Technical Overview

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Impact of Temperature on the Efficiency of High-Temperature GC Columns

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Abstract

The best practices for performing gas chromatography (GC) at temperatures above 360 °C are disputed. High-temperature gas chromatography applications using fused silica columns can be problematic for applications that run above 400 °C. Even if a phase is stable enough to be maintained for extended periods of time above 400 °C, the polyimide coating on fused silica will eventually burn off, causing the column to become brittle. This Technical Overview examines the effects of temperatures above 400 °C on the integrity of the Agilent J&W DB-5ht column phase and brittleness of the column over extended periods of time.

Introduction

When working with high-temperature applications exceeding 360 °C, the temperature range of the column tubing and stationary phase must be considered. Standard polyimide-coated fused silica columns are easy to use, and can operate up to 360 °C with no degradation of the polyimide coating. Operating these columns between 360 and 400 °C however, creates a problem for standard tubing. For applications in the temperature range of 360 to 400 °C, polyimide-coated columns that have been designed to operate at higher temperatures must be used. High-temperature fused silica columns can only operate up to temperatures of 400 °C. As the temperature of the oven increases above 400 °C, the polyimide will start to flake off and leave the column brittle, and sensitive to breakage.[1–3] The stability of the stationary phase must also be considered when working with high-temperature applications. Maximum allowed operating temperatures (MAOTs) are stated for each phase. If taken above the MAOT for an extended period, the phase will be irreversibly damaged, leading to an increase in adsorption sites, which cause peak tailing.[4]

The DB-5ht GC column has an operating temperature range of up to 400 °C, where the fused silica tubing and the phase can operate for extended periods of time. This Technical Overview compares the thermal stability and efficiency of a DB-5ht GC column to a competitor's 5ht column to demonstrate the increased stability of the DB-5ht column phase. We also examined what can happen to the polyimide coating of a high-temperature GC column as it is taken above the MAOT. Finally, we demonstrated the advantages of Agilent high temperature fused silica compared to a competitor's high-temperature tubing.

Materials and methods

An Agilent 7890 GC/FID equipped with a multimode inlet and an Agilent 7693 automatic liquid sampler with Agilent MassHunter software was used for GC/FID experiments. The method was set up to perform dual injections.

GC conditions

Parameter	Value
Column	Agilent J&W DB-5ht, 30 m × 0.25 mm, 0.10 µm (p/n 122-5731) Brand X 5ht column, 30 m × 0.25 mm, 0.10 µm Brand Y-5ht column, 30 m × 0.25 mm, 0.10 µm
Carrier	Helium, constant flow, 1 mL/min
Oven	90 °C (30.0 minutes), ramp 20 °C/min to 400 °C (60 minutes) 90 °C (30.0 minutes), ramp 20 °C/min to 430 °C (60 minutes)
Inlet	MMI inlet, split mode, 300 °C, split ratio 50:1
Inlet Liner	Ultra Inert, split, low pressure drop, glass wool (p/n 5190-2295)
GC/FID	Agilent 7890B GC equipped with FID
Sampler	Agilent 7693 autosampler
FID Conditions	
Temperature	380 °C
Hydrogen	30 mL/min
Air	400 mL/min
Col + Make Up	25 mL/min

Flowpath supplies

Septum	Bleed and temperature optimized (BTO), 11 mm septa (p/n 5183-4757, 50/pk)
Vials	2 mL, screw top, amber, write-on spot, certified (p/n 5182-0716, 100/pk)
Vial inserts	150 µL glass inserts (p/n 5183-2088, 100/pk)
Vial caps	9 mm blue screw cap, PTFE/red silicone septa (p/n 5185-5820, 500/pk)
Inlet/FID	Graphite ferrules (p/n 500-2114, 10/pk)

Standards preparation

Individual analytes were purchased from Sigma-Aldrich and prepared at a concentration of 0.25 mg/mL in hexane.

Results and discussion

A standard mix was injected simultaneously on a DB-5ht GC column and a brand X 5ht column and held isothermally at 90 °C for 30 minutes, before being ramped up to a final temperature of 400 °C and held for one hour. This experiment was repeated until the total time the columns were held at 400 °C reached 40 hours. Figure 1 demonstrates the breakdown of the brand X 5ht phase over 40 hours operating at 400 °C. After 20 hours operating at 400 °C, peak tailing is most visible with naphthalene, tridecane, and methyl dodecanoate. After 40 hours operating at 400 °C, however, all the peaks in this test mix have significant tailing. The tailing of an alkane, such as *n*-tridecane, proves that the active sites causing peak tailing to occur are due to the progressive breakdown of the stationary phase, which has created adsorption sites.

Figure 2 demonstrates the same test mix, injected at the same time, over the same 40 hours operating at 400 °C on the DB-5ht column. Over the 40 hours operating at 400 °C, the peak shapes of the analytes are still symmetrical, indicating that the phase is stable after prolonged periods at its stated MAOT.

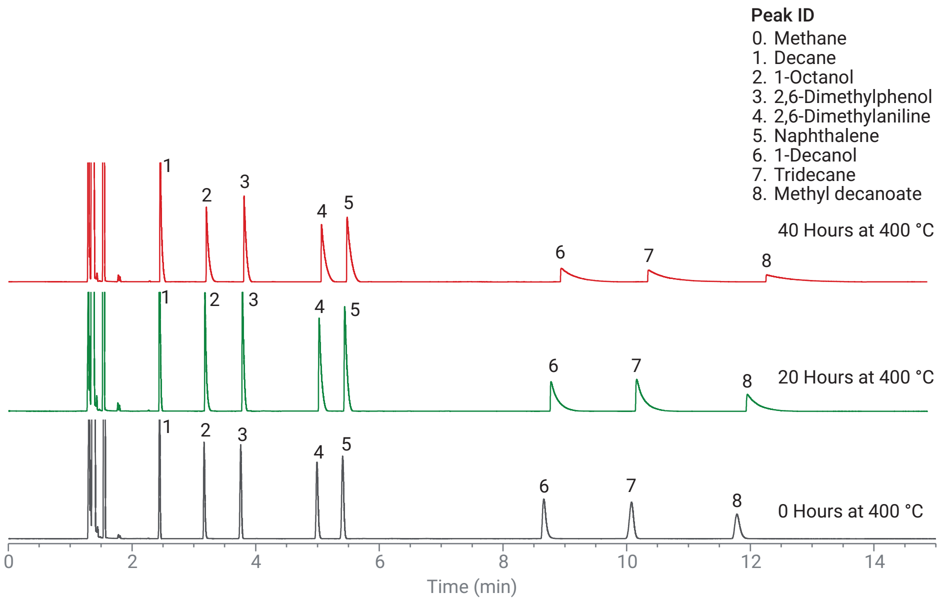

Figure 1. Test mix analyzed on a brand X 5ht column over 40 hours operating at 400 °C.

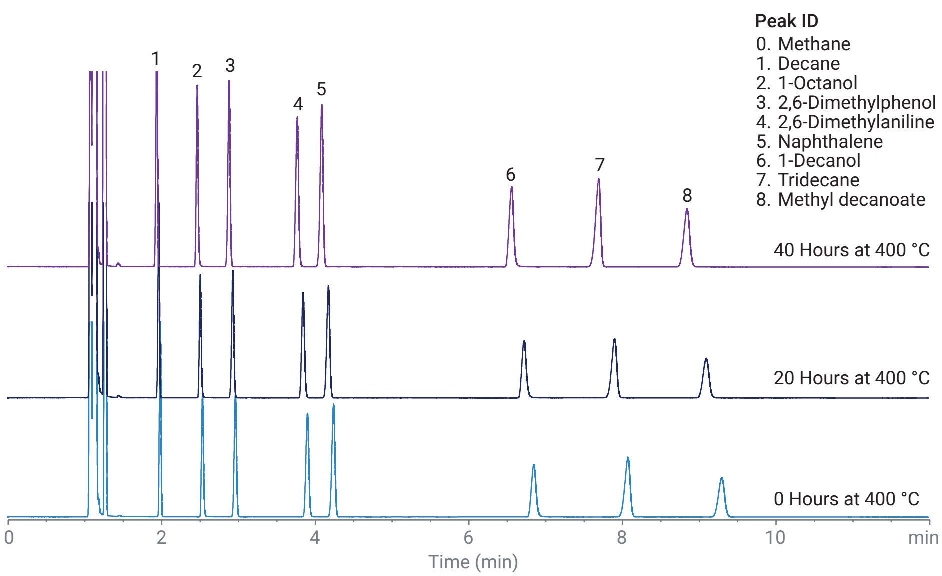

Figure 2. Test mix analyzed on an Agilent J&W DB-5ht over 40 hours operating at 400 °C.

The loss in peak symmetry is not the only indication that the phase in the brand X 5ht column has been degraded, while the DB-5ht phase is still stable, as shown in Figure 3. Figure 4 shows how the plates per meter for tridecane decrease drastically in brand X's 5ht after 15 hours operating at 400 °C. Conversely, the DB-5ht plates per meter for tridecane remain consistent and only decrease slightly after 40 hours. The stability of the plates per meter of the DB-5ht over long periods of time operating at 400 °C indicates that the DB-5ht will have an increased column lifetime compared to the brand X 5ht column.

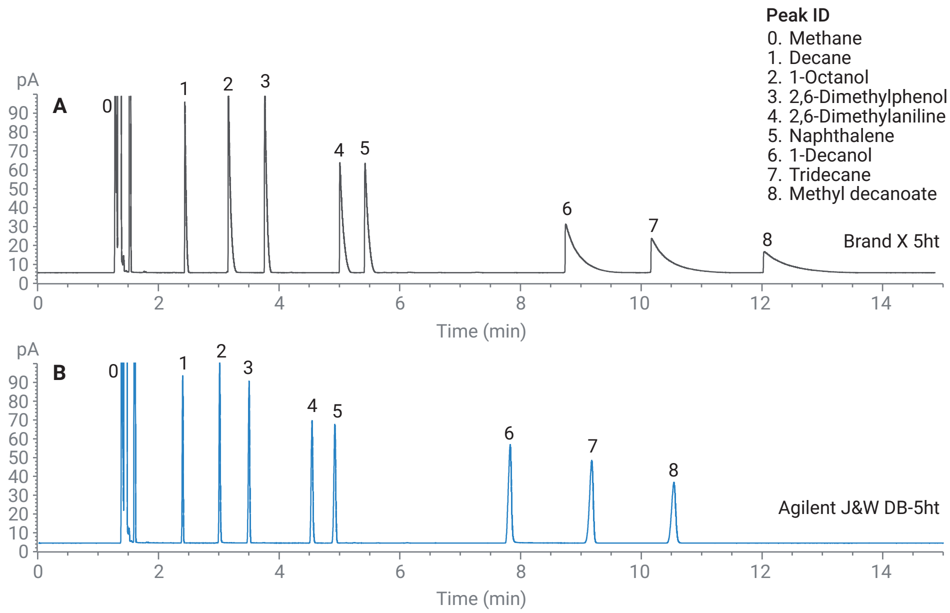

Figure 3. Analysis of the test mix after 40 hours at 400 °C, injected simultaneously on an Agilent J&W DB-5ht and a brand X-5ht column.

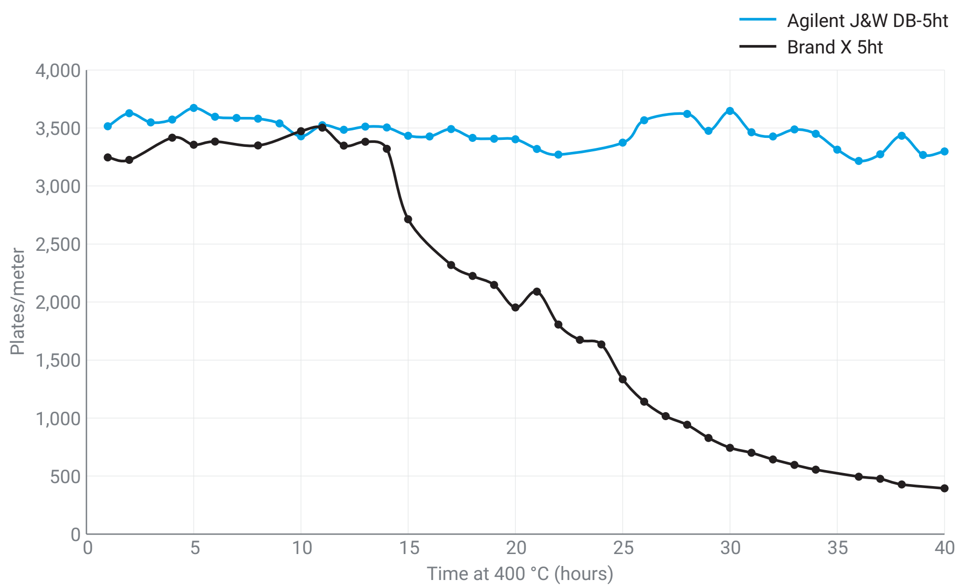

Figure 4. A comparison of the efficiency of the Agilent J&W DB-5ht column compared to the brand X 5ht column over 40 hours operating at 400 °C.

The stated MAOT, for a DB-5ht fused silica column is 400 °C, which is set to guarantee robustness and extended column lifetime even for demanding applications. Other competitors however, state that it is possible to achieve an upper-temperature limit of 430 °C with a 5ht fused silica column. Figure 5 shows a direct comparison of a competitor column with a stated maximum temperature of 430 °C to a DB-5ht over eight hours operating at 430 °C. Similar to Figure 3, in Figure 5, significant peak tailing can be seen with the brand X 5ht column, but not with the DB-5ht column, indicating that the DB-5ht column phase is more stable at 430 °C than the competitor's 5ht column phase.

In Figure 6, much as in Figure 4, a drastic drop in the plates per meter of tridecane can be seen for the brand X 5ht column in comparison to the DB-5ht. The difference observed when the final temperature is increased to 430 °C is that the plates per meter begin to decrease after four hours at 430 °C for the brand X 5ht, whereas they decrease after 15 hours at 400 °C. This indicates the brand X 5ht phase degrades faster at 430 °C than 400 °C. There is a slight decrease in efficiency of the DB-5ht after operating at five hours at 430 °C, which is 30 °C above the stated MAOT, but it is not as dramatic as that seen with the brand X 5ht column.

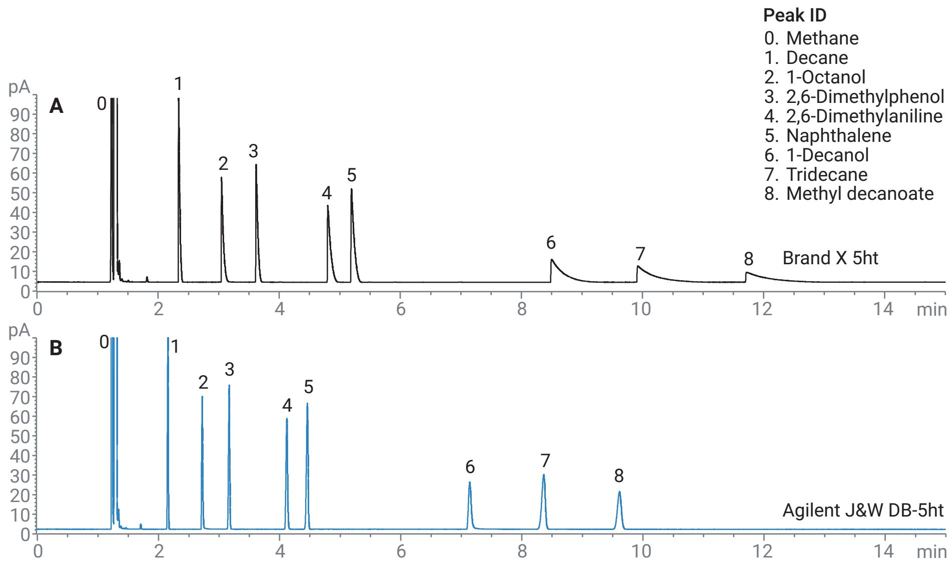

Figure 5. Analysis of the test mix after eight hours at 430 °C, injected simultaneously on an Agilent J&W DB-5ht column and a brand X 5ht column.

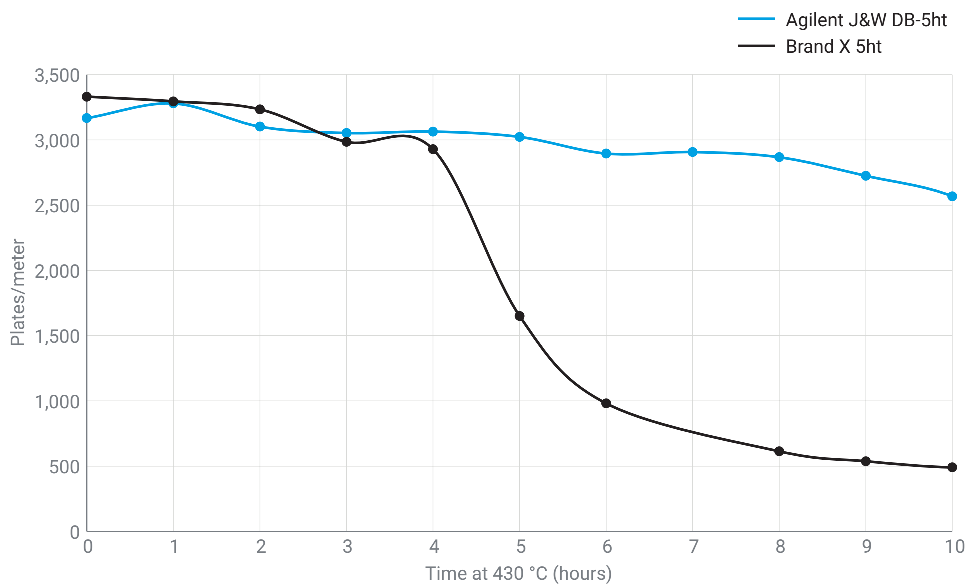

Figure 6. A comparison of the efficiency of the Agilent J&W DB-5ht compared to a brand X 5ht column over 10 hours operating at 430 °C.

Standard polyimide begins to breakdown, and will flake off, after prolonged exposure to temperatures above 360 °C, but high-temperature polyimide is able to operate up to 400 °C. Figures 7A and 7B demonstrate what the polyimide breakdown process looks like. Uneven coating of polyimide on fused silica can cause weak spots where the oxidation of polyimide will occur first, then continue for the entire column. In Figure 7A, the coating of brand Y's 5ht column has mostly flaked off, with some spots of faint polyimide remaining, indicating uneven polyimide coating of the column. This loss of polyimide caused the column to become very fragile. The DB-5ht column, in Figure 7B, still has a uniform coating of polyimide, even after 25 hours operating at the MAOT, and remained flexible.

Conclusion

The Agilent J&W DB-5ht GC column is more stable at the maximum temperature of 400 °C than brand X 5ht columns, making it a better choice for high-temperature applications. The peak shape and efficiency of the test mix compounds stayed consistent throughout extended operation at 400 °C, indicating an overall increase in column lifetime compared to brand X 5ht columns. The polyimide coating of the DB-5ht column also lasted longer than a brand Y 5ht column when exposed to extremely high temperatures, allowing the DB-5ht to remain flexible, longer. If a temperature greater than 400 °C is required, use a deactivated stainless steel GC column.

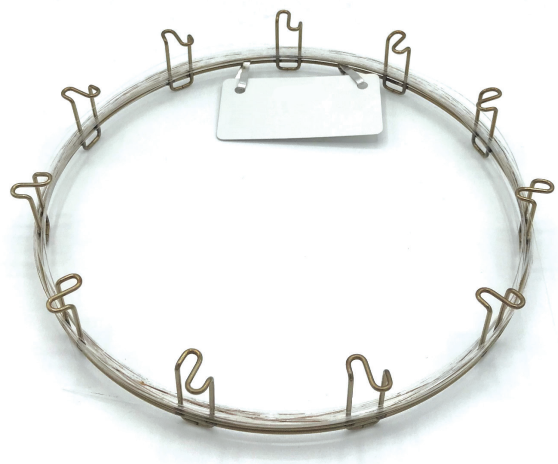

Figure 7A. Brand Y 5ht column after operating at 400 °C for 25 hours

Figure 7B. An Agilent J&W DB-5ht after operating at 400 °C for 25 hours.

References

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