Fast Detection of Trace Haloanisole and Halophenol Off-Flavor Compounds in Cork Wine Stoppers

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Haloanisole and Halophenol Off Flavors in Wine

The flavor and aroma of wine can be negatively altered by the presence of unwanted off-flavor compounds, leading to consumer dissatisfaction and rejection of purchased wines. So-called “cork taint” in wine and other alcoholic beverages is most commonly caused by haloanisole compounds and their halophenolic precursors, which can be present in the water supplies of production sites or released by natural wood and cork materials used for processing and packaging.

Natural wood and cork materials contain halophenols which can be transformed to haloanisoles via fungal metabolism.1,2 The detection of haloanisole and halophenol compounds throughout the supply chain and during quality control of cork and wood products is complicated by their extremely low concentrations and the complex sample matrices.

The most used method for haloanisole and halophenol analysis in the wine industry is HS-SPME-GC-MS (Headspace solid-phase microextraction gas chromatography–mass spectrometry). Unfortunately, HS-SPME-GC-MS analyses are time consuming, limiting how frequently product quality and process control measurements can be made. Further, the small number of samples analyzed at the laboratory level are not statistically representative of entire product batches, as the presence of these compounds in cork and wood is strongly localized. Therefore, there is a need for a high-throughput instrument that can rapidly measure many individual samples.

Fast and Sensitive Measurement of Haloanisoles and Halophenols in Cork Stoppers With the Vocus CI-TOF

The Vocus chemical ionization time-of-flight mass spectrometer (Vocus CI-TOF) can rapidly measure haloanisoles and halophenols in cork samples at trace concentrations, even below the human sensory threshold. The non-destructive measurement simultaneously quantifies all detectable compounds with high precision in 3 seconds or less. These

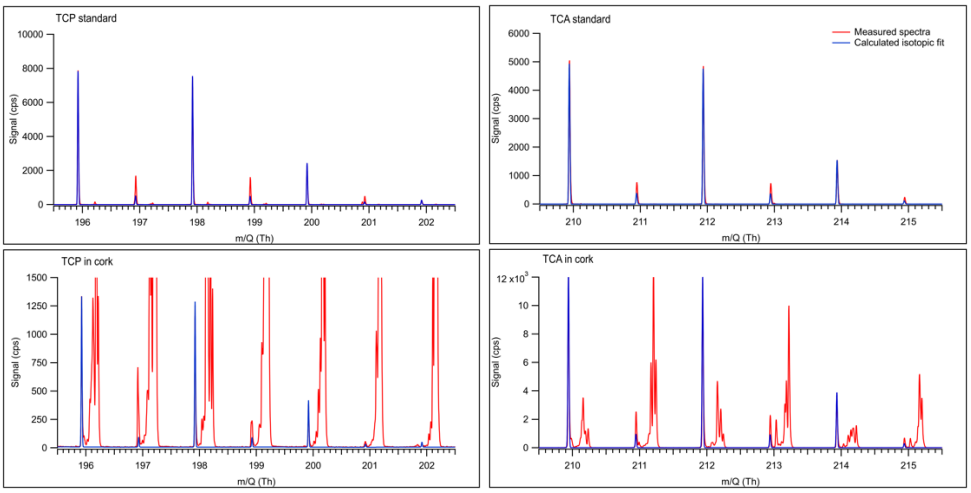

Figure 1 *Mass spectra of the off-flavor compounds trichlorophenol (TCP) and trichloroanisole (TCA). Red lines show mass spectra measured with the Vocus CI-TOF; Blue lines overlaid on the spectra show the predicted mass spectra based on the isotopic composition of each molecule. Measured TCP (left) and TCA (right) mass spectra for the standard (upper) and a cork (lower) samples.*

Molecule	Acronym	Formula
Trichloranisole	TCA	$C_7H_5Cl_3O$
Dichloroanisole	DCA	$C_7H_6Cl_2O$
Tetrachloroanisole	TeCA	$C_7H_4Cl_4O$
Pentachloroanisol	PCA	$C_7H_3Cl_5O$
Pentachlorophenol	PCP	C_6HCl_5O
Trichlorophenol	TCP	$C_6H_3Cl_3O$
Chloroanisole	CA	C_7H_7ClO
Tribromoanisole	TBA	$C_7H_5Br_3O$

Table 1 *Eight off flavor compounds that were determined to have significant concentrations in the 4060 cork stoppers screened with the Vocus CI-TOF.*

capabilities allow for automated, high throughput screening in industrial settings, which is exemplified by the Vocus Cork Analyzer.

Figure 1 shows example Vocus CI-TOF mass spectra for the off-flavor compounds trichlorophenol (TCP) and trichloroanisole (TCA) measured from permeation tubes of standards and in cork stopper samples. Comparison of recorded peak distributions to known isotopic patterns ensures that compounds are properly identified and that false negatives/positives are minimized. Recorded signal intensities are precisely calibrated to report concentrations with 1 pptv limits of detection (which correspond approximately to a LOD of 0.03 ng/L in the case of TCA released from cork stoppers according to the ISO20752 method).

More than four thousand natural cork stoppers were screened with a

Vocus CI-TOF to measure concentrations of haloanisole and halophenol off-flavor compounds. Individual stoppers were measured for 2 seconds, with the Vocus CI-TOF simultaneously recording signal intensities at mass-to-charge (m/Q) values corresponding to thousands of different chemical compounds, including the target off-flavor compounds. Table 1 list eight off-flavor compounds that were found to have significant concentrations in the screened stoppers.

Figure 2 (on page 4) shows histograms of recorded concentrations of these eight compounds in the 4060 cork stoppers. The x-axis is the concentration in parts-per-trillion by volume (pptv) and the y- axis is the number of stoppers with the particular concentration. The Vocus CI-TOF detects many of these compounds below the sensory perception threshold.

This unique capability to rapidly quantify many off flavor compounds simultaneously makes the Vocus CI-TOF a valuable tool for the high-throughput quality control of different natural products used in the wine industry (corks, wood barrels, etc.). Further, multi-target analysis, as demonstrated here, opens up new directions for research on the origin of off flavors in natural matrices, which were not possible with GC-MS approaches used so far. In the case of chloro- and bromoanisoles contamination in cork, for example, it is possible to rapidly analyze large batches of cork samples for the presence of their phenolic precursors and thus to obtain additional information about their microbiological formation, allowing the mapping of the extraction zones in cork oak forests.

References

1. H.-R. Buser et al., J. Agric. Food Chem., 1982, 30, 359 – 362

2. P. Chatonnet et al., J. Agric. Food Chem., 2004, 52, 1255 - 1262

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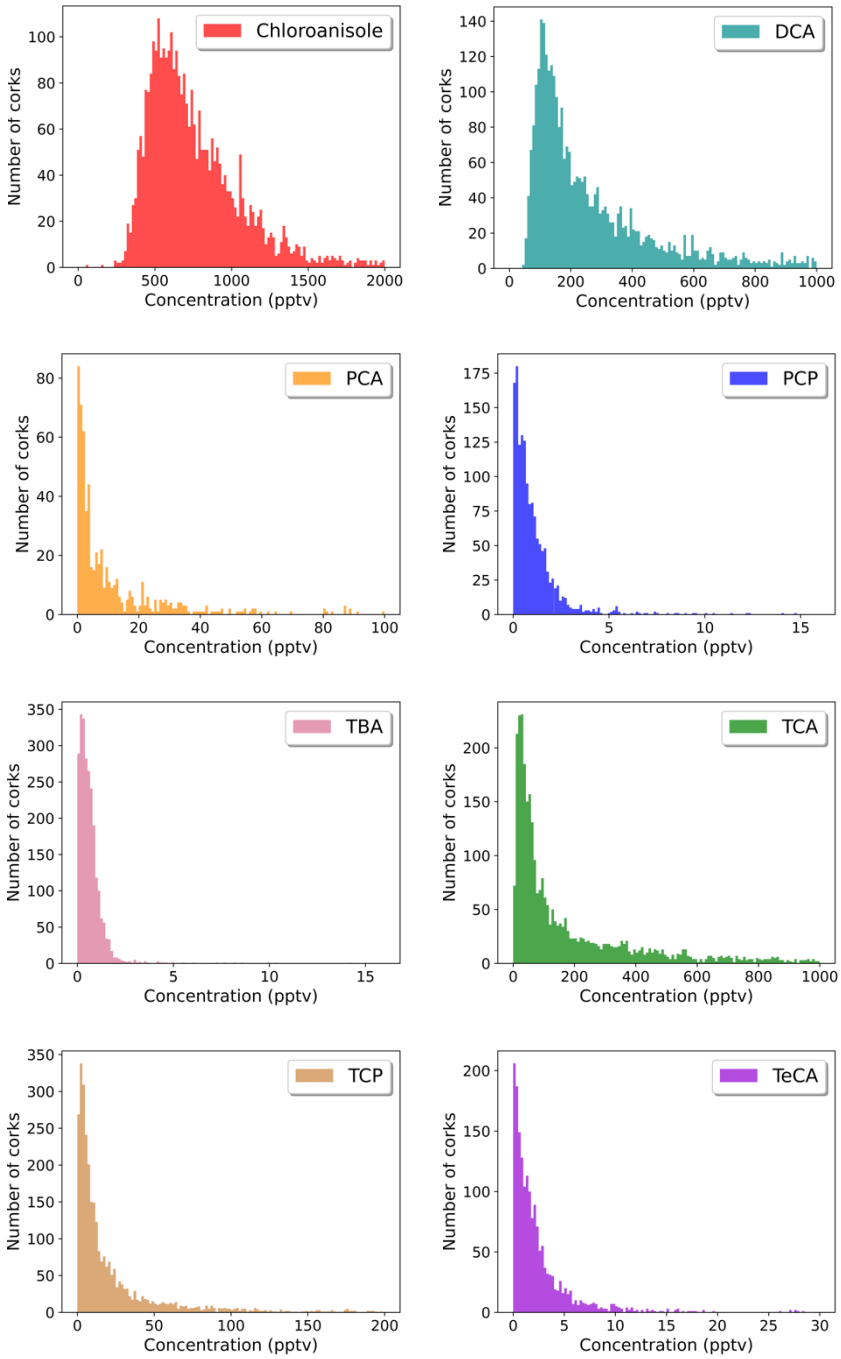

Figure 1 *Histograms of measured concentrations of the target taint compounds in the 4060 cork stoppers screened with the Vocus CI-TOF*