Examination of the efficiency on high temperature GC columns and Strategies for Successful high temperature applications

Vanessa Abercrombie; Gustavo Serrano-Izaguirre; Phil Stremple; Daron Decker

ISCC 2019
POSTER #55

Agilent
Trusted Answers

Introduction

Gas Chromatography utilizes a wide variety of temperature ranges, and depending on the application may need to exceed temperatures greater than 360°C. In industries such as petrochemical, it is not unheard of to require temperatures of up to 400°C for the analysis of hydrocarbons.

When working with applications exceeding 360°C, such as high temperature applications, the temperature range of the column tubing and stationary phase of the column must be considered. Even if a phase is stable enough to maintain extended periods of time above 360°C, the polyimide coating on fused silica will eventually burn off, causing the column to become brittle.

We will examine what affect temperatures above 360°C will have on the integrity of the column polyimide coating, stationary phase, and brittleness of the column over extended periods of time. We will also look into strategies for more efficient and successful high temperature applications, such as utilizing UltiMetal or Pro Steel Deactivated Stainless Steel GC columns.

Experimental

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

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

GC Conditions

Column	**Agilent J&W DB-5ht (p/n 122-5731)** 30m x 0.25 mm x 0.10 µm **Brand X and Brand Y-5ht Column** 30 m × 0.25 mm × 0.10 µm
Carrier	**Helium, constant flow, 1 mL/min**
Oven	**90 °C (30.0 min), Ramp 20 °C/min to 400 °C (60 min)** **90 °C (30.0 min), Ramp 20 °C/min to 430 °C (60 min)**
Inlet	**MMI Split mode, split ratio 50:1, 300°C**
Inlet Liner	**Ultra Inert, split, low pressure drop, glass wool (p/n 5190-2295)**
GC/FID	**Agilent 7890B GC equipped with FID**

Flow Path Supplies for High Temperature Applications

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)**

Phase Degradation Above 360 °C

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, and after 40 hours operating at 400°C all of the peaks in this test mix have significant tailing. This tailing is not due to active sites in the first part of the column but is due to the breakdown in the integrity of the phase, and the creation of adoption sites.

Figure 2 demonstrates 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 shape of the analytes are still consistent, indicating that the stationary phase is stable for use for prolonged periods at its stated MAOT.

In Figure 3 we can see how the comparison of the column efficiency. The theoretical plates per meter for Tridecane decreases drastically in Brand X's 5ht after 15 hours operating at 400°C whereas the DB-5ht theoretical plates per meter for Tridecane remains consistent and only decreases slightly after 40 hours.

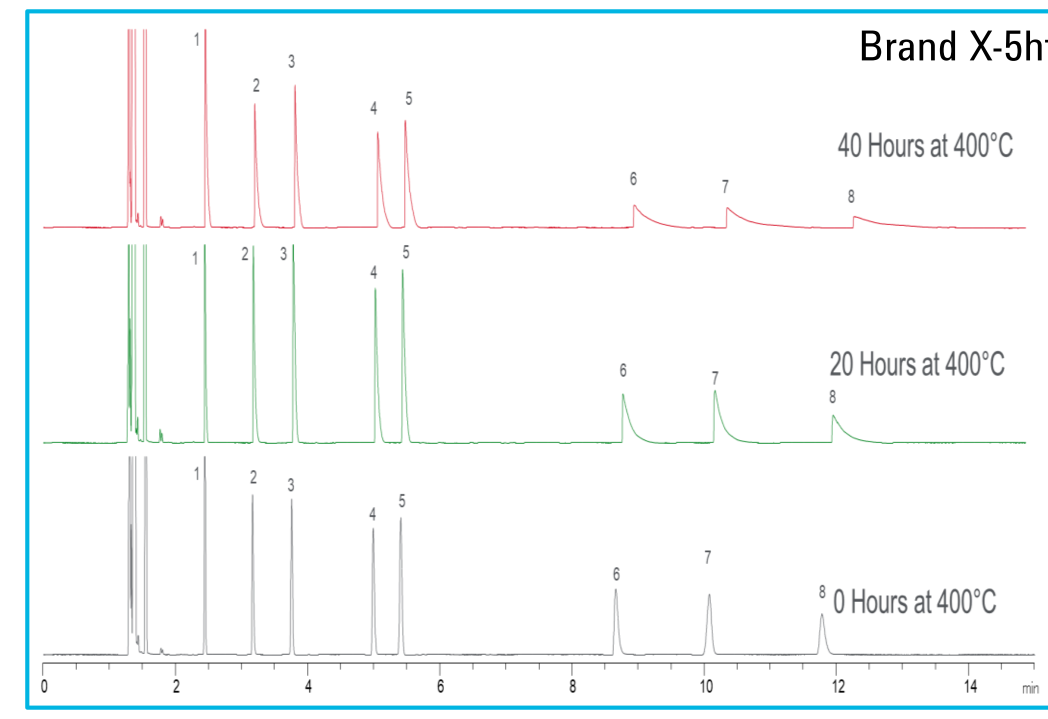

Figure 1. Test Mix analyzed on Brand X-5ht over 40 hours operating at 400°C

Peak Identification: (1) Decane, (2) 1-Octanol, (3) 2,6-Dimethylphenol, (4) 2,6-Dimethylaniline, (5) Naphthalene, (7) Tridecane, (8) Methyl Decanoate

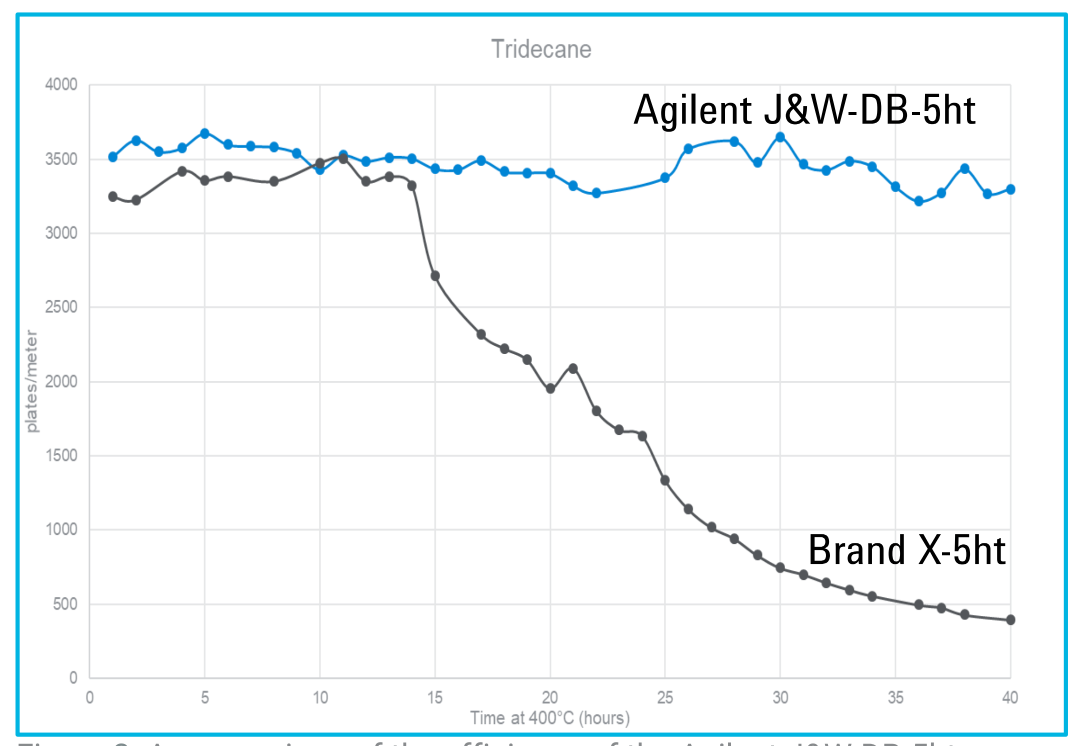

Figure 3. A comparison of the efficiency of the Agilent J&W DB-5ht compared to Brand X-5ht column over 40 hours operating at 400°C.

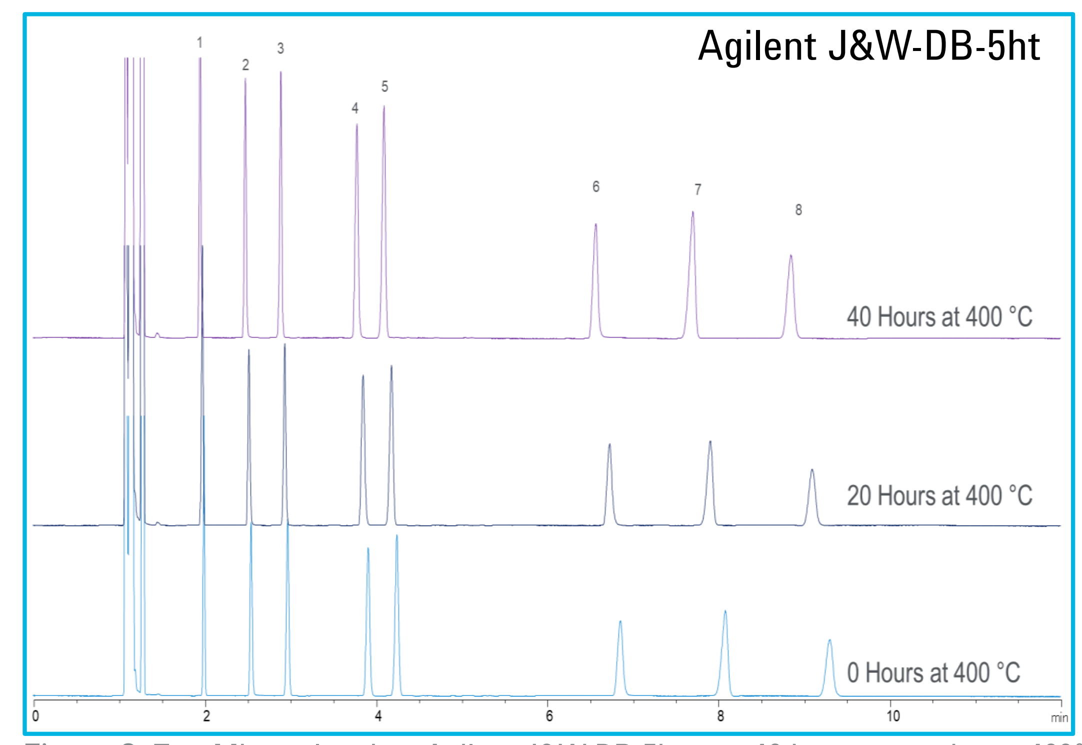

Figure 2. Test Mix analyzed on Agilent J&W DB-5ht over 40 hours operating at 400°C

Peak Identification: (1) Decane, (2) 1-Octanol, (3) 2,6-Dimethylphenol, (4) 2,6-Dimethylaniline, (5) Naphthalene, (7) Tridecane, (8) Methyl Decanoate

Metal Columns Provide a Safer Option for Operating Above 400 °C With the Same Phase

Metal columns have been used since the beginning of Gas Chromatography, and while early metal columns were difficult to deactivate because of uneven surfaces, the metal columns of today have been greatly improved with uniform internal surfaces. Agilent UltiMetal and Pro Steel GC columns are made using Deactivated Stainless Steel and have a maximum operating temperature of up to 450 °C. When working with Agilent metal columns there is no need to worry about potential heat damage to the exterior of the column, which can cause brittleness.

Agilent UltiMetal and Pro Steel metal GC columns utilize the same phases as their fused silica counterparts, and behave the same way chromatographically, as is demonstrated in Figure 6. UltiMetal and Pro Steel GC columns allow your upper temperature limit be determined by the stationary phase MAOT and not the upper limit of the tubing.

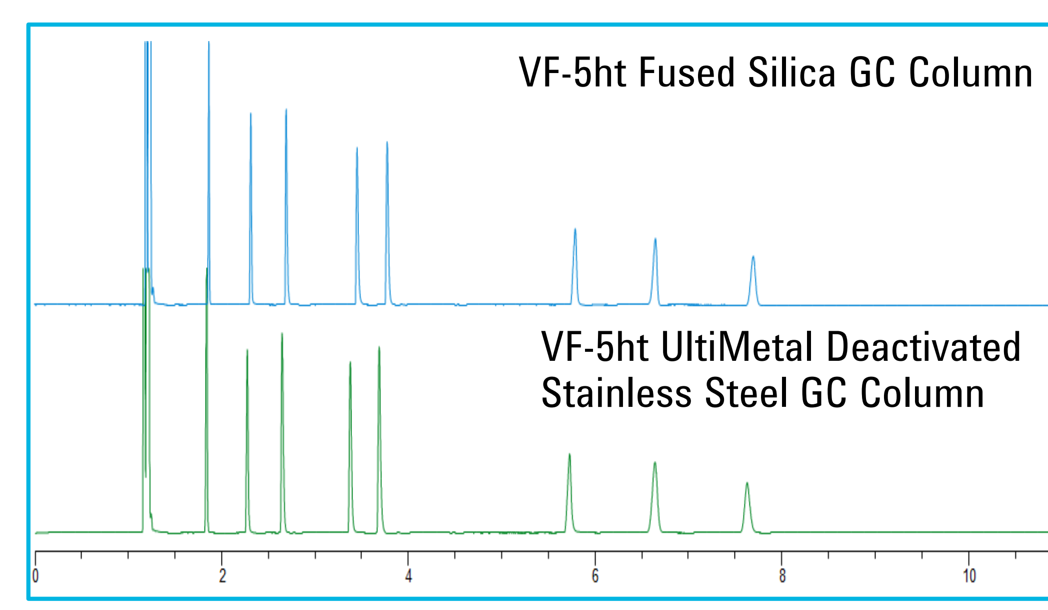

Figure 6. Test mix analyzed on Agilent J&W VF-5ht fused silica GC column and Agilent J&W VF-5ht UlitMetal GC Column

Polyimide Breakdown above 400°C for Competitor 5HT GC Column

It is known that polyimide begins to breakdown and will flake off after prolonged exposure to temperatures above 400°C. Figure 4a and 4b demonstrate what the polyimide breakdown process look like. Uneven coating of polyimide on fused silica can cause weak spots were the oxidation of polyimide with occur first.

As is seen in Figure 4a, the polyimide coating of Brand Y's 5ht column has flaked off from most of the column, but still has some dark spots, indicating uneven polyimide coating of the column. This loss of polyimide caused the column to become very fragile. The DB-5ht column, in figure 4b still has a uniform coating of polyimide, even after 25 hours operating at the MAOT, and remained flexible.

Figure 5 demonstrates a test mix that had be injected on Brand Y's 5ht column, after operating at 400 for 25 hours, and prior to it being taken out of the GC and imaged for Figure 4a. In addition to the polyimide breaking down, the phase of Brand Y's column has degraded, as is indicated by the peak tailing of the test mix components.

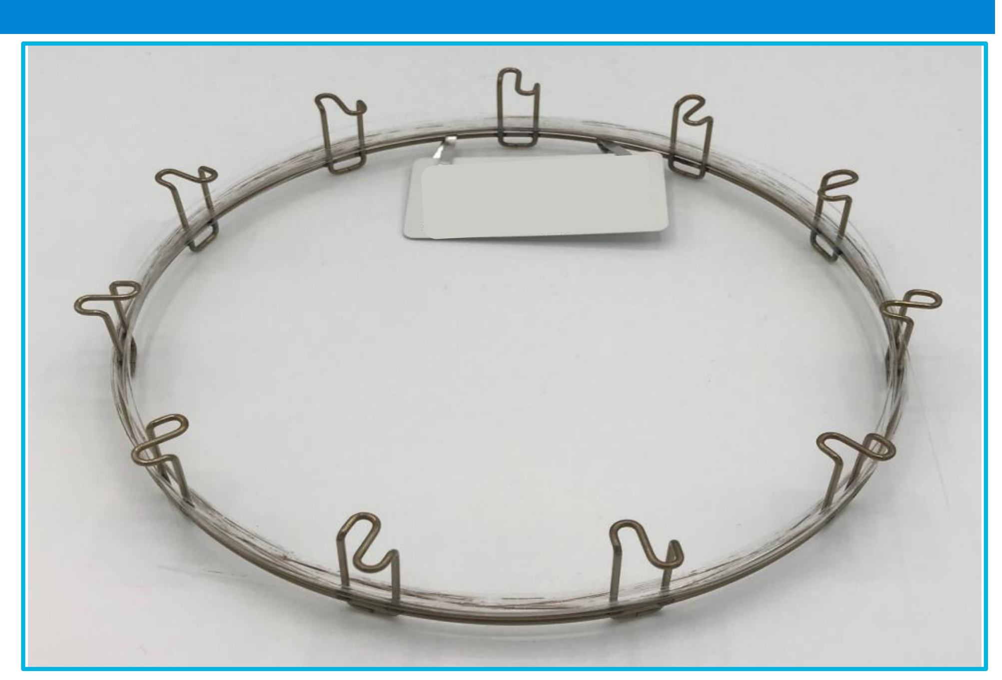

Figure 4a. Brand Y-5ht GC Column after 25 hours operating at 400°C

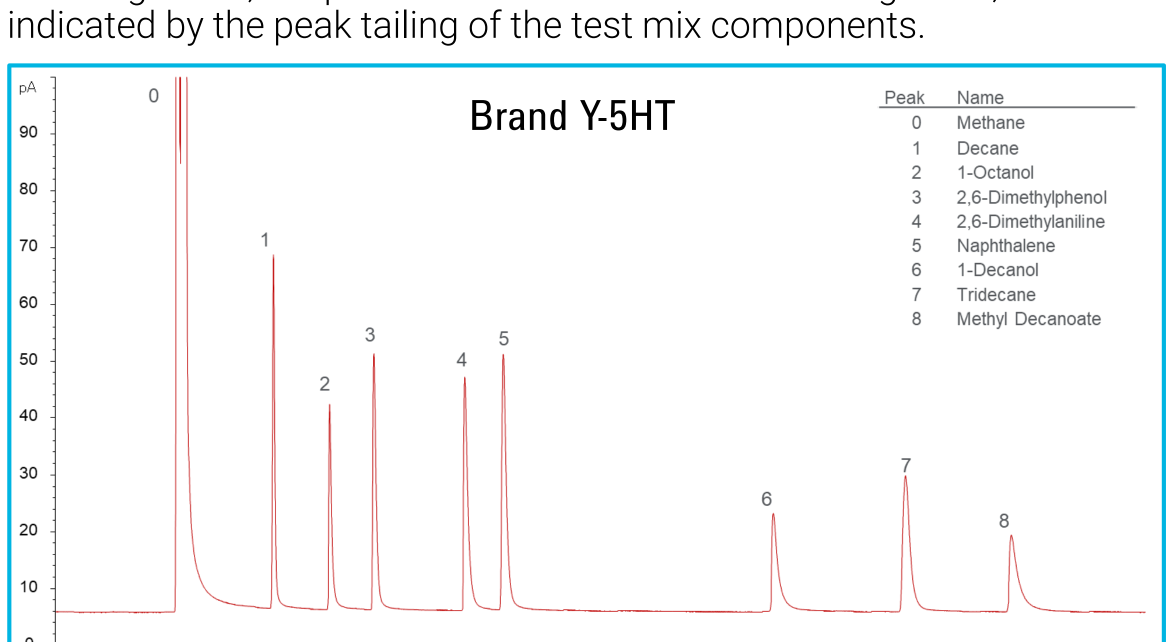

Figure 5. Test Mix analyzed on Brand Y-5ht over 25 hours operating at 400°C

Figure 4b. Agilent J&W DB-5ht GC Column after 25 hours operating at 400°C

Conclusions

The Agilent J&W DB-5ht GC column is more stable at the stated maximum temperature of 400°C than competitor 5HT columns, making it a better choice for high temperature application. The peak shape of the test mix compounds and the column efficiency stayed consistent throughout extended operation at 400°C, indicating an overall increase in column lifetime in comparison with other Brands of 5ht columns. The polyimide coating of the DB-5ht column also lasted longer when exposed to extremely high temperatures, allowing the DB-5ht to remain flexible, longer.

Agilent UltiMetal and Pro Steel GC columns provide the same stationary phase as their fused silica counterparts, with the benefit of a temperature limit of 450°C, making them the best option for applications with a final temperature greater than 400°C with decreased risk of tubing failure.

References

1. L. S. Ettre, "Evolution of Capillary Columns for Gas Chromatography" LCGC, Volume 19, Issue 1, pg 48-59, January 2001
2. John V. Hinshaw, "The Making of a Column" LCGC Europe, Volume 19, Issue 2, pg 93–98, Feb 01, 2006
3. Steve Griffin, "Fused-Silica Capillary -The Story behind the Technology" LCGC North America Volume 20 Number 10 October 2002
4. A. Reese; A. Vickers; C. George. GC Column Bleed: A MASS PerSPECtive. Agilent Technologies, Publication Number: B-0442 (2001).

Printed in USA, May 7, 2019
5994-0963EN