

NYWGF RESEARCH -Progress Report

SECTION 1:

Project title: Expanding the range of rapid analysis approaches to semi-polar volatiles and non-volatile precursors in grapes

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New Research **Continued Research**

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SECTION 2:

Project Summary Impact Statement: Targeted measurements of volatiles or volatile precursors in grapes are useful for grape and wine quality evaluation, but these analyses are typically slow, and routine fee-for-service analyses are typically prohibitively expensive. Our group has previously demonstrated that sorbent sheets (SPMESH) could be used for rapid extraction of non-polar odorants from sample headspace. In the past year, we evaluated two novel extensions of SPMESH to make it more appropriate for analysis of semi-polar, lower volatility and non-volatile compounds (e.g. “Brett” phenols). We demonstrated that directly contacting the SPMESH with samples (“immersive” SPMESH) and pre-treating SPMESH sheets with organic solvents (“Swelled” SPMESH) could improve extractability of these analytes. However, due to technical challenges in real matrices, we are planning to evaluate alternative techniques going forward.

(Maximum 5 sentences)

Objectives:

- 1) Using “immersive” SPMESH-DART-MS and a lower-cost triple quadrupole MS, develop and optimize a single platform for accurate, rapid quantification of volatiles important to grape quality evaluation
- 2) Evaluate new approaches (“swelled” SPMESH-DART-MS and Coated Blade Spray – MS) for selective extraction and subsequent analyses of non-volatile precursors

Materials & Methods: For Objective 1, we expanded upon previous work using polydimethylsiloxane based thin-film sorbent sheets (SPMESH). Previous versions of SPMESH have only been appropriate have previously been used for parallel headspace (HS) extraction prior to direct analysis in real time mass spectrometry (DART-MS) for rapid quantitation of odorants in complex matrices. However, HS-SPMESH extraction is poorly suited for less volatile odorants, e.g. volatile phenols. We modified the SPMESH extraction device which make it amenable to parallel extraction of low volatility analytes from multiwell plates under direct immersion (DI) conditions. A schematic of the DI-SPMESH process is shown in Figure 1. Following parallel extraction, compounds

could be analyzed directly from SPMESH sheets by direct analysis in real time mass spectrometry (DART-MS). Optimization and validation of the DI-SPMESH-DART-MS approach was performed on four volatile phenols (4-ethylphenol (4-EP), 4-ethylguaiacol (4-EG), 4-methylguaiacol (4-MG), and guaiacol (G)) in wine and juice.

For Objective 2, Swelled Microextraction (SweME) devices were prepared by coating a thin layer of polydimethylsiloxane (PDMS) grafted onto a stainless-steel support. Pre-treating the SweME device with small volumes of organic solvent causes the PDMS to swell. The swollen SweME device was then immersed directly into juices for absorptive extraction of low-molecular weight, non-polar analytes. Following storage, analytes can be solvent desorbed prior to subsequent characterization. Coated blade-spray (CBS) was not attempted because the materials could not be readily used in a parallel manner, which would result in slow sample analysis times.

Results/Outcomes/Next Steps: For Objective 1, the use of DI-SPMESH-DART-MS resulted in greatly improved sensitivity for the four volatile phenols (4-ethylphenol (4-EP), 4-ethylguaiacol (4-EG), 4-methylguaiacol (4-MG), and guaiacol (G)), with detection limits in the range of 0.5-3 µg/L in water observed for all compounds. The approach analyzed 24 samples in < 1 hr, including extraction time. However, a major drawback was that interferences were observed in juice samples. The source of these interferences was unclear, but it limited the usefulness of DI-SPMESH, especially for analysis of guaiacol (G) and 4-methylguaiacol (4-MG). However, reasonable accuracy and recovery (71-135%) could be achieved for 4-EP and 4-EG.

For Objective 2, proof-of-principle work with both non-volatile (carotenoids in carrots and tomatoes) and volatile (odorants in wines and grapes) analytes demonstrate that SweME is appropriate for quantitative analyses (Fig 3) and increases the stability of air-sensitive analytes during storage at ambient temperatures as compared to solvent extracts. However, the extraction rate of semi-polar odorants and non-volatile precursors was too low to be useful for future applications.

In summary, although DI-SPMESH-DART-MS and SweME-MS were successful for certain compounds, they do not seem appropriate for routine use on grape or wine samples. For Future Steps in 2022-23, we will evaluate two other alternative approaches for rapid extraction and analysis of semi-polar odorants and non-volatile precursors, derivatization with HS-SPMESH-MS and Low Pressure GC-MS.

Technology Transfer Plan: Results from Objective 1 were recently published (Rafson and Sacks, *J Ag Food Chem*, 2021. DOI: 10.1021/acs.jafc.1c04197. Results from Objective 2 are in preparation for publication in a peer-reviewed journal.

Figures and Tables

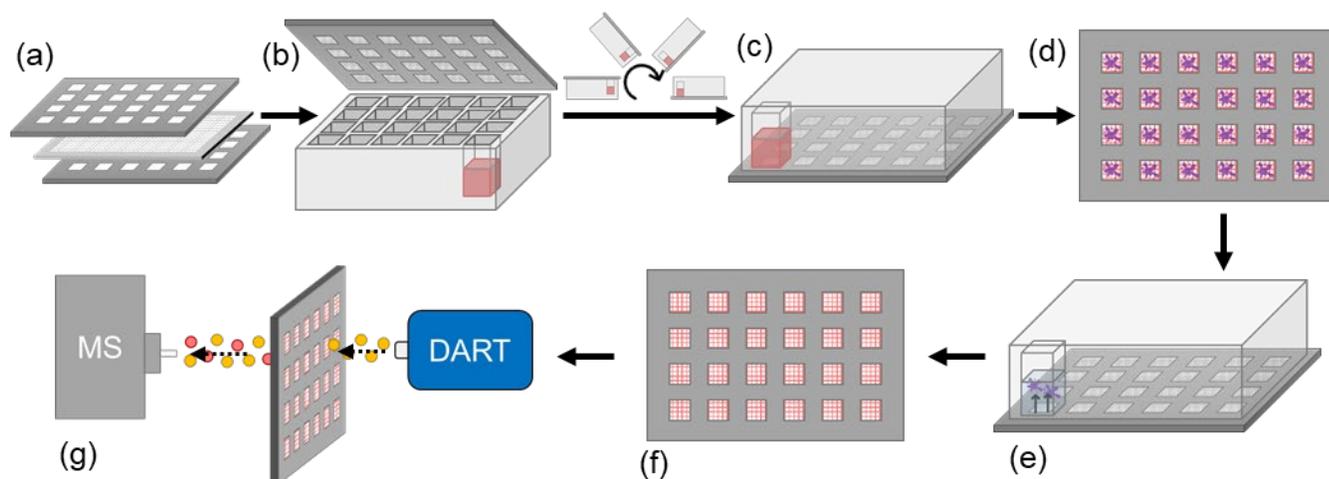


Figure 1. SPMESH-DART-MS workflow: (a) SPMESH is positioned in stainless steel frame, (b) the SPMESH is then placed on a 24-wellplate. (c) Parallel immersion extraction is performed by inverting the wellplate. (d) After, the SPMESH has absorbed the compounds of interest while large, non-volatile interferences remain on the surface. (e) SPMESH is rinsed with water to remove interferences, (f) leaving only the compounds of interest. (g) Desorption and MS analysis is then performed using DART-MS.

	4-EP ^a		4-EG ^b		G ^b	
	Recovery ^c	SE ^d	Recovery	SE	Recovery	SE
Juice						
Cab Franc	89%	7%	128%	17%	138%	46%
Chardonnay	118%	8%	117%	12%	67%	31%
Concord	98%	14%	135%	28%	50%	13%
Lemberger	75%	8%	72%	11%	369%	52%
Pinot Noir	71%	14%	83%	17%	397%	134%

Table 1: Recoveries of volatile phenols (4-EP, 4-EG, G) spiked into grape juices. Recoveries in the range of 70-120% are acceptable for routine use.

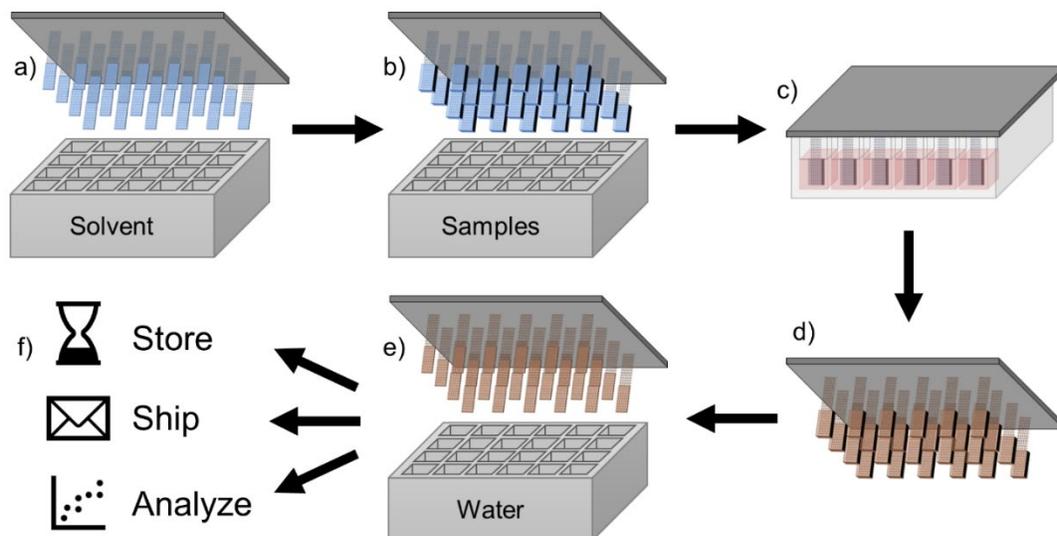


Figure 2. SweME workflow: (a) the SweME device is swollen in an appropriate solvent, (b) then the swollen device is inserted into a wellplate with samples for (c) extraction. After extraction, (d) the solvent evaporates from the polymer in a fume hood (e) then rinsed with water. (f) The individual SweME devices can then be stored, shipped, and/or analyzed.

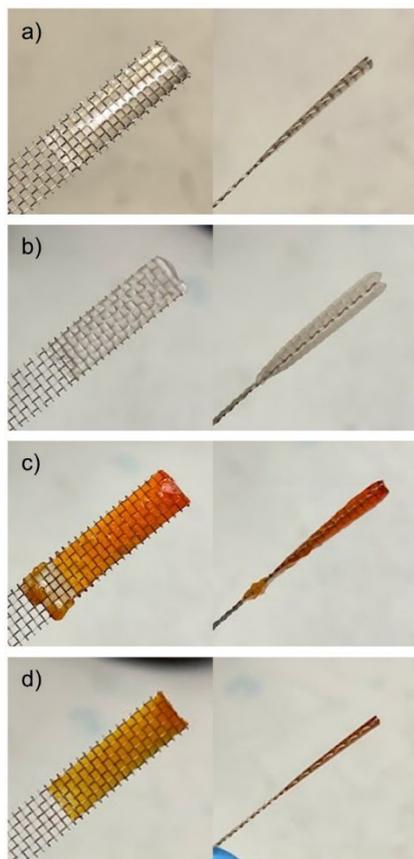


Figure 3. (a) An unswelled SweME, (b) a swelled SweME, (c) a swelled SweME after extraction from a tomato juice sample, and (d) the SweME after it is deswelled. Tomato juice was used for this experiment to make it easier to observe the absorption process.