Low Level Detection of Trichloroanisole in Red Wine

Application Note

Food/Flavor

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Abstract

Trichloroanisole (TCA) has an extremely low odor threshold. This compound is primarily responsible for "cork taint" in wines. TCA levels can often be detected by analytical instrumentation but not by consumers and many wines that contain TCA have won awards. TCA does not pose a health risk for anyone who detects a musty odor in their wine. However, the odor of TCA can be off putting and for that reason, wineries prefer to limit consumer exposure to this compound.

Introduction:

Wine corks have taken the blame for the musty, TCA, odors in wines. However, TCA can also be attributed to wine barrels or exposure to other wood sources when manufacturing or preserving wine. For this reason, many wineries have resorted to stainless steel wine barrels and synthetic corks. Still, many wineries prefer the use of wooden barrels as the wood can contribute to the overall flavor of the wine. Furthermore, market research has shown a preference for natural cork over synthetic corks or screw tops by U.S. consumers.[1]

TCA is formed when 2, 4, 6-Trichlorophenol (TCP) is exposed to either mold or chlorine. Any exposure can cause the TCP to undergo methylation and produce TCA. The process of simply cleaning the floor with a chlorinated detergent can cause TCA formation. Furthermore, fungal strains present in the wood or cork also have the ability to methylate the TCP thus forming TCA.

The human threshold for the detection of TCA is extremely low. In fact, most people can smell TCA down to part per trillion levels. In order to detect TCA at such low levels of contamination, analysts need to optimize the sampling and analysis of the wine. This application note will demonstrate the efficacy of using the FLEX autosampler and its drag and drop sampling software coupled with a Gas Chromatograph Mass Spectrometer (GCMS) for the detection of TCA at part per trillion levels.

Experimental:

The sampling system used for this study was the Flex Autosampler. A 100µm Polydimethylsiloxane (PDMS) SPME fiber was used for headspace sampling of the samples. Agitation of the samples was performed through an oscillation motion which is unique to the Flex and provides less wear and tear on the fiber. The Flex was coupled to a Shimadzu QP2010 SE GCMS analytical system while the GC was configured with a Restek Rxi-5Sil MS 30m x 0.250mm x 0.250µm column. Tables 1 and 2 list the experimental parameters for the Flex and the GCMS respectively.

Autosampler	FLEX
General	
Method Type	SPME
Sample Incubate Agitate	
Incubation Temp.	28ºC
Incubation Time	1.0min
Agitation	No
Extraction	
Fiber Guide Depth	65%
Sample Vial Fiber Depth	1.0cm
Fiber Extraction Time	30.0min
Fiber Extraction Agitation	Yes
Agitation Type	Oscillate
Agitation Delay	0.1min
Agitation Duration	29.0min
Wait	
Wait Input	GC Ready
Desorbtion	
Fiber Guide Speed	40%
Fiber Guide Depth	50%
Fiber Insertion Speed	75%
Fiber Insertion Depth	1.0cm
Fiber Desorbtion Time	3.0min
Injection Start Input	Start

Table 1: Flex Autosampler Experimental Parameters

GC/MS	Shimadzu QP2010 SE GCMS
Inlet	Split/Splitless
Inlet Temp.	270ºC
Pressure	57.4kPa
Mode	Splitless
Injection Pressure	50kPa for 3.0min.
Carrier Gas Saver	2:1 Split for 3.0min
Desorbtion	3.0min
Column	Rxi-5 Sil MS 30m x 0.25mm I.D. x 0.25µm film thickness
Oven Temp. Program	60ºC hold for 2.0 min, ramp 8ºC/min to 200ºC hold for 0.5min, total run time 20 min
Column Flow Rate	1.0ml/min.
Gas	Helium
Linear Velocity	36.5cm/sec
Source Temp.	220ºC
MS Transfer Line Temp.	300ºC
SIM Ions	m/z 195, 197, 210, 212
SIM Time	3.01 to 20.0min
Solvent Cut Time	3.0min

Table 2: GC/MS Experimental Parameters

Pure TCA was procured from Sigma Aldrich and a standard was made with methanol in order to calibrate the GCMS system. Each headspace vial was prepared with one gram of sodium

chloride. The calibration curve was prepared as described in Table 3. Next, the calibration curve was run using the parameters outlined in Tables 1 and 2. The results are displayed in Figure 1.

Trichloroanisole Standard			
Standard Concentration (ppb)	**Volume (µl)**	**Final Volume (µl)**	**Final Concentration (ppt)**
113	20	10000	226
113	10	10000	113
113	5	10000	56.5
113	2	10000	22.6
113	1	10000	11.3
113	0.5	10000	5.65

Table 3: Calibration Curve Preparation

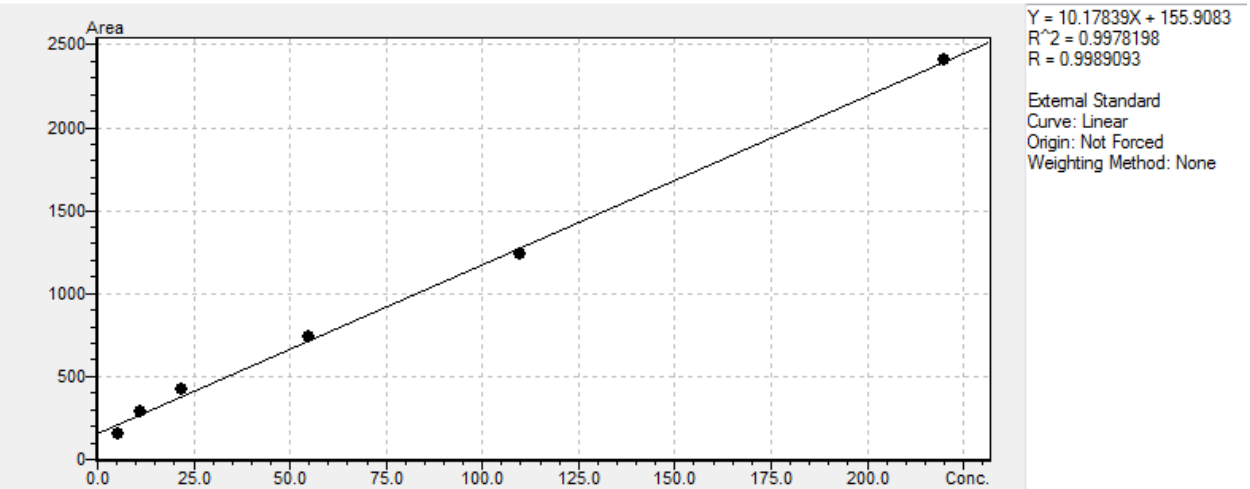

Figure 1: Calibration Curve.

After the calibration curve was established. Red wine was acquired from a local market. Next, it was recognized that the wine was sealed with a natural cork. Finally, ten milliliters of the wine was poured into a 20ml prepared headspace vial. The headspace vial was prepared with one gram of sodium chloride. The wine was then tested with and without 5ppt of TCA standard. The results are shown in Figures 2 and 3.

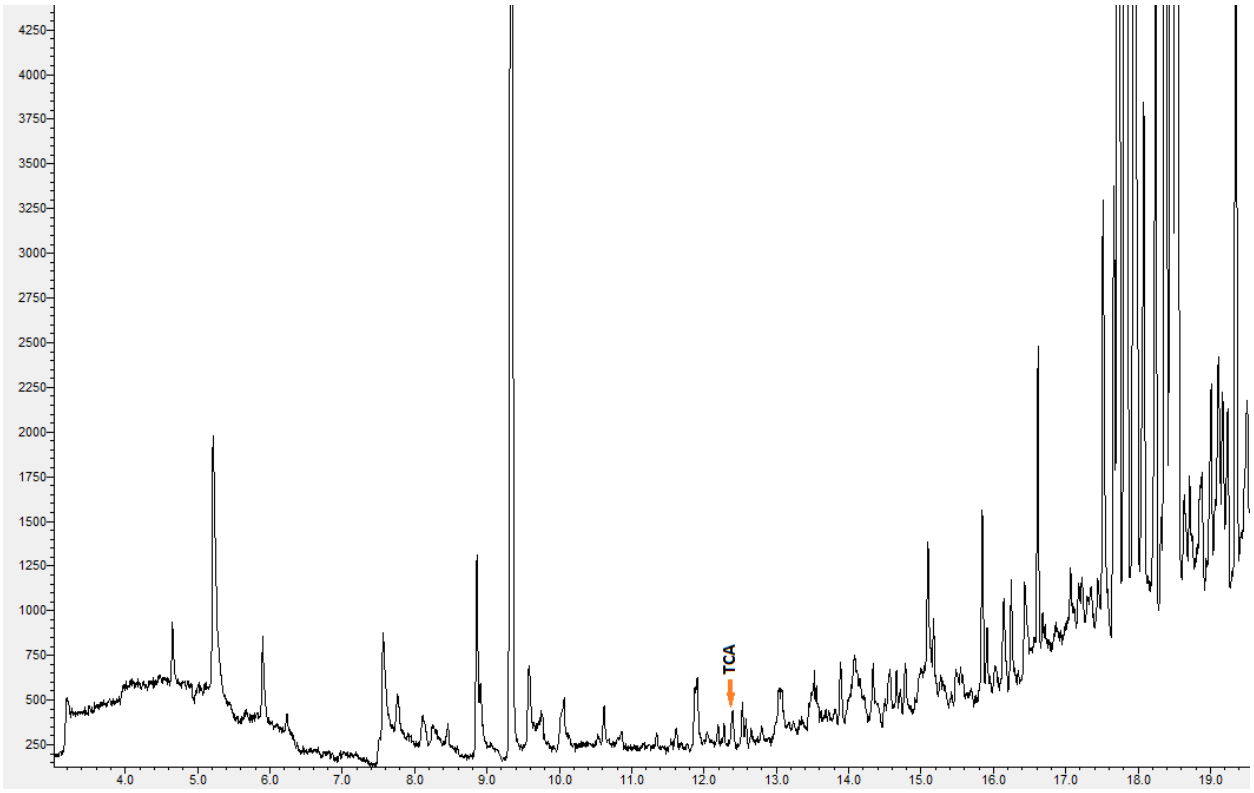

Figure 2: Chromatogram of 5.6ppt TCA in Wine

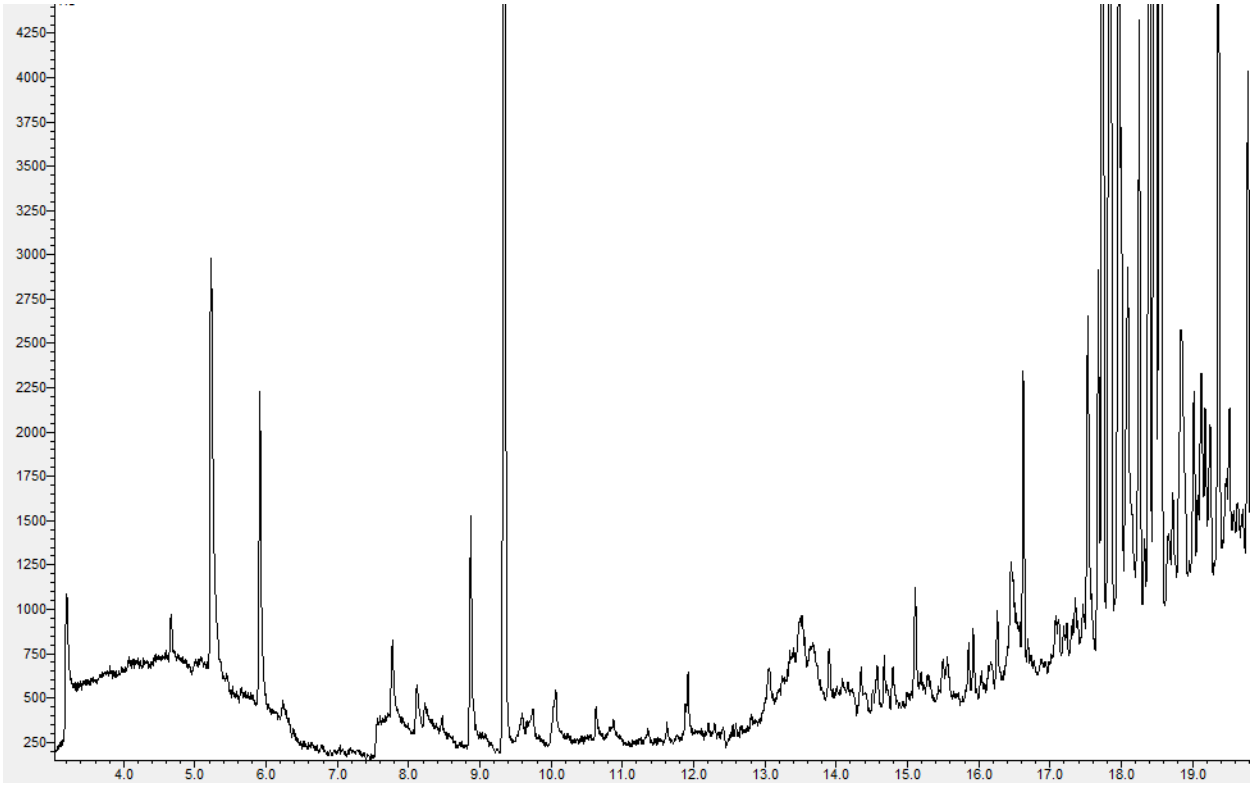

Figure 3: Chromatogram of Unspiked Wine

Conclusions:

The Flex Series autosampler with its distinctive oscillating agitation provided an excellent platform for the development of a Solid Phase Micro Extraction (SPME) technique for the detection of TCA in wine. The software facilitated effortless method development as there is a convenient drag and drop menu for an extensive array of agitation, incubation and sampling techniques. With the use of Selective Ion Monitoring, the TCA was detected at the 5ppt level both in a calibration curve and in spiked wine samples.

References:

"Growing Preference Among U.S. Wine Consumers for Natural Cork Stoppers", 100% Cork, June 24, 2014, **http://www.prnewswire.com/news-releases/growing-preference-among-us-wine-consumers-for-natural-cork-stoppers-264392581.html**, April 7, 2016.

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