Quantification of 2,4,6-trichloroanisole to Detect Cork Taint Fault in Wine with the Pegasus® BT

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

1. Introduction

Cork taint is a common wine fault that leads to off-putting odors in a wine. Predicting this fault is challenging as it can occur in any naturally corked wine of any variety, vintage, price point, or geographical region. Analytically detecting cork taint is also challenging because the sensory threshold for 2,4,6-trichloroanisole (TCA), an analyte that is a large contributor to the off-odor and taste, is in the low part-per-trillion (ppt) levels for most people. Here, detection and quantification of TCA at levels well below the threshold are demonstrated. HS-SPME was used for sample preparation and analysis was performed with LECO's *Pegasus* BT GC-TOFMS system. The *Pegasus* BT provides full m/z range data and sensitivity which make it ideal for screening target analytes and/or general unknowns. This robust tool makes your routine analyses easy and has the potential to uncover what you've been missing.

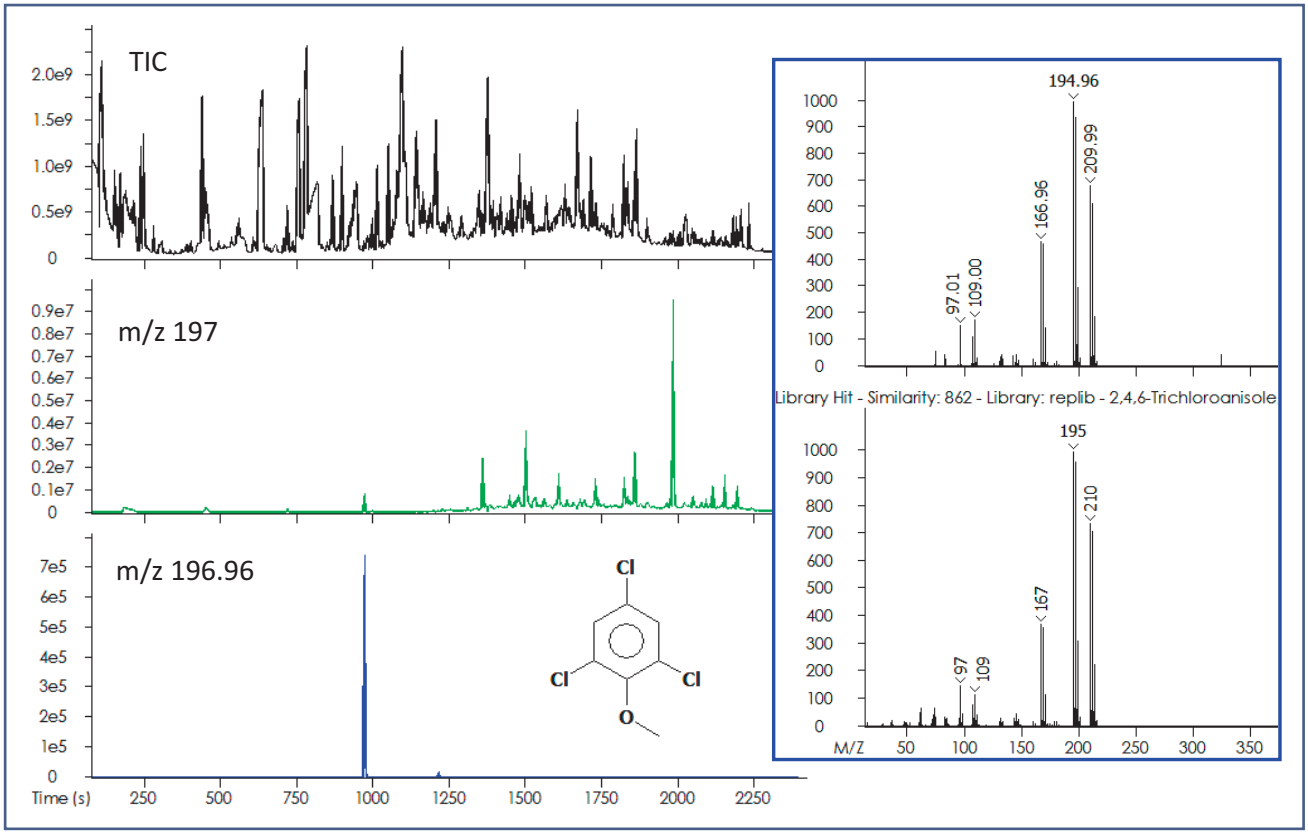

Figure 1. A GC-TOFMS chromatogram for a Shiraz wine sample spiked with TCA at 100 ppt is shown. Many aroma analytes are observed in the chromatogram. TCA is highlighted with extracted ion chromatograms (XIC) of m/z 197 and m/z 196.96. The narrowed mass range helps focus on the target analyte rather than other peaks with the same nominal m/z. The deconvoluted spectrum (top) is shown along with the NIST library match (bottom spectrum) for TCA at this level.

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2. Experimental

TCA (Sigma Aldrich, USA), was spiked into a commercially available Shiraz wine matrix at concentrations ranging from 0.1 ppt to 10 ppb. The wine selected as the matrix was sealed with a screw cap to minimize the chance of naturally occurring TCA from contaminated cork. The 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. The samples were incubated for 5 minutes and extracted for 30 minutes at 65°C with a 2 cm DVB/CAR/PDMS fiber (Sigma Aldrich). Instrument conditions are listed in Table 1.

Table 1. GC-TOFMS (*Pegasus* BT) Conditions

Gas Chromatograph	**Agilent 7890 with LECO L-PAL3 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, ramp 5°C/min to 200°C, ramp 20°C/min to 300°C hold 1 min
Transfer Line	250°C
Mass Spectrometer	**LECO *Pegasus* BT**
Ion Source Temperature	250°C
Mass Range	33-650 m/z
Acquisition Rate	10 spectra/s

3. Results and Discussion

TCA was spiked into the Shiraz wine matrix, which was then sampled with HS-SPME, and analyzed with GC-TOFMS. A representative chromatogram is shown in Figure 1. A data processing tool, Target Analyte Find, was used to quickly screen the samples for TCA based on a user-defined retention window and a list of required masses to locate and determine a peak area for the target analyte on the order of seconds. For target screening applications, this fast processing option complements comprehensive peak finding that provides general characterization when you don't know what you're looking for. A calibration curve was created by determining the peak area of each standard with m/z 197, as shown in Figure 2.

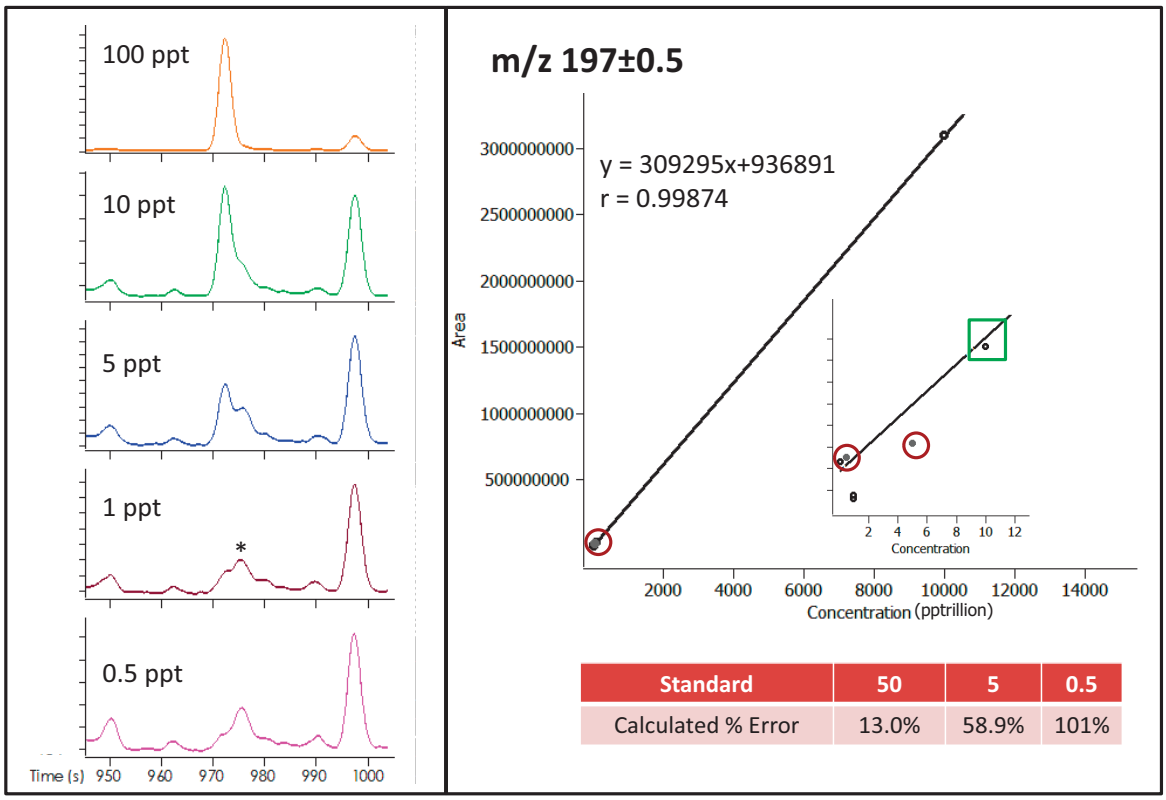


Figure 2. The calibration for TCA in wine matrix is shown. The calibration range was from 0.1 ppt to 10 ppb with an r-value of 0.99874. While the r-value is good and the levels extend below the sensory threshold (10 ppt, boxed in green), there are problematic deviations at the low levels. The samples circled red were omitted when creating the calibration equation and used as check standards. The percent error for these samples is unacceptably high. A comparison of XIC 197 for decreasing concentrations shows that a coelution from the matrix has very low levels of m/z 197 that cause problems at the lowest TCA concentrations.

The *Pegasus* BT provides better than nominal mass resolution, therefore, some coelutions with shared nominal m/z can be further distinguished based on their more accurate m/z if there is a sufficient mass difference. In this case, the chlorinated fragment from TCA is slightly less than 197 while the interference is slightly higher than 197 with a mass difference of approximately 0.2 Da. A spectrum showing both m/z is shown in Figure 3.

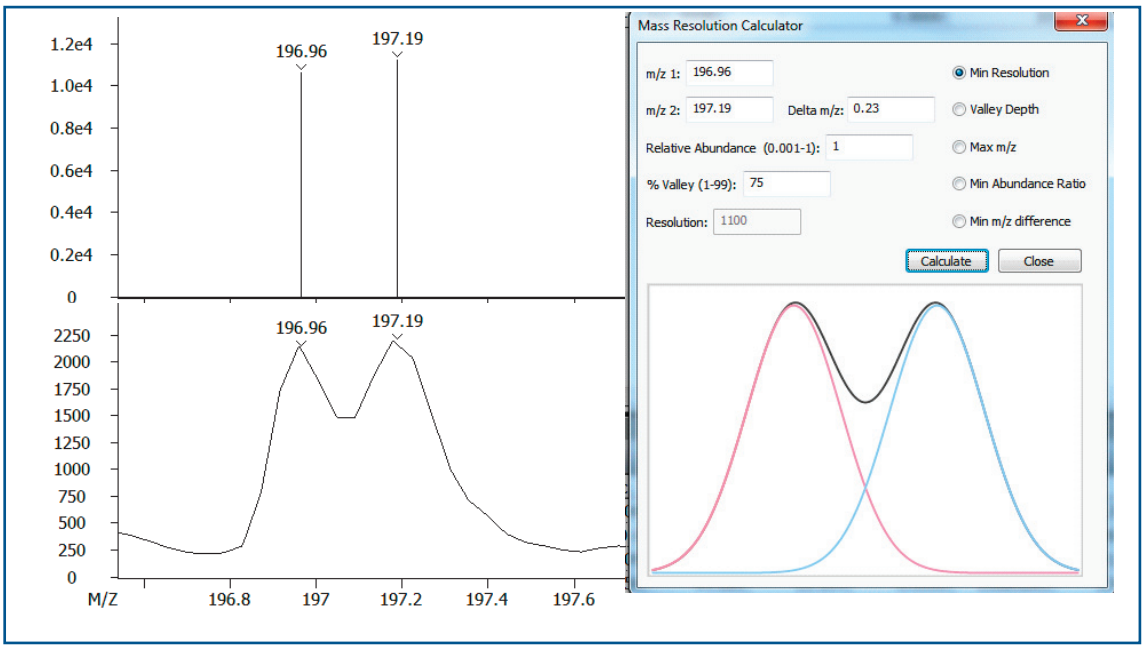
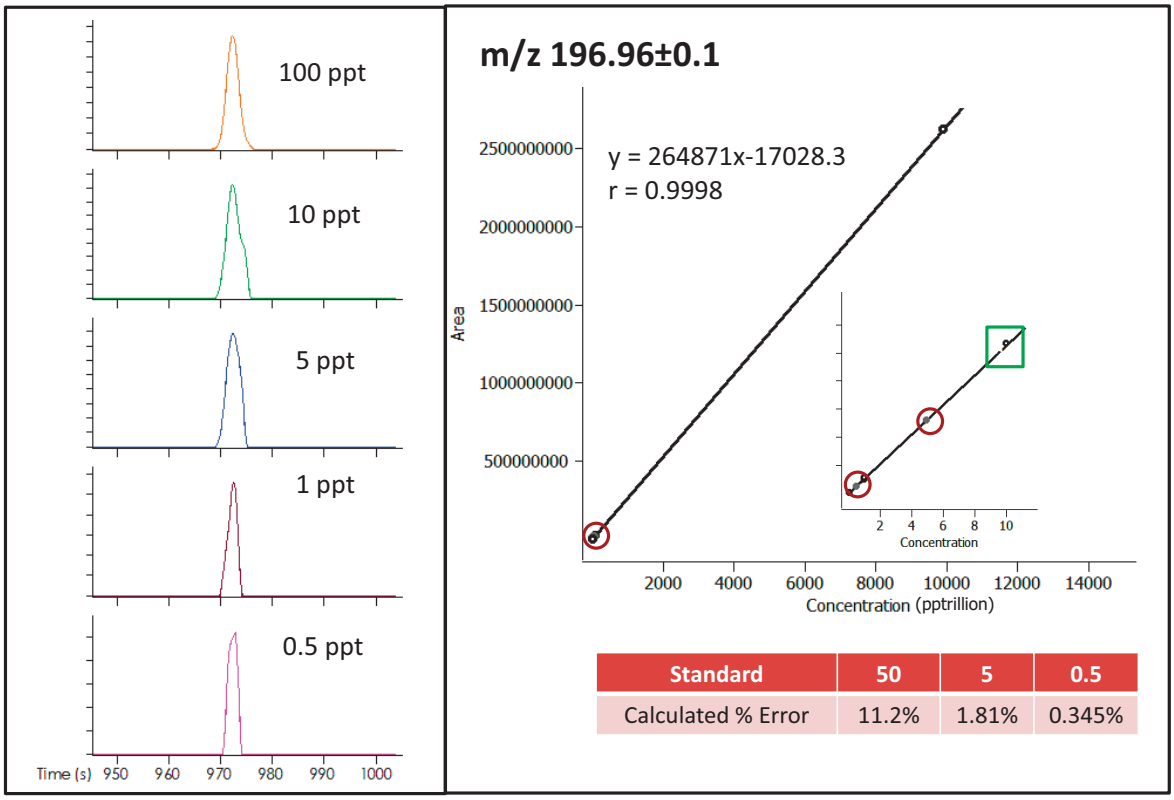


Figure 3. The Pegasus BT has enough mass resolution to distinguish the m/z from the target analyte and from the matrix interference. This caliper spectrum is from the 1 ppt sample (indicated with an asterisk in Figure 2). The calculated required resolution is similar to what was observed and within the capabilities of the instrument.

The calibration was repeated using a narrowed mass tolerance to determine peak areas with the accurate m/z, 196.96, and the results are much improved as shown in Figure 4.



Standard	50	5	0.5
Calculated % Error	11.2%	1.81%	0.345%

Figure 4. The calibration for TCA using m/z 196.96 is shown. The calibration range was from 0.1 ppt to 10 ppb with an r-value of 0.9998. Using this tighter mass tolerance separated the target analyte from the matrix interference and provided more accurate peak areas. This can be observed in the XICs as well as the improved percent errors for the check standards (circled red and omitted when creating the calibration equation). The calibration range extends well below the sensory threshold (boxed green).

The instrument also provides non-targeted information, therefore, the coelution can be further investigated. A zoomed view of the TIC around the target analyte, shown in Figure 5, indicates that two analytes elute together with TCA. Deconvolution, incorporated to peak finding, provides pure spectral information for each analyte, and XICs for m/z unique to each show the pure peak profiles. A siloxane peak is the source of the interfering m/z 197 previously described, and an aroma analyte, whiskey lactone with known odor properties, was identified as the other coeluting analyte.

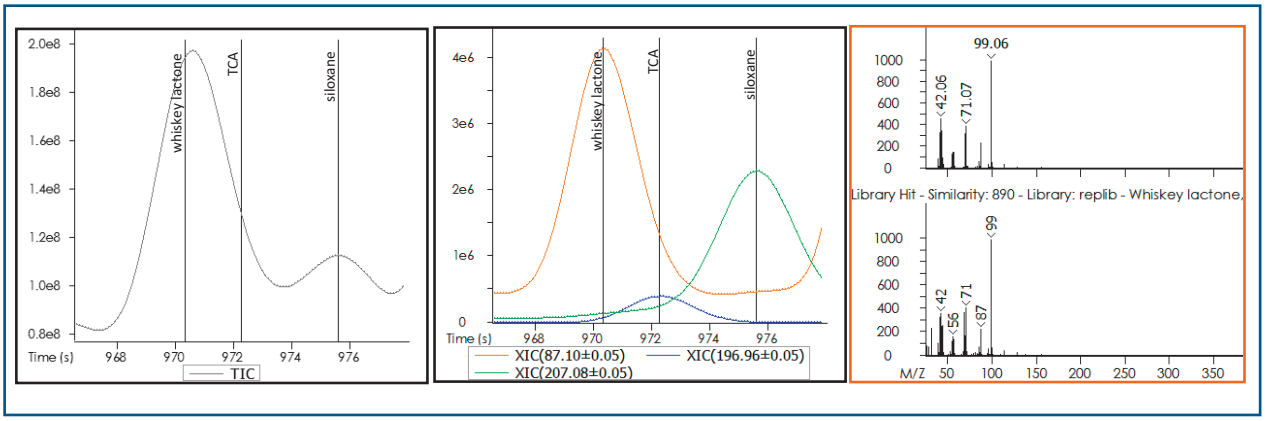


Figure 5. Non-targeted information is also available and an example is shown here. The target analyte, TCA, coelutes with two other analytes; a siloxane peak that contains the interfering m/z 197 and whiskey lactone a known odor analyte. All three analytes are determined with deconvolution. The peak profiles are shown with XICs unique to each analyte. Pure spectral information for the non-targeted, whiskey lactone, is also shown (top spectrum) compared to the NIST library match (bottom spectrum).

4. Conclusion

This study demonstrates the *Pegasus* BT's ability to detect and quantify 2,4,6-trichloroanisole at parts-per-trillion levels within a wine matrix. TCA is attributed to the cork taint wine fault and these detected concentrations are below the typical sensory thresholds. The better than nominal mass information generated by the *Pegasus* BT allowed for further distinction of the target analyte from a matrix interference with a shared nominal mass that was problematic at the very lowest concentrations. This analytical tool facilitates your routine analyses, and also provides full m/z range information for comprehensive characterization in non-targeted applications.

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