The Determination of 2,4,6-Trichloroanisole in Wine using Headspace Trap with GC/MS

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Introduction

2,4,6-trichloroanisole (TCA) is found in the cork used to seal glass wine bottles. The determination of TCA in wine is necessary due to the extremely low level of sensory perception for this compound. The literature reports taste thresholds to be between 4 and 10 parts per trillion (ppt) in white wines and between 10 and 30 ppt for the heavier red wines.[1] Above these thresholds, wines have an undesirable flavor.

The cork that is used to store wine contains many inherent phenolic compounds. These phenolic compounds can become chlorinated in the production of the cork and/or during sanitization with chlorine-based agents. The chlorinated phenols (Figure 2) are then methylated by the natural microbes in wine, producing TCA. Other chlorinated phenols such as 2,3,4,6-tetrachloroanisole are also produced. These phenols have a higher sensory threshold – thus they do not adversely affect the wine quality and do not require testing.

Wineries require a fast, reliable technique that can produce accurate and precise results for TCA analysis. Existing headspace technologies can produce the required accuracy and precision, as well as the high throughput, but they cannot reach the low parts-per-trillion detection-limit requirement for taste.[2] A static (equilibrium) headspace injection typically only injects a small aliquot (1/100) of the available headspace. This technique would be ideal if a large percentage of the available headspace vapor was injected onto the chromatographic system.

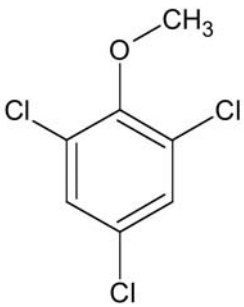

Figure 1. Structure of TCA.

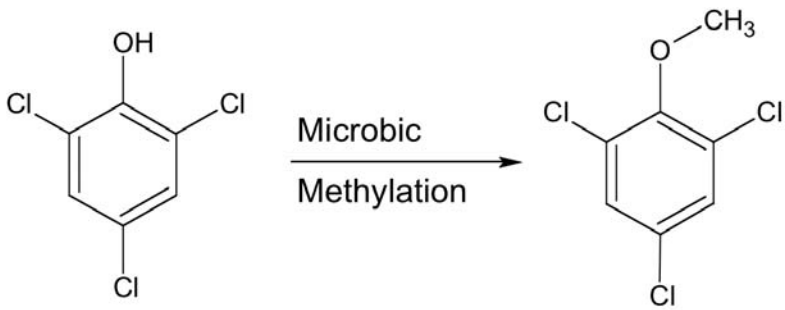

Figure 2. Production pathway.

The PerkinElmer® TurboMatrix™ Headspace Trap (HS Trap) with the Clarus® 500 GC/MS (Figure 3) meets all of the requirements for TCA analysis. The HS Trap functions by concentrating the vapor contents in the headspace vial onto a low-mass trap containing a chromatographic sorbent just above room temperature. The trap is then heated quickly to volatize the analytes onto the chromatographic system in a narrow band. This technique provides up to a 100-fold increase in sensitivity over standard headspace technology.

Experimental

A California white wine (bottled in 2000) was purchased in Toronto, Ontario, Canada. This wine was selected due to the synthetic cork used in the bottle, so it should have a minimum level of TCA. Ten grams of this wine were added to a 22-mL headspace vial (PerkinElmer part number B0104236). The vial was then sealed with silicone/PTFE septa (PerkinElmer part number B0104241). These septa had been baked overnight at 150 ˚C to ensure they were free from any volatile impurities before being used to seal the headspace vials.

A stock solution of 100 ppm (µg/mL) was prepared of 2,4,6-trichloroanisole in purge-and-trap grade methanol (Sigma-Aldrich, St. Louis, MO, USA). This stock solution was used to produce a 100-ppb (µg/L) spiking solution using 95% ethanol. Ethanol was selected to minimize the change in the matrix and minimize the sample's natural headspace pressure.

Several different sorbents were evaluated on the HS Trap, including Air Toxics (PerkinElmer part number M0413628), Tenax™ (PerkinElmer part number M0413535), and Carbopack Y and C (Supelco Inc., Bellefonte, PA, USA). All of these sorbent traps worked well, except for Carbopack C. The recovery of TCA from Carbopack C was poor – hence it was not used for this study. The data reported here were obtained using the Carbopack Y trap.

The TurboMatrix HS-40 Trap was controlled using the TurboMatrix control software and was coupled to the Clarus 500 GC/MS. The Clarus 500 GC was equipped with a programmable split/splitless (PSS) injector and programmable pneumatic control (PPC). A piece of deactivated fused silica (0.32 mm) was used as the transfer line from the TurboMatrix HS-40 Trap. The GC column was directly connected to this transfer line using a universal union (PerkinElmer part number N9302149). The Clarus 500 MS was controlled via TurboMass™ 5.0 control software and operated in EI mode. The SIFI™ (Single Ion + Full Ion scan acquired in the same injection) acquisition technique was used to collect data.

Table 1. Instrument Parameters.

Clarus 500 GC		**Clarus 500 MS**	**SIFI Conditions EI+**
Injector Temperature:	150 ˚C	Mass Range:	50-300 u; (SIR) m/z 195 + 210
Oven Program - Initial Temperature:	50 ˚C	Scan Time:	0.20 sec; 0.25 sec/each ion
Initial Time:	Hold 4 min	InterScan Delay:	0.01 sec; 0.01 sec
Ramp:	40 ˚C/min	Transfer Line Temperature:	200 ˚C
Final Temperature:	240 ˚C	Electron Energy:	70 eV
Final Time:	Hold 5 min	Detector Voltage:	600 V
Column:	Elite-5MS*	Threshold:	0
TurboMatrix HS-40 Trap		Thermostatting Time:	30 min
Needle Temperature:	75 ˚C	Pressurization:	1 min, 3 cycles
Transfer Line Temperature:	75 ˚C	Decay Time:	1.2 min
Oven Temperature:	70 ˚C	Outlet Split:	OFF
Trap Low Temperature:	40 ˚C	Vial Pressure:	40 PSI
Trap High Temperature:	280 ˚C	Column Pressure:	25 PSI
Dry Purge Time:	5 min	Desorb Pressure:	NA
Trap Hold Time:	5 min	Carrier Gas:	Helium (99.999%)
Desorb Pressure Time:	0 min	Trap Sorbent:	Carbopack Y

* PerkinElmer part number N9316282 (30 m, 0.25 mm, 0.25 µ)

Figure 3. Clarus 500 GC/MS with TurboMatrix HS Trap.

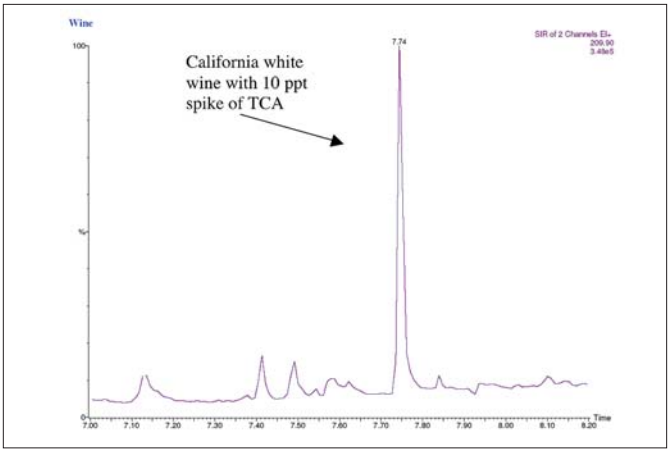

Figure 4. 10-ppt spike of 2,4,6-trichloroanisole in California white wine.

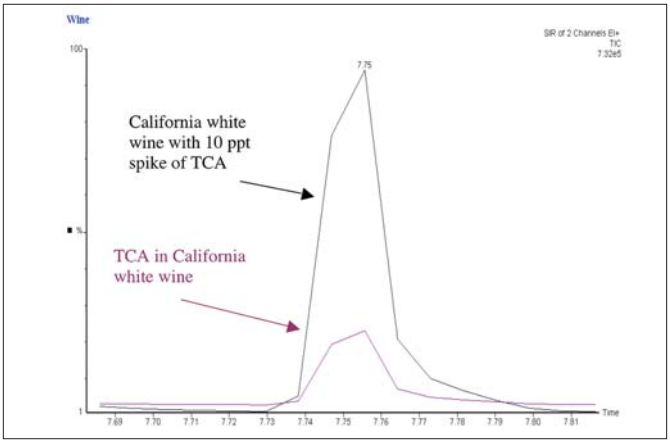

Figure 5. Overlay view of white wine with a 10-ppt spike of 2,4,6-trichloroanisole in the same white wine.

Figure 7 displays the mass spectrum of TCA, obtained in full scan mode. The ions at m/z 195 and 210 are two of the most intense, characteristic ions of TCA. The m/z 210 ion is the most abundant molecular isotope of TCA, while the m/z 195 ion represents the same molecular isotope of TCA, after the loss of a methyl group. These ions were chosen for the selected ion recording (SIR) acquisition mode used for quantifying TCA. Instrument parameters for the GC/MS and HS Trap system are listed in Table 1.

Results

The TurboMatrix HS-40 Trap was successful in meeting the low detection limit required for TCA analysis (Figure 4). The white wine with the synthesized cork appeared to contain a small quantity of TCA. Spiking this wine with 10 ppt TCA, both confirmed the retention time of TCA and the ability of the TurboMatrix HS Trap system to reach the low-ppt detection level. Figure 5 is an overlay of the SIR data obtained from the white-wine sample and the same wine spiked with 10 ppt of TCA.

Because of the multitude of components in wine, the SIR trace in Figure 4 shows a number of other components in the chromatographic run that produce ions at m/z 210 or 195. However, identification of TCA is confirmed through both the retention time and the comparison of the NIST-library mass spectrum of TCA (Figure 6) with the mass spectrum obtained from the 100-ppt spike of TCA in white wine (Figure 7).

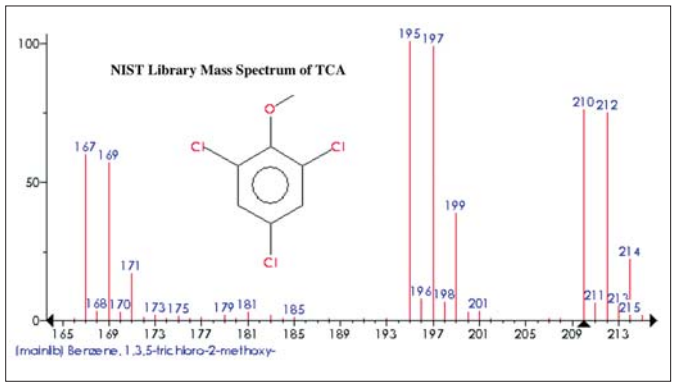

Figure 6. Expanded TCA mass spectrum obtained from NIST library.

Conclusions

The PerkinElmer TurboMatrix HS Trap with the Clarus 500 GC/MS meets all of the requirements for TCA analysis. The first requirement is the rigorous detection limit required. As demonstrated here, TCA can easily be determined in wine at low part-per-trillion levels. The second requirement is that the TCA determination be fast and easy. Using the system described in this report, all that is required is to place the sample in the HS Trap vial and then place the vial into the HS Trap's autosampler tray for complete automation. In addition, the HS Trap's overlapping thermostatting allows up to 12 samples to be processed simultaneously, thus allowing 50-75 TCA determinations to be made each day.

References

1. *For Quality Control of Natural Corks,* 11/23/2004, http://www.corkqc.com/SPMEFAQ.htm.

2. M.P Marti et al, Fast Screening Method for Determining 2,4,6-Trichloroanisole in Wines using a Headspace-Mass Spectrometry (HS-MS) System and Multivariate Calibration. Anal. Bioanal. Chem (2003) 376:497-501.

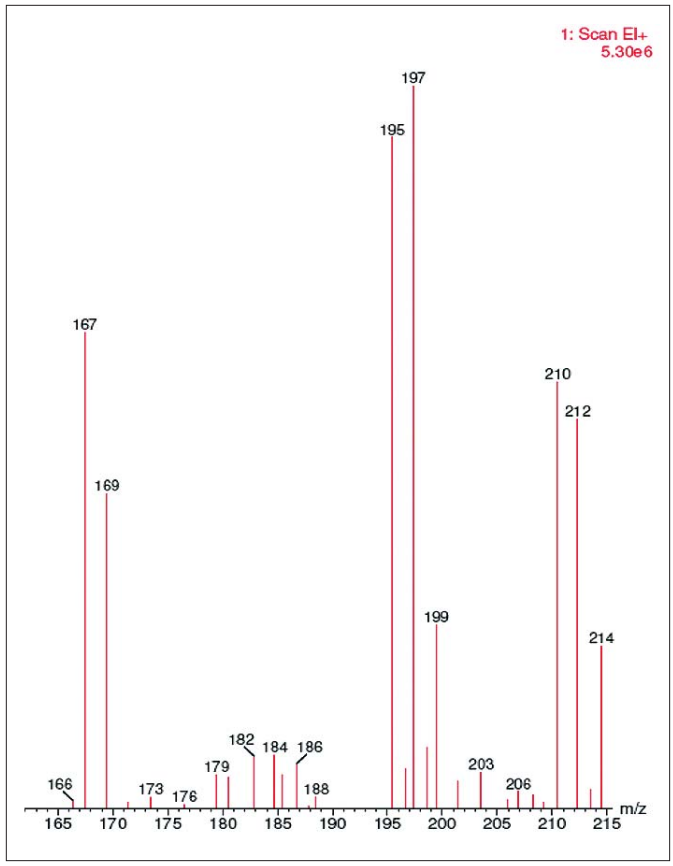

Figure 7. Expanded mass spectrum obtained from GC/MS analysis of 100-ppt spike of TCA in white wine.

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