Detection of Cork Taint Fault in Wine Using HS-SPME and GC-TOFMS for the Quantification of 2,4,6-trichloroanisole

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Key Words: 2,4,6-trichloroanisole (TCA), Cork Taint, HS-SPME, GC-TOFMS, Pegasus HT, Deconvolution, Calibration, Wine Aroma

1. Introduction

Cork taint is a common fault in wine and can occur in naturally corked wines of all varieties, vintages, price points, and from any geographical region, so its presence is difficult to predict. This fault is largely attributed to 2,4,6-trichloroanisole (TCA) that can develop in a natural cork and migrate into the wine. Very small amounts of TCA can render a wine undrinkable as the sensory threshold for most people is in the low parts per trillion (ppt) range. Detecting this analyte in wine samples is useful for both confirming and understanding cork taint. HS-SPME paired with GC-TOFMS is an effective approach to monitor for TCA in a wine sample, and to see what you're missing in a standard analysis. The headspace analytes are concentrated onto the SPME fiber allowing for low level detection, while GC effectively separates analytes within the complex samples for TOFMS detection which provides identification information through full-mass range library searchable mass spectral information. Here, we highlight the benefits of these analytical technologies to calibrate and quantify TCA in a wine sample.

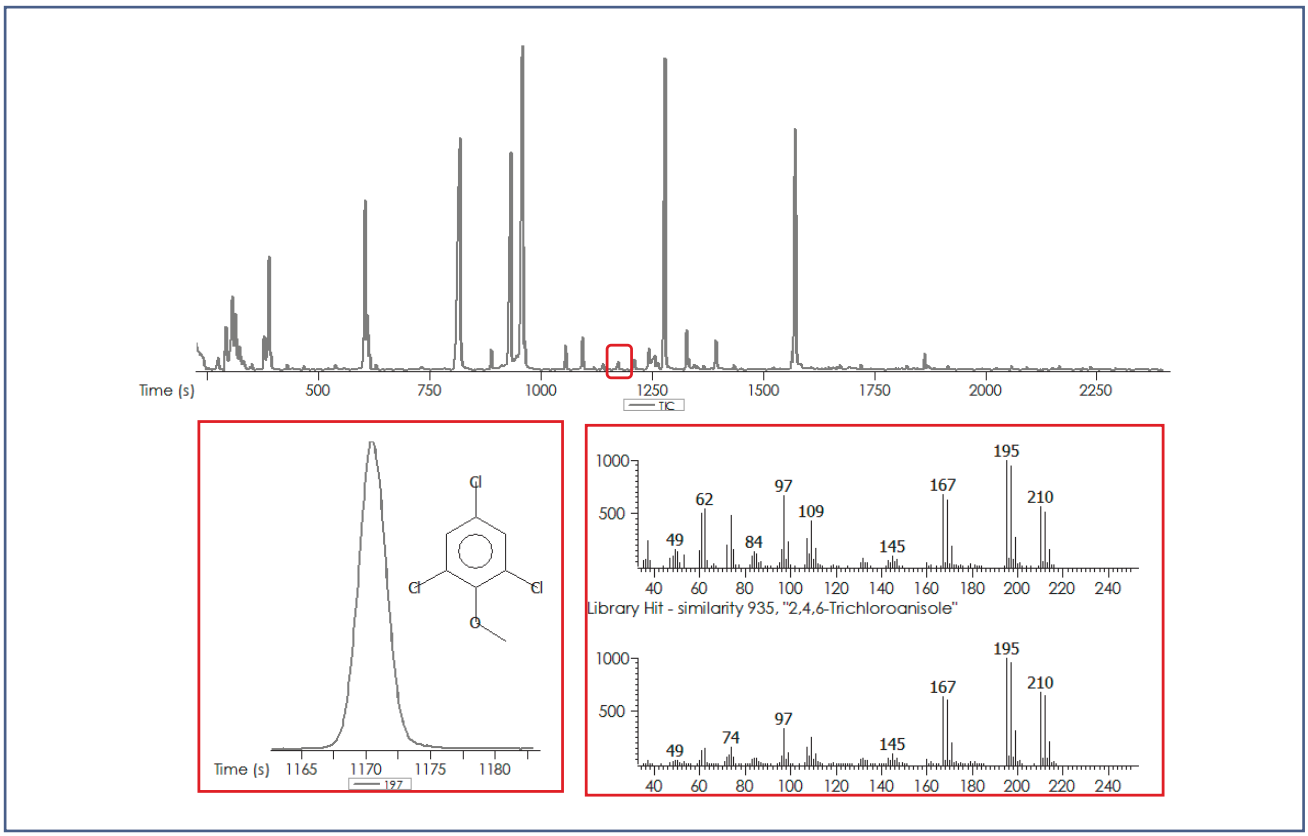

Figure 1. A GC-TOFMS chromatogram for a Shiraz wine sample spiked with 1 ppb TCA is shown. Many aroma analytes are observed in the chromatogram and TCA is highlighted in the red box. An XIC (m/z 197) shows the chromatographic peak and the deconvoluted spectral data (top spectrum) is shown with the NIST library match (bottom spectrum).

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2. Experimental

A commercially-available wine sealed with a screw cap was used for the wine matrix, so naturally occurring TCA was not anticipated. 2,4,6-tricholoranisole (Sigma Aldrich, USA) was spiked into the wine matrix at concentrations ranging from 5 ppt to 10 ppb. Wine samples were prepared for HS-SPME by sealing 10 mL of wine and 3 g of salt into a 20 mL vial with a septum cap. Samples were incubated for 5 minutes at 65°C just prior to extraction, performed at the same temperature for 30 minutes using a 2 cm DVB/CAR/PDMS fiber (Sigma Aldrich). Additional instrument conditions are listed in Table 1.

Table 1. GC-TOFMS (Pegasus® HT) Conditions

Gas Chromatograph	**Agilent 7890 with MPS2 Autosampler**
Injection	2 min fiber desorption with inlet @ 250°C, splitless
Carrier Gas	He @ 1 ml/min
Column	Rxi-5ms, 30 m x 0.25 mm i.d. x 0.25 µm coating (Restek)
Oven Program	2 min at 40°C, ramped 5°C/min to 200°C, ramped 20°C/min to 300°C held 1 min
Transfer Line	260°C
Mass Spectrometer	**LECO *Pegasus* HT**
Ion Source Temperature	250°C
Mass Range	33-500 m/z
Acquisition Rate	15 spectra/s

3. Results and Discussion

TCA was spiked into the Shiraz wine matrix as shown in Figure 1. All of the calibration standards were sampled with HS-SPME and analyzed with GC-TOFMS. TCA was located and the calibration equation was determined from the peak area of each standard, as shown in Figure 2. The calibration range spanned 5 ppt through 10 ppb with an R^2 value of 0.9999.

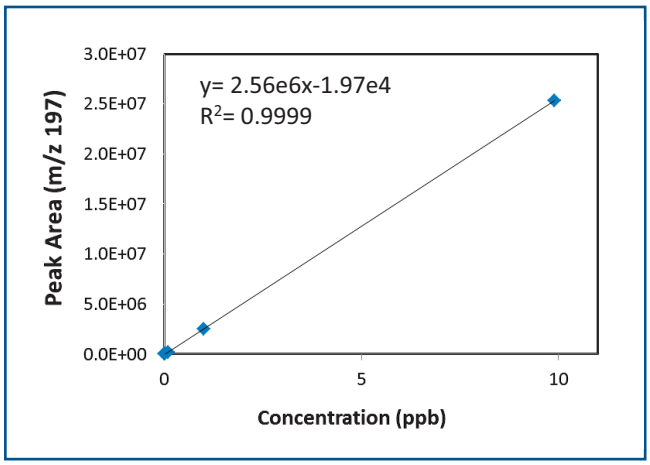

Figure 2. The calibration equation for TCA in a wine matrix sample is shown. The calibration range was from 5 ppt to 10 ppb with an excellent R^2.

One benefit of LECO's *Pegasus* HT that is particularly important in these analyses is the ability to handle matrix interferences and coelutions with ChromaTOF's® mathematical deconvolution tools. In this case, the target analyte, TCA, coelutes with an interference from the matrix, as shown in Figure 3. *ChromaTOF's* Automated Deconvolution algorithms mathematically separate these coelutions and provide mass spectral and chromatographic peak profile information for both analytes.

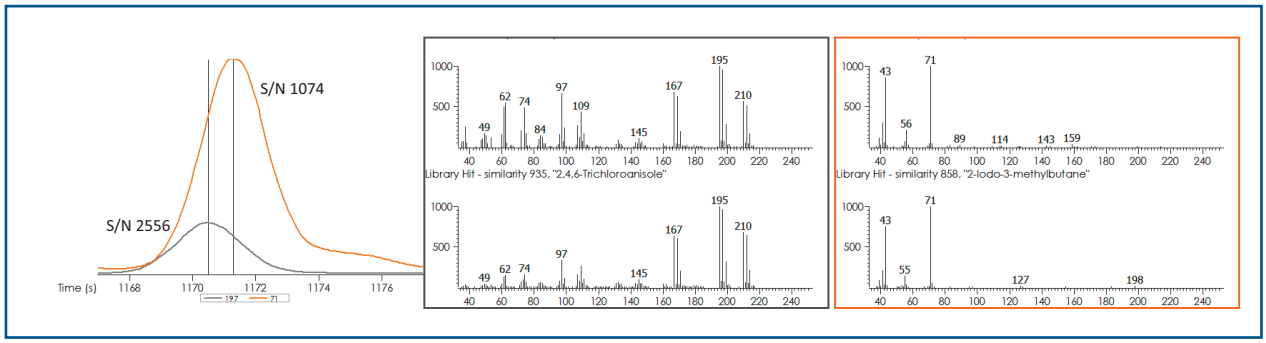

Figure 3. TCA (at 1 ppb) coelutes with a matrix interference. Information (pure chromatographic profiles and spectra) for both analytes is determined with ChromaTOF's deconvolution algorithms. In each displayed window, the deconvoluted spectrum is on the top and the associated NIST library match is on the bottom.

In Figure 3, the coeluting analytes are present at comparable S/N, but deconvolution can also accommodate coelutions when the S/N differs between the analytes. As shown in Figure 4, the S/N for the matrix analyte is roughly the same in every sample, while the S/N for the target analyte decreases with decreasing concentration as expected. The deconvolution algorithm still separates these coelutions at the different concentration levels. In this example, the S/N for the target analyte ranged from 20-fold higher to 40-fold lower than the matrix coelution. Examples of the deconvolution for the 10 and 0.1 ppb standard with larger S/N differences compared to the matrix analyte are shown in Figure 5.

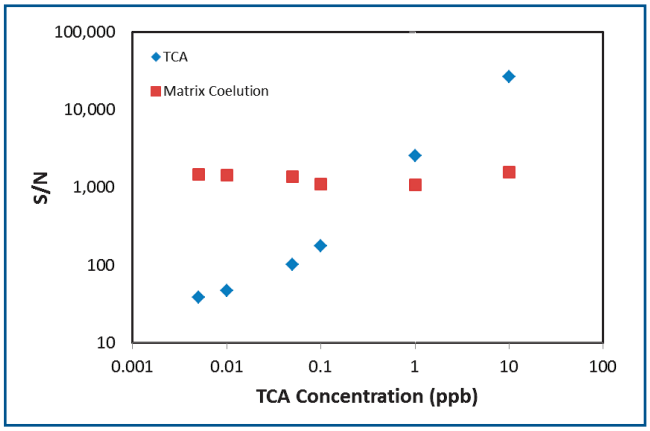

Figure 4: Deconvolution accomodates coelutions that occur where the analytes have vastly different S/N. Here the target analyte S/N decreases with concentration while the coelution S/N is consistent.

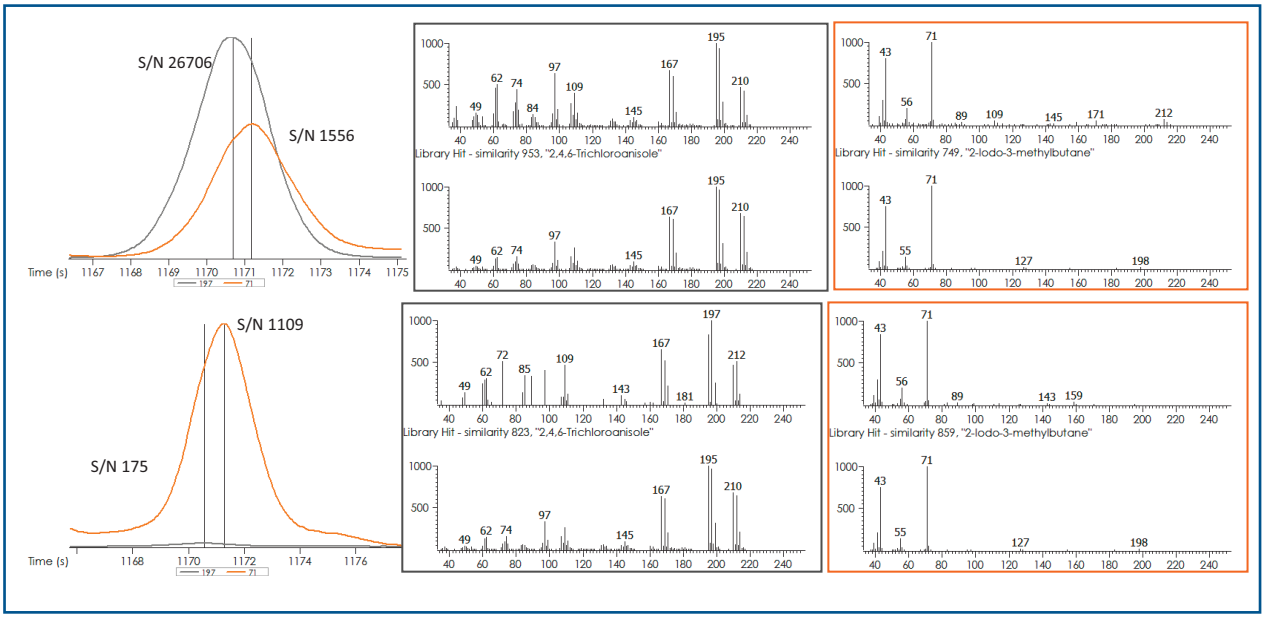

Figure 5: TCA and the matrix coelution are shown for different S/N levels. In each displayed window, the deconvoluted spectrum is on the top and the associated NIST library match is on the bottom.

The calibration equation was then applied to a wine sample spiked with TCA at a known concentration (50 ppt), as shown in Figure 6. The unknown sample, not included in the calibration, is shown as a red square superimposed on the calibration plot. XIC chromatograms for the spiked sample and the two bracketing standards are also shown. The calculated concentration had a percent error of 7.8% compared to the expected concentration at this very low ppt level.

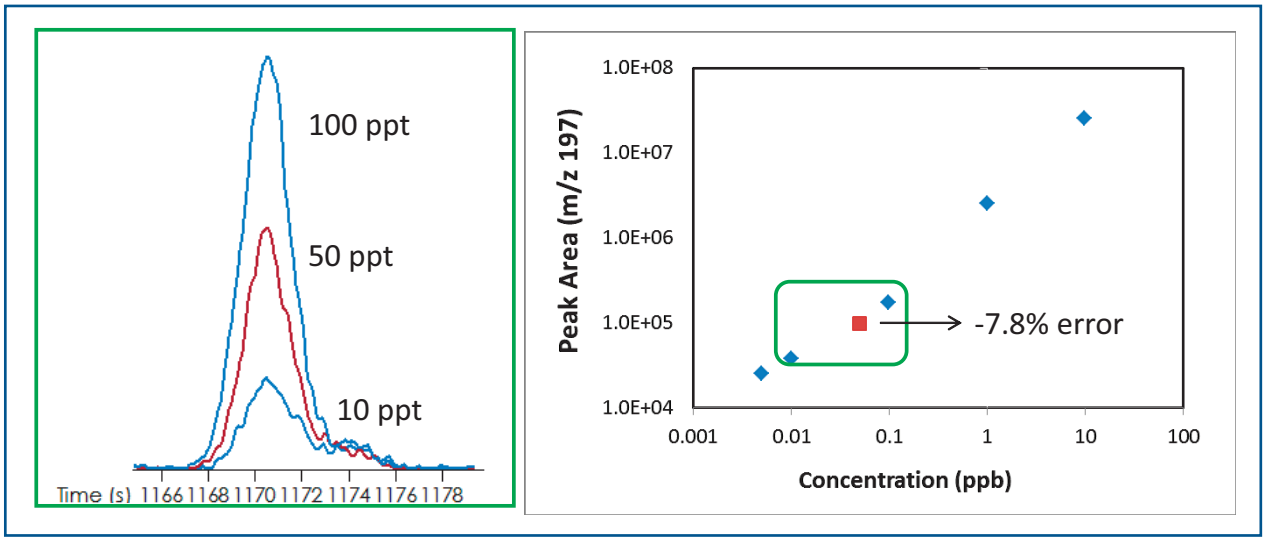

Figure 6. The calibration equation was applied to a wine sample spiked with 50 ppt TCA, but not included in the calibration. The chromatographic peak profile is shown in red, along with the two bracketing concentrations (10 ppt and 100 ppt) shown in blue. The calculated concentration from the equation agreed with the spiked concentration.

4. Conclusion

This study demonstrates the ability to detect a target analyte—2,4,6-tricholoranisole—at parts-per-trillion levels within a wine matrix. TCA is attributed to the cork taint wine fault and these detected concentrations are comparable to typical sensory thresholds. Calibration data were demonstrated and applied to a known spiked sample with good accuracy, even in the presence of a matrix coelution. *Pegasus* HT's full mass range sensitivity and speed with unparalleled deconvolution capabilities allow you to get more out of your standard analyses without needing to run in selected ion monitoring mode to optimize quantitative results. This provides quantitation for target compounds, and the ability to determine what else may be in your sample all in the same analysis.

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