

Using the Agilent J&W DB-HeavyWAX Column as the Second Dimension in Comprehensive 2D Chromatography (GC×GC) for the Analysis of Diesel Oil

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Abstract

This Application Note evaluates the performance of the Agilent J&W DB-HeavyWAX column as secondary column in comprehensive two-dimensional gas chromatography (GC×GC) for the characterization of diesel oil. This analysis is challenging due to matrix complexity. To achieve suitable 2D resolution, a two-dimensional chromatographic technique, as well as careful choice of the column set, is required. The J&W DB-HeavyWAX can operate at higher temperatures than traditional WAX columns, allowing good polarity-based selectivity, while providing faster analysis times and an extended operational range.

Introduction

To provide enhanced separation power and superior peak capacity, GC×GC combines two analytical columns, called dimensions, within one analytical method. Thanks to these unique features, GC×GC has become the method of choice for the detailed characterization of highly complex samples that cannot be approached with traditional GC. This is the case for many petrochemical products, which are very challenging due to the huge number of compounds covering a wide range of volatilities and chemistries.

From a theoretical point of view, first and second dimensions should have independent separation mechanisms to maximize resolution. In practice, it is accepted that this is not feasible. However, to make best use of the 2D space, phases are generally selected to be as different as possible.

Typical column sets encountered in petrochemical analysis are made of a nonpolar and a midpolar column. The goal is to couple separations based on boiling point and polarity, respectively. Midpolar phases are selected for their ability to separate based on polarity and their wide temperature range. This flexible, robust setup is widely used with good results. Conversely, their separation mechanism is only partially determined by polarity, due to the significant role played by volatility.

In some cases, using a highly polar column with nonpolar phases may be desirable to maximize the role played by polar interactions and improve resolution for specific compounds/groups. In general, WAX-type stationary phases are a natural choice for this purpose. These phases are, for instance, very efficient in separating aliphatic and aromatic fractions, and in providing additional separation of the latter into subgroups (for example, mono-/di-/tri-aromatics). However, their use is limited by their low maximum temperature of 240 °C.

The J&W DB-HeavyWAX has an extended temperature limit of up to 280 °C under isothermal conditions (290 °C when programmed). This higher limit permits analysis of higher boiling compounds without risking the integrity of the column. This Application Note examines the use of the J&W DB-HeavyWAX as the second dimension for GC×GC with thermal modulation to obtain extended operational range.

Experimental

Materials and methods

All measurements were performed with an Agilent 7890B GC equipped with a Zoex ZX2 cryogen-free thermal modulator and an Agilent 5975C MSD with triple-axis detector controlled with the Agilent MassHunter software. 2D data were visualized and processed with the GC Image software package.

Results and discussion

A sample of diesel oil was injected undiluted, and analyzed by GC×GC with a final oven program temperature of 280 °C (full details in Table 1). Figure 1 shows the highly structured 2D plot and the efficient separation. Different chemical groups that fully coeluted on the nonpolar primary column were efficiently separated based on polarity on the secondary J&W DB-HeavyWAX. Additionally, several individual peaks were fully resolved, providing a detailed picture of the diesel oil used as the test sample.

Table 1. Instrument conditions.

GC conditions	
Column set	First dimension: Agilent J&W HP-5ms (30 m × 0.25 mm, 0.25 µm) Modulation loop: deactivated empty fused-silica (1 m × 0.10 mm, 0.10 µm) Second dimension: J&W DB-HeavyWAX (1 m × 0.1 mm, 0.10 µm)
Carrier	Helium, constant flow, 0.7 mL/min
Inlet	0.1 µL, 250 °C, split mode, split ratio 1:150
Oven	45 °C (5 minutes), 3 °C/min to 280 °C (6.7 minutes)
Transfer line	280 °C
Modulator conditions	
Modulation period	6 seconds
Hot jet pulse	350 ms
Hot jet temperature	250 °C (5 minutes), 3 °C/min to 400 °C
MSD conditions	
Acquisition mode	EI, Full scan
Mass range	50–300 <i>m/z</i>
Scan rate	12,500 u/s

The analysis was replicated 60 times to assess the thermal stability of the column after re-iterated heating cycles to 280 °C with final hold time. Figure 2 shows the comparison of a complex area, and highlights some test compounds selected as reference. The chromatographic pattern is consistent through the sequence, and no negative effects were observed in terms of peak width or shape after repeated exposure at 280 °C. Changes in terms of retention time in the second dimension were marginal. Only a small loss in retention was observed for the most retained compounds (Figure 3). Overall repeatability was satisfactory: standard deviations were in the order of 0.02–0.03 seconds, and RSDs were mostly <1 %, and always ≤ 2 % even for compounds with a retention time <1 second (Table 2).

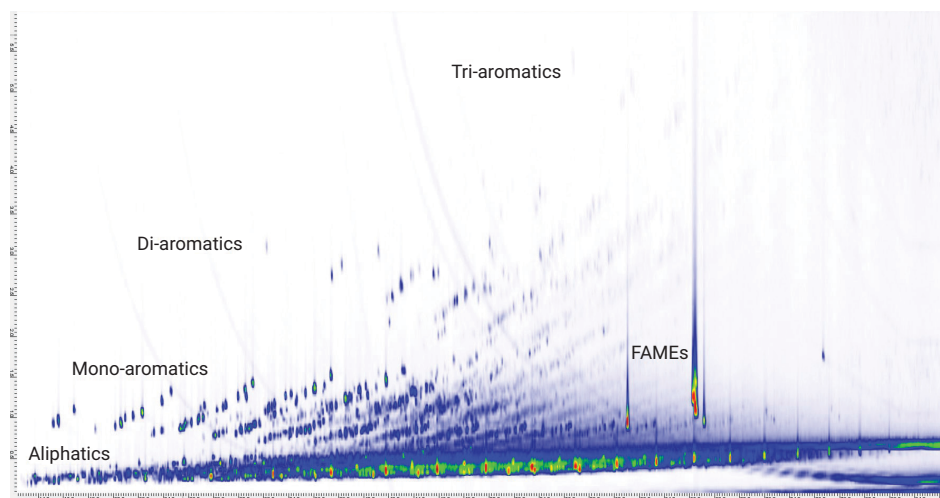


Figure 1. GCxGC run for a diesel oil with a nonpolar primary column and a J&W DB-HeavyWAX second dimension.

Table 2. Retention time (in seconds) and repeatability (n = 60) for selected test compounds for the J&W DB-HeavyWAX second dimension.

Compound	Mean (sec)	Std. dev.	% RSD
Methyl palmitate	0.92	0.02	1.7
Methyl stearate	0.93	0.02	2.0
1,2,3,4-Tetrahydro-naphthalene	1.38	0.02	1.2
1,2,3,4-Tetrahydro-5-methyl-naphthalene	1.48	0.02	1.5
2-Methyl-naphthalene	2.69	0.03	0.9
1-Methyl-naphthalene	2.81	0.03	1.0
Biphenyl	2.99	0.03	0.9
Naphthalene	3.02	0.03	1.0
Fluorene	3.85	0.03	0.8
Anthracene	5.33	0.03	0.6

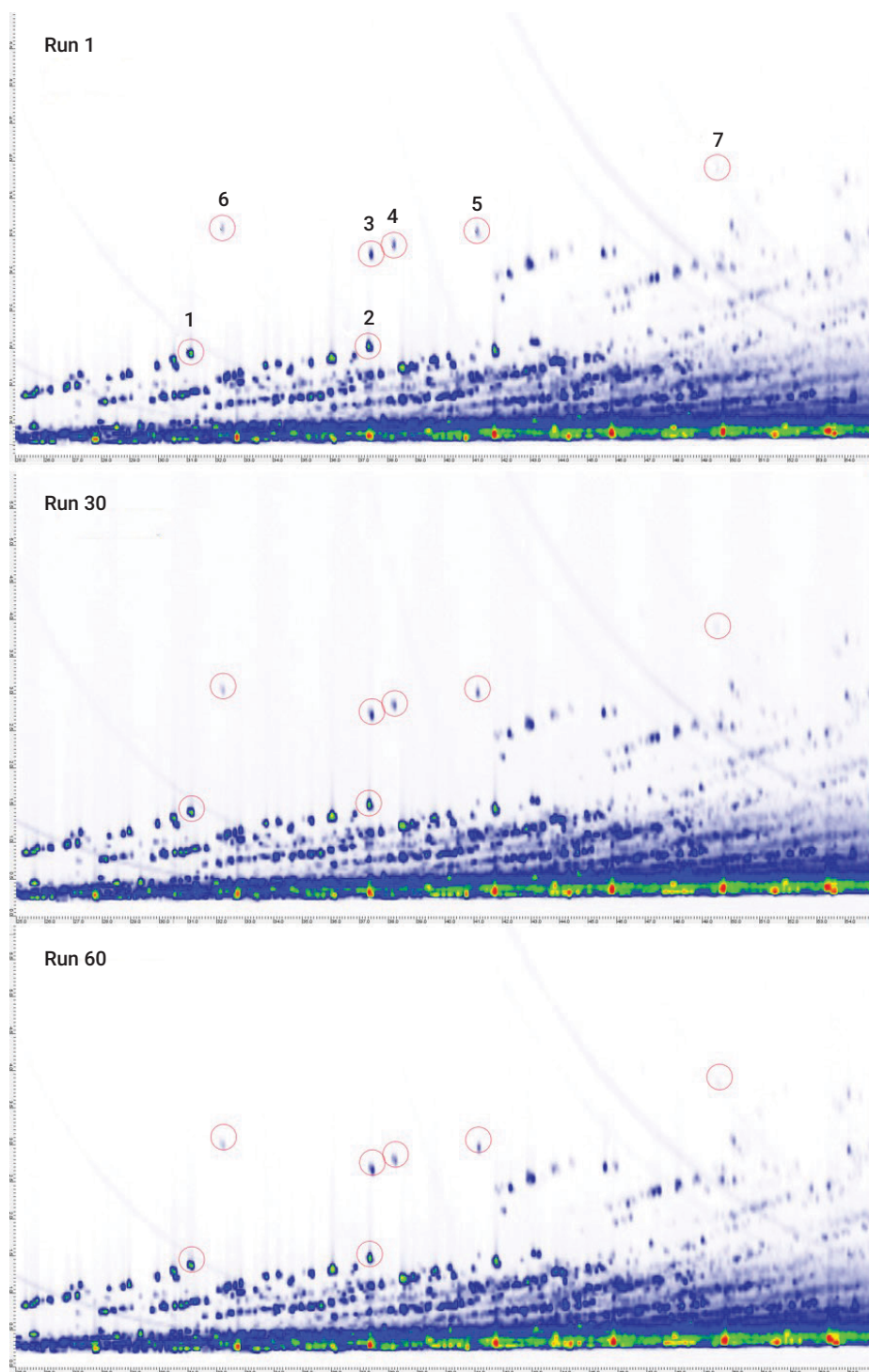


Figure 2. Comparison of a complex area for GCxGC runs with a J&W DB-HeavyWAX second dimension with a final temperature of 280 °C. Test compounds: 1. 1,2,3,4-tetrahydro-naphthalene; 2. 1,2,3,4-tetrahydro-5-methyl-naphthalene; 3. 2-methyl-naphthalene; 4. 1-methyl-naphthalene; 5. biphenyl; 6. fluorene; 7. naphthalene.

These results are remarkable, considering the very short retention times in the second dimension and the extremely narrow peaks (widths at half height were in the range of 80–150 milliseconds). These features make this test highly sensitive and unforgiving to poor column efficiency.

The same diesel oil was analyzed under identical conditions on a typical J&W DB-WAX second dimension with a final oven temperature of 240 °C. In general, the J&W DB-WAX shows increased retention, but the selectivity and overall chromatographic 2D resolution obtained with the J&W DB-HeavyWAX are comparable (Figure 4). Due to the limited final temperature, a longer hold time was required to elute the sample, leading to a slower analysis. High boiling point peaks that elute in the final isothermal window are broader and shifted towards longer elution times, with negative impact on resolution. Figure 5 shows an example for the paraffins. The J&W DB-HeavyWAX phase eliminates, or at least reduces, this effect. Figure 6 shows that the two WAX phases are also similar in terms of retention time repeatability (10 repeated runs), with RSDs mostly <0.8 %, and always <1.3 % (standard deviations ≤ 0.02 seconds).

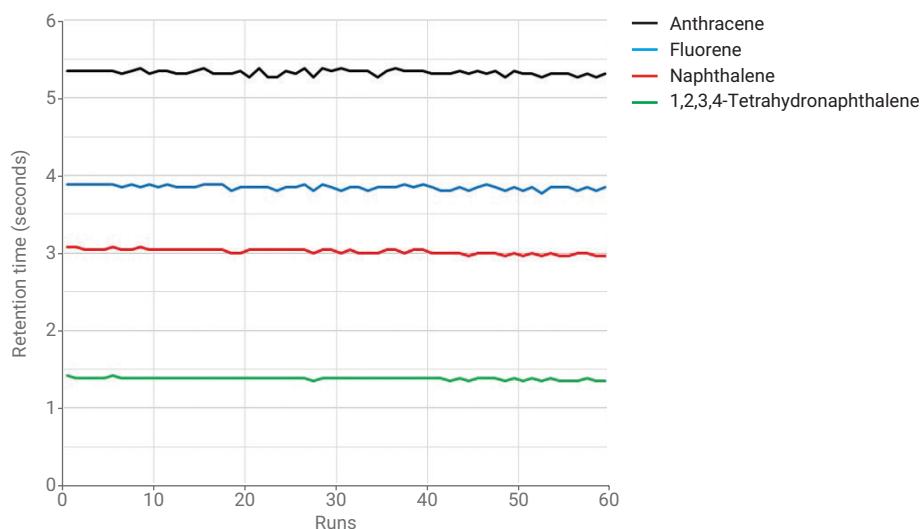


Figure 3. Trend of retention time on the J&W DB-HeavyWAX second dimension over 60 repeated injections.

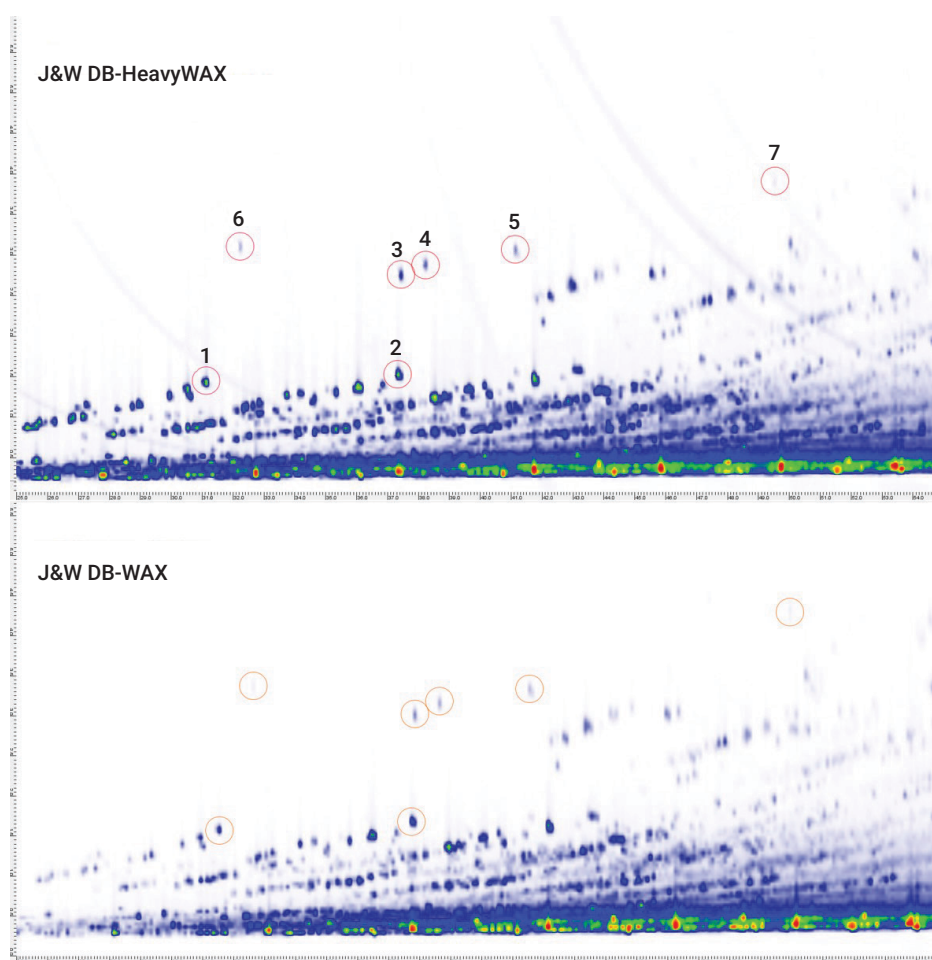


Figure 4. Comparison of a complex area for GCxGC runs with a J&W DB-HeavyWAX and a J&W DB-WAX second dimension, respectively. Test compounds: 1. 1,2,3,4-tetrahydro-naphthalene; 2. 1,2,3,4-tetrahydro-5-methyl-naphthalene; 3. 2-methyl-naphthalene; 4. 1-methyl-naphthalene; 5. biphenyl; 6. fluorene; 7. naphthalene.

Conclusion

The J&W DB-HeavyWAX column was tested as the second dimension for GC×GC with thermal modulation for a diesel oil sample. The J&W DB-HeavyWAX provides a higher maximum temperature of 280/290 °C (isothermal/programmed) than standard WAX-type stationary phases. This allows shorter analysis times and an extended operational range towards higher boiling compounds. Good thermal stability was observed after repeated heating cycles up to 280 °C. Performance did not show significant signs of deterioration, even for the critical test provided by the fast, sharp two-dimensional peaks. Chromatographic performance matched that of typical J&W DB-WAX columns.

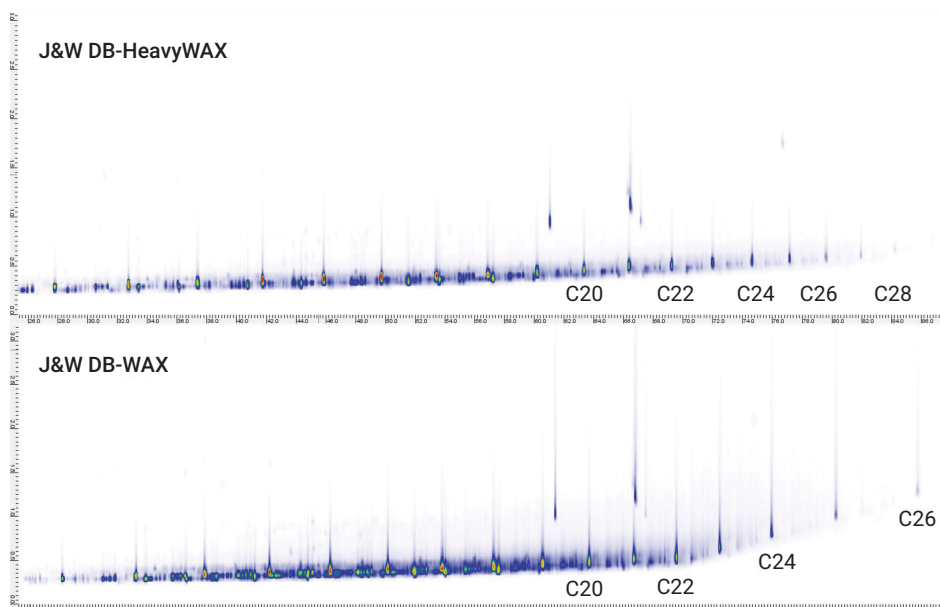


Figure 5. Comparison of selected ion chromatograms for m/z 57 with a J&W DB-HeavyWAX and a J&W DB-WAX second dimension, respectively.

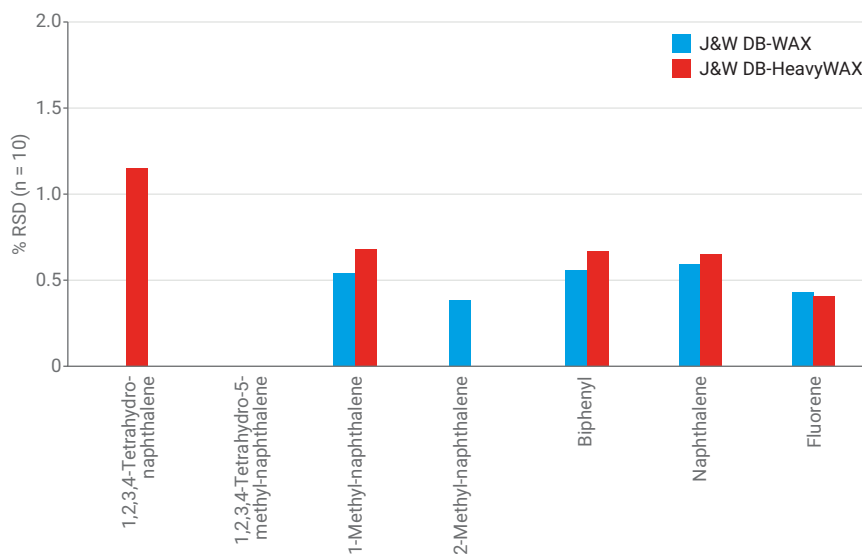


Figure 6. Comparison of repeatability (n = 10) with a J&W DB-HeavyWAX and a J&W DB-WAX second dimension, respectively. For the columns not shown, RSD <0.01 %.

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