Headspace gas chromatography (HS-GC) is a well-established method of chemical analysis. Agilent has a portfolio of HS instrumentation that makes use of a six-port gas sampling valve and a headspace sample loop. Work is described here that has focused on engineering control of the pneumatic and timing systems and developing standard operating procedures that improve the pneumatic and temporal control of Agilent’s products. The result of this work was the development of new headspace instrumentation (Agilent P/N 7697A). Results from the new instruments show industry leading performance for HS-GC applications.

**Introduction**

HS-GC selectively samples the volatile components of a complex matrix thereby providing the ability to analyze for compounds of interest with little to no sample preparation. The minimal sample preparation inherent to HS-GC has led to the implementation of the technique in a myriad of uses ranging from forensic applications to environmental monitoring. HS-GC offers the ability to perform not only qualitative analyses but also to provide quantitative information. The quality of the quantitative results is based on the instrumental ability to provide accurate and precise measurements. The precision of the quantitative results is based on the instrumental ability to provide accurate and precise measurements.

**Experimental**

Instrumentation

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Advanced Pneumatic Control for Headspace Gas Chromatography

111-vial capacity 7697A headspace sampler

Figure 1: Headspace pneumatic system

The control system provides the user with the ability to operate the headspace sampler with either active or passive backpressure regulation of the vent path. Experiments were performed under both conditions to evaluate system performance.

Several application-specific experiments have been conducted to demonstrate the benefits of advanced pneumatic control. These experiments were performed on samples of representative standards of concentrations in a water matrix and analyzed to evaluate system linearity, carryover, precision, and detection limit.

**Results and Discussion**

For HS-GC to provide accurate and precise results the pressure conditions at which the sample vials and the instrument control tubing must be controlled exactly. Incorporating Agilent’s Advanced Pneumatic Control into the design of the 7697A control systems resulted in accurate control of gas flows and pressure as well as valve timing. Figure 2 demonstrates the accuracy and precision by overlaying the pressure traces associated with 100 consecutive HS vials sampled using advanced pneumatic control.

Figure 3 illustrates the differences between operating the pneumatic system in active versus passive mode.

A common forensic application for HS-GC is the detection and quantification of ethanol in blood and urine. Figure 4 contains representative chromatograms of a mixture containing ethanol and other standards in water using a DB-ALC1 column.

Using a 7697 with optimized parameters, analytic peak areas obtained from Agilent 7697A GC equipped with flame ionization detectors (FID) were acquired with area precision of ≤0.5% RSD. Table 1 compares the performance of the 7697, using active backpressure control, with existing systems operated in passive backpressure control and a competitor’s HS-GC system.

The pressures, flows, and valve timing of existing Agilent headspace systems is ≤10% thereby making the units less amenable to application oriented work. Units operated under typical conditions contained the greatest potential for improving overall instrument performance. An on-board pneumatic system that has the ability to perform active or passive backpressure regulation was designed and implemented. Figure 1 contains a representative of the pneumatic scheme. The results contained of new hardware (e.g., solenoid and proportional valves) and electronic circuitry (i.e., electronic pneumatic control, EPC modules).

Figure 2: EPC control of vial pressurization and sample loop filling

In Figure 2, the headspace vial was pressured to 16psi (gage) by having PV2 (see Figure 1) closed and PV1 being controlled to the pressure sensor and/or the flow sensor (gauge). The pressures were controlled from the pneumatic control and instrument timing that could improve the precision and accuracy of Agilent’s HS-GC instrumentation.

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Figure 3: Active versus passive control of sample loop filling

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**Figure 4: Dual column separation using 7697 HS**

The linearity demonstrated in Figure 5 is also readily achievable using a DB-ALC1 column. Solution concentrations of 0.001%, 0.01%, 0.1%, 0.2%, and 0.5% are represented in Figure 5. The area precision achievable at each concentration level in Figure 5 is in agreement with the values represented in Table 1. Analyses performed at the 0.001% level demonstrated signal-to-noise ratios of >100.

**Table 1: Performance comparison of headspace pneumatic technologies (n = 24 per instrument)**

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Active Area (pA*)</th>
<th>Passive Area (pA*)</th>
<th>Area Precision</th>
<th>Area Passive Area as % of Active Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>203.65</td>
<td>251.93</td>
<td>25%</td>
<td>70.38%</td>
</tr>
<tr>
<td>n-Propanol</td>
<td>701.04</td>
<td>458.82</td>
<td>25%</td>
<td>65.45%</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>1428.57</td>
<td>919.82</td>
<td>25%</td>
<td>64.76%</td>
</tr>
<tr>
<td>1-Octanol</td>
<td>3705.85</td>
<td>2427.53</td>
<td>25%</td>
<td>65.39%</td>
</tr>
<tr>
<td>Butanol</td>
<td>127.34</td>
<td>91.98</td>
<td>25%</td>
<td>72.07%</td>
</tr>
</tbody>
</table>

**Conclusions**

Active backpressure control using modified Agilent EPC technology allows industry leading performance in peak area precision and area response in static headspace analyses using a conventional valve and loop sampling system. For HS-GC, the 7697A sampler has shown to provide excellent robustness and repeatable precision and provides the user the ability to tailor their analyses by using either active or passive backpressure control or adjusting the user-selectable backpressure parameters.

**References**