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Stainless-Steel Column for Robust High Temperature Microchip Gas Chromatography

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Abstract

This paper reports the first results of a robust, high performance, stainless-steel microchip gas chromatography (GC) column that is capable of analyzing complex real world mixtures as well as operating at very high temperatures. Using a serpentine design, a 10 m column with an approximately semicircular cross section with a 52 μm hydraulic diameter (D_h) was produced in a 17 cm x 6.3 cm x 0.1 cm rectangular steel chip. The channels were produced using a multilayer chemical etch and diffusion bonding process, and metal nuts were brazed onto the inlet and outlet ports allowing for column interfacing with ferrules and fused silica capillary tubing. After deactivating the metal surface, channels were statically coated with a layer of 0.16 μm (5%-phenyl)(1%-vinyl)-methylpolysiloxane (SE-54) stationary phase, and cross-linked with dicumyl peroxide. By using *n*-tridecane (*n*-C13) as test analyte with a retention factor (*k*) of 5, a total of 44,500 plates (≈ 4500 plates/m) was obtained isothermally at 120 °C. The column was thermally stable to at least 350 °C, and rapid temperature programming (35 °C/min) was demonstrated for the boiling point range from *n*-C5 to *n*-C44 (ASTM D 2887 simulated distillation standard). The column was also tested for separation of two complex mixtures: gasoline headspace and kerosene. These initial experiments demonstrate that the planar stainless-steel column with proper interfacing can be a

viable alternative platform for portable, robust microchip GC that is capable of high temperature operation for low volatility compound analysis.

Introduction

Since the introduction of silicon microchip gas chromatography (GC) columns by Terry et al. (1) in 1979, there has been tremendous interest among researchers in fabricating such columns in various substrates such as ceramics (2,3) glass (4), polymers (5, 6) and metals (2, 7-9). Despite the wide variety of substrates employed, silicon accounts for the majority at approximately 80% of all microchip GC columns fabricated. The advantages of silicon include established micromachining technology, capability of generating high aspect ratio features, cost effectiveness due to batch processing, low thermal mass, high thermal conductivity, chemical inertness and familiar silanol (Si-OH) chemistry to the popular fused-silica capillary column technology (10). It is worth mentioning that although there are reports of all-silicon microcolumns (both etched in and bonded with silicon wafers), in most cases, the channels are microfabricated in a silicon substrate followed by anodically bonding to a Pyrex glass top layer (1, 11,12). This design is not ideal as such silicon/glass hybrid systems exhibit thermal expansion coefficient (CTE) mismatch (13), non-uniformity in temperature profile (silicon has 2 orders of magnitude higher thermal conductivity compared to Pyrex glass) (14), and high thermal capacitance (15), as well as variable surface chemistries (16). Furthermore, these columns have been mainly limited to the analysis of volatile organic compounds (VOCs) due to the use of adhesive-based interfacing techniques to connect the chip to the injector and detector. These adhesives usually have limited thermal stabilities at temperatures above 200°C and have significantly different CTE values (17) from silicon and glass, leading to cracks upon repeated thermal cycling.

Unsatisfied by the performance of first generation silicon-glass hybrid systems that were mainly limited to isothermal operations due to high thermal capacitance and low thermal conductivity, Bhushan et al. (7) became the first to report on the use of a metal microchip GC column in 2004. This initial report was followed by several detailed descriptions of metallic columns in later years (15,18). These columns were fabricated by X-ray LIGA using two substrates: one sacrificial (titanium or silicon) and the other

61 final (nickel), where the sacrificial substrate was used as an initial support, which was
62 eventually etched away, leaving the final electrodeposited substrate. However, these
63 metal columns used epoxy as an interfacing adhesive, which prevented good
64 deactivation of active sites in the channel (requiring 380 °C) and limited the application
65 range to 250 °C.

66 In 2005, Lewis and Wheeler (8) (US7273517 B1) fabricated a non-planar
67 microchip GC column consisting of numerous parallel vertical through-holes coated with
68 stationary phase in a nickel substrate. The nickel substrate was bonded to the top and
69 bottom cover plates containing etched channels that connect the through-holes into a
70 continuous winding channel. They claimed that this microfabricated GC column was
71 superior to planar microfabricated GC columns, because it allowed for a longer column
72 to fit within a smaller footprint, and it allowed for a uniform stationary phase to be
73 deposited, avoiding the pooling effect generated by the sharp corners found in
74 rectangular channels. In their patent, the authors did not report the type of interfacing
75 technique they used; however, they performed their analyses isothermally at 80 °C,
76 which produced very broad *n*-alkane (*n*-C8 to *n*-C12) peaks. In 2010, while describing a
77 unique column design, called a "folded passage column," Adkins and Lewis (19) (US
78 2001/0226040 A1) listed nickel as one of the possible substrate. The concept of this
79 column design involved joining a channel within a surface through a slot to another
80 channel in a separate surface. This process of connecting channeled surfaces was then
81 repeated to achieve the desired column length. A commercial version of such a column
82 is used in the FROG (Defiant Technologies, Albuquerque, NM, USA.) portable GC
83 instrument for which columns are fabricated in metals: nickel and stainless steel. The
84 interfacing is dependent on 1/16" ports that are welded in place, and columns are
85 connected to injector and detector using compression fittings (i.e., O-ring or ferrule
86 seals). Technically, such columns should be able to operate at high temperature.
87 However, as the devices use ambient air as carrier gas, to avoid oxidation, the
88 application range of such columns was limited to the boiling point range of -13.3 °C to
89 244.7 °C at 1 atm.

In 2012, Iwaya et al. (20) wet-etched semi-circular cross-section channels into stainless-steel plates, and fusion bonded them, to produce a metal microfabricated GC column. After bonding the channels, stainless steel connection tubes were brazed to the plate for connection to the inlet and detector. Unlike epoxy-based adhesives, since brazing can handle high temperatures, chemical vapor deposition of silicon for deactivating channels was performed at 550 °C. However, the steel microchip column was coupled to a planar surface acoustic wave (SAW) sensor to produce a Ball SAW GC, which was never demonstrated for high temperature applications. The highest column temperature used was 35 °C for normal hydrocarbon analysis (*n*-C6 to *n*-C8). In 2013, Darko (2) reported the fabrication of 0.1 m and 15 m columns from titanium tiles for packed and open tubular GC, respectively. The highest temperature attained by these columns was 210 °C, and baseline elevation was markedly present for an *n*-C8 to *n*-C20 mixture. In 2017, Raut and Thurbide (9) reported a 7.5 cm x 15 cm rectangular monolithic titanium device that contained a 5 m x 100 µm x 100 µm serpentine column with integrated FID. Gas-tight custom fittings were used with nuts/ferrules for attaching fused silica tubing for interfacing. The highest reported temperature was 100 °C and the separations of *n*-alkane mixtures shown were not impressive and had poor peak shapes.

Considering the fact that metal open tubular columns have been, and continue to be, a very integral part of modern GC analysis, exploring the full potential of such columns seems to be an obvious direction for further research for two reasons: (1) metal columns are robust in nature, making them ideal for application in portable devices, and (2) interfacing of such columns can be achieved with nuts and ferrules through brazed fittings that can withstand high temperature GC application. However, a potential drawback inherent to metal columns is the difficulty and high cost of fabrication as compared to silicon microchips. Additionally, deactivation of highly active metal surfaces and increased thermal mass can also be disadvantageous. Earlier this year (2018), we showed some initial separations using a stainless-steel microfabricated column in both temperature programming (TPGC) and thermal gradient (TGGC) modes of operation (21). The chip was heated using a conventional GC oven for conventional TPGC analyses; however, for TGGC studies, the chip was electrically insulated with a

thin ceramic coating. Two resistive heaters were then silk screened onto the backside of the chip with silver conductive paste (ESL ElectroScience, King of Prussia, PA, USA). In this paper, we report a 10 m microfabricated stainless steel column with a 52 μm hydraulic diameter (D_h) semicircular cross section that was etched into 304 stainless steel plates, diffusion bonded, and brazed with inlet and outlet ports for interfacing. The column was deactivated and statically coated with SE-54 stationary phase. Using this method, we were able to successfully integrate the column into a benchtop GC system, and separate compounds in gasoline vapors, kerosene and an *n*-alkane (*n*-C5 to *n*-C44) standard mixture (ASTM D 2887) using temperatures up to 350 °C. It is worth mentioning that the first semi-volatile analysis in microchip GC using a similar temperature range was reported by Gaddes et al. (22), in which compression-based seals were applied to a 2 m silicon microchip column for temperature programmed GC. Although the authors reported a significant advance in high temperature microchip GC, relatively poor separation performance was demonstrated compared to conventional capillary GC. A subsequent compression-based heater/clamp device reported by Ghosh et al. (23) extended the upper temperature of a silicon microchip GC column to 375 °C. However, due to the use of a thermal gradient along the chip, only part of the microchip reached this high temperature. To our knowledge, this paper reports the highest temperature applied (350 °C) and best performance attained by any metal microfabricated column to date. It also reports the longest metal microfabricated column and best performance for semi-volatile compound analysis by any microchip GC column reported to date.

Materials and Methods

Materials

N-pentane was purchased from Alfa Aesar (Ward Hill, MA, USA); dicumyl peroxide was purchased from Sigma–Aldrich (St. Louis, MO, USA); 1% vinyl, 5% phenyl, 94% methylpolysiloxane (SE-54, catalog no. 21106) was purchased from Supelco (Bellefonte, PA, USA); ASTM D2887-12 calibration standard (31674 and kerosene standard (31229) were purchased from Restek (Bellefonte, PA, USA); a gasoline sample was obtained from a local Shell gas station in Provo, UT, USA; a solid

phase micro extraction (SPME) fiber assembly (100 μ m PDMS, 23 gauge needle, 57342-U was purchased from Supelco (Bellefonte, PA, USA); helium, air, and ultrapure hydrogen were obtained from Air Gas (Radnor, PA, USA); polyimide ferrules (FS.25-5) were purchased from Valco (Houston, TX, USA). Silver conductive paste (ESL 599-E) was obtained from ESL ElectroScience (King of Prussia, PA, USA). An Agilent 6890 GC (Agilent Technologies, Santa Clara, CA, USA) was used for testing of the microchip column.

Column fabrication and preparation

The 304 stainless steel microchip column was produced from thin, stacked layers by VACCO Industries (South El Monte, CA, USA,) using a proprietary procedure. The layers were diffusion bonded into a single chip under high pressure and at high temperature. The resultant chip was welded with stainless steel nuts for capillary interfacing at the inlet and outlet holes (**Figure 1**). Brigham Young University's Precision Machining Laboratory used a precision laser welder to ensure leak free seals between the nuts and the stainless steel chip. The column was then thoroughly cleaned using *n*-pentane and methanol. A proprietary surface deactivation of the channel was performed by Silcotek (SilcoNert® 2000) using chemical vapor deposition.

Column coating

The inlet and outlet ends of the microchannel were accessed with 100 μ m i.d. x 240.7 μ m o.d. fused silica capillaries. Stainless steel nuts (3/16 in.) and polyimide ferrules were used to achieve proper sealing. The stationary phase solution contained 0.5% (w/v), 1% vinyl, 5% phenyl, 94% methylpolysiloxane (SE-54) and ~1% dicumyl peroxide (used as crosslinking agent) in *n*-pentane. The coating solution was filtered using a sterile syringe filter (0.2 μ m) before filling the microchannel using a syringe pump (PHD 2000, Harvard Apparatus, Holliston, MA, USA). Once the channel was filled, the end of one capillary lead was sealed with both RTV sealant (732 multi-purpose sealant, Dow Corning, Midland, MI, USA) and a silicone GC septum.

Coating of microchip columns using the static coating method has been difficult in the past because of cavitation at interfaces, adsorption of air on channel surfaces, or

from bubbles present in the coating solution. This was addressed in our previous publication (23) by applying pressure to the column after filling it with coating solution. Specifically, the coating solution was pressurized at 100 psi for 4 h with helium. Next, the open end of the microchip capillary lead was connected to a vacuum pump for static coating and left overnight. During solvent evaporation, the microchip was submersed in a water bath at room temperature to ensure a constant and uniform temperature. Curing of the stationary phase was performed by heating the microcolumn from 40 °C to 275 °C at 2 °C/min and holding at 275 °C for 6 h followed by further conditioning for several h at 375 °C, all while purging with helium gas. The capillaries attached to the ends of the microchips during static coating were replaced with ~25 cm long uncoated fused silica leads at each end. The film thickness of the stationary phase was calculated to be approximately 0.125 µm. Two such columns were prepared for testing.

Results and Discussion

Measurement of column efficiency

The efficiency of the column was determined by chromatographing *n*-tridecane (*n*-C13) in *n*-pentane isothermally at a temperature of 120 °C with a split ratio of 400:1. Golay plots (**Figure S1**) were generated at various velocities to determine the optimum velocity, and the retention factor ($k = 5$) was determined by injecting methane. **Figure S 2** (Supporting Information) shows the *n*-C13 peak obtained from a 1-µL injection. The total number of theoretical plates for the 10 m column (N) was found to be 44,500, which corresponds to ~4,500 plates/m. Any possible leakage was periodically examined at the interface with a commercial leak detector as well as by submerging the chip in water with helium flowing through the channel. The brazed interfacing provided very robust connections that did not leak even after hundreds of injections and temperature program cycles.

Analysis of gasoline headspace by SPME-GC

SPME was carried out by transferring several drops of neat gasoline into a 2-mL glass vial fitted with a septum cap and equilibrated for 5 min at ambient temperature. An SPME holder was used for headspace sampling, with a polydimethylsiloxane stationary

phase coated fiber, which was exposed to the sample headspace for 30 s to extract volatile organic compounds. The fiber was then introduced directly into the injection port of the GC to thermally desorb the analytes, which was equipped with a 10 m x 52 μ m hydraulic diameter (D_h) SE-54 coated stainless steel microchip column. The injector and detector temperatures were held at 250 °C. The split was set at 125:1 with a helium flow of 0.3 mL/min at 40 °C at constant pressure. The oven temperature was raised from 40 °C to 150 °C at 10 °C/min. **Figure 2** shows a chromatogram obtained from headspace analysis of gasoline vapors. Although no effort was made to identify the individual peaks, it is clear from the chromatogram that complex VOC mixtures can be resolved using this stainless steel microchip column.

Liquid injection analysis of kerosene

A 1- μ L volume of neat kerosene (unweathered) in CH_2Cl_2 was injected into the microchip with a 50:1 split. Helium carrier gas at 1 mL/min at 40 °C, and an FID were used. The injector and detector were held at 260 °C and 300 °C, respectively. After injection, the oven temperature was increased at a rate of 15 °C/min from 40 °C to 275 °C and held constant. **Figure 3** shows a chromatogram of the kerosene standard. The abundant *n*-alkane peaks in the chromatogram were identified by chromatographing an *n*-C8 to *n*-C20 mixture using the same programming rate. *Analysis of n-C5 to n-C44 ASTM D2887 standard*

The purpose of analyzing an *n*-C5 to *n*-C44 ASTM 2887 standard using a microfabricated stainless steel column was to illustrate the high temperature applicability of the column, which requires that the GC column reach a temperature of 350 °C. It is worth mentioning that the first report of a similar analysis using microchip GC was by Gaddes et al. (22) in 2014 using a silicon microchip column interfaced to injector and detector using a ferrule-based compression system; the separation showed poor peak shapes, peak tailing and major baseline elevation. A 1- μ L volume of the 20-component mixture was injected using a split of 50:1. The inlet temperature was held at 325 °C and the detector was at 350 °C. The carrier gas was helium at 1 mL/min at 40 °C, and the oven was ramped from 40 °C to 350 °C at a rate of 35 °C/min and held constant. **Figure 4** shows a chromatogram obtained, which clearly demonstrates the

ability of the column to perform at high temperature. The peaks were well separated from each other and there was no baseline drift due to stationary phase degradation, even while holding at 350 °C for a considerable period of time. Due to the limited thermal stability of the stationary phase above 350 °C, the columns were not operated at higher temperatures. The components of the simulated distillation standard are listed in **Table S3** (Supporting Information) according to their retention times (t_r), along with their peak widths at half maximum (w_h) and resolution (R_s).

Conclusions

In this paper, we report the development and demonstration of stainless-steel microchip columns that can operate at high temperatures. Overall, these columns provide a series of advantages over previously reported metal microchip columns. First, they are rugged in nature and suitable for portable applications. Second, brazing of fittings for interfacing proved also to be robust, and provided leak free connections up to a temperature of 350 °C. Finally, with these microchip columns, the upper temperature limit of GC is no longer determined by the column support and interfacing materials, but by the temperature stabilities of the stationary phases and analytes themselves.

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Figure 1. (A) Photograph of a microfabricated stainless steel GC column with attached capillary leads for connecting to injector and detector; (B) SEM image of channel cross section.

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342 Figure 2. Chromatogram of commercial gasoline vapor analyzed by SPME- microchip
343 GC-FID.

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349 Figure 3. Chromatogram of neat kerosene standard obtained using stainless steel
350 microchip column.

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356 Figure 4. Chromatogram of an *n*-alkane standard mixture according to ASTM D2887
357 using a stainless-steel microchip column.

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