



Quantification of “smoke taint” compounds in wine by SPME-GCMS

Madeleine DiGregorio, Alan Owens, Andy Sandy, Rick Karbowski, Eberhardt Kuhn, Nicole Lock
Shimadzu Scientific Instruments, Inc., Columbia, MD 21046

1. Introduction

“Smoke taint” refers to the aroma that wine takes on when grapes in a vineyard are exposed to smoke from wildfires during ripening, a frequent occurrence in Australia and the western US which has significantly increased in recent years. Wines afflicted with smoke taint are often described as “campfire” or “ash tray” and are typically not accepted by consumers. Because of this, a fast and accurate screening method for smoke taint is necessary for winemakers who are faced with remediation, blending, or discarding decisions when grapes are being harvested during or after a wildfire.

Guaiacol and 4-methylguaiacol are two compounds typically analyzed as markers of smoke taint, as they are most abundant compared to other smoke-derived odorants like 4-ethylguaiacol, 4-ethylphenol, and eugenol.

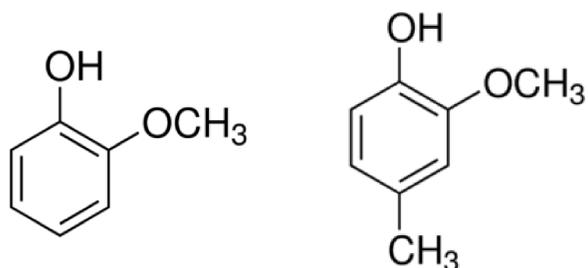


Figure 1. Molecular structures of guaiacol (left) and 4-methyl guaiacol (right)

By combining solid phase microextraction (SPME) sampling prior to analysis by triple quadrupole gas chromatography-mass spectrometry (GCMS), sensitivity of volatiles increases while matrix effects decrease. In SPME, a sorbent fiber is exposed to the headspace of a sample allowing volatiles to adsorb to the fiber, which is then injected into the system where desorption occurs immediately prior to analysis. This technique is ideal for the analysis of ppb-level odorants, such as smoke taint compounds, because of the sensitivity it can achieve while minimizing sample preparation.

In this work, a multiple-reaction monitoring (MRM) method with SPME preconcentration was developed for quantification of guaiacol and 4-methylguaiacol in smoke taint-afflicted wines. Method validation was performed on wines containing low-ppb levels of analytes. Sub-ppb detection limits were achieved for both compounds with the use of a deuterated internal standard.

2. Experimental Methods

The table below specifies the instrument conditions used on the Shimadzu GCMS-TQ8050 NX equipped with an AOC-6000 autosampler throughout this work.

“Model wine” samples were prepared as follows: 1.5 g of NaCl was weighed into 20 mL standard headspace vials containing 5 mL 10% ethanol solution, prior to spiking in guaiacol and 4-methylguaiacol standards, plus internal standard *d*₃-guaiacol (at 20 ng/L).

Table 1. GCMS instrument conditions for SPME, GC, and MRM parameters

GCMS-TQ8050 NX with AOC-6000	
SPME Fiber	PDMS/DVB/Carboxen
Incubation	60 °C, 15 min
Extraction	60 °C, 15 min
Desorption	10 min
Gas Chromatography	
Injection Port	230 °C splitless (1 min); split 10:1
Column	SH-Rxi-5MS column (30 m × 0.25 mm × 0.25 μm) He carrier gas Constant Linear Velocity, 31.4 cm/s
Oven Temperature	40 °C > 180 °C (50 °C/sec) > 210 °C (5 °C/sec) > 250 °C (50 °C/sec) – 2 min
Mass Spectrometry	
Interface Temperature	250 °C
Ion Source Temperature	200 °C
Detector Voltage	+0.5 kV Relative to tune result
Scan Range	40 to 400 m/z
Event Time	0.3 seconds
Ions for Quantification	Guaiacol – 124 > 109 4-methyl guaiacol – 138 > 123.1, 123 > 95.1, 123 > 67.1 <i>d</i> ₃ -guaiacol – 127 > 109.1, 127 > 81.1, 127 > 53.1

3. Results

3.1 SPME Calibration curves for guaiacol and 4-methyl guaiacol

Calibration curves levels were each run in triplicate, with blanks run in between every sample to eliminate carryover. Internal standard calibration curves were built for both guaiacol and 4-methyl guaiacol with *d*₃-guaiacol as the internal standard. Excellent linearity ($R^2 = 0.99$) was observed for both analytes, as shown in Figures 2 and 3.

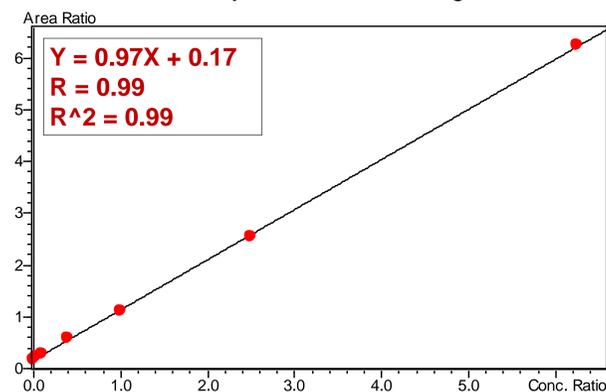


Figure 2. Calibration curve for guaiacol with *d*₃-guaiacol internal standard by SPME

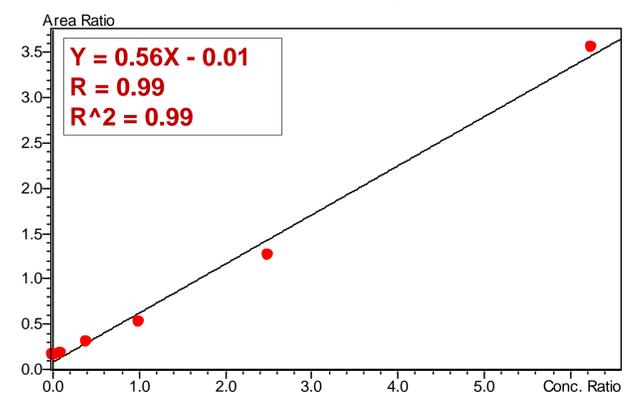


Figure 3. Calibration curve for 4-methyl guaiacol with *d*₃-guaiacol internal standard by SPME

3.2 Limits of detection

Limits of detection were calculated from the 0.5 ng/L calibration level; based on 3 x signal-to-noise (S:N) ratio. For both guaiacol the limit of detection for this method was 0.05 ng/L and for 4-methyl guaiacol it was 0.5 ng/L, roughly 2 orders of magnitude below their odor thresholds (approximately 20 μg/L guaiacol and 60 μg/L 4-methyl guaiacol).

3.3 Real wine samples

Real wine samples were run to assess the recovery of this method. Both red and white wines were spiked with 8 ng/L of guaiacol and 4-methylguaiacol standards, and 20 ng/L of internal standard. Samples were run in duplicate.

Recovery in real samples		
	guaiacol	4-methyl guaiacol
Red wine	88%	4%
White wine	56%	56%

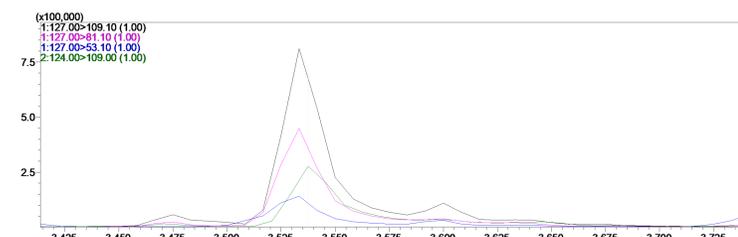


Figure 4. Representative chromatogram of guaiacol and *d*₃-guaiacol internal standard in white wine

The lower recovery for 4-methyl guaiacol in red wine is due to significant interferences at the monitored transitions. Other recoveries may be improved with further optimization of extraction conditions (e.g. higher temperature, longer time).

4. Conclusion

The method reported in this work is fast (30 min per sample by overlapping autosampler extraction with GCMS analysis) and appropriate for trace-level detection of smoke taint volatiles in wine. Limits of detection are well below the odor thresholds for these compounds, and the reproducibility is excellent at the lowest calibration level (0.5 ng/L).

