Advanced Pneumatic Control for Headspace Gas Chromatography

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Summary

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 fixed volume sample loop. Work is described here that has focused on engineering solutions 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 PN: 7697A). Results from the new instruments show industry leading performance in HS-GC applications.

Introduction

HS-GC selectively samples the volatile components of a complicated matrix thereby providing the ability to analyze 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 data. It was the purpose of this work to identify areas in the pneumatic control and instrument timing that could improve the precision and accuracy of Agilent's HS-GC instrumentation.

111-vial capacity 7697A headspace sampler connected to a 7890GC

Experimental

The pressures, flows, and valve timing of existing Agilent headspace units (i.e., G1888 units) were monitored while the units were operated under typical conditions representing a variety of user applications. From these measurements it was determined that the pneumatic and temporal control associated with the loop filling process 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 representation of the pneumatic scheme. The modules consisted of new hardware (e.g., solenoid and proportional valves) and pneumatic circuitry (i.e., electronic pneumatic control, EPC, modules).

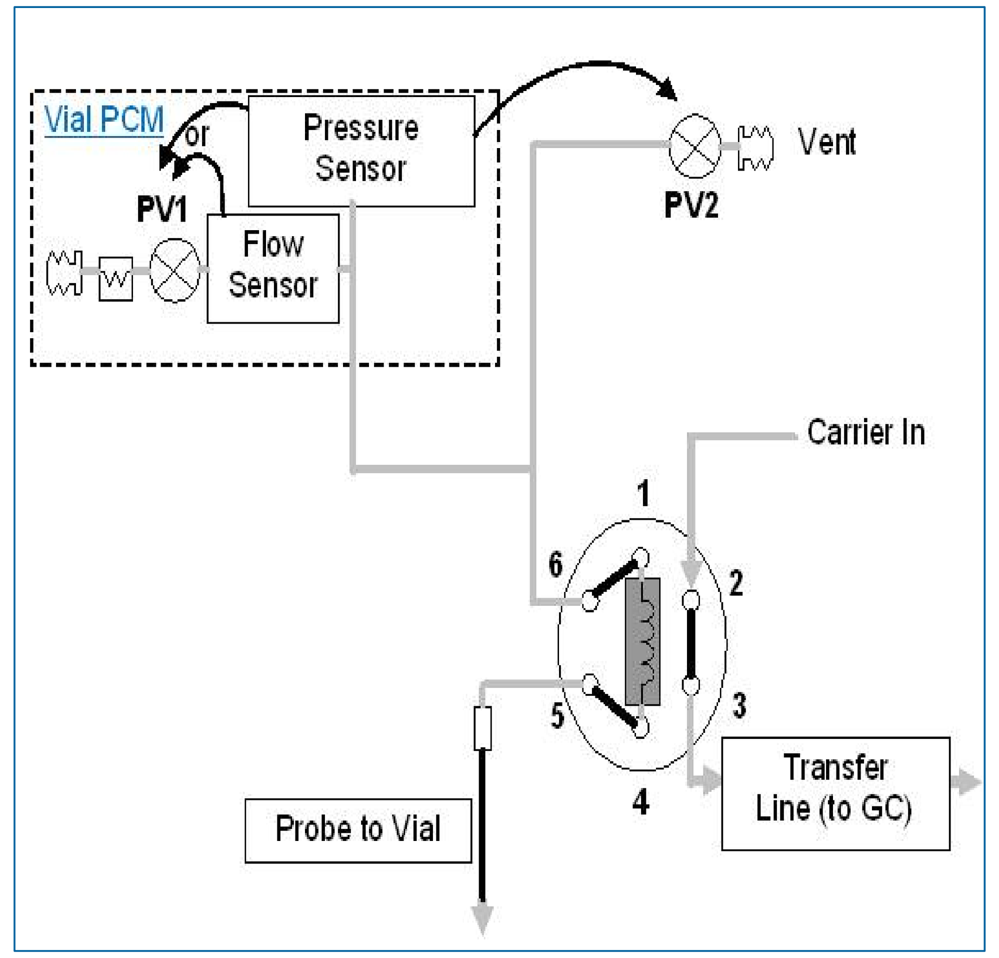


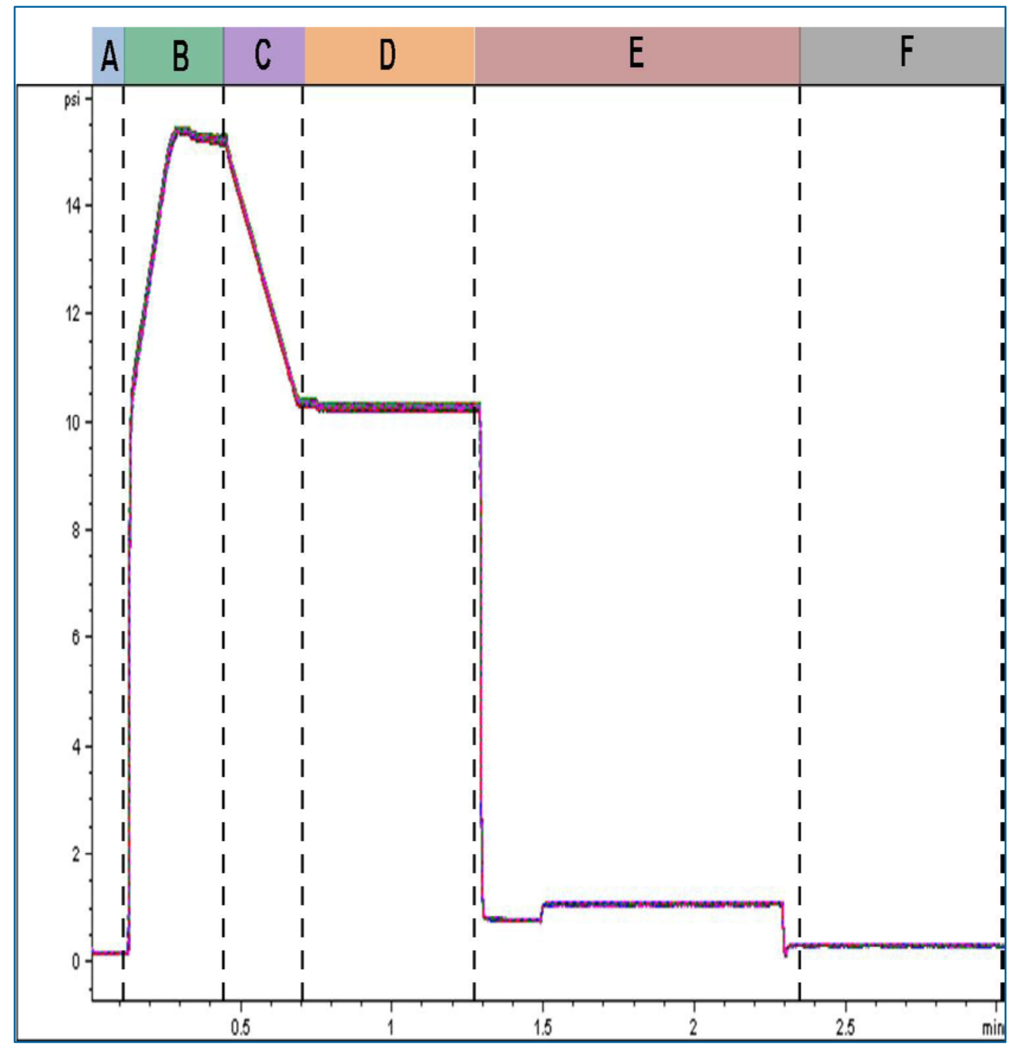
Figure 1: Headspace pneumatic system

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 verify system operation. Reported here are the results from tests targeted at blood alcohol applications. Standards were prepared at different concentrations in a water matrix and analyzed to evaluate system linearity, carryover, area precision, and detection limit.

Results and Discussion

For HS-GC to provide accurate and precise results the pressures associated with the sample vials and the instrument control timing must be controlled exactly.[1] Incorporating Agilent's proven EPC technology into the design of the 7697A control systems resulted in accurate control of gas flows and pressures as well as valve timing. Figure 2 demonstrates this accuracy and precision by overlaying the pressure traces associated with 100 consecutive HS vials sampled using advanced pneumatic control.

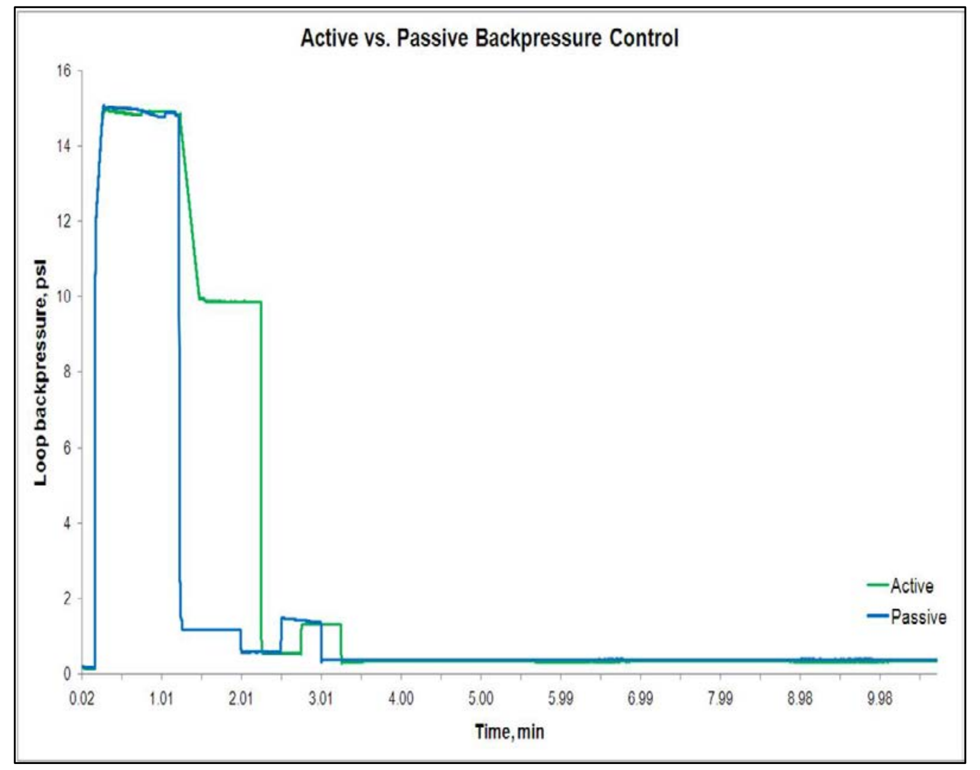


A = End of oven equilibration
B = Vial pressurization
C = Loop filling
D = Six port injection
E = Recovery period
F = Start of standby

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

In Figure 2, the headspace vial was pressurized to 15psi (gauge) by having PV2 (see Figure 1) closed and PV1 being controlled by the pressure sensor and/or the flow sensor. Using the pneumatic system in Figure 1, sample is transferred from the pressurized vial to the sample loop by converting the system from forward pressure regulated (pressure controlled by PV1) to backpressure regulated (pressure controlled by PV2 in the vent path). The amount of sample in the sample loop, and ultimately what is injected to the GC, is proportional to the pressure in the loop (Ideal gas law), so by actively controlling the backpressure to a pressure above ambient, this EPC system is able to provide a sample of both higher concentration and precision than a passive system.

Figure 3 illustrates the difference between operating the pneumatic system in active versus passive modes.



Analyte	Active Area (pA*s)	Passive Area (pA*s)	Passive Area as % of Active Area
Ethanol	357.98	251.93	70.38
n-Propanol	701.04	458.82	65.45

Figure 3: Active versus passive control of sample loop filling

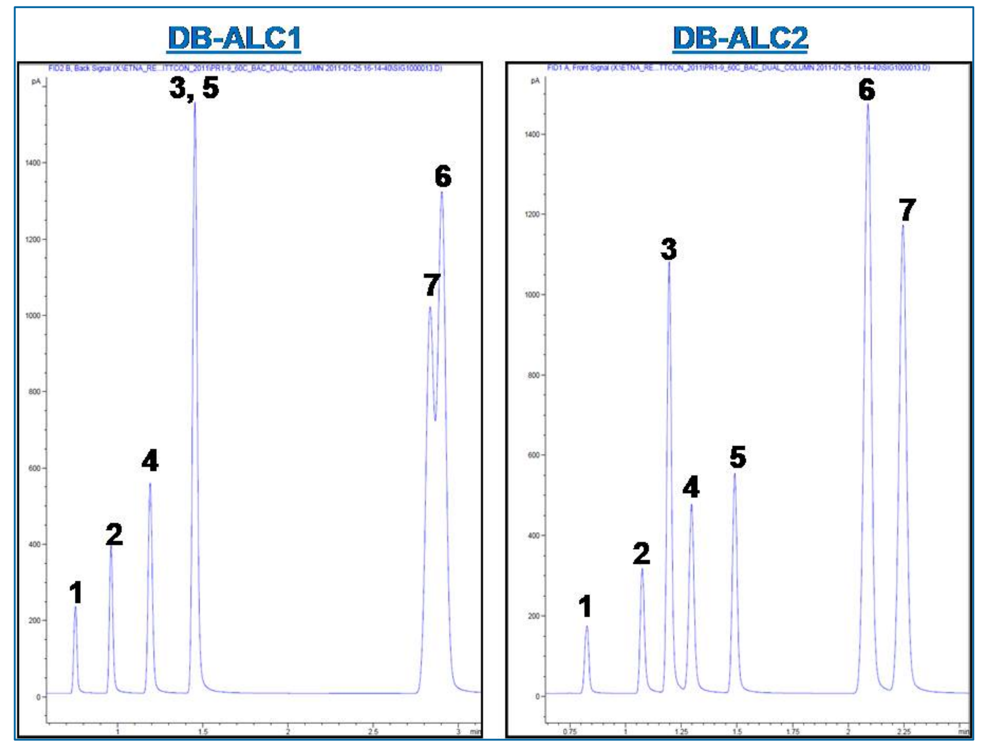
Using a 7697 with optimized parameters, analyte peak areas obtained from Agilent 7890 GCs equipped with flame ionization detectors (FID) were acquired with area precision of ≤1% RSD. Table 1 compares the performance of the 7697, using active backpressure control, with existing systems operated in passive backpressure control and a competitor's HS-GC system.

Pneumatic System	Ethanol Area Precision, %RSD	Acetone Area Precision, %RSD	n-Propanol Area Precision, %RSD
Existing G1888	2.87	1.10	2.36
Competitor	0.82	0.86	0.88
7697A	0.60	0.49	0.56

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

Results and Discussion

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 7697HS-GC system.



GC:
Oven: 35C isothermal
Inlet: Split/splitless, 5:1 split at 200C

Column I: DB-ALC1
(30m x 0.32mm x 1.8μm)
Column II: DB-ALC2
(30m x 0.32mm x 1.2μm)

7697 Headspace:
Oven: 60C
Vial equilibration: 15min at shaking of 1

Sample: 0.05% ea. vol/vol
1. Methanol
2. Ethanol
3. Acetone
4. Isopropanol
5. Acetonitrile
6. Ethyl acetate
7. MEK

Figure 4: Dual column separation using a 7697 HS

Using the same sample as in Figure 4, six different concentrations were used to evaluate the system linearity. The concentrations ranging from 0.005% to 0.5% are representative of levels used in various state crime labs for quantitative sample analysis. The resulting calibration curve is given in Figure 5.

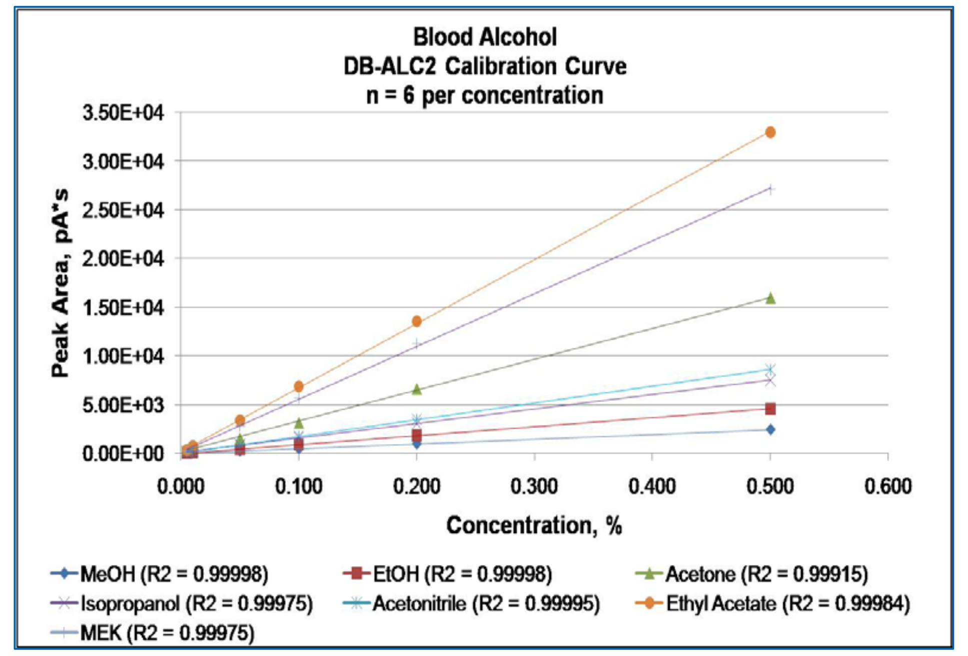


Figure 5: Calibration curve demonstrating linearity of 7697 HS

The linearity demonstrated in Figure 5 is also readily achievable using a DB-ALC1 column. Solution concentrations of 0.005%, 0.01%, 0.05%, 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.

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 The new 7697 sampler has shown to provide excellent linearity and robust operation and provides the user the ability to tailor their analyses by using either passive backpressure control or adjusting the user-settable active backpressure parameters.

References
[1]Kolb, B. and Ettre, L.S. Static Headspace-Gas Chromatography: Theory and Practice 2nd ed., Wiley & Sons, NJ, 2006.