separations shown in Fig. 4. (A) Isothermal data at 50 °C ($\triangle$) (data from Fig. 4A) and temperature programmed data at 26 °C/s ($\blacktriangle$) (data from Fig. 4C). (B) Detail of the plot in (A) containing only the temperature programmed data at 26 °C/s. Methane was the dead time marker, $t_M = 632$ ms.

(for the separation shown in Fig. 4C). The previously reported device has a peak capacity of approximately 6 for the same 1.5 s time frame (see p. 5642, Fig. 4C). The fact that the average linear flow velocity for the previously reported micro-GC chip is approximately 12-fold higher than the average linear flow velocity of the new micro-GC chip should be an advantage. In most cases the faster the velocity, the higher the peak capacity of the resulting separation. For this particular case, the new device has a higher peak capacity even though it was operated at a much lower velocity.

The new micro-GC chip has a separation channel that is 30 cm with a 50 μm × 50 μm cross-section. The previously reported micro-GC chip had a separation channel 50 cm in length with a 100 μm × 100 μm cross-section. The dependence on channel dimensions for the anticipated peak width, in the absence of any extra-column band broadening, can be estimated from Golay theory [11]. The improvement in the new micro-GC chip is a combination of factors. These factors include, but are not limited to, the new nanotube growth recipe that led to a uniform thickness of the nanotube "mat" in the channel (as per Fig. 1), the uniform size of the nanotubes (length and diameter), and the different chip bonding technique. The major improvements in peak shape suggest that the presented micro-GC chip utilizing CNTs as the stationary phase is a significant enhancement of the previously reported chips.

4. Conclusions

The micro-GC chip reported herein utilized a carbon nanotube (CNT) stationary phase grown utilizing a new growth recipe, which resulted in a more uniform stationary phase morphology and an improvement in peak symmetry, peak capacity, and overall separation performance. Micro-GC chips can be fabricated in a batch format because multiple columns can be etched onto one wafer. The lower energy and carrier gas consumption make these chips more appealing and likely more applicable for field portable applications of micro-GC.

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