Thermal Zone Considerations for the Agilent 7697A Headspace Sampler

White Paper

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Executive summary

- Mechanical design of the Agilent 7697A headspace sampler removes the need to operate the oven and loop zones at different temperatures.
- The best peak area precision from the 7697A headspace sampler is observed when the oven and loop zones are operated at the same temperature.

Article

Headspace (HS) sampling is a popular technique for the analysis of volatile components that are contained within a nonvolatile, condensed phase matrix. Heating the matrix increases the vapor pressure of volatile analytes in the vial's headspace thus providing a more sensitive analysis. Once the concentration of analytes has reached a thermodynamic equilibrium between the condensed phase and the vial's headspace, an aliquot of the headspace is injected into a gas chromatograph (GC) for subsequent analysis.

A detailed discussion regarding the theory of headspace gas chromatography has been provided by Kolb and Ettre [1] and is beyond the scope of this article. However, the fundamental equation that describes the technique is pertinent and is given in Equation 1 where it is assumed that a thermal equilibrium has been established between the condensed phase and the vial's headspace:

$$A \propto C_{HS} = \frac{C_{sample}}{K + \beta} \qquad (1)$$

According to Equation 1, the area (A) observed following a chromatographic run is directly proportional to the concentration of sample in the vial's headspace (C_{HS}). Equation 1 shows that the area is directly related to the analyte concentration in the condensed phase (C_{sample}), and inversely related to the sum of the partition coefficient (K) and the phase ratio (β). The phase ratio is the ratio of vial headspace volume to condensed phase sample volume and the partition coefficient is the equilibrium constant that describes the distribution of analytes between the headspace and condensed phases.

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Equation 1 shows that K and β must be precisely controlled to precisely analyze a sample. Assuming a constant volume of sample is deposited into each headspace vial to be analyzed, the phase ratio can be taken as constant. With the phase ratio held constant, the precision of repeatedly analyzing the same sample that has been distributed into multiple headspace vials is dependent upon how precisely the partition coefficient remains the same. Since K describes a thermodynamic process, the precision of K will depend on how precisely the sample's thermal environment is controlled.

The 7697A valve and loop headspace sampler is the latest in the Agilent portfolio for static headspace analyses. The 7697A unit leverages technology from previous products that have made Agilent a leader in gas phase chemical analysis such as electronic pneumatic control (EPC) technology and the accurate control of thermal zones. Similar to other valve and loop systems, the 7697A consists of a heated oven where the vial is allowed to thermally equilibrate, a heated loop zone where the vial is pressurized and sampled, and a heated transfer line that serves as the conduit through which the sample will pass from the HS to the GC. While these three heated zones can be controlled independently, it is recommended that in the 7697A, the oven and loop zones be set to the same temperature. Considering the earlier discussion regarding the need to precisely control a vial's thermal environment, it is deleterious to operate the oven and loop zones at different temperatures.

In operating the 7697A, a vial containing sample is thermally equilibrated in the oven for the requisite amount of time. The length of time needed to reach a thermodynamic equilibrium between the vial's headspace and the sample's condensed phase depends on the sample type, the sample volume, the ability to agitate the vial, and the temperature at which the equilibrium must be established. Figure 1 shows the area response, normalized to the area acquired with a vial equilibration time of 5 minutes, as a function of vial equilibration time where 1.5 mL of aqueous sample was added to 20 mL vials. For the results in Figure 1, the HS oven was set to 60 °C, the loop zone was also set to 60 °C, and the transfer line was set to 100 °C and the vials entered the oven at room temperature, 22 °C. The data in Figure 1 clearly shows that a thermodynamic equilibrium was not reached until the vial had been in the HS oven for 15 minutes. Using a vial equilibration time less than 15 minutes would create the scenario where the vial's headspace contents are sampled before equilibrium had been established which would lead to imprecise data.

Another part of experimental space that would lead to imprecise data on the 7697A is when the unit's oven and loop zones are operated at different temperatures. In the 7697A design, the vial is thermally equilibrated in the HS oven for a requisite amount of time then the vial is physically moved to the loop zone for sampling. A thermodynamic equilibrium is established within the vial while the vial is in the HS oven; to maintain that equilibrium the vial's temperature must remain constant. If the loop zone of the 7697A HS oven is set to the same temperature as the oven then the vial's equilibrium is maintained. However, if the loop zone is set at a different, higher temperature than the oven then the vial would need to reside in the loop zone for the necessary length of time to reestablish the new equilibrium. Under default conditions, the 7697A HS sampler has the vial in the loop zone for less than 1 minute before sampling its contents. As seen in Figure 1, if the temperature difference between the loop zone and oven is great enough, several minutes may be required to reestablish equilibrium.

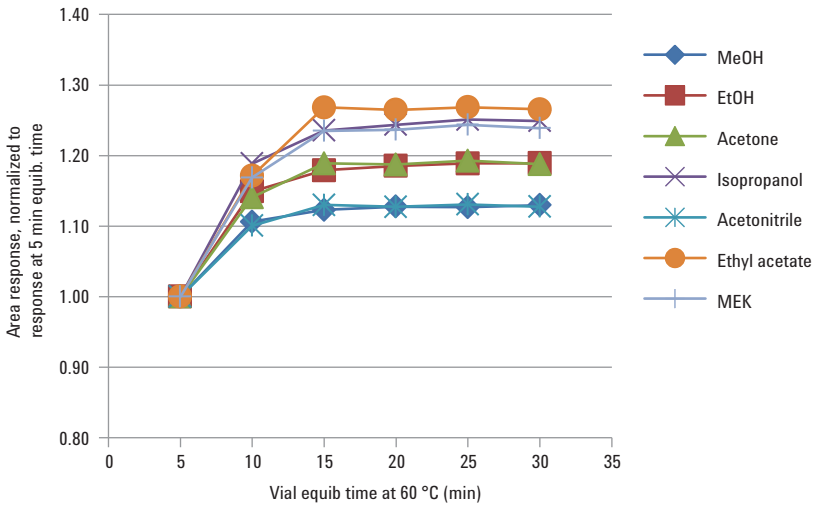

Figure 1. Area response dependence on vial equilibration time.

To demonstrate the impact of operating the oven and loop zones of the Agilent 7697A headspace sampler at different temperatures, a series of experiments were run using a blood alcohol resolution check standard. One milliliter of sample was added to each 20 mL headspace vial, the headspace oven was at 60 °C, the transfer line temperature was at 100 °C, the vial equilibration time in the HS oven was 15 minutes with a shaking level of 1, and the loop zone temperature was changed from 60 °C to 120 °C in increments of 10 °C. The area precision for each analyte under each thermal condition was determined and the results are given in Figure 2.

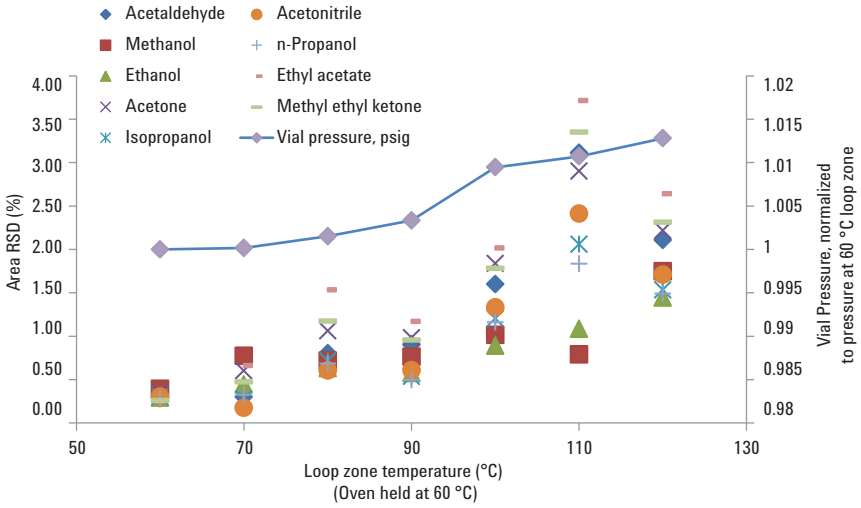

Figure 2. Area precision dependence on loop zone—oven temperature difference.

In Figure 2, replicate measurements were made at each thermal condition. The results in Figure 2 clearly show that the best area precision was achieved when the oven and loop zones were at the same temperature, 60 °C. As the temperature differential between the oven and loop zones increased the spread in area precision increased as did the %RSD. Also shown in Figure 2 is the vial pressure that was achieved under each condition before the start of the loop filling process. The plot shows that as the loop zone temperature increased so too did the recorded pressure. In fact, at loop temperatures greater than 80 °C the vial pressure was above set point and thus was no longer controlled by the system. In addition to the pressure increasing there was a concomitant 15% decrease in peak areas observed for all analytes; data not shown.

1. Kolb, B. and L.S. Ettre, *Static Headspace-Gas Chromatography: Theory and Practice*. Second ed. **2006**, Hoboken, New Jersey: John Wiley & Sons, Inc. 349.

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