

Thin Film, Laser-Etched Sorbent Sheets for Spatially Resolved and High Throughput Analysis of Volatiles

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Principal Investigator(s): Gavin Sacks

User(s): Jessica Rafson, Madeleine Bee

Affiliation(s): Department of Food Science, Cornell University

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Contract: gls9@cornell.edu, myb8@cornell.edu, jr2255@cornell.edu

Website: <http://blogs.cornell.edu/winechemistry/>

Primary CNF Tools Used: VersaLaser engraver/cutter tool

Abstract:

The analysis of trace-level volatiles responsible for odor of foods, beverages, and other systems is challenging because of their low concentrations, often down to part-per-trillion (nanogram-per-liter) levels. Because of this, trace volatile analyses often require pre-concentration and extraction steps, followed by lengthy analysis on gas chromatography — mass spectrometry (GC-MS). Often, analyses require 30 min per sample. Using tools available through the Cornell NanoScale Facility (CNF), we have prepared etched sorbents sheets. These sheets can be used to extract multiple samples in parallel, either from multiwell plates or other planar surfaces. The etched geometry of the sheets facilitates their direct coupling with mass spectrometers, and allows for very rapid analyses of trace volatiles — up to 24 samples in 17 min, or over 10-fold faster than conventional approaches. Additionally, because the extraction step preserves the spatial distribution of volatiles, it can also be used for imaging analyses of volatiles.

Summary of Research:

The odors associated with common foods, beverages, and fragrances are due to range of odorants, many present at concentrations as low as a part-per-trillion (nanogram-per-liter, or ng/L). Because of these low concentrations, analysis of these trace volatiles often requires initial steps to concentrate them and remove interferences, followed by analysis by techniques like gas chromatography — mass spectrometry (GC-MS).

GC-MS analyses often require 30 min per sample and represent a common bottleneck in characterization of large numbers of samples. So-called “ambient-ionization” — MS techniques like direct analysis in real time (DART) — are much faster than GC-MS, but coupling automated extraction approaches to DART-MS has not been straightforward. To overcome this, our group developed an approach called Solid Phase Mesh Enhanced Sorption from Headspace (SPMESH), which is readily coupled to DART-MS, as shown in Figure 1.

Our group used the VersaLaser cutting tool at the CNF to generate mesh patterns on poly(dimethylsiloxane) (PDMS) sheets shown in Figure 2. We could then position the sheets over multiwell plates pre-loaded with samples, e.g. macerated grapes. The silicone sheets then absorbed the volatiles in the headspace above each well in parallel.

Following extraction, the SPMESH sheet with extracted volatiles is then transferred to an automated positioning stage. Using three representative odorants, we were able to use SPMESH-DART-MS to analyze 24 samples in 17 min with detection limits in the ng/L range, shown in Figure 3 [1]. We also showed that the approach had excellent day-over-day repeatability (< 25% in signal over two weeks).

In a follow-up study [2], we reported that SPMESH absorption could also be performed from headspace of other planar surfaces, including samples spotted on thin-layer chromatography (TLC) plates. The use of TLC plates greatly enhanced the extraction rate, such that extraction only required 2-3 min to reach equilibrium. We also demonstrated that spatial distribution of volatiles could be preserved during imaging, allowing SPMESH to be used for imaging of volatiles from a surface, as shown in Figure 4.

In summary, laser-etched SPMESH sheets can be used for both high-throughput extraction and analysis of trace volatiles, as well as imaging of the spatial distribution of volatiles.

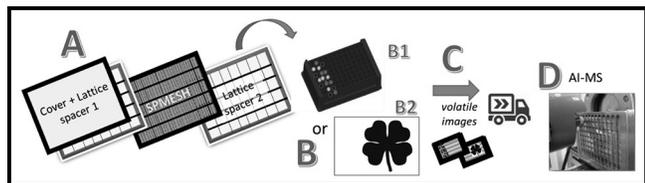


Figure 1: Overview of new approach to volatile analyses. Sorbent coated laser-etched meshes (SPMESH, A), are situated between inert lattice spacers, and positioned over well plates for high-throughput quantification (B1) or over an intact sample for imaging analyses (B2). Following parallel headspace extraction to create volatile images (C), the SPMESH sheet can be rapidly analyzed by ambient ionization - mass spectrometry (AI-MS, e.g., DART-MS (D)).

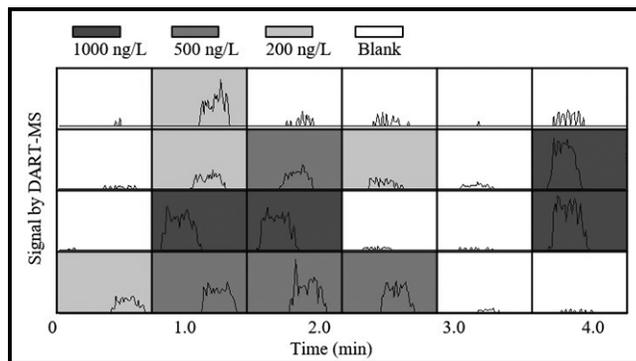


Figure 3: High-throughput SPMESH-DART-MS analyses of a trace level volatile (IBMP, "green pepper aroma") from a multi-well plate. Each cell represents a sample on a 24-well plate, containing 0-1000 ng/L IBMP.

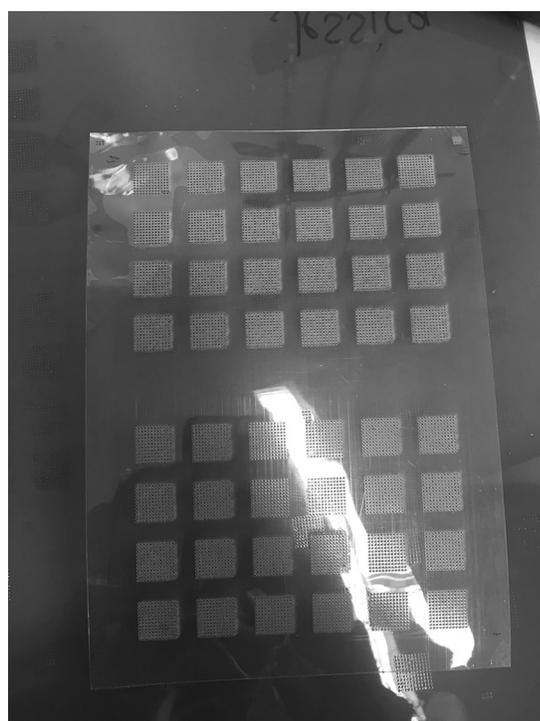


Figure 2: Etched silicone SPMESH sheet produced at the CNF. The grid size is 0.5 mm × 0.5 mm.

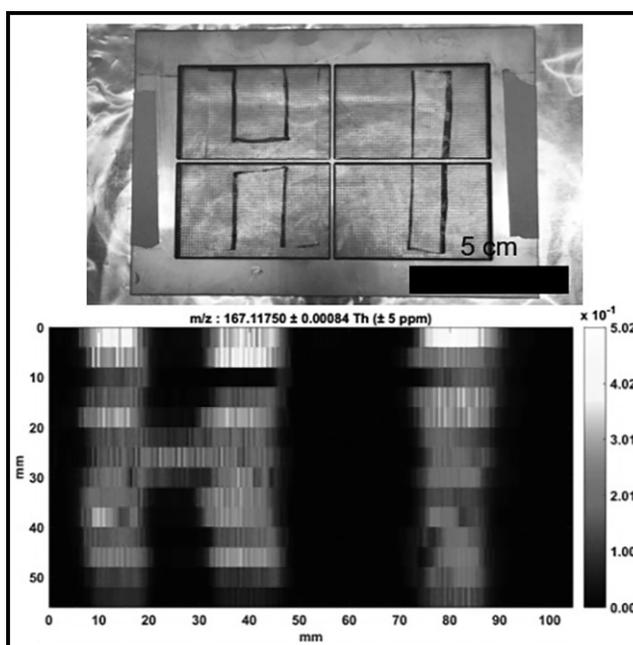


Figure 4: Spatially resolved image (bottom) of a volatile deposited on a polyethylene film (top) using SPMESH-DART-MS.

References:

- [1] Bee MY, Jastrzembki JA and Sacks GL. Parallel headspace extraction onto etched sorbent sheets prior to ambient-ionization mass spectrometry for automated, trace-level volatile analyses. *Analytical Chemistry*. 90, pp. 13806-13813. <https://pubs.acs.org/doi/10.1021/acs.analchem.8b04465> (2018).
- [2] Rafson J, Bee MY, Sacks GL. Spatially resolved headspace extractions of trace-level volatiles from planar surfaces for high-throughput quantitation and mass spectral imaging. *Journal of Agricultural and Food Chemistry*. <https://pubs.acs.org/doi/10.1021/acs.jafc.9b01091> (2019).