Analysis of Pinot Noir Wines by HS-SPME GC/Q-TOF: Correlating Geographical Origin with Volatile Aroma Profiles

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Introduction

Methodologies utilizing GC/MS for characterization of wine are used extensively in both research and production environments. Improvements in sampling, data acquisition and data analysis have increased the quality, accuracy and ease of interpretation of such complex data. In this work, headspace solid phase microextraction (HS-SPME) was performed in combination with an accurate mass high resolution GC/Q-TOF on wine samples as part of a much larger project to correlate the volatile profile of Pinot noir wines with the soil and microclimate of their vineyards of origin.

Experimental

Pinot noir grapes from the same clone were grown in 15 different vineyards in California and Oregon (Figure 1). In ten cases, the vines were grafted onto the same root stock. The grapes were harvested and brought to the UC Davis winery (Figure 2) where wines were made in quadruplicate from each vineyard using identical enological conditions. Included in the facility is a state-of-the art winery with 152 highly automated research fermenters with precise temperature control, stirring and brix measurements. Every 15 minutes, measurements are sent wirelessly to a control room that monitors and charts all of the data. Attempts were made to remove as many variables as possible in the wine making process so that differences in the chemical make-up of the wine would be due to the grape growing conditions – soil and microclimate. Triplicate samples of each wine were transferred to 60 mL bottles which were capped with no headspace. Three of the replicate wines from each vineyard were analyzed in triplicate using HS-SPME (Figure 3) with an Agilent 7200B GC/Q-TOF (Figure 4).

Figure 1. American Viticulture Areas (AVA) supplying grapes for this study.

Experimental

Figure 2. UC Davis is renowned for its Viticulture and Enology program.

Figure 3. PAL 3 Autosampler for SPME, Liquid or HS Injections

Figure 4. 7200B High Res. Accurate Mass GC/Q-TOF

Experimental

From each of the 45 wine samples (15 vineyards, 3 replicate fermentations), 10 mL of wine and 3 g NaCl were added to each of three headspace vials and data were acquired:

HS-SPME Conditions:

100 µm, 1 cm Fiber
Pre-extraction sample equilibration = 5 min @ 30°C
Headspace extraction = 45 min @ 30°C
Fiber desorption in MMI inlet = 2 min @ 240°C
Fiber conditioning = 10 min @ 250°C

GC/Q-TOF Conditions

Column: 30 m X 0.25 mm X 0.25 µm DB-WAXETR
Oven: 40°C (5 min); 3°C/min→180°C (0 min); 30°C/min→240°C (10 min)
Acquisition: 33 – 300 m/z, 5 spec/s, 4GHz High Res Mode

Results and Discussion

UC Davis has state-of-the-art fermenters that can produce wine in precisely controlled conditions allowing excellent reproducibility between batches made in a single year and from year to year. This is significant as this project will continue for 5 years. In future years, recording weather stations will be placed in each vineyard located where the grapes are growing to provide accurate weather data.

The project will utilize multiple techniques to analyze wines in determining how soil & microclimates affect flavor. This work describes analysis by HS-SPME GC/Q-TOF.

- **Volatile Analysis- HS-SPME GC/Q-TOF**
- Elemental Analysis- ICP-MS
- Polyphenolic Analysis- LC-DAD
- Sensory Analysis- Descriptive Analysis

HS-SPME GC/MS has proved to be very sensitive for the analysis of wine volatiles. As shown in Figure 5, HS-SPME GC/Q-TOF was able to detect 2,4,6- trichloroanisole (responsible for a musty or "cork taint" aroma in wine) at 0.1/L (parts per quadrillion).

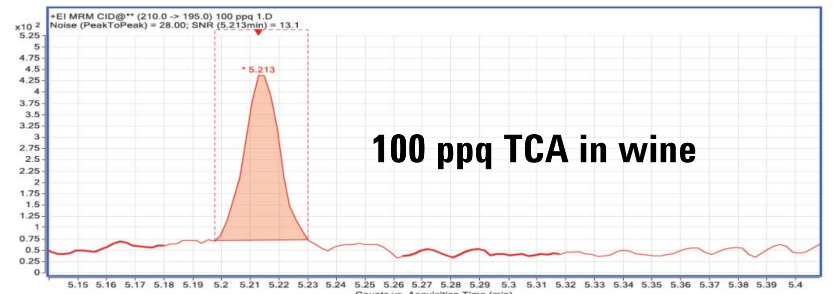

Figure 5. HS-SPME GC/Q-TOF analysis of 2,4,6-trichloroanisole at 0.1 ng/L. The sensory threshold for TCA is ~2 ng/L .

Results and Discussion

Chromatography

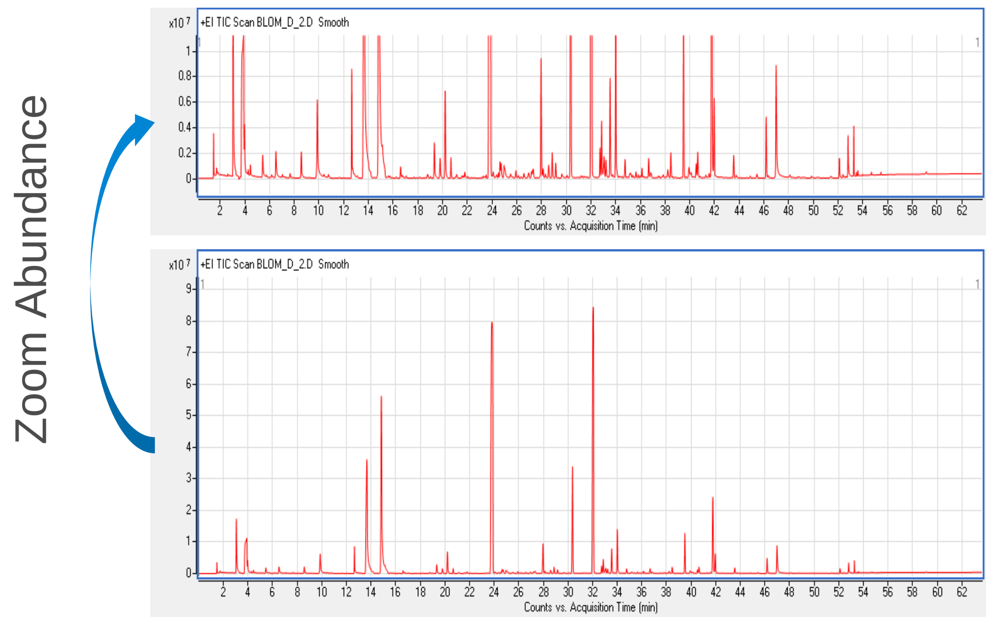

Figure 6. Typical HS-SPME GC/Q-TOF of a Pinot noir wine used in this study. >250 peaks could be integrated in each wine sample.

Peak Identification

In Figure 7, compounds indicated by a # were identified previously by injecting known standards using the same retention time locked method as used in this study. Other compounds were *tentatively identified* by spectral matching (to NIST unit mass library) and by comparison of the compound's Retention Index to literature values. Some compounds could be classified only as terpenes and sesquiterpenes.

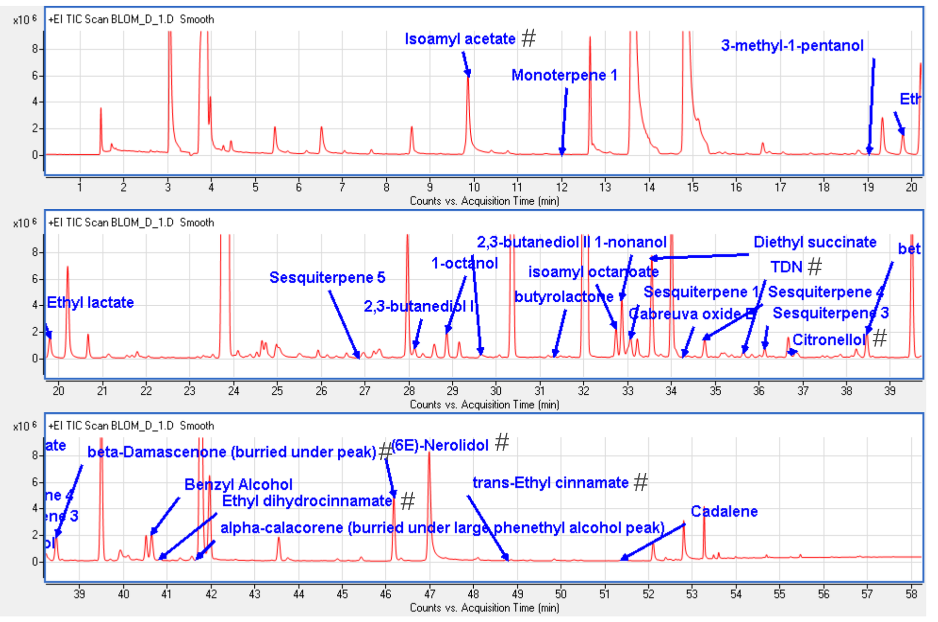

Figure 7. Significant aroma compounds identified in the Pinot noir wines studied. Compounds marked with a # were identified by injecting an authentic standard. Others were tentatively identified by spectral matching and comparison of retention index values.

Results and Discussion

Statistical Analysis

66 compounds were positively or tentatively identified. Areas for these peaks (relative to 2-undecanone ISTD) were determined for all samples and ANOVA was performed using R statistical software. These data were imported into Agilent Mass Profiler Professional (MPP) for Principle Component Analysis (PCA).

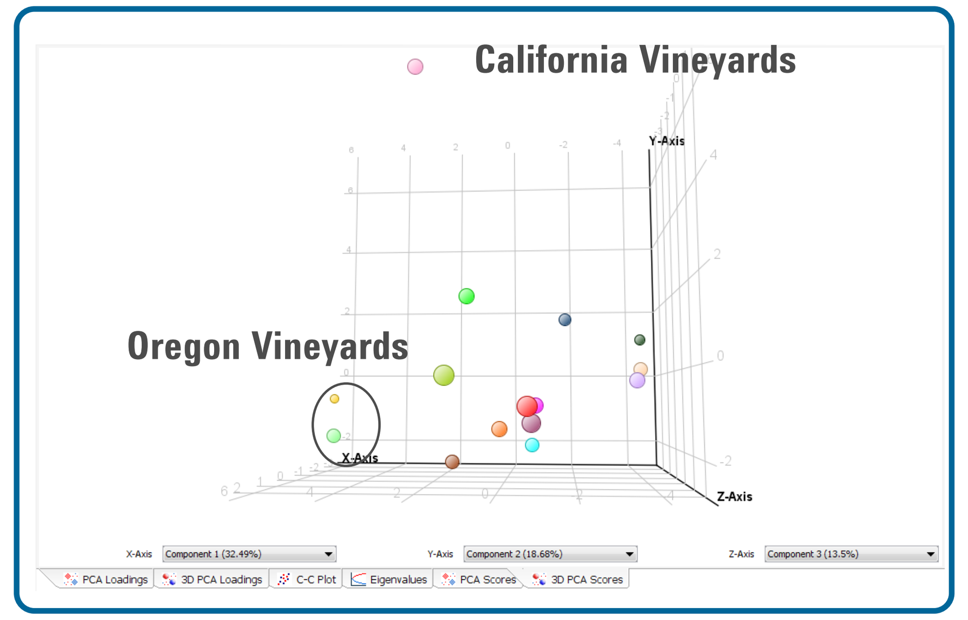

Figure 8. PCA Scores plot for all 15 vineyards. Each point represents 9 measurements – 3 SPME injections of 3 replicate wines. Oregon wines are distinctly different than California wines.

Analysis of wines having identical root and vine stock

Of the 15 vineyards sampled, 10 had grapes harvested from plants with the same root and vine clones. These were analyzed separately as shown in Figures 9 and 10.

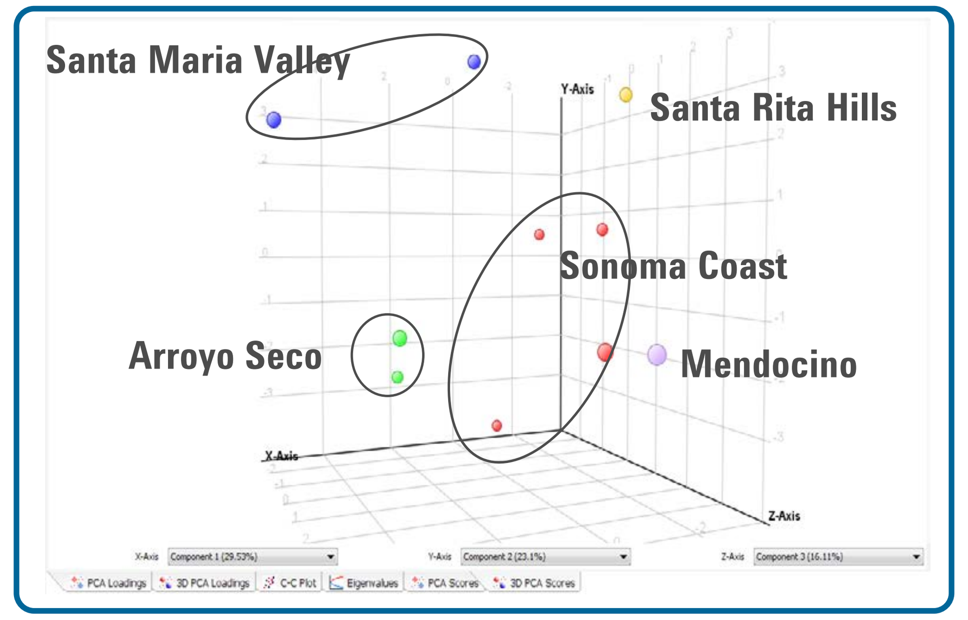

Figure 9. PCA Scores plot for 10 vineyards producing grapes from identical root and vine clones. Regional differences can be seen. The names are the American Viticulture Areas (AVA) where the grapes were grown.

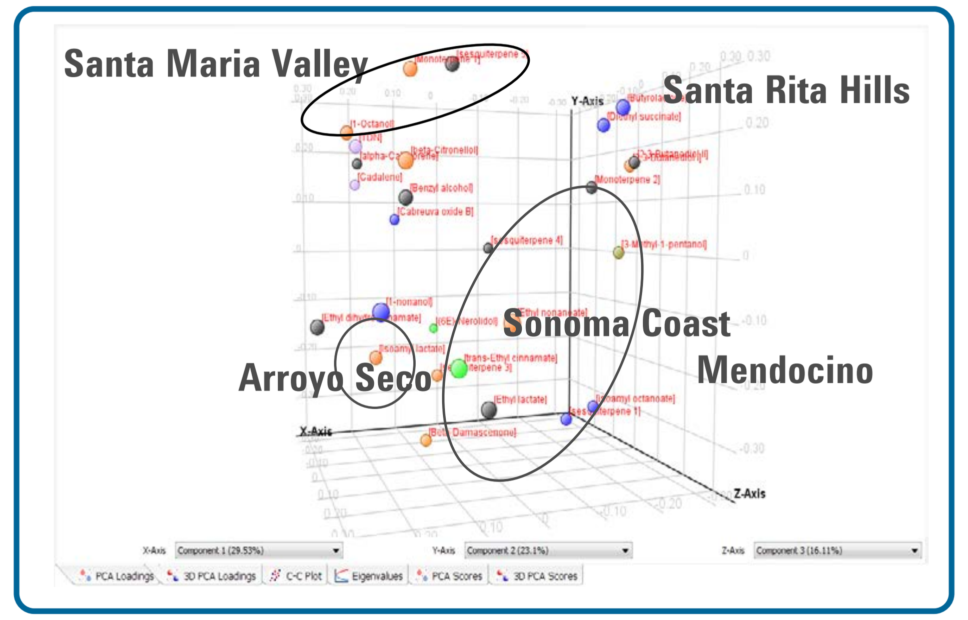

Figure 10. PCA Loadings plot showing the most significant flavor and aroma compounds that differentiate the Pinot noir wines. Superimposed are the regional clusters shown in Figure 9.

Future work to be performed

- ✓ Place recording weather station at each vineyard location
- ✓ Obtain climate information for each AVA and each vineyard
- ✓ Correlate GC/Q-TOF results with
  - o Vineyard microclimate
  - o Unit resolution GC/MS results
  - o Metals/Elemental analysis by ICP-MS
  - o Polyphenolic analysis by LC/DAD
  - o Sensory Analysis
- ✓ Continue investigation over multiple years
- ✓ Add more vineyards with same grape clone and same root stock

Conclusions

- ✓ Four batches of wine were made (per vineyard) from Pinot Noir grapes harvested from 15 different vineyards in California and Oregon (3 batches used for GC/Q-TOF analysis).
- ✓ Three replicate HS-SPME injections made for each wine batch
  - o 15 vineyards X 3 wine batches X 3 replicates = 135 analyses
  - o 9 analyses for each vineyard
- ✓ Volatile profile differs between vineyards in Oregon, California north coast and California central coast.
- ✓ All vineyards could be separated in PCA based on volatile profiles of significant aroma compounds.

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