Micro-Etched Sorbent SPMESH Sheets for High Throughput, Trace-Level Analysis of "Smoke Taint" Compounds in Grapes and Wines

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Primary CNF Tools Used: VersaLaser Engraver/Cutter Tool

Abstract:

Exposure of grapes to the smoke of forest or brush fires may result in "smoky" off-aromas ("smoke taint") in resulting wines due to several odorants, including volatile phenols like cresol and guaiacol. These volatile phenols are detectable at low ppb (ng/g) concentrations, and their analysis typically requires lengthy analyses (20-40 min) by gas chromatography - mass spectrometry (GC-MS). The slow analytical throughput of GC-MS creates bottlenecks during smoke exposure events during harvests, and limits the ability of vineyards and wineries to make data-driven decisions. Using tools available through the Cornell NanoScale Facility (CNF), we have prepared etched sorbents sheets ("SPMESH") designed for selective extraction of volatile phenols. The sheets are designed to fit over multiwell plates and allow for parallel extraction of odorants prior to rapid mass spectrometric analysis. The optimized method can analyze 24 samples in < 10 min, or nearly a 100-fold improvement in throughput over the gold standard method.

Summary of Research:

SPMESH sheets were prepared by etching a grid pattern in thin silicone sheets using the VersaLaser Cutter/Engraver at CNF, using a previously described protocol (Figure 1, left) [1]. SPMESH sheets were positioned over multiwell plates containing wine or grape samples to extract volatile phenols from the sample headspace. Extracted sample sheets were then analyzed by direct analysis in real time mass spectrometry (DART-MS) (Figure 1, right). Poor signal response and detection limits (>1 mg/L) were initially observed. This was determined to be due to the high polarity of the analytes. This problem was addressed by derivatization with deuterated acetic anhydride (Figure 2). The full workflow is shown in Figure 3.

Following optimization, figures of merit were determined in juice and wine. Detection limits for target compounds were ~ 1 μg/L for the three target VPs, below sensory threshold. Good linearity and reproducibility were also achieved. The DART-MS analysis requires < 10 min to analyze 24 samples, or about 50-100 faster than gas chromatography-mass spectrometry (GC-MS), the current gold standard. Including derivatization and extraction time, the entire approach requires ~ 60 min for 24 samples. For validation, juice and wine samples were sourced from an industry cooperator. Samples were analyzed by both the new SPMESH-DART-MS method and the gold standard GC-MS method. Good agreement was observed between the two methods for all analytes (r2 = 0.7-0.9). Results of the work have been published ([2] Bates and Sacks, 2023) and the approach is being shared with commercial fee-for-service analytical labs.

References:

[1] Bee, Madeleine Y., Jillian A. Jastrzembski, and Gavin L. Sacks. "Parallel headspace extraction onto etched sorbent sheets prior to ambient-ionization mass spectrometry for automated, trace-level volatile analyses." Analytical chemistry 90.22 (2018): 13806-13813.

[2] Bates, Terry L., and Gavin L. Sacks. "Rapid headspace solid-phase microextraction sheets with direct analysis in real time mass spectrometry (SPMESH-DART-MS) of derivatized volatile phenols in grape juices and wines." Analytica Chimica Acta (2023): 341577. https://www.sciencedirect.com/science/article/pii/S0003267023007985.

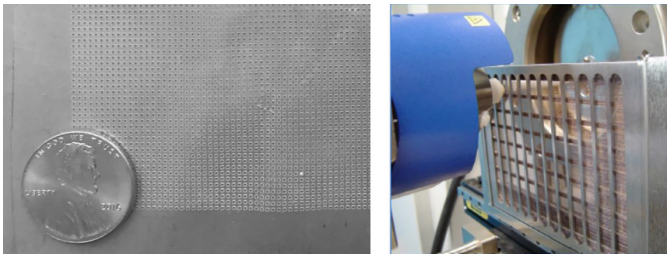

Figure 1: (left) Etched silicone SPMESH sheet produced at the CNF. The grid size is 0.5 mm × 0.5 mm, and (right) SPMESH sheet positioned during DART-MS analysis.

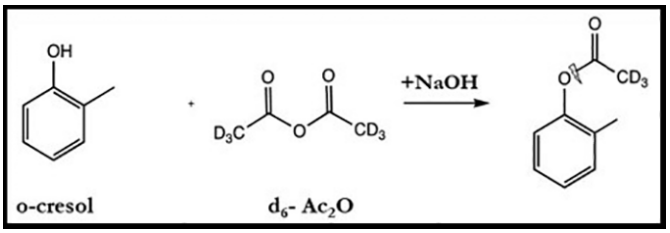

Figure 2: Acetylation scheme used to increase hydrophobicity and extractability of targeted phenols.

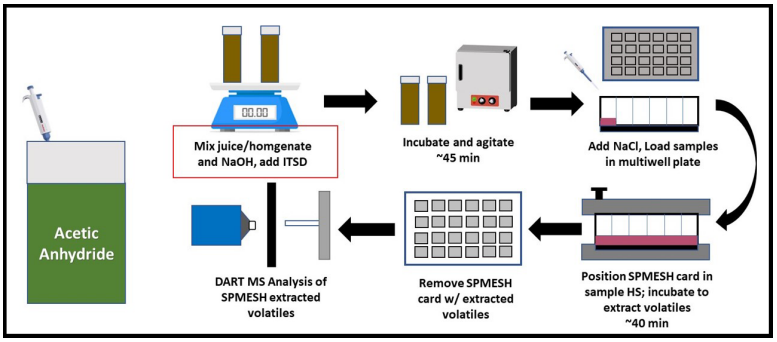

Figure 3: Workflow for rapid analyses of "smoke taint" odorants (volatile phenols) in grapes and wines.