

Successful High-Temperature GC with Agilent J&W Deactivated Stainless Steel GC Columns

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Abstract

This Technical Overview examines successful strategies for working with high temperature GC Applications and the implementation of metal GC columns. Agilent UltiMetal and ProSteel GC columns use the same phase as their fused silica counterparts, with the advantage of being able to operate at temperatures up to 430 °C for extended periods of time. For applications analyzing high molecular weight alkanes, short, thin filmed GC deactivated stainless steel UltiMetal or ProSteel columns are needed to elute these heavy compounds off the column and have low enough bleed to maintain sensitivity to detect up to C₁₁₄ to C₁₂₀.

Introduction

Two factors are considered when a maximum allowed operating temperature (MAOT) is determined for a GC column a:

- MAOT for the phase and
- MAOT for the column material

While some phases such as polyethylene glycol may have a lower MAOT of 250/260 °C for an Agilent J&W DB-WAX UI and 280/290 °C for an Agilent J&W DB-HeavyWAX column, the phase MAOT will be the limiting factor in the maximum temperature.^{1,2} Other phases, such as dimethylpolysiloxane (PDMS) or 5% phenyl dimethylpolysiloxane, are so thermally stable that the limiting factor for the isothermal temperature limit is determined by the capillary tubing on which it is coated.

Standard polyimide-coated, fused-silica columns have a MAOT of 360 °C; for applications operating between 360 and 400 °C, specially designed, high-temperature, polyimide-coated columns are required. High-temperature, fused-silica columns operate up to 400 °C. As the temperature of the oven increases, the polyimide will start to flake off and leave the column brittle and prone to breakage.³ For applications that require temperatures greater than 400 °C, it is necessary to use deactivated stainless steel GC columns. Agilent UltiMetal or ProSteel GC columns are two types of deactivated stainless steel GC columns offered by Agilent. These columns can operate up to 430 to 450 °C, and use the same phases as their fused silica counterparts. The increased temperature limit of the deactivated stainless steel tubing along with the same Agilent phases allow for the same selectivity with an increased temperature range.

For applications such as simulated distillation (Sim Dis), ASTM (ASTM D2887) has established guidelines to analyze samples with a range of atmospheric equivalent boiling points (AEBP) of approximately –42 to 615 °C. If using longer high-resolution, high-temperature metal columns, extremely long hold times at a final temperature of 430 °C would be required to elute off all compounds, and could still pose a risk of carryover. Using shorter and wider bore columns, such as 5 m × 0.53 mm with thin film, provides a solution that allows for elution of up to C₁₂₀ within a reasonable time.

Agilent J&W DB-HT Sim Dis ProSteel GC columns are easy to cut, durable for extended periods of time at high temperatures, and have a low bleed, enabling detection of compounds up to C₁₁₄ to C₁₂₀ without the need for baseline correction.

Experimental

Materials and methods

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

GC conditions

High-resolution Columns	
Column	Agilent J&W VF-5ht, fused silica, 30 m × 0.25 mm × 0.10 μm (p/n CP9046)
	Agilent J&W VF-5ht, UltiMetal, 30 m × 0.25 mm × 0.10 μm (p/n CP9092)
Carrier	Helium, constant flow, 1 mL/min
Oven	90 °C (30.0 minutes), ramp 20 °C/min to 430 °C (60 minutes)
Inlet	MMI inlet, split mode, 300 °C, split ratio 501
Inlet Liner	Ultra Inert, split, low pressure drop, glass wool (p/n 5190-2295)
GC/FID	Agilent 7890B GC equipped with FID
Sampler	Agilent 7693A automatic liquid sampler
High-temperature Metal Columns	
Column	Agilent J&W DB-HT Sim Dis ProSteel, 5 m × 0.535 mm × 0.15 μm (p/n 145-1001)
	Brand X metal Sim Dis column, 5 m × 0.535 mm × 0.15 μm
Carrier	Helium, constant flow, 18 mL/min
Oven	40 °C (0 minutes), ramp 10 °C/min to 430 °C (20 minutes)
Inlet	MMI inlet, splitless mode, 100 °C (0.5 minutes), ramp 10 °C/min to 430 °C
Inlet Liner	Ultra Inert, 2 mm dimpled, splitless (p/n 5190-2297)
GC/FID	Agilent 7890B GC equipped with FID
Sampler	Agilent 7693 automatic liquid sampler
FID conditions	
Temperature	430 °C
Hydrogen	30 mL/min
Air	400 mL/min
Column plus Makeup	25 mL/min
Flowpath supplies	
Septum	Bleed and temperature-optimized, BT0, 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 0.25 mm ID column (p/n 500-2114, 10/pk)
	Graphite ferrules 0.80 mm ID column (p/n 500-2118, 10/pk)
FID Jet	H temp adaptable 61.5 mm (p/n 19244-80620)

Standards preparation

Individual analytes were purchased from Sigma-Aldrich, and prepared at a concentration of 0.25 mg/mL in hexane for high-resolution, high-temperature column comparison. Standards of *n*-paraffins Polywax 500, 655, and 1000 were purchased from Sigma-Aldrich, and prepared at a concentration of 2.0 mg/mL in toluene and carbon disulfide.

Results and discussion

High-resolution, high-temperature GC columns

A standard mix was injected simultaneously on a J&W VF-5ht fused silica GC column and a J&W VF-5ht UltiMetal GC column and held isothermally at 90 °C for 30 minutes, before being ramped up to a final temperature of 430 °C and held for one hour. This experiment was repeated until the columns were held at 430 °C for 17 hours. Figure 1 demonstrates the similarities between the 5% phenyl polydimethylsiloxane phases in the fused silica and UltiMetal columns after operating at 430 °C for five hours. Retention times, peak shape, and resolution are similar in both the fused silica and UltiMetal columns because they are the same phase, but with different tubing materials.

Figure 2 demonstrates what happens to the efficiency of the column as the polyimide begins to degrade. The stated MAOT for J&W VF-5ht fused silica column is 400 °C, which is set to guarantee robustness and extended column lifetime under the limitations of the high-temperature, fused-silica tubing. However, this MAOT is not phase-related. Even polyimide from a high-temperature, fused-silica tubing will eventually start to degrade and flake off when operated for extended periods of time above 400 °C. After 12 hours operating at 430 °C, 30 °C above the recommended MAOT for high-temperature fused silica, the efficiency starts to decline for tridecane.

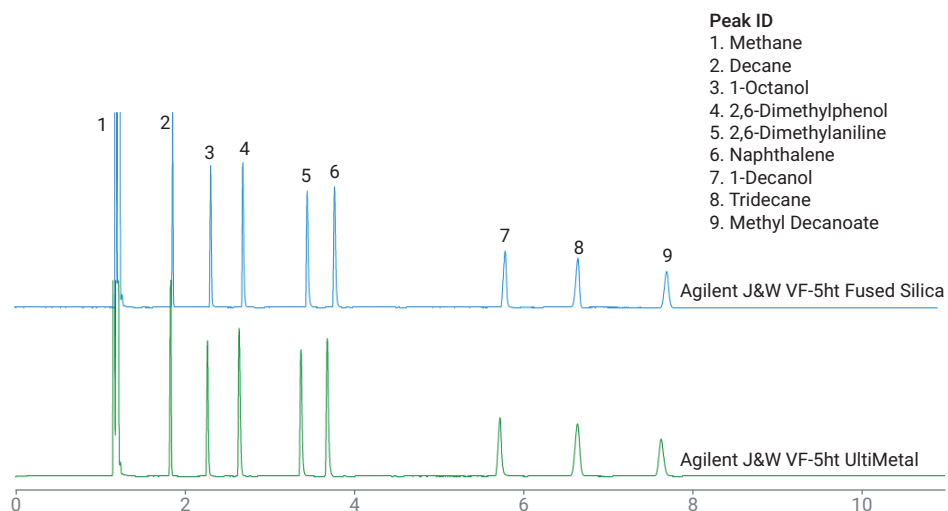


Figure 1. Test mix analyzed on an Agilent J&W VF-5ht fused silica and an Agilent J&W VF-5ht UltiMetal GC column after five hours operating at 430 °C.

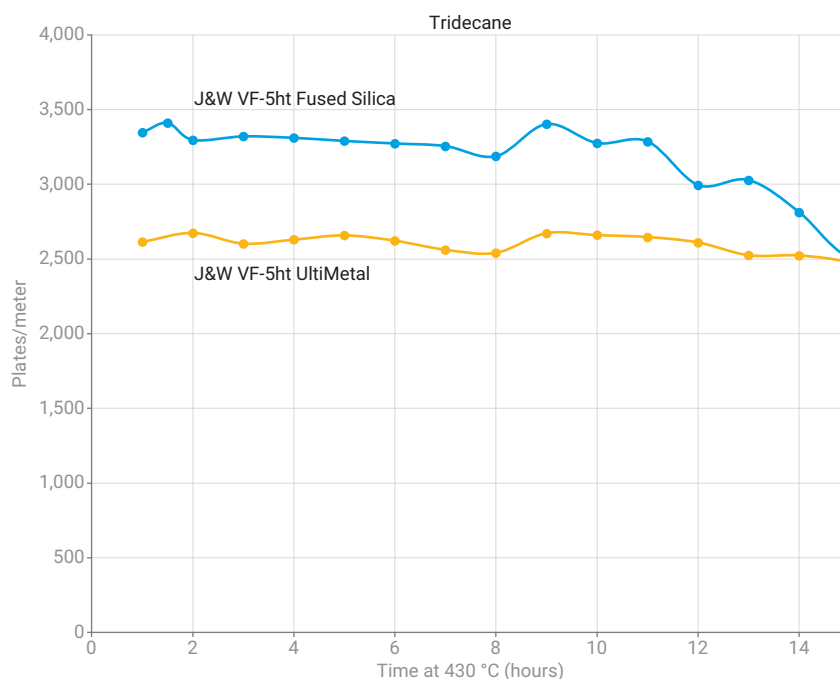


Figure 2. Efficiency of Agilent J&W VF-5ht fused silica and J&W VF-5ht UltiMetal over 15 hours operating at 430 °C.

Figure 3 shows what the fused-silica column looked like after operating 30 °C above the stated MAOT for an extended period. After 15 hours of being used above the MAOT, the polyimide has burned off, creating weak spots in the fused silica where the phase can be exposed to oxygen, and degradation of the phase has begun.

It is normal for metal GC columns to have less column efficiency than fused-silica columns, as seen in Figure 2. This is due to differences in surface energy between the stationary phase and the metal surface of the column, which does not allow the liquid stationary phase to disperse as efficiently as it does on a silica surface. Although this lower column efficiency may affect resolution of compounds with similar boiling points, such analysis is not typical of high-temperature applications. The advantage of high-temperature GC columns is reflected in Figure 2. For applications above 400 °C, metal GC columns provide consistent column efficiency, demonstrating robustness for demanding applications when operating at high temperatures for extended periods of time.

Ideal GC column configuration for high-temperature applications

Best practices for successful high-temperature GC applications are:

- To use the combination of deactivated stainless steel columns that can withstand temperatures greater than 400 °C
- To decrease the column length and increase the diameter of the column to speed up the time it takes for compounds to reach the detector
- To use thinner column phases to decrease column bleed and compound retention and increase the ability to detect higher molecular weight compounds

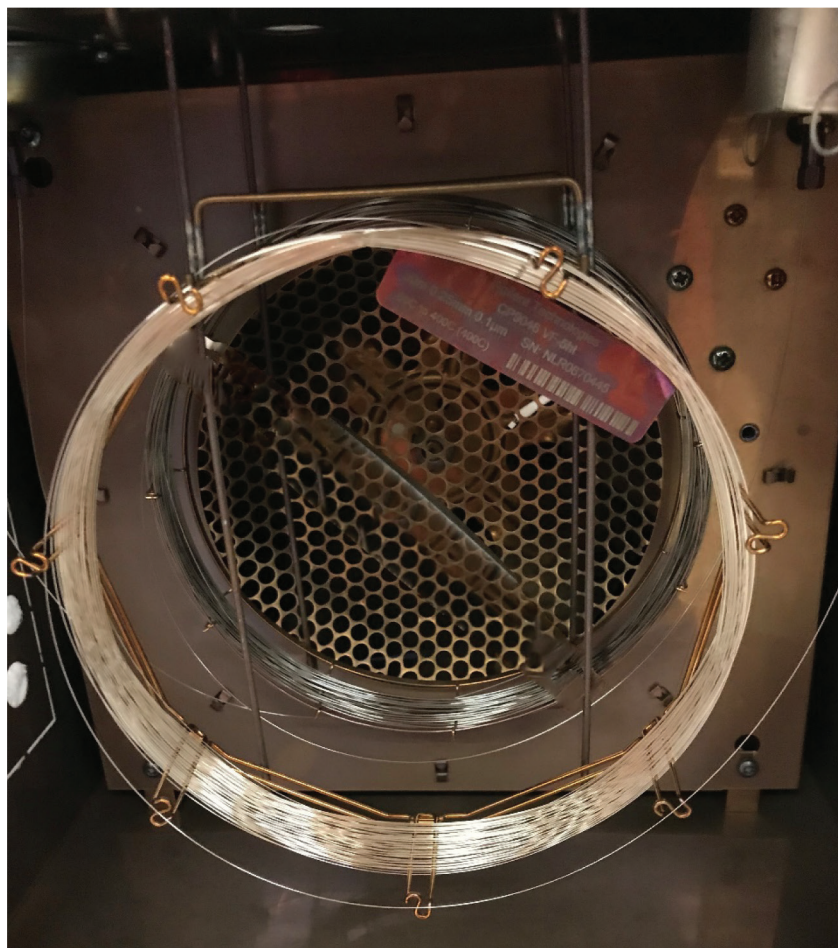


Figure 3. Agilent J&W VF-5ht fused silica and Agilent J&W VF-5ht UltiMetal columns after over 15 hours at 430 °C. Metal Columns are stable at high temperatures longer than fused-silica columns.

While standard films are needed for high resolution of lower boiling compounds, thinner films such as 0.15 μm or less are needed to analyze higher boiling compounds in heavy crude oils.

Decreased bleed with Agilent ProSteel deactivated stainless steel GC columns

Figure 4 shows a standard of Polywax 655 simultaneously injected onto a J&W DB-HT Sim Dis ProSteel GC column and Brand X metal Sim Dis GC column. Polywax 655 contains an alkane range up to C_{90} . In both GC columns, all hydrocarbons are detected, but the Brand X metal Sim Dis column has a significantly higher column bleed than the DB-HT Sim Dis. The increase in column bleed that is seen in the Brand X metal Sim Dis column begins as the oven is increasing above 400 $^{\circ}\text{C}$, and continues up to a final column bleed of 87.0 pA at 430 $^{\circ}\text{C}$, making integration and detection of the later eluting hydrocarbons more difficult. Conversely, the DB-HT Sim Dis GC column only has a bleed of 17.3 pA, showing the higher quality of the Agilent phase, and allowing for easier detection of heavier molecular weight hydrocarbons.

Increase carbon range

With the remarkably low bleed at temperatures up to 430 $^{\circ}\text{C}$, it is possible to analyze a greater range of alkanes and to elute and clearly detect materials up to C_{114} with the DB-HT Sim Dis without carryover. In Figure 5, overlaid injections of the paraffin standards of Polywax 500, Polywax 655, and Polywax 1000 analyzed on the DB-HT Sim Dis demonstrate the ability to analyze a carbon range of C_{12} up to C_{114} without the need to alter the background signal. The decrease in bleed on the DB-HT Sim Dis GC column allows for more accurate integration of peaks and increased accuracy of quantitative results.

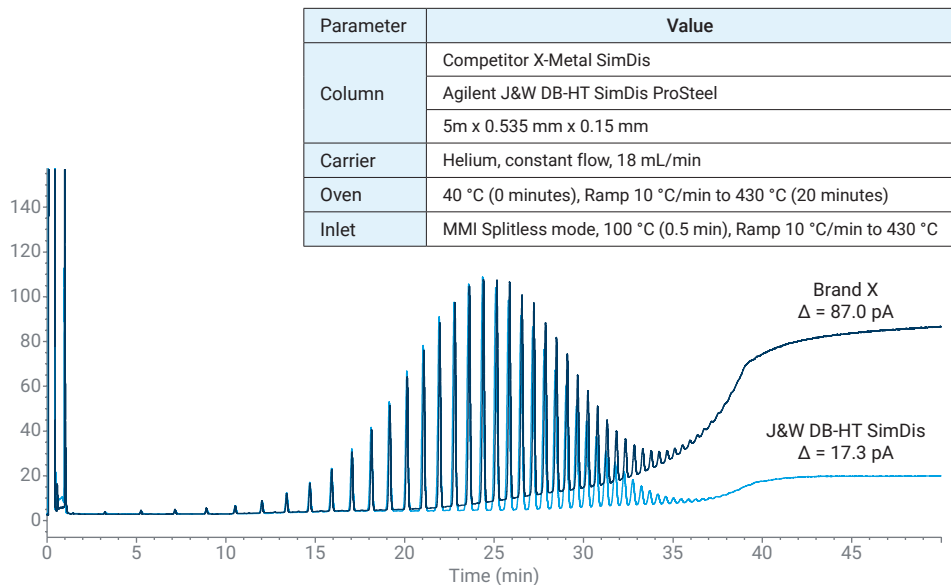


Figure 4. Polywax 655 analyzed on an Agilent J&W DB-HT Sim Dis ProSteel and Competitor X Sim Dis metal GC column.

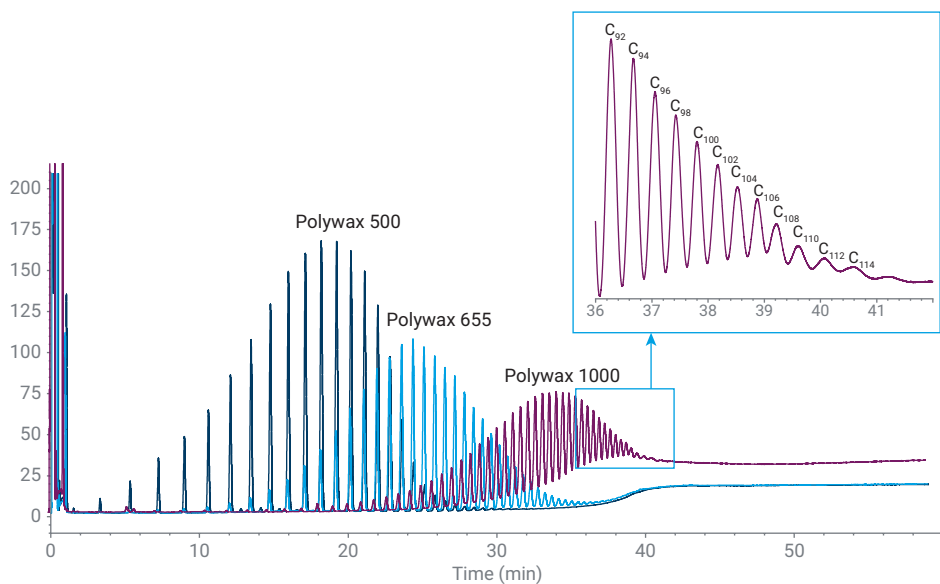


Figure 5. Paraffin Polywax standards analyzed on an Agilent J&W DB-HT Sim Dis ProSteel column.

Carryover in high-temperature applications

The extremely high temperatures that are required to perform applications such as simulated distillation may not be high enough to elute some of the heaviest compounds, and they will be carried over into subsequent injections. Common causes of carryover are an inadequate maximum oven temperature and inlet vaporization of the compounds. Thermal discrimination in the inlet can occur when there is not enough surface area in an inlet liner to vaporize heavier compounds at the same time as lighter compounds, or the inlet temperature is not hot enough to vaporize the heavier compounds. Conversely, if an inlet is too hot, there is a potential for compound breakdown. For this reason, when analyzing a sample with a wide range of molecular weights, it is important to use an inlet that can increase the temperature independently of the GC oven. Such inlets include programmable temperature vaporization (PTV) or multimode inlet (MMI), which can fully vaporize all compounds. A liner that has enough surface area to efficiently transfer heat to the sample to minimize thermal discrimination, such as the 2 mm dimpled liner, can also be used.

Figure 6 demonstrates an injection of the combined Polywax 500 and Polywax 1000, and the subsequent blank injection. As shown in the chromatogram, the blank injection immediately after the injection of the paraffin compounds does not contain any carryover, and still maintains a low bleed at 430 °C.

Ease of use of Agilent J&W deactivated stainless steel GC columns

Deactivated stainless steel columns have a reputation of being difficult to use. Agilent UltiMetal and ProSteel columns only require one tool to clip properly, and are easy to clip and install when using the proper ferrule. Other manufactures recommend the use of two tools to cut then file the end of their metal GC columns. It is extremely difficult to achieve a clean cut without using both tools. Using a file to clean up the edges of a column can cause

tiny metal shavings to end up in the GC column. These shavings can cause activation sites, as well as potentially clog up a flame ionization detector (FID) and lead to unplanned downtime for instrument maintenance. Conversely, both Agilent UltiMetal and ProSteel deactivated stainless steel GC columns only require one ceramic tool for properly clipping the column. This feature decreases the risk of activity due to metal shavings falling in the column and allows for better chromatography to be achieved with a clean column cut.

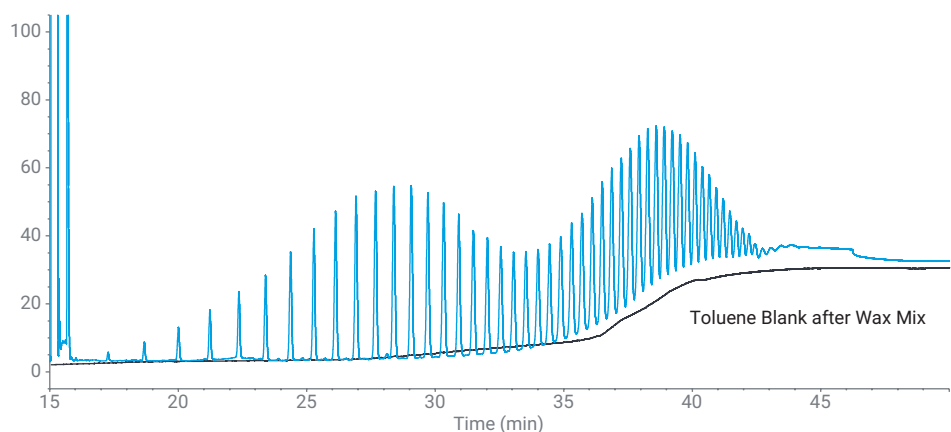


Figure 6. Mixture of Polywax 500 and 1000 on an Agilent J&W DB-HT SimDis ProSteel column and subsequent blank injection of toluene.

Conclusion

When working with applications that require temperatures greater than 400 °C, deactivated stainless steel GC columns are recommended. Polyimide on high-temperature fused silica will eventually start to break down when exposed to temperatures above 400 °C for extended periods of time. Agilent J&W UltiMetal GC columns offer an option for high-resolution, high-temperature GC analysis and Agilent ProSteel columns are a great option for application-specific, high-temperature analysis. Both the UltiMetal and ProSteel GC columns are made from deactivated stainless steel, and are offered in the same phase as their fused silica counterparts, and only require one tool to cut them properly.

To perform the most successful high-temperature GC applications and analyze heavy molecular weight compounds up to C₁₁₄ to C₁₂₀, use short 5 m deactivated stainless steel GC columns that have a phase thickness of 0.15 µm or less. ProSteel GC columns have a maximum temperature limit of 430 °C and maintain a low column bleed, enabling better detection and quantitation of high-molecular-weight compounds. The high quality of the proprietary J&W brand deactivation process, polymer bonding and cross-linking, and ease of use of Agilent deactivated stainless steel GC columns, produce robust and durable GC columns that are ideal for high-temperature applications.

References

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