

Microscale Sorbent Sheets for Rapid Extraction and Analysis of Volatiles

CNF Project Number: 2513-16

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Primary Source(s) of Research Funding: New York Wine and Grape Foundation

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Primary CNF Tools Used: VersaLaser Engraver/Cutter Tool

Abstract:

The quality and safety of raw agricultural products is often determined by small molecules present at trace, sub-part-per-million levels. Measurement of these components during production and manufacturing is critical – and sometimes compulsory – for ensuring a healthy, palatable, and safe food supply. Gold-standard methods like chromatography coupled to mass spectrometry (MS) are slow, expensive and must often be performed off-site, and rapid methods often suffer from poor selectivity or sensitivity. Our group has previously demonstrated that etched sorbent sheets (SPMESH) can be used for rapid parallel extraction prior to direct analysis in real time mass spectrometry (DART-MS). This SPMESH-DART-MS approach can achieve part-per-trillion detection limits in <30 s per sample. Using tools available through the Cornell NanoScale Facility (CNF), we have explored the impact of varying the etch pattern on the performance of SPMESH sheets. For square apertures, an optimum aperture size of 1.5 mm was observed. At lower and higher aperture sizes, a decrease in sensitivity and increase in detection limits was observed. Sensitivity and detection limits could be further improved by using circular mesh patterns. These findings will lead to improved throughput and better sensitivity for trace level 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

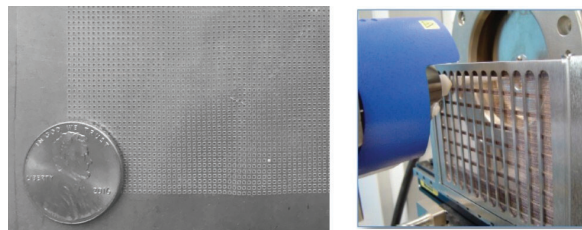


Figure 1: Example of an etched silicone SPMESH sheet produced at the CNF.

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. Our group used the VersaLaser Cutting Tool at the CNF to generate mesh patterns on poly(dimethylsiloxane) (PDMS) sheets (Figure 1). We could then position the sheets over multiwell plates pre-loaded with samples, e.g. macerated grapes (Figure 2). 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 representative odorants, we have previously reported that SPMESH-DART-MS can analyze 24 samples in 8.5 min with detection limits in the ng/L range.

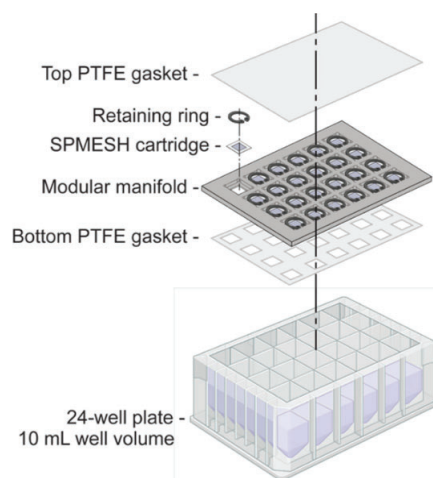


Figure 2: Diagram of the SPMESH assembly. Following parallel headspace extraction, the SPMESH manifold can be transferred to ambient ionization – mass spectrometry (AI-MS, e.g., DART-MS) for rapid characterization.

Optimization of SPMESH mesh pattern geometry has not been previously reported. Using the VersaLaser Cutting Tool, we prepared PDMS meshes of varying aperture shape (circular, square), size, and surface areas. We then used DART-MS to evaluate two target volatiles. We determined that maximum signal and the lowest detection limits were achieved with an aperture size of 1.5 mm. A decrease in sensitivity and increase in detection limits was observed at lower and higher aperture sizes, and further improvements could be achieved with circular mesh apertures in place of square apertures. This is likely because the optimum mesh pattern allows for maximum extraction and desorption from the interior faces of the SPMESH sheet. The optimum mesh could improve detection limits by 20-fold (Figure 3).

Conclusions and Future Steps:

In summary, optimization of the geometry of laser-etched SPMESH sheets can result in improved performance for high-throughput analysis of trace level volatiles.

References:

- [1] Kalenak AP and Sacks GL. Mesh Geometry Optimizes Parallelized Sorbent Sheet Extraction from Headspace (SPMESH) DART-MS. Submitted to Analytical Chemistry. 2026.

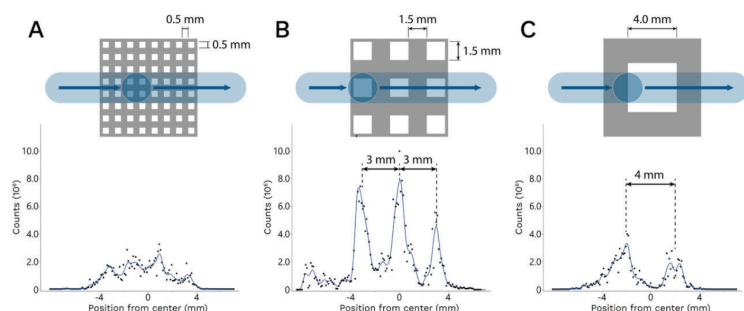


Figure 3: Chronograms of 0.5 x 0.5 mm (aperture x gauge) (A), 1.5 x 1.5 mm (B), and 4 x 4 mm (C) SPMESH cartridges following extraction of a 1 $\mu\text{g/L}$ 3-isobutyl-2-methoxypyrazine (IBMP) standard. Depictions of DART scan paths for each SPMESH geometry are shown over each chronogram.