NYWGF RESEARCH - FINAL REPORT

Funding for fiscal year: 2024-25

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 ☒

Amount Funded $ 121,670

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 often slow and prohibitively expensive for routine use. Over the last several years, the Sacks lab developed a new approach for increasing throughput and decreasing costs for routine volatile analyses by using sorbent sheets (SPMESH) coupled to direct-analysis in real time mass spectrometry (DART-MS).

In 2024, a new commercial SPMESH-DART-MS prototype was evaluated, allowing for development of new volatile assays. The system evaluated was a improvement on a 2023 version of the same instrumentation which was determined to have unacceptable sensitivity and robustness for routine grape and wine analyses, as well as serious deficiencies in software control. The new 2024 system was determined to be acceptable for routine grape and wine analyses. Additionally, improved SPMESH-DART-MS methods for detection of C6 alcohols (“green”), C8 alcohols (“moldy”) and free volatile phenols (“smoky”).

Objectives:

Objective 1: Using a modified turnkey commercial SPMESH-DART-MS system, validate previously developed assays for total volatile phenols, methoxypyrazines, and C_6 aldehydes

Objective 2: Validate SPMESH-DART-MS for new analyte classes (free vs. bound volatile phenols and C_6 alcohols)

Objective 3: Validate SPMESH-DART-MS for sampling and analysis of volatiles from fermentations.

Materials & Methods:

For Objective 1, we attempted to validate our recently developed methods for IBMP, C6 aldehydes, and total volatile phenols using a new commercial prototype SPMESH-DART-MS. The instrument was provided by Bruker. Evaluation used only standards in model juice and wine systems. Grape samples were collected from New York State vineyards, but were not used in analysis due to challenges with

instrument performance. The SPMESH-DART-MS system was used to analyze three classes of commonly measured grape and wine odorants at varying concentrations.

- IBMP (“bell pepper”)
- C6 aldehydes (“grassy”)
- Total volatile phenols (“smoky”).

For Objective 2, we developed and evaluated new methods for expanding the existing range of analytes for rapid SPMESH-DART-MS

C6 alcohols (“green”) and C8 alcohols (“moldy”) – Pyridine was added to samples to enhance DART-MS sensitivity. Figures of merit (e.g. detection limits, reproducibility, linear range) were determined for a dilution series of standards.

Free vs. Bound phenols (“smoky, clove, band-aid”) – Previous work had measured total (free + bound) volatile phenols only. In 2023-24, we determined that by decreasing pH from 13 to 10.5, we could selectively measure only free phenols using standards. In 2024-25, we evaluated the selectivity of the protocol using authentic smoke taint samples.

For Objective 3, we used the new SPMESH-DART-MS system to quantify six common fermentation metabolites (ethyl esters, acetate esters, and higher alcohols).

Results/Outcomes/Next Steps:

In 2024, a commercial prototype of a turnkey SPMESH-DART-MS system from an industry collaborator (Bruker) was evaluated. Several problems were identified with the system, especially with the coupling of the DART interface with the MS unit. As a result, the new unit showed unacceptably low sensitivity for many target analytes. Based on feedback from our team and others, Bruker has released a new version of the mass spectrometer (EVOQ TQ+) with an improved DART to MS coupling. At Bruker’s research lab, our group confirmed that the new instrument could achieve acceptable detection limits (Figure 1), and the new instrument is scheduled for installation in the Sacks lab at Cornell in Jan 2025.

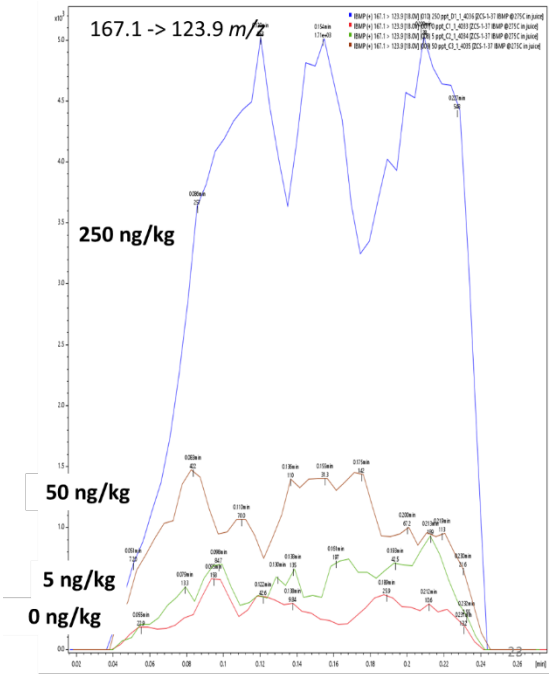

Figure 1 *–SPMESH-DART-MS of IBMP ("green pepper") using new EVOQ TQ+ turnkey instrument. Detection limits are ~ 5 ng/kg, or about 10-fold lower than the previous iteration of Bruker instrument.*

As a result of these issues, we were not able to analyze samples from NYS wineries and vineyards in 2024. With the new instrumentation, in 2025-26, we will execute our previous plan and solicit samples from New York State producers (n=300 grape and wine samples), and analyze IBMP, volatile phenols, and/or C6 aldehydes by both our new SPMESH-DART-MS method and conventional GC-MS analyses.

In 2024, we also made further progress on targets that were previously not accessible to SPMESH-DART-MS.

- For **C_6 aldehydes ("green, unripe")**, a validated method was published (Bates & Sacks, 2024).
- For **C_6 alcohols ("green") and octen-3-ol ("moldy")**, figures of merit were evaluated following addition of nitrogenous bases. The lowest detection limits were achieved with addition of either pyridine or quinoline to samples to form adducts in the DART-MS source (Figure 2).
- For **free and bound volatile phenols ("smoky, Brett")**, we confirmed that derivatization at pH 10.5 with acetic anhydride will allow for selective measurement of free phenols, and derivatization at pH 13 will measure both free and bound phenols.

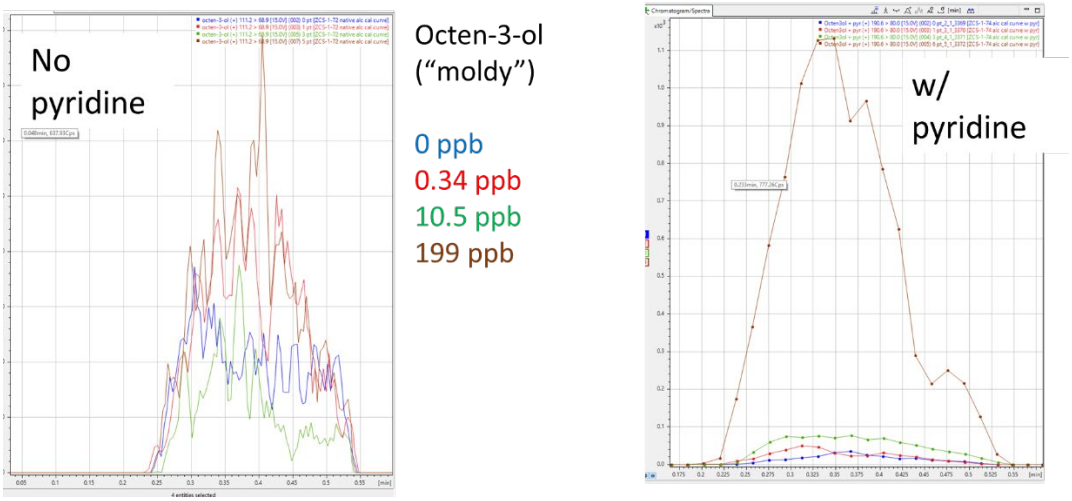

Figure 2 *– SPMESH-DART-MS of octen-3-ol with (left) or without (right) addition of pyridine prior to analysis. Detection limits are improved by almost two orders of magnitude.*

A summary of SPMESH-DART-MS methods developed and validated through Mar 2025 are reported in Table 1.

	Compound or compound class	Status for SPMESH-DART-MS	Notes	Detection limits
	IBMP	Validated method (Bates, 2022)	Direct extraction, no derivatization	Low ppt
	Total monoterpene alcohols (combined signal of linalool, geraniol, and isomers)	Validated method (Bee, 2020)	Direct extraction, no derivatization	Low ppb
	Free + bound volatile phenols (guaiacol, methylguaiacol, cresols)	Validated method (Bates, 2023)	Acylation at pH 13 w/ d6-acetic anhydride	Low ppb
	C_6 aldehydes (Hexanal and *trans*-2-hexenal)	Validated method (Bates, 2024)	**PFBOA** derivatization to produce oximes	Low ppb
	Damascenone	Detectable (Jastrzembski, 2017)	Direct extraction	Low ppb
	Free volatile phenols (guaiacol, methylguaiacol, cresols)	Validated (Kalenak, 2024)	Acylation at pH 10 w/ d6-acetic acid.	Low ppb (?)
	C_6 alcohols (Hexanol and *trans*-2-hexenol) and octenol	Validated (Scott, 2024)	In source derivatization with **pyridine**.	Low ppb (?)

Table 1 *–SPMESH-DART-MS methods developed in the Sacks lab.*

Technology Transfer Plan: Results from this work are currently in preparation for publication in the Journal of Agricultural and Food Chemistry. We also expect to publish in Cornell Extension Enology publications (Veraison to Harvest, or Appellation Cornell).

SECTION 3:

Project summary and objectives: Measurement of trace-levels of odorants or their precursors in grapes and wines are useful to winemakers, but existing analytical approaches are prohibitively expensive. We evaluated a new commercial system – based on innovations in our lab – for rapid inexpensive odorant analyses. Using this system, we also investigated new approaches to measurements of odorants in grapes, wines, and fermenting must.

Importance of research to the NY wine industry: Analysis of many components of juices and wines, such as acids, sugars and alcohol is routine. However, analysis of most odorants in grapes or wines is prohibitively expensive for many wineries. Decreasing the cost of these volatile analyses will allow for their more frequent usage by winemakers and grapegrowers in decision making.

Project Results/next steps: Previous SPMESH-DART-MS analyses focused on a single analyte class at a time. In 2025, we propose to validate the improved turnkey SPMESH-DART-MS commercial system for performance in simultaneous analyses of multiple analytes. We also propose to evaluate SPMESH-DART-MS using 96-well plates in place of the current 24-well plates for multiplexed analyses, which will allow for higher throughput during multi-target analyses.