Journal of Chromatography A, 1374 (2014) 216–223

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Axial thermal gradients in microchip gas chromatography

Anzi Wang[a], Sampo Hynynen[b], Aaron R. Hawkins[b], Samuel E. Tolley[a,c], H. Dennis Tolley[c], Milton L. Lee[a,*]

[a] Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT 84602, United States
[b] Department of Electrical and Computer Engineering, Brigham Young University, Provo, UT 84602, United States
[c] Department of Statistics, Brigham Young University, Provo, UT 84602, United States

ARTICLE INFO

Article history:
Received 23 September 2014
Received in revised form
12 November 2014
Accepted 13 November 2014
Available online 18 November 2014

Keywords:
Gas chromatography
Microfabrication
Thermal gradient
Peak focusing
Resolution

ABSTRACT

Fabrication technologies for microelectromechanical systems (MEMS) allow miniaturization of conventional benchtop gas chromatography (GC) to portable, palm-sized microfabricated GC (μGC) devices, which are suitable for on-site chemical analysis and remote sensing. The separation performance of μGC systems, however, has not been on par with conventional GC. Column efficiency, peak symmetry and resolution are often compromised by column defects and non-ideal injections. The relatively low performance of μGC devices has impeded their further commercialization and broader application. In this work, the separation performance of μGC columns was improved by incorporating thermal gradient gas chromatography (TGGC). The analysis time was ~20% shorter for TGGC separations compared to conventional temperature-programmed GC (TPGC) when a wide sample band was introduced into the column. Up to 50% reduction in peak tailing was observed for polar analytes, which improved their resolution. The signal-to-noise ratios (S/N) of late-eluting peaks were increased by 3–4 fold. The unique focusing effect of TGGC overcomes many of the previous shortcomings inherent in μGC analyses.

1. Introduction

Although conventional benchtop GC systems are efficient and reliable for routine analysis in the laboratory, their bulky sizes, low heating/cooling rates and high power consumption restrict their use for field analysis. As a result, samples collected for environmental monitoring and biomedical diagnostics are subject to loss, contamination and degradation during transport to the laboratory and storage before analysis [1]. Also, applications that require fast response (e.g., toxic/explosive compound detection) must be performed in the field. To fill the need for small, low-power instruments that can provide rapid analysis of volatile and semivolatile organic compounds (VOCs and SVOCs), researchers have been developing μGC devices based on MEMS [2–6]. By assembling micropreconcentrator/injector, microcolumn and microsensor components into compact, low-cost, battery-operated packages, μGC systems have demonstrated promise for field applications including ambient air monitoring, hazardous materials detection, industrial exposure measurement, food quality analysis, and point-of-care diagnostics.

Despite the potential of μGC systems, their separation performance lags significantly behind conventional GC. Efficiencies of microcolumns range typically from 2500 to 5500 plates per meter [7–10], while commercial narrow-bore fused-silica open tubular columns can achieve over 10,000 plates per meter [11]. The lower efficiency of microcolumns is mostly caused by stationary phase non-uniformity (pooling). Giddings [12] investigated the relationship between surface structure and column performance as early as 1962. Non-uniformities in stationary phase coating due to pooling lead to inefficient columns. It was found that when coating a capillary column, a slight variation in cross-section curvature could result in significant liquid accumulation. Therefore, a uniform circular inner surface is required for producing a uniform stationary phase coating. Conventional fused-silica capillaries are manufactured by melting a raw synthetic silica tube in a high-temperature furnace and drawing it down to capillary tubing of precise dimensions [13]. The nearly perfect round cross-section and low surface roughness allow uniform stationary phase coating with accurately determined thickness. Unfortunately, the ideal column profile is rarely achieved in microfabricated columns. Thicker and less uniform films formed at the corners of rectangular/trapezoidal cross-sections increase the plate heights for μGC separations. While researchers have made progress in fabricating circular cross-sectional columns [14,15] and micropillar array columns [16,17] to

* Corresponding author. Tel.: +1 801 422 2135.
E-mail address: milton_lee@byu.edu (M.L. Lee).

http://dx.doi.org/10.1016/j.chroma.2014.11.035
0021-9673/

yield higher numbers of theoretical plates per meter, the fabrication processes are more complex and difficult.

Because a variety of materials and processes are involved for microcolumn fabrication, surface active sites (i.e., reactive functional groups and trace impurities that are introduced into the column during fabrication) are typically more problematic for microcolumns compared to conventional fused-silica columns. For example, the Pyrex glass used for wafer bonding contains B_2O_3, Na_2O, Al_2O_3, Fe_2O_3, CaO, MgO and Cl in addition to its main SiO_2 composition. These oxides remain on the column surface after fabrication, and obviously interact with certain analytes, which affects their separation. Ceramic-based columns [18,19] create similar problems from their mixed oxide composition. When using metal columns [20], analytes are exposed to the metal surface, which is more reactive than silica. Polymer-based microcolumns [21] often have chemical impurities (e.g., initiators and additives) in the polymer composition; the molding process can also add impurities from surface contact between different substrate/template materials. Another source of active sites is the adhesives used for capillary connection, which can potentially adsorb certain compounds as well as outgas various contaminants. Although little has been reported in the literature concerning the surface characterization of microchip columns, the negative effects of active sites are evidenced by the poor peak symmetry observed in many μGC chromatograms. Interactions between analytes and surface active sites are most common for compounds containing hydroxyl, amine, carboxyl, and sulfur- and phosphorus-containing functionalities [22]. Significant tailing poses problems for identification and quantitation. Complete elimination of active sites (i.e., deactivation) is more difficult and sometimes technically impossible for μGC columns due to the complex surface chemistry on the column walls. In some cases, multi-step deactivation procedures and prolonged pre-conditioning have shown success [9,23]; however, the long preparation times and extra costs are undesirable.

Dead volume concerns are also magnified when using μGC columns. If capillary tubing is used for connections between the injector, column and detector, even a slight mismatch between the tubing and the channel introduces dead volume. Dead volumes at connections interfere with static coating [7,24] as well as create extra band broadening and peak tailing in separations [20,25]. Integration of a microfabricated injector, column and detector on a single wafer can eliminate the use of connecting tubing and fittings, and, thus, reduce the dead volume. In this case, the whole μGC system would have to be replaced, even if only one component failed, since disassembling is not possible with such integrated systems.

In addition to column defects that deteriorate chromatographic efficiency and peak symmetry, the sample injection process also affects the performance of μGC. In field analysis, analytes of interest are often present in water/air/soil at low levels [26] and, therefore, large injection volumes are desired to lower the detection limits. Regardless of injection type (i.e., liquid injection, headspace injection or thermal desorption), a few seconds to several minutes may be needed for the carrier gas to carry most of the sample into the column. Large injection bandwidths require focusing at the front of the column, usually at low temperature, in order to preserve column efficiency and obtain adequate resolution. During the low-temperature part of the temperature program, analytes are trapped in the stationary phase at the beginning of the column and little separation occurs. μGC devices are usually faster than their benchtop counterparts because of the use of resistive heating, low thermal mass, and short column length. Therefore, sample focusing becomes a large percentage of the analysis time and restricts analysis throughput.

Regardless of the different sources and effects of the above mentioned defects/factors, they all result in unwanted band broadening. Theoretically, a negative temperature gradient along the column should mitigate band broadening by focusing the sample bands and separating them from each other at the same time. When a sample band migrates through a negative temperature gradient, the back of the band always resides at a higher temperature and travels faster than the front of the band. Separation occurs simultaneously, as less volatile analytes are slowed down at higher temperatures than volatile ones. This technique is known as TGGC, pioneered by Zhukhovitskii et al. [27] and studied by a number of research groups in the last few decades [28–33]. While the work on TGGC by Liu and Phillips [34] led to the introduction of comprehensive two-dimensional GC (GC × GC), TGGC itself has rarely been implemented in practice. The recent work by Contreras et al. [35,36] explored some unique features of TGGC and pointed out the possibility of improving μGC separation performance by utilizing static and moving thermal gradients.

This paper describes the first use of TGGC on a microfabricated column format. Separations under TGGC and temperature-programmed GC (TPGC) conditions were compared to demonstrate the focusing effect of the thermal gradient and improvements in analysis time, peak symmetry, resolution, and peak capacity.

2. Experimental

2.1. Reagents and standards

Pentane was purchased from EMD Millipore (Billerica, MA, USA); hexanes were purchased from Mallinckrodt Baker (Phillipsburg, NJ, USA); carbon disulfide was purchased from Fisher Scientific (Fair Lawn, NJ, USA); dicumyl peroxide, n-decane, n-undecane, n-dodecane, n-pentadecane, n-nonylamine, n-decylamine, 2-octanol and tributylphosphate were purchased from Sigma–Aldrich (St. Louis, MO, USA); and 2,4,6-trichlorophenol was purchased from Acros Organics (Morris Plains, NJ, USA). Silicone SE-54 (catalog No. 21106) and D3710 test mixture (catalog No. 4-8884) were purchased from Supelco (Bellefonte, PA, USA). The D3710 mixture contained 19 components: n-propane, 2-methylpropane, n-butane, 2-methylbutane, n-pentane, 2-methylpentane, n-hexane, 2,4-dimethylpentane, n-heptane, toluene, n-octane, p-xylene, n-propylbenzene, n-decane, n-butylbenzene, n-dodecane, n-tridecane, n-tetradecane, and n-pentadecane.

2.2. Column fabrication

Through-holes, 400 μm in diameter, were laser-drilled on a 1000-μm thick 4-in. silicon wafer to form the column inlet and outlet. After drilling, the wafer was re-polished using a chemical-mechanical polisher to restore its smooth, particle-free surface. Anisotropic KOH wet etch was used to create two 1.4-m-long and one 2.7-m-long serpentine channels on a single wafer. Briefly, the wafer was (1) heated in a furnace to form a thick layer of thermal oxide on the surface, (2) patterned with AZ P4620 photoresist and AZ 400K developer (AZ Electronic Materials, Branchburg, NJ), (3) etched in HF to remove the exposed oxide layer, (4) cleaned in Nano-Strip (Cyantek, Fremont, CA, USA) to remove residual photoresist, and (5) etched in KOH to form the channel. Fig. 1A shows the trapezoidal cross section of the wet-etched channel, and Fig. 1B displays the serpentine pattern and critical dimensions.

During KOH etching, the surface oxide layer was slowly thinned and became less uniform, especially around the channel. To ensure a uniform layer thickness for the subsequent wafer bonding process, surface oxide was removed by HF after KOH etching. To seal the channel, the etched wafer was bonded to another silicon wafer through fusion bonding. In the absence of commercial wafer bonders, an alternative method was employed to ensure a hermetic