Application Note

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Influence of Sample Pressure on Response when Using the Agilent 990 Micro GC

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Abstract

The Agilent 990 Micro gas chromatography system thrives on its fast analysis speed, accurate results, and small volume in several industries. The external standard method is one of its most used quantitative methods. Consistency of response is challenged by variation of sample pressure. In this application note, the influence of sample pressure on response and retention time was studied in a simulated natural gas analysis setup. The maximum relative standard deviation of both the average retention time and response under six sample pressures ranging from 10-100 kPa were observed to be less than 0.10%, demonstrating the minimal impact of sample pressure on response on a functioning 990 Micro GC. Troubleshooting suggestions are also included as part of this study.

Introduction

The external standard method is a commonly used quantitative technique, especially for automated analysis (an area of expertise for the Agilent 990 Micro gas chromatography system). It involves analyzing standards of various concentrations to establish a calibration curve, from which the concentration of the target analyte can be calculated. This method enables quantitative analysis with simple operation without a requirement for determining correction factors.

When using an external standard method to measure the concentration of components, the stability of the chromatographic response is one of the most important parameters that determine the accuracy of the measurement results.

By unifying the sample pressure in the sample loop before pressurization through the equilibration process, the consistency of sample composition and pressure, as well as the hardware environment related to injection, is ensured on the 990 Micro GC.[1] In principle, the response of sample components on a properly functioning instrument is independent of sample pressure.

The purpose of this application note is to quantify the actual effect of sample pressure on the response of the 990 Micro GC under normal conditions, and to analyze the possible causes for the observed influence of sample pressure on response encountered in practice.

Taking natural gas analysis as an example, two analytical channels of the 990 Micro GC were used, namely 40 cm HayeSep A (HSA) and 8 m CP-Sil 5CB (5CB). HayeSep A enables the separation of O_2/N_2, CH_4, CO_2, and C_2H_6, while 5CB enables the separation of alkanes.[2]

Experimental

The 990 Micro GC was equipped with a 40 cm HayeSep A straight channel, and an 8 m CP-Sil 5CB straight channel. Table 1 shows the experimental conditions for the analysis. Standard gas was purchased from Air Liquide Inc. The composition is shown in Table 2.

Table 1. Experimental conditions for natural gas analysis using the Agilent 990 Micro gas chromatography system.

	Channel Type	
	40 cm HayeSep A, Straight	**8 m CP-Sil 5CB, Straight**
Carrier Gas	Helium	Helium
Column Pressure	260 kPa	175 kPa
Injector Temperature	60 °C	70 °C
Column Temperature	60 °C	70 °C
Injection Time	40 ms	40 ms
Sample Time	30 s	30 s

Table 2. Composition of the standard gas.

Component	Concentration (%)
O_2	0.473
N_2	4.03
CH_4	88.5
CO_2	1.51
C_2H_6	3.98
C_3H_8	1.01
i-C_4H_{10}	0.197
n-C_4H_{10}	0.196
i-C_5H_{12}	0.0472
n-C_5H_{12}	0.0487

The sample pressure is regulated by a pressure reducing valve (Air Liquide FMD32014 BCF1.5 W21.8RHF CL1/8), and the actual pressure is monitored with a pressure gauge (Supmea SUP-P300, -100 kPa to 100 kPa) to ensure that it remains close to the set value. Since the allowable sample pressure is 0 to 100 kpa, six pressure points are selected for testing to simulate the extreme pressure changes that may occur during analysis. Figure 1 shows the pressure variation at the front end of the sample connector (G3588-67018) as a function of analysis time (only pressure data during the analysis period are retained for data readability). Cyclic, rather than unidirectional pressure experiments were adopted here to evaluate the influence of the pressure rampup and rampdown process, and to clarify the effect of time factors through the A-B-A experiment. Due to the use of pump, the recorded pressure decreases during sampling, resulting in a characteristic comb-shaped pressure pattern.

To minimize the potential effect of negative pressure leakage in the external sample line on the response (the influence of external leakage on response is not the subject of this study), the minimum stable pressure was set to approximately 14 kPa (still labeled as 10 kPa). This ensures positive sample pressure (close to 0 kPa during sampling) at the sample connector. Twenty injections are conducted at each sample pressure, and the last ten injections are used for calculation in this application note.

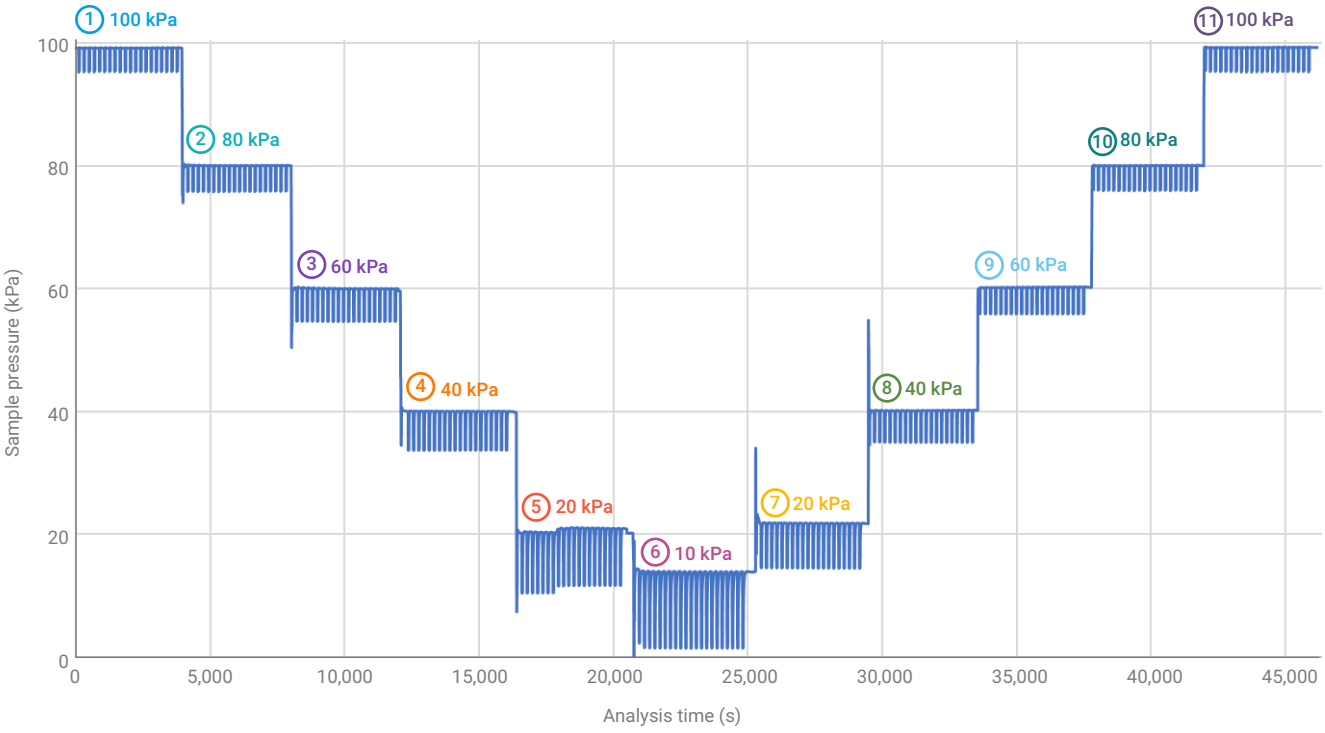

Figure 1. Sample pressure at sample connector in this analysis.

Results and discussion

The analysis results of simulated natural gas at different sample pressures are as follows. The chromatograms are stacked through response offset. The serial numbers next to the stacked chromatograms indicate the experimental sequence. Figure 2A shows the chromatogram of standard gas on the 40 cm HayeSep A straight channel. O_2/N_2, CH_4, CO_2, and C_2H_6 were resolved. On the 8 m CP-Sil 5CB straight channel, C_3H_8, i-C_4H_{10}, n-C_4H_{10}, i-C_5H_{12}, and n-C_5H_{12} were separated as shown in Figure 2B. As can be seen from the figure, the peak retention times and responses of each component are nearly identical at different sample pressures.

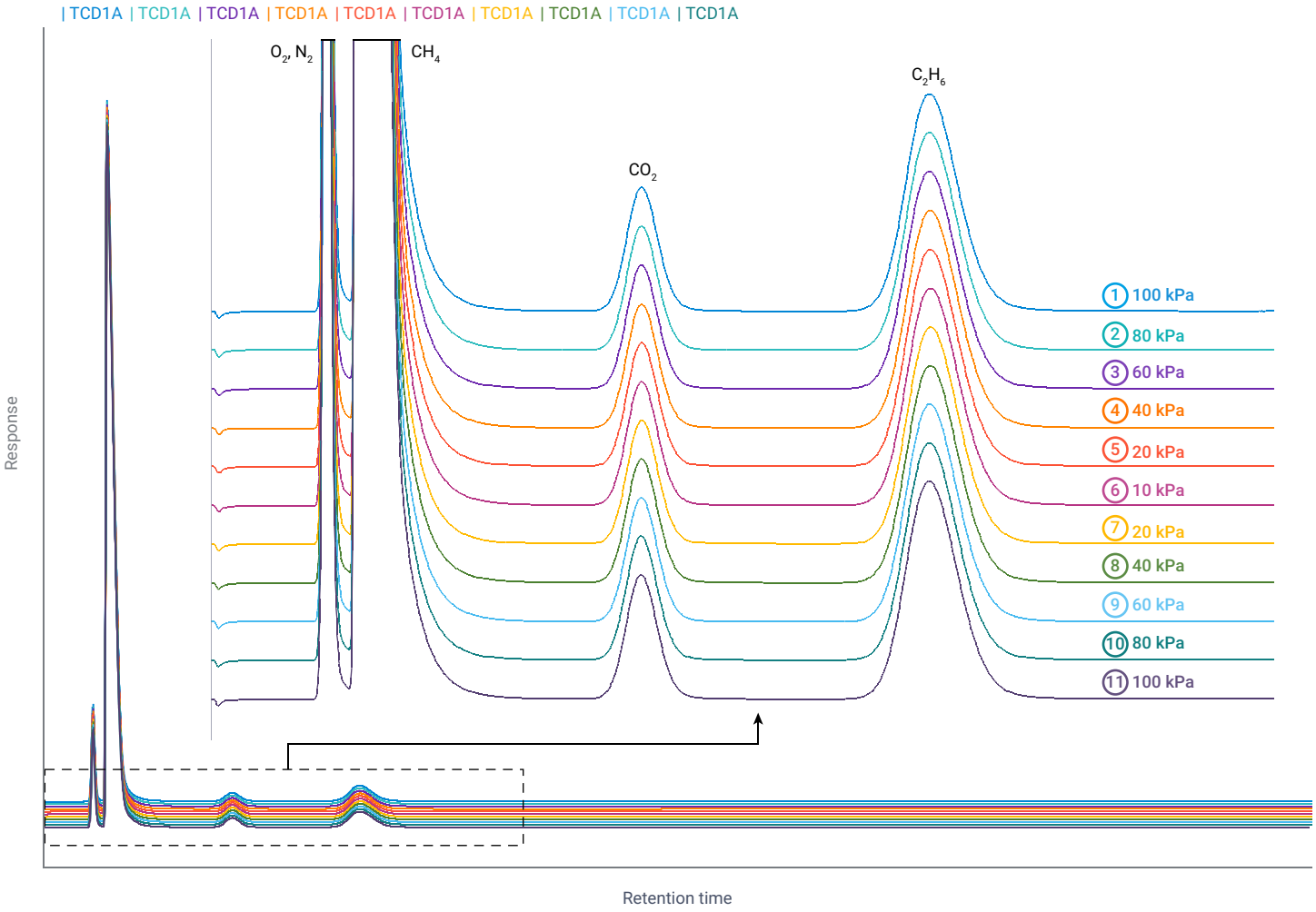

Figure 2A. Chromatogram of standard gas on the 40 cm HayeSep A straight channel at different sample pressures.

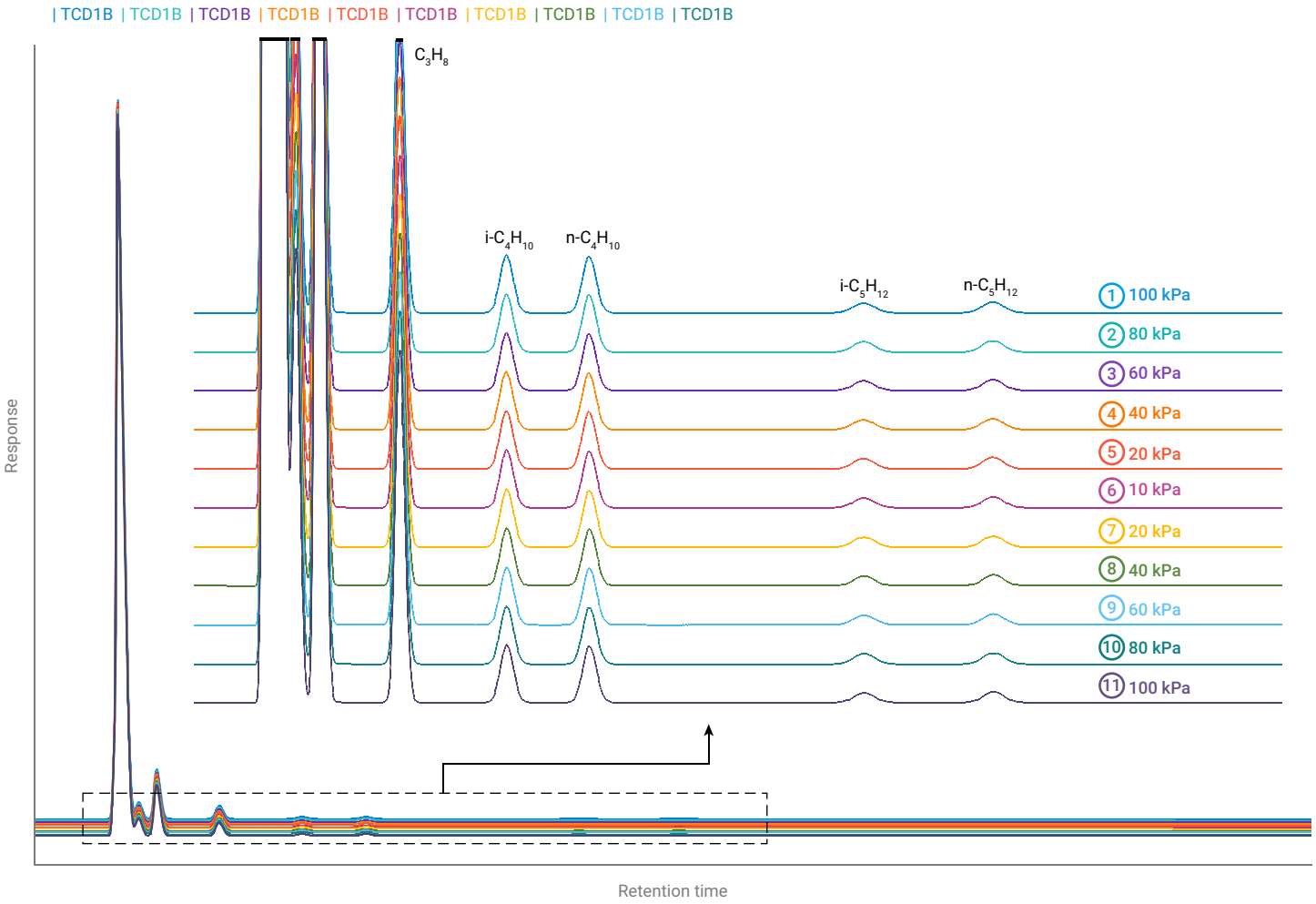

Figure 2B. Chromatogram of standard gas on the 8 m CP-Sil 5CB straight channel at different sample pressures.

Table 3 shows the chemical performance for a sequence of 10 runs of the standard gas at different sample pressures in the form of numerical values. As there are 11 sets of data results, the table lists the value range (minimum to maximum) for each item, rather than individual data points. The largest retention time (RT) and area relative standard deviation (RSD) among all sample pressures are less than 0.10% and 0.050%, respectively. These low RSD values demonstrate the ability of the 990 Micro GC to provide quantitative results with a high level of confidence, repeatability, and quality, at least when the sample pressure is constant.

Table 4 shows the calculated gross heating value (HV) in different experimental steps along with their RSDs, which are all below 0.0020%. The RSD of average HVs is 0.0011%, which is a very small number, indicating that the effect of sample pressure on heating value is negligible.

Table 3. Retention time, area, and repeatability ranges for 10 injections of standard gas during the entire experimental process of sample pressure variation.

Component	Concentration (%)	RT (min)	RT RSD (%)	Area (mV × s)	Area RSD (%)	Analysis Channel
O_2 and N_2	4.51	0.0585–0.0586	0.016–0.099	27.940–28.003	0.022–0.041	40 cm HayeSep A, straight
CH_4	88.5	0.0755–0.0756	0.0088–0.046	466.432–467.539	0.012–0.040	40 cm HayeSep A, straight
CO_2	1.51	0.217–0.217	0.0061–0.022	11.219–11.250	0.0053–0.017	40 cm HayeSep A, straight
C_2H_6	3.98	0.362–0.363	0.0065–0.016	32.800–32.876	0.0046–0.016	40 cm HayeSep A, straight
C_3H_8	1.01	0.359–0.359	0.0021–0.050	14.100–14.134	0.0043–0.054	8 m CP-Sil 5CB, straight
i-C_4H_{10}	0.197	0.419–0.419	0.0020–0.032	3.217–3.225	0.0040–0.033	8 m CP-Sil 5CB, straight
n-C_4H_{10}	0.196	0.466–0.466	0.0018–0.027	3.293–3.299	0.0037–0.037	8 m CP-Sil 5CB, straight
i-C_5H_{12}	0.0472	0.620–0.620	0.0015–0.035	0.885–0.886	0.0032–0.037	8 m CP-Sil 5CB, straight
n-C_5H_{12}	0.0487	0.693–0.693	0.0013–0.016	0.984–0.987	0.0032–0.046	8 m CP-Sil 5CB, straight

Table 4. Calculated gross heating value (HV) and repeatability from the measurement results of the standard gas (theoretical HV = 887.831 kJ/mol).

Experimental Step	HV RSD (%) of 10 Injections Under Corresponding Sample Pressure	Average HV of 10 Injections Under Corresponding Sample Pressure (kJ/mol)
(1) 100 kPa	0.0012	887.826
(2) 80 kPa	0.0018	887.815
(3) 60 kPa	0.0016	887.815
(4) 40 kPa	0.0011	887.826
(5) 20 kPa	0.0014	887.832
(6) 10 kPa	0.0010	887.831
(7) 20 kPa	0.0013	887.846
(8) 40 kPa	0.0011	887.838
(9) 60 kPa	0.0013	887.834
(10) 80 kPa	0.0018	887.838
(11) 100 kPa	0.0014	887.825
Average HV at Different Sample Pressures (kJ/mol)		887.830
RSD (%) of Average HVs at Different Sample Pressures		0.0011

Figure 3 shows the variation of the relative response of each component with sample pressure. The maximum deviation of the average response for each component under different sample pressures is less than 0.30%, and the maximum relative standard deviation is less than 0.10%. These indicate that the response of each component is almost unaffected by the sample pressure.

The whole experiment lasted three days, and minor overall drift (~ 0.2%) in response is to be expected. When calculating the heating value, concentrations are normalized, so the impact on the heating value is negligible.

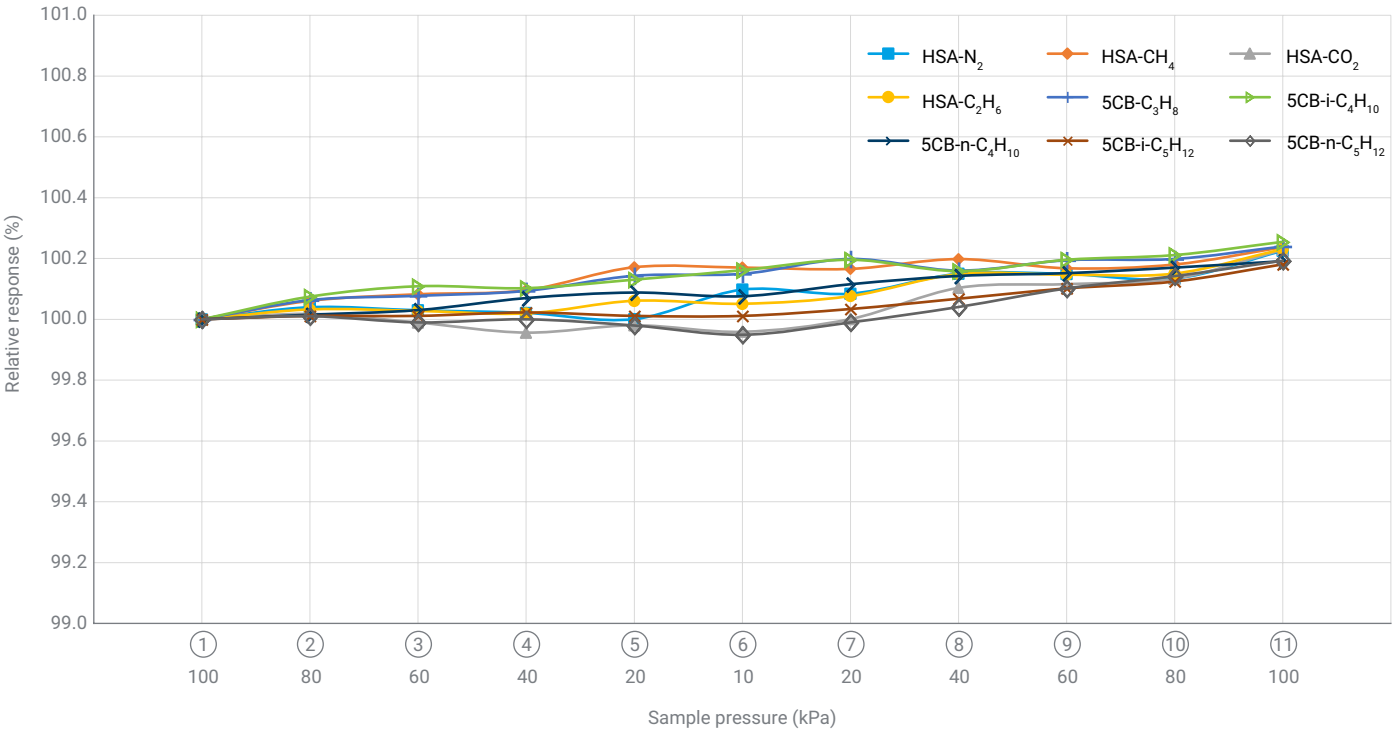

Figure 3. Relative response of each component under different sample pressures.

Figure 4 shows the variation of the relative retention time of each component with sample pressure. The maximum deviation of the average retention time for each component under different sample pressures is less than 0.20%, and the maximum relative standard deviation is less than 0.10%. These indicate that the retention time of each component is also almost unaffected by the sample pressure.

Therefore, being unaffected by sample pressure is an inherent characteristic of the 990 Micro GC. If this is found to vary, then there must be faults somewhere. The faults include, but are not limited to: Adsorption, leakage and/or carryover along the sample line, ambient temperature variation, and damage to instrument components. Troubleshooting suggestions are only provided here for cases where the response is affected by the sample pressure due to damage to instrument components. Typically, it is related to the injector die. Common root causes include:

a. Leakage of the injection membrane valve on the injector die. Carrier gas flows out from the leak point and continuously dilutes the sample entering the sample loop. The lower the sample pressure, the higher the leakage rate, and the higher the column head pressure, the greater the reduction in response.

b. Leakage of the sampling membrane valve on the injector die. During pressurization, the pressurized carrier gas pushes the sample back into the sample container. The sample in the sample loop is diluted by carrier gas, resulting in an overall reduced response. The lower the sample pressure, the higher the leakage rate, and the higher the column head pressure, the greater the reduction in response.

c. Both a and b.

To determine whether the injector die is at fault, troubleshooting methods are as follows:

1. Set the instrument to normal test conditions and ensure it remains in the idle state throughout the entire troubleshooting process.
2. Block the inlet of the sample connector with a plug. Disconnect the "Sample In" line from the pump box. Monitor the "Sample In" line to measure any gas venting. If the injection membrane valve on the injector die is functioning properly, no flow will be detected. Otherwise, it will leak and the injector die should be replaced.

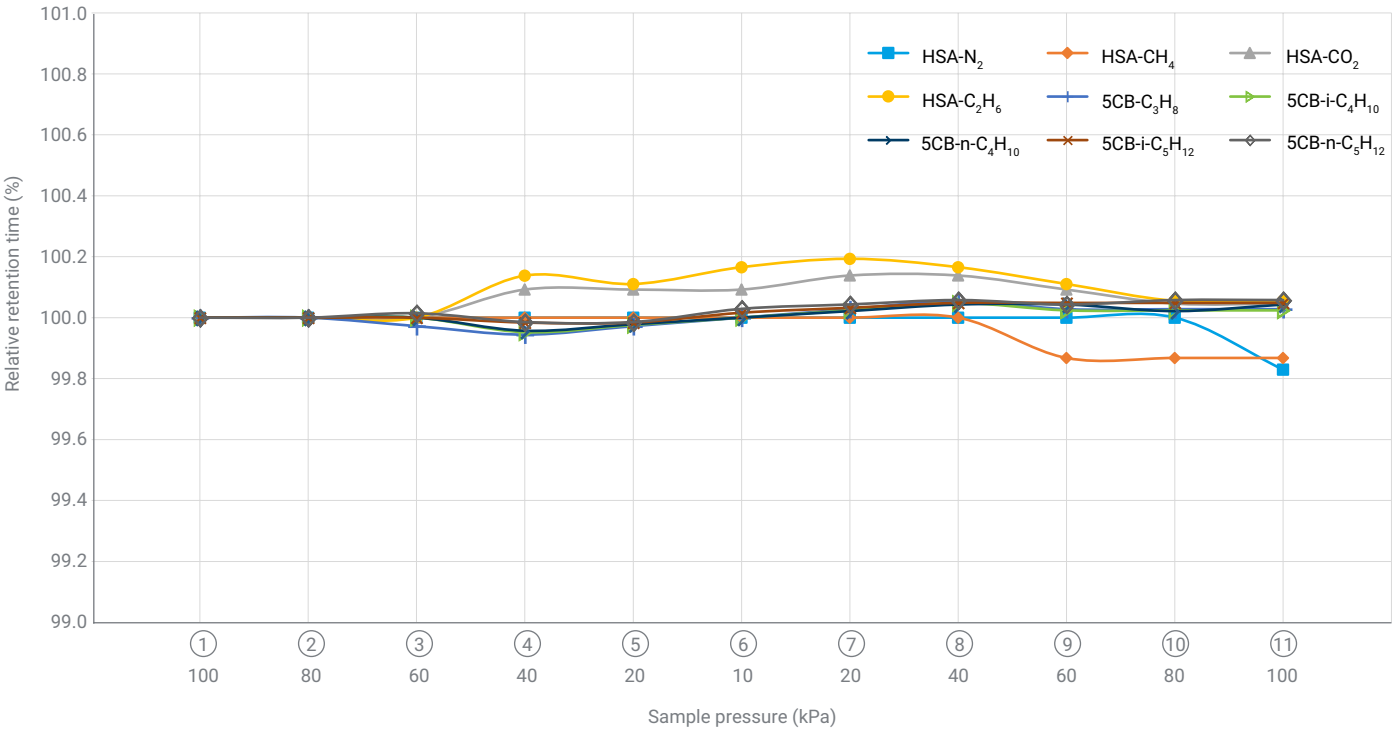

Figure 4. Relative retention time of each component under different sample pressures.

3. If no flow is detected in Step 2, remove the plug. Connect the 100 kPa Air/N_2 supply to the sample connector. Monitor the "Sample In" line to measure any gas venting. If the sampling membrane valve on the injector die is functioning properly, no flow will be detected. Otherwise it will leak and the injector die should be replaced.

Damage to the membrane valves on the injector die mostly results from particles or fibers entering the valve body. Some preventive proposals are listed below:

- The sample should be free of particles and fibers; it should not be highly corrosive or oxidative; and it should remain gaseous throughout the analysis.
- Use sample tubing provided by Agilent.
- The sample connector (G3588-67018) provides filtration. Ensure the sample enters the channel via sample connector (or through a similar filter) rather than directly connecting to the sample inlet. It is also recommended to add an external filter provided by Agilent, such as a Genie filter (effective for capturing droplets, oil mist, and particles) if the cleanliness of the sample is highly challenging. Note that adding extra filters may introduce additional carryover and/or air contamination.
- Seal the sample inlet on channel when storing or transporting the 990 Micro GC.
- Purge new sample tubing before connection.
- When replacing the column plate or injector die, purge the connector first, and wait for dust and particles to settle before disconnecting and reconnecting. Be careful not to let particles and fibers contact the internal part during the process.

Conclusion

The influence of different sample pressures on the Agilent 990 Micro gas chromatography system response was investigated under the same operating conditions, using natural gas analysis as an example. The results show excellent relative standard deviation of both average retention time and response at all six sample pressures ranging from 10 to 100 kPa, demonstrating the inherent characteristic of the 990 being unaffected by sample pressure. The response of the 990 Micro GC can be affected by sample pressure when hardware is damaged or not working properly. The faults are listed and root cause analyzed. Some troubleshooting methods and preventive measures are also proposed for the possible damage of the injector die instrument component.

References

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