A New Approach to Creating Microfluidic Flow Switching Devices for Complex Capillary GC Applications

James McCurry, Heing He, and Matthew Giardina

Introduction

In 2004 Agilent Technologies introduced the first planar microfluidic device optimized for heat-cutting 2-D capillary gas chromatography. Shortly thereafter, Agilent employed this Capillary Flow Technology (CFT) to create devices for eluent splitting, column selection, back flushing, and flow-modulated GCxGC. Over the last decade these devices have made a significant impact on the practice of modern capillary GC. The planar form factor of CFT is best suited when large, complex flow paths must be etched into the monolithic metal structure, but for the simpler flow paths the excess metal structure supporting the device contributes to thermal mass. Additionally, fabrication involves etching the flow path using chemical, mechanical or laser techniques along with diffusion bonding (solid-state welding). Both etching and diffusion bonding are relatively simple, time consuming, and expensive, and the process yield from fabrication utilizing such techniques is limited. In this paper, we show a new approach to creating microfluidic flow devices where the flow path consists of simple, narrow bore metal tubes and connectors uniquely aligned and welded to side ports in the tubes. The result is a device with less thermal mass and a flow path completely surrounded by the heated air bath. Figure 1 shows a Deans switch made using this design and technique.

Figure 1: A microfluidic Deans Switch constructed from simple thin tubing and capillary GC connectors

Thermal Performance Measurements

Microfluidic flow devices are typically heated in the main oven air bath along with the capillary columns. To maintain optimal performance, any device should respond to oven temperature changes in a similar way to the columns. Cortez and Shellie suggested a device’s thermal performance is a function of mass, with lower mass devices exhibiting superior performance. However, they did not offer any measurements or data to support this conjecture.

For this work, we tested the thermal performance of the new Thin Tube based device along with two microchannel planar devices, Agilent CFT (thin plate) and SilFlow™ (thick disk). Each device is shown in Figure 2 along with their mass. The devices’ thermal response during temperature programming was measured in two ways. First, a single K-type thermocouple was threaded into the interior flow paths. This allowed us to directly measure the temperatures inside the device flow path as the column oven temperature changes. Next, we performed a chromatographic separation of polyaromatic hydrocarbons (PAH) with each device installed at the outlet of the column flow path. Any thermal lag between the column and the flow device would manifest as tailing in the PAH peak shape.

Figure 2: Three microfluidic Deans switch devices and their respective masses

Internal Temperature Measurements

Each device was installed separately in an Agilent 7890 Series GC. Device mounting location was on the center of the left oven wall using the same placement mounts. The K-type thermocouple was threaded into a 3 cm piece of 0.32 mm i.d. underivatized fused silica tubing and then inserted into the devices’ flow path using the supplied ferrules and nuts. Open ports were sealed using the supplied plugs and 3 mL/min of helium flowed through the devices. The main column oven was held at 40 °C for 0.3 min., ramped at 30 °C/min. to 210 °C, held for 0.3 min., ramped at 15 °C/min. to 325 °C and held for 0.3 min.

Figure 3 shows the difference in the column oven temperature and the devices’ internal temperatures. The K-type thermocouple had a small offset of a few degrees compared to the main oven’s ceramic thermocouple (black trace). The new Thin Tube design showed the smallest temperature lag of 10 to 15 °C. The Thin Plate had the larger lag of 15 to 23 °C while the Thick Disk exhibited the largest lag of 16 to 24 °C.

PAH Peak Tailing Measurements

The effects of thermally induced peak tailing were measured using a mixture of 16 PAHs. The PAH sample was first run on a DB-5ms column without any Deans switch device in order to establish a reference peak shape and tailing factor. The chromatography for the PAH Mix is shown in Figure 4.

The outlet of a DB-5ms column was then installed into each Deans switch device (Figure 5). In this configuration, each chromatographically separated PAH passes from the column outlet and then through the Deans switch flow path where significant thermal lag could cause peak tailing.

Figure 4: A soil sample contaminated with petroleum hydrocarbons was prepared using the protocol described in ISO 16703. This preparation removes any PAHs in the sample extract. Prior to MDGC analysis, the TPH extract spiked with 2.5 µg/mL of each PAH listed in Figure 4. Using the GC conditions from Figure 8 and the two multiple heart analysis methods (Figure 9), the spiked TPH sample was analyzed for individual PAHs (Figure 10). Recoveries for each PAH were between 2.4 and 2.7 µg/mL.

Conclusions

- A small, light microfluidic switching Deans switch was successfully made using thin, inert metal tubing.
- The thin tube Deans switch showed better temperature performance when compared to microchannel planar devices.
- The Thin Tube Deans switch design was successfully used to heat-cut multiple PAH samples from a TPH soil extract.

Figure 5: The USP Tailing Factor calculation is shown in Figure 6. The tailing factors calculated for three PAH peaks are shown in Figure 7. Each device did induced some thermal peak tailing (T > 1), however, these effects were small.

<table>
<thead>
<tr>
<th>Device Type</th>
<th>Mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thin Tube</td>
<td>3.6</td>
</tr>
<tr>
<td>Thin Plate</td>
<td>7.2</td>
</tr>
<tr>
<td>Thick Disk</td>
<td>11.0</td>
</tr>
</tbody>
</table>


Figure 6: The tailing factors calculated for three PAH peaks are shown in Figure 7. Each device did induced some thermal peak tailing (T > 1), however, these effects were small.

Figure 7: The USP Tailing Factor calculation is shown in Figure 6.