Application Note

Flavors and Fragrances

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Fast Analysis of Smoke Taint Compounds in Wine with an Agilent J&W DB-HeavyWax GC Column

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Abstract

The analysis of smoke taint compounds such as guaiacol and 4-methylguaiacol in wine requires a sensitive GC/MS detection method such as Selective Ion Mode (SIM) or Multiple Reaction Mode (MRM). The DB-HeavyWAX GC column is ideal for the analysis of these polar aromatic compounds in wine. The increased maximum isothermal temperature of the DB-HeavyWAX, of 280 °C, allows for baking off heavier compounds in wine. In addition, the improved thermal stability of the DB-HeavyWAX column allows for retention time stability over long periods of injections of wine, and increases reproducibility.

Introduction

In the wine making process, the growth and maturation of the grape is arguably the most important step. During the period of veraison, acid concentration decreases and sugar concentration increases while aromatic and flavor compounds start to develop. There are many external factors, weather conditions being the most influential, that determine when grapes have matured and are ready for harvest. Other environmental conditions, unrelated to temperature, such as smoke from nearby fires, can have a large and negative impact on the sensory quality of the wine.

Wildfires are not uncommon near vineyards, especially in Australia and the American West. When these fires occur after verasion, the grape leaves absorb the smoke. Then, photosynthesis drives the conversion of carbon dioxide into carbohydrates, and sugar levels increase in the berries, but it also transfers the precursors of smoke compounds from the leaf to the berry[1]. During fermentation, strong acids hydrolyze these precursors, forming the aromatic compounds guaiacol and 4-methylguaiacol. The presence of these compounds, because of smoke, is often referred to as smoke taint. The longer the berries hang on the vine after exposure to smoke, the greater the potential for smoke precursor compounds to contaminate the berries, risking contamination of the finished wine[2].

While aging wine in oak barrels can also contribute to the concentration of guaiacol and 4-methylguaiacol, the ratio of these two compounds will differ. Smoke-tainted berries contain almost four times as much guaiacol as 4-methylguaiacol[3]. The aroma contributed by oak barrels will be perceived as smoke and char. In contrast, when the two compounds are present due to smoke taint, it will be more reminiscent of campfires and ashtrays, which is not desirable in wine.

Detection limits for the analysis of smoke taint compounds must be sensitive enough to detect 1 ppb, which is why SIM is commonly used in the GC/MS analysis[4]. Direct analysis of wine can be challenging because sugars and aromatic compounds with higher retentions require a higher final temperature to bake off from the column than is safe with traditional WAX type columns. The improved temperature limit of the DB-HeavyWAX GC column, of 280 °C isothermal and 290 °C programmed, allows for safe bake-out of the column after the direct injection of undiluted wine[5]. In addition, using faster ramping rates and a higher final temperature of 280 °C, the analysis of smoke taint compounds in wine can be decreased to under 15 minutes.

Materials and methods

For these experiments, an Agilent 7890 GC coupled with an Agilent 7010 triple quadrupole GC/MS equipped with a split/splitless inlet, and an Agilent 7693 sampler with Agilent MassHunter control software was used.

Sample preparation

A 10 % ethanol solution was prepared by diluting pure ethanol (Sigma-Aldrich) in distilled water using Class A volumetric glassware. Standards of guaiacol and 4-methylguaiacol were from Sigma-Aldrich, and prepared at a concentration of 10 ppb in the 10 % ethanol solution. Commercially available red and white wine was purchased at local markets, and 0.5 µL was injected neat.

Instrument conditions

GC conditions	
Column	DB-HeavyWAX 30 m × 0.25 mm, 0.25 µm (p/n 122-7132)
Carrier	Helium, constant flow, 1.2 mL/min
Oven	150 °C (2.0 minutes), Ramp 30 °C/min to 280 °C (8 minutes)
Inlet	Split mode, 250 °C, split ratio 200:1
Inlet liner	UI-Low pressure drop (p/n 5190-2295)
Sampler	Agilent 7693 autosampler
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	2 mL, screw top, amber, write-on spot, certified, (p/n 5182-0716, 100/pk)
Vial inserts	250 µL glass inserts, deactivated (p/n 5181-8872, 100/pk)
Vial caps	9 mm blue screw cap, PTFE/red silicone septa (p/n 5185-5820, 500/pk)
Inlet/MSD	85:15 Vespel: graphite ferrules (p/n 5062-3508, 10/pk)

7010 triple quadrupole MSD conditions

Peak	Compound	Quantifier			Qualifier			Qualifier		
		Precursor ion (*m/z*)	Product ion (*m/z*)	Collision energy (V)	Precursor ion (*m/z*)	Product ion (*m/z*)	Collision energy (V)	Precursor ion (*m/z*)	Product ion (*m/z*)	Collision energy (V)
1	Guaiacol	180.9	81.0	10	123.9	81.1	20	123.9	108.9	10
2	4-Methylguaiacol	137.9	122.9	10	122.9	66.9	10	122.9	95.0	5

Results and discussion

The analysis of aromatic fragrance compounds in wine can be difficult by liquid injection. This is because wine contains a wide variety of compounds, including heavier and higher boiling compounds, which require a higher final temperature or longer run time to completely elute from the column. With the ability to run to a final temperature of 280 °C, all compounds could be eluted off the DB-HeavyWAX column in 15 minutes. Figure 1 demonstrates the ability to elute compounds such as *m*-phenethyl alcohol, identified by NIST search, and only hold the final temperature of 280 °C for eight minutes. If a lower final temperature were used, a longer final hold time would be needed for this compound to elute off the column, resulting in a longer overall run time.

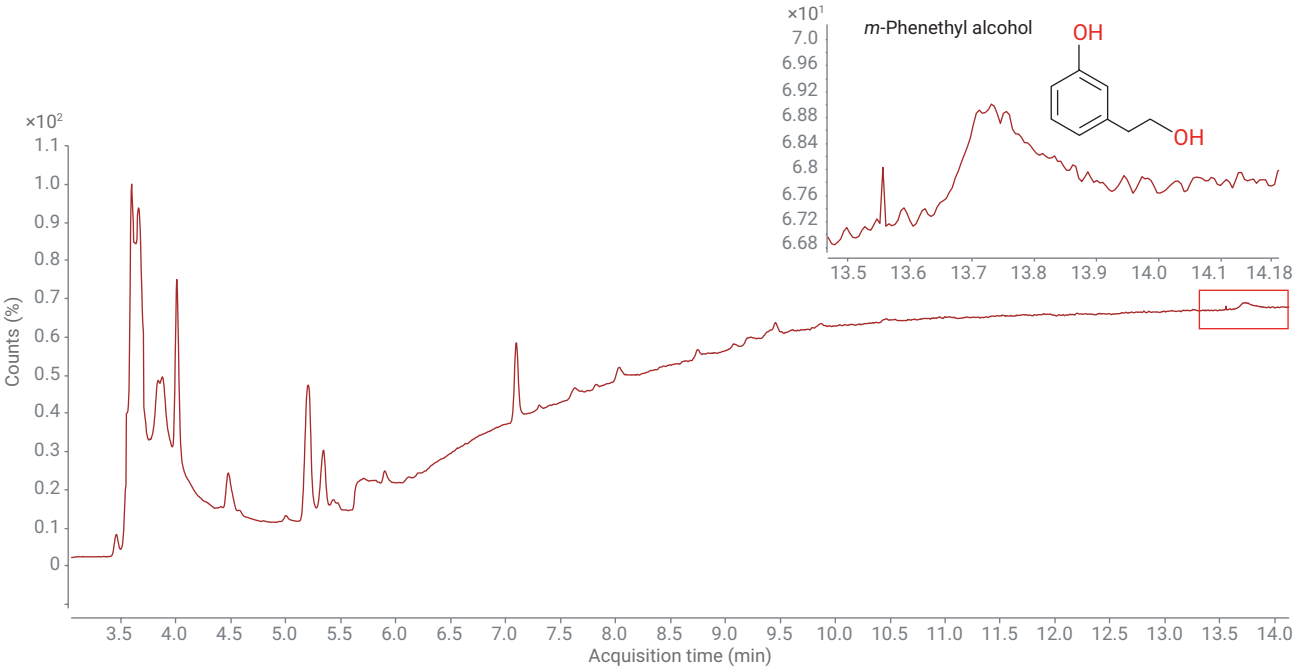

Figure 1. Full scan of injection of red wine.

Because the olfactory system can detect smoke taint compounds at low levels, approximately 1 ppb in wine, sensitive methods for detection, such as SIM or MRM, are required. Injecting wine without any sample preparation can result in interferences that can be problematic. However, by using a GC/QQQ operated in MRM, the required sensitivity is achievable without requiring time-consuming sample preparation. Figure 2 shows that a standard of smoke taint compounds at 10 ppb was injected and analyzed using MRM. The good peak shape of the standard demonstrates the sensitivity of this method.

Figure 3 shows a sample of unoaked, or bag-n-box, white wine analyzed with and without a spike of 10 ppb of smoke taint compounds. Even in the sample matrix of white wine, the peaks for guaiacol and 4-methylguaiacol were clearly detected.

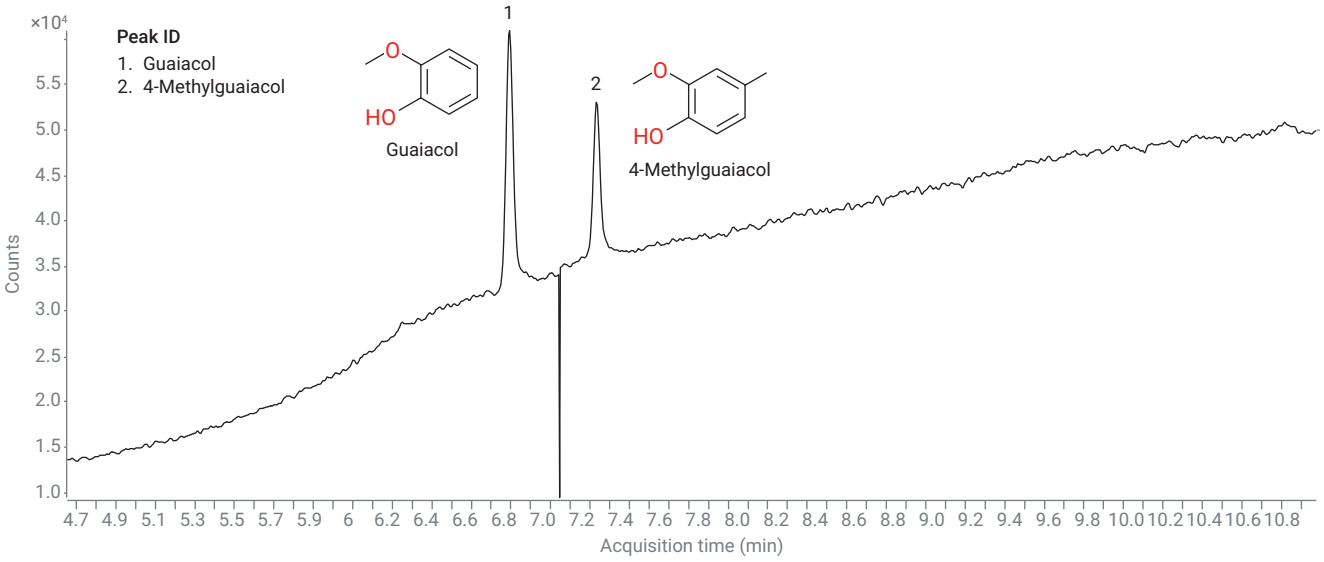

Figure 2. Standard of 10 ppb smoke taint compounds collected using MRM mode.

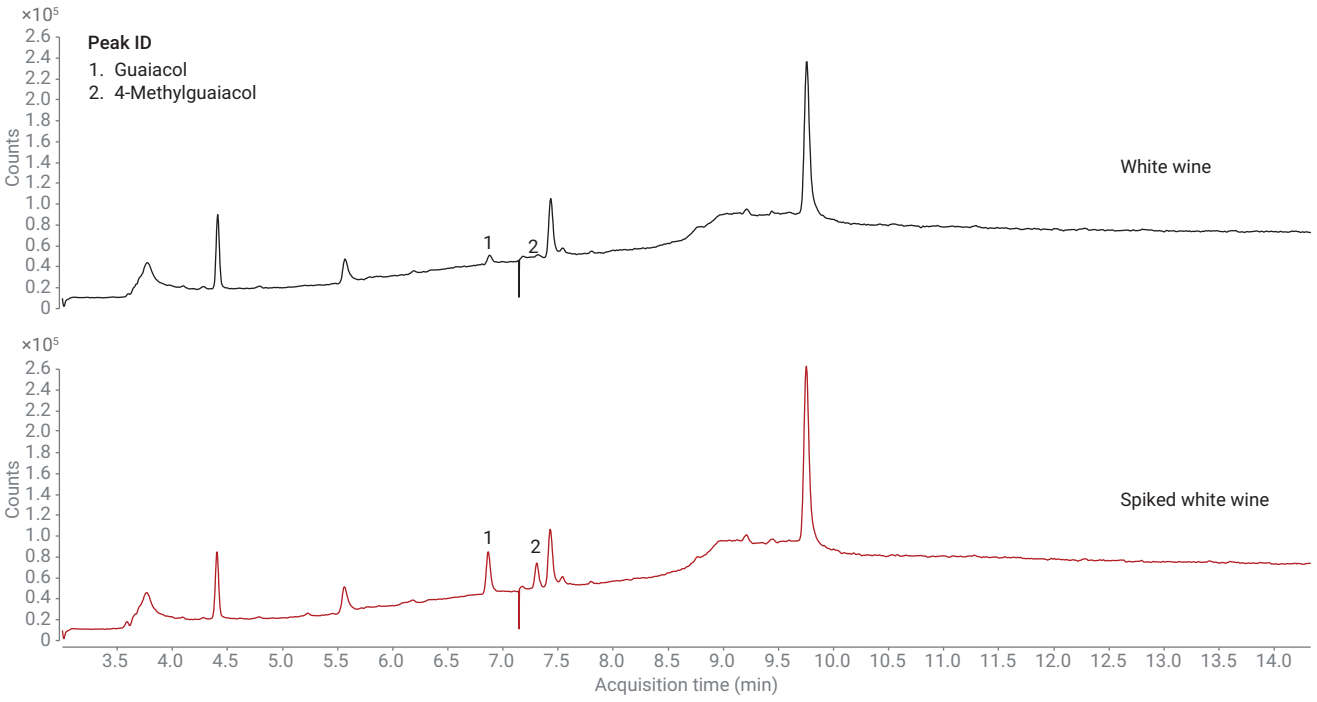

Figure 3. White wine without and with spike of 10 ppb of smoke taint compounds collected using MRM mode.

Reproducibility

Figures 4A and 4B demonstrate the reproducibility and ruggedness of the DB-HeavyWAX column for the analysis of smoke taint compounds over 100 injections of an aqueous matrix. A standard of 10 ppb smoke taint in Figure 4A and red wine in Figure 4B, was injected before and after 100 injections of 10 % ethanol in water. Both matrices, the standard in 10 % ethanol and red wine, were reproducible after many aqueous injections, demonstrating the ruggedness of the DB-HeavyWAX for multiple aqueous injections.

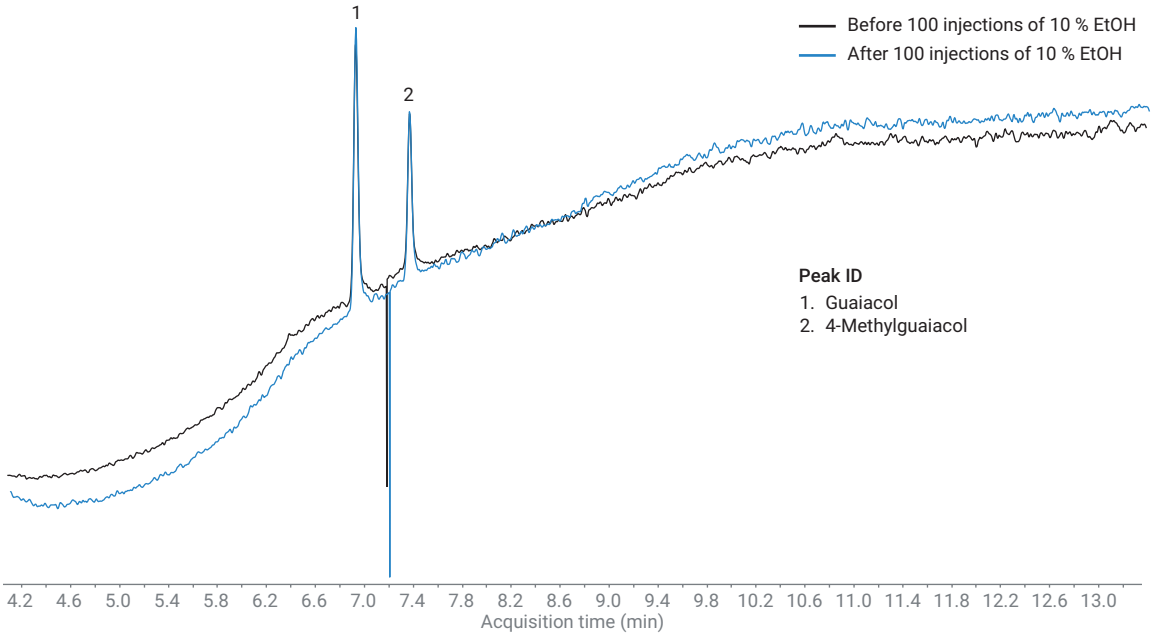

Figure 4A. Standard of 10 ppb smoke over 100 injections of 10 % ethanol, collected by MRM.

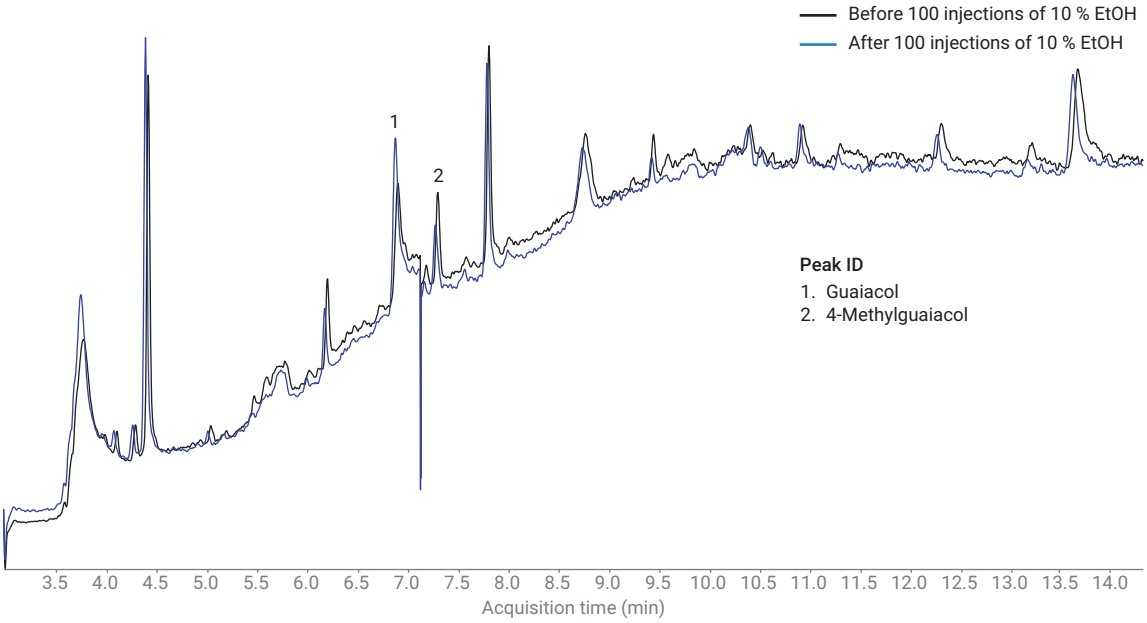

Figure 4B. Red wine before and after 100 injections of 10 % ethanol, collected by MRM.

Conclusion

The analysis of smoke taint compounds in wine by multireaction mode mass spectrometry using the DB-HeavyWAX GC column provides a sensitive and robust method. To ensure that the later eluting compounds in wine samples elute off the column, the increased temperature range of the DB-HeavyWAX, of 280 °C isothermal and 290 °C programmed, allows for a safer bake-out of the column, and decreases the risk of carryover compounds. With the improved thermal stability of the DB-HeavyWAX, retention times are stable even after 100 aqueous injections, demonstrating the robustness of the DB-HeavyWAX.

References

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3. Herve, E.; Price, S.; Burns, G. Free Guaiacol and 4-Methylguaiacol as Markers of Smoke Taint in Grapes and Wines: Observations from the 2008 Vintage in California. *Proceedings of the 9e Symposium International d'Œnologie*, Bordeaux, France, **2011**.
4. Wilkinson, K. L.; *et al.* Comparison of methods for the analysis of smoke related phenols and their conjugates in grapes and wine. *Australian Journal of Grape and Wine Research* **2011**, *17*, S22–S28
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