Application Note

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Reduced carryover and improved reproducibility in pyrolysis gasoline ASTM D6563 analysis

Using an Agilent J&W DB-HeavyWAX gas chromatography column

Author

Vanessa Abercrombie

Abstract

This Application Note evaluates the performance of the Agilent J&W DB-HeavyWAX column for the analysis of pyrolysis gasoline. This analysis is challenging due to presence of higher molecular weight aromatic compounds, which can cause carryover or extended analysis times. The J&W DB-HeavyWAX, with a maximum temperature of 280 °C isothermal and 290 °C programmed, can operate at higher temperatures than traditional WAX-type columns, allowing faster and more reproducible analysis of pyrolysis gasoline.

Introduction

Using the steam cracking process, pyrolysis gasoline is a by-product of the production of ethylene, and can be used as an octane booster for fuels or a feedstock for industrial chemicals. The goal of the steam cracking process is to break down long chain hydrocarbons into smaller chains, ranging from C5 to C12. While approximately 80 to 90 % of pyrolysis gasoline is made up of benzene, toluene, and xylene, often referred to as BTEX, the remaining amount can contain higher molecular weight hydrocarbons and aromatics[1].

Due to the probability of finding those higher boiling compounds, the analysis of pyrolysis gasoline, per ASTM D6563[2], can create an analytical challenge. Increasing the final hold time on a GC run may facilitate the elution of some later eluting compounds. However, it will also increase the overall GC run time, and reduce column lifetime. The risk of taking a column above the stated maximum allowable operating temperature (MAOT) to elute all of the semivolatile compounds risks damage to the phase. This damage can cause:

- Shifting retention times
- Increased column bleed
- A change in elution order of certain compounds over extended periods of time[3]

In general, WAX-type columns have greater bleed levels compared to polysiloxane stationary phases at higher operating temperatures; the less thermally stable the column, the greater the column bleed. This decrease in thermal stability can pose difficulties for applications of industrial chemicals and pyrolysis gasoline.

The Agilent J&W DB-HeavyWAX has an extended temperature limit of up to 280 °C isothermal, and 290 °C programmed. This extended temperature limit permits analysis of the higher boiling compounds in pyrolysis gasoline samples without risking the integrity of the column phase. This Application Note examined the advantages of the extended temperature limit of the DB-HeavyWAX and how it can increase reproducibility and decrease carryover in ASTM method D6563 for the analysis of pyrolysis gasoline.

Materials and methods

An Agilent 7890 GC/FID equipped with a split/splitless inlet, and an Agilent 7693 Sampler with Agilent MassHunter control software was used for GC/FID experiments.

Results and discussion

A sample of pyrolysis gasoline was injected undiluted into an Agilent J&W DB-HeavyWAX column, and analyzed according to ASTM D6563, with the final oven temperature extended from 250 to 280 °C. To compare column bleed with the DB-HeavyWAX column, this analysis was repeated on a traditional commercially available WAX-type column, with a final oven temperature of 250 °C. Figure 1 shows that the DB-HeavyWAX has a lower bleed at 280 °C than a traditional WAX column has at 250 °C. The bleed level of the DB-HeavyWAX at a final temperature of 280 °C was 8.2 pA, compared to the 18.2 pA bleed of a traditional WAX column at a final temperature of 250 °C. This decrease in column bleed at high temperatures of DB-HeavyWAX, compared to the traditional WAX-type column, demonstrates the overall improvement in thermal stability of the DB-HeavyWAX column.

In samples of pyrolysis gasoline that contain heavier hydrocarbons, the increased MAOT of DB-HeavyWAX has the added benefit of eluting these higher boiling compounds much faster. Figure 2 shows that by operating at higher temperatures, compounds such as anthracene elute from the column and do not pose a carryover risk in subsequent injections.

Instrument conditions

GC conditions	
Column	Agilent J&W DB-HeavyWAX, 60 m × 0.25 mm, 0.25 µm (p/n 122-7162) Agilent J&W DB-WAX, 60 m × 0.25 mm, 0.25 µm (p/n 122-7062) Traditional commercially available WAX column, 60 m × 0.25 mm, 0.25 µm
Carrier	Helium, constant flow, 1.2 mL/min
Oven	70 °C (10.0 minutes), ramp 5 °C/min to 280 °C (30.0 minutes)
Inlet	Split mode, 250 °C, split ratio 200:1
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	280 °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)
Gold seal	Ultra Inert gold seals (p/n 5190-6145, 10/pk)
Vials	Screw top, amber, write-on spot, certified ,2 mL (p/n 5182-0716, 100/pk)
Vial inserts	Glass inserts, deactivated, 250 µL (p/n 5181-8872, 100/pk)
Vial caps	Blue, screw cap, PTFE/red silicone septa, 9 mm (p/n 5185-5820, 500/pk)
Inlet/FID	85:15 Vespel: graphite ferrules (p/n 5062-3508, 10/pk)

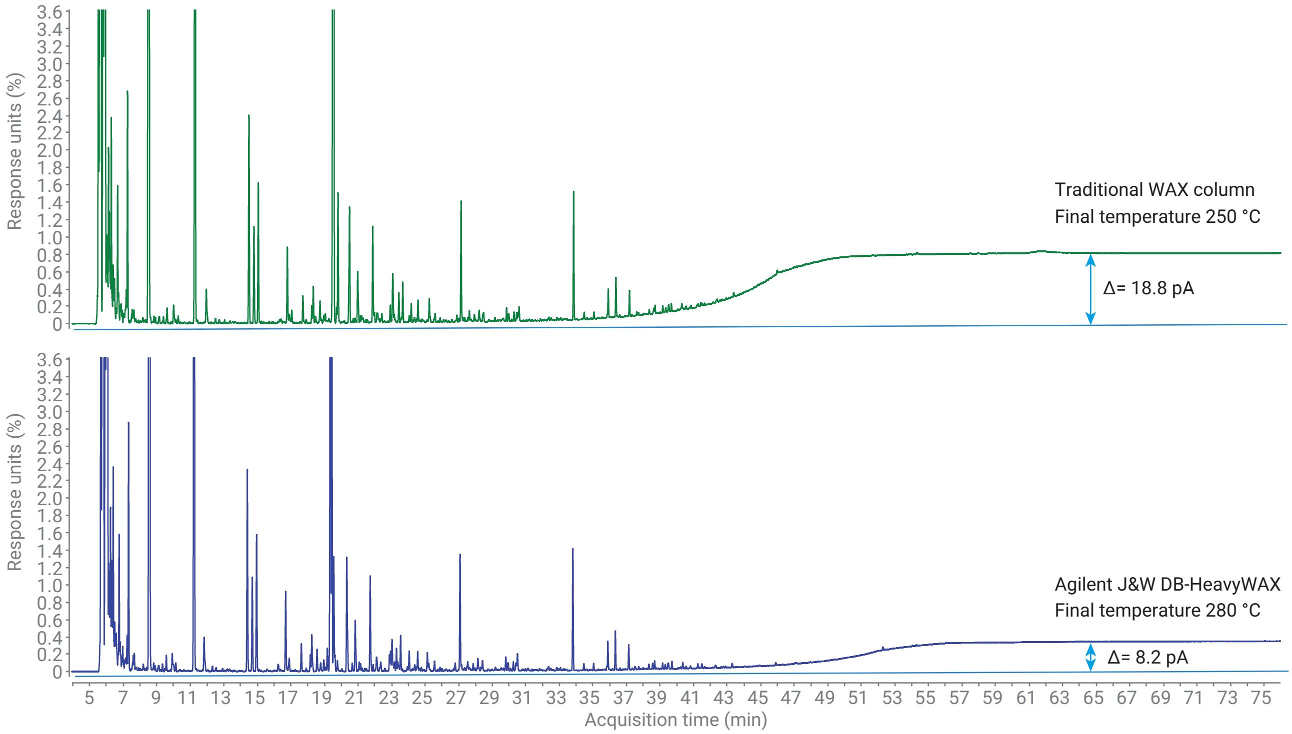

Figure 1. Comparison of a sample of pyrolysis gasoline run on a traditional WAX column with a final temperature of 250 °C, and an Agilent J&W DB-HeavyWAX column with a final temperature of 280 °C, and their associated column bleed levels.

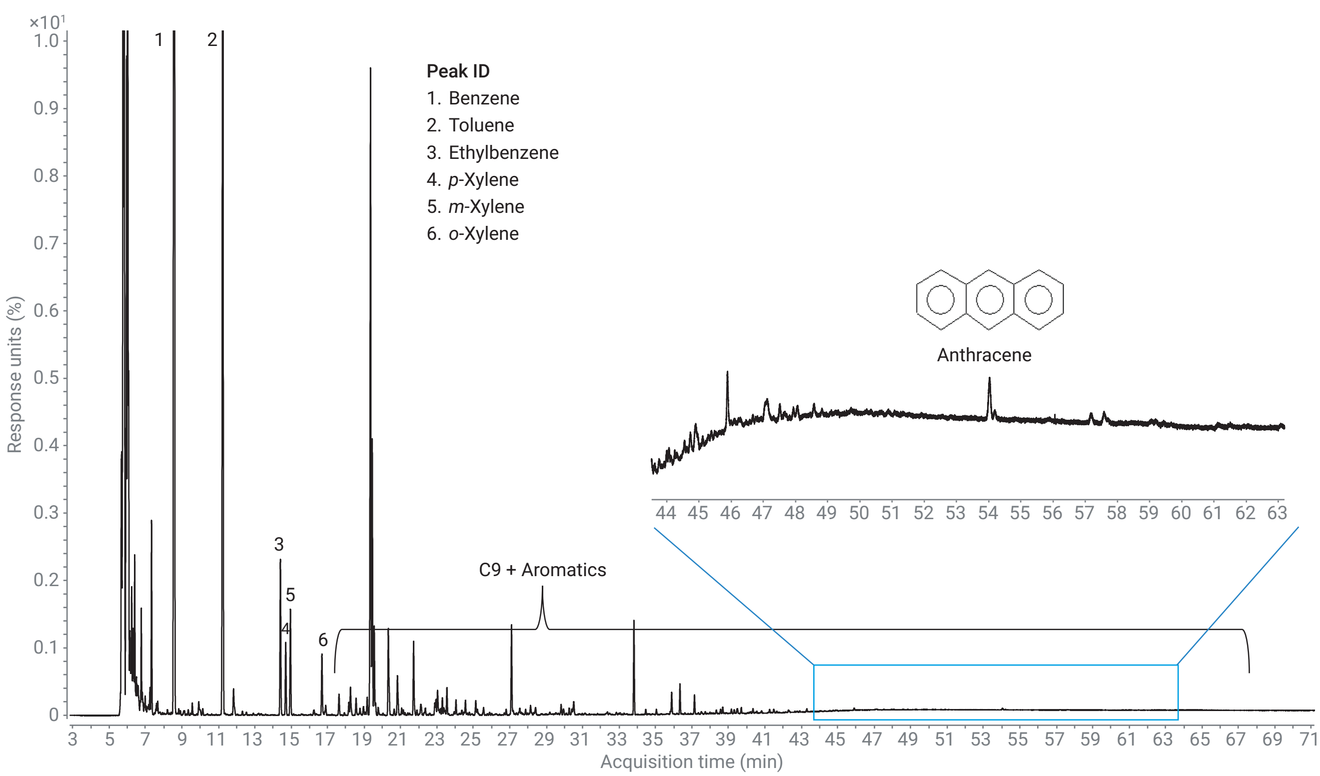

Figure 2. Demonstration of later eluting compounds in pyrolysis gasoline on an Agilent J&W DB-HeavyWAX run to a final temperature of 280 °C.

Figure 3 shows the same sample of pyrolysis gasoline analyzed on a DB-HeavyWAX and an Agilent J&W DB-WAX to a final temperature of 250 °C. Both columns show similar selectivity for the analysis of pyrolysis gasoline.

Conclusion

The Agilent J&W DB-HeavyWAX column provides an increased maximum temperature range. This permits analysis of higher boiling compounds in pyrolysis gasoline, while minimizing the possibility of carryover from sample to sample. The decrease in column bleeding demonstrates the increase in thermal stability of the DB-HeavyWAX compared to traditional WAX columns. In addition, DB-HeavyWAX has a similar selectivity to Agilent J&W DB-WAX. This selectivity provides easier method translation when replacing a traditional WAX column with a DB-HeavyWAX. This column replacement gives the added benefits of:

- Extended temperature limit
- Improved stability
- More complete analysis of larger aromatic compounds

References

1. Yang, D.; *et al.* Pyrolysis Gasoline Hydrogenation in the Second-Stage Reactor: Reaction Kinetics and Reactor Simulation; *Industrial & engineering chemistry research* **2008**, *47*, 1051–1057.
2. ASTM D6563. Standard Test Method for Benzene, Toluene, Xylene (BTX) Concentrates Analysis by Gas Chromatography.
3. Abercrombie, V.; Provoost, L. Increased Thermal Stability and Maximum Temperature of the Agilent J&W DB-HeavyWAX Column. *Agilent Technologies Application Note*, publication number 5991-9035EN, **2018**.

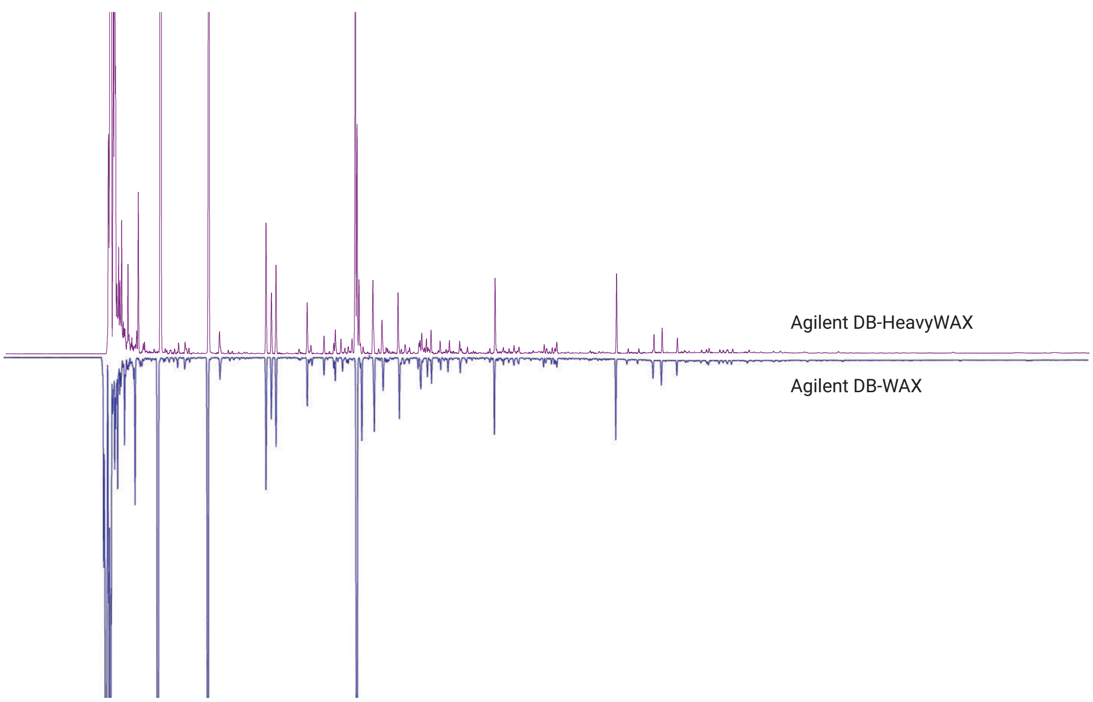

Figure 3. A Pyrolysis gasoline sample analyzed on an Agilent J&W DB-HeavyWAX (60 m × 0.25 mm, 0.25 µm) and Agilent J&W DB-WAX (60 m × 0.25 mm, 0.25 µm) column by ASTM D6563, to compare selectivity.

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