APPLICATION NOTE

Gas Chromatography/
Mass Spectrometry

Authors:

Sharanya Reddy

Thomas Dillon

PerkinElmer, Inc.
Shelton, CT

Profiling of Aroma Components in Wine Using a Novel Hybrid GC/MS/MS System

Introduction

The global wine industry is an established market with more than one million wine makers globally. The present market size is approximately three billion U.S. dollars with an annual growth rate of ~3%.

Aroma profiling of wine is important for wine formulation and quality control because aromas are known to contribute to the organoleptic/sensory properties of wine. Wine aroma is determined by hundreds of volatile compounds present at a wide range of concentrations. Characterization of these aroma contributing compounds can help with wine characterization and therefore with quality control of wine.

The AxION® iQT™ GC/MS/MS is a novel hybrid mass spectrometer system that offers full scan mass spectral information with excellent sensitivity at fast data acquisition speeds. It is ideal for detection of components present at both trace levels and at high concentrations compared to scanning instruments such as quadrupoles.

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The eCipher™ data analysis package, provided with the instrument, includes a deconvolution algorithm with automatic "spectral library" database searching for identification of components in complex matrices including wine. The results obtained can be imported into the PerkinElmer TIBCO Spotfire® Software for Principle Component Analysis (PCA) to identify the chemical components that are unique to the wine varieties.

Experimental

Sample Preparation

Wine (Merlot, Chardonnay or Rosé, 20 mL each) was mixed with dichloromethane (10 mL) and stirred at room temperature for 30 min. The samples were centrifuged at 3500 RPM. The dichloromethane layer was carefully removed into a centrifuge tube containing anhydrous sodium sulfate (2 g), vortexed for 0.5 secs and centrifuged at 3500 RPM for 10 min. The organic layer was removed, dried under nitrogen gas to 1 mL and injected (1 µL).

Table 1. GC conditions.

Gas Chromatograph	PerkinElmer Clarus® 680
Injector Type:	Programmable Split/Splitless
Injector Temperature:	250 °C
Injection:	1 µL, splitless
Oven Program:	40 °C, hold for 2 min., ramp to 180 °C at 12.5. °C/min., ramp to 240 °C/min. and hold for 5 min.
Analytical Column:	PerkinElmer ELITE-5 MS, 30 m X 0.25 mm X 0.25 µm
Carrier Gas:	1 mL/min. Helium

Table 2. MS conditions.

Mass Spectrometer	PerkinElmer AxION iQT MS/MS
GC Transfer Line Temperature:	250 °C
Source Temperature:	250 °C
Acquisition Time:	0.2 sec
Mass Range:	40-400
Ion Source:	EI
Solvent Delay:	3 min.

Results and Discussion

A full scan chromatogram of Chardonnay wine analyzed by the AxION iQT system is shown in Fig. 1. Deconvolution of data by eCipher™ resulted in 107 peaks being detected, including peaks representing <1% of the total ion current. The user set thresholds for peak area and signal-to-noise (S/N) determine the number of peaks detected by the deconvolution software. The spectra of peaks detected were matched against the NIST[1] library database. Table 3 shows representative components tentatively identified in white wine.

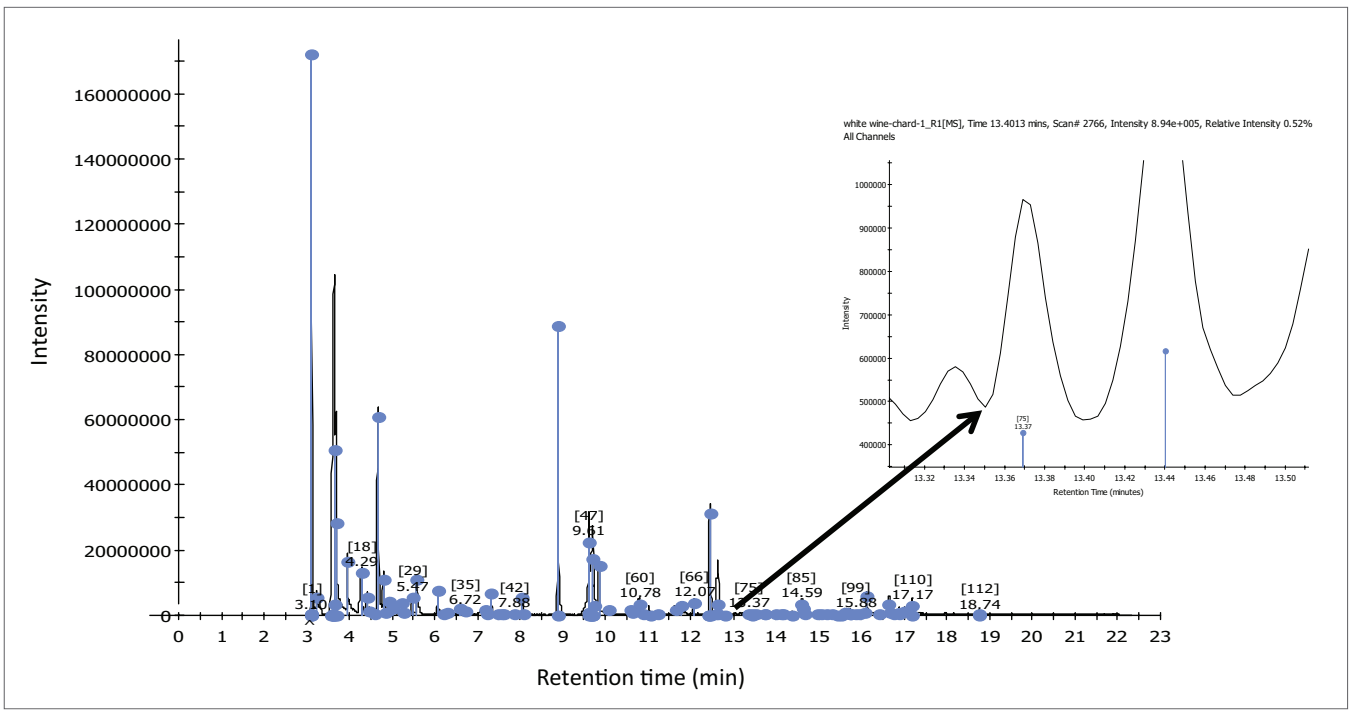

Figure 1. Peaks identified in Chardonnay (in blue) with thresholds settings for S/N at 10 and area of 500. Inset shows peaks identified at <1% of the total ion current.

Table 3. Representative components tentatively identified in Chardonnay by matching against NIST library.

RT Found	% Area	Match	Reverse Match	Name
4.364	0.31	928	928	1-Propanol
4.480	0.30	840	840	Butanoic Acid, ethyl ester
5.031	2.99	912	912	1-Propanol, 2-methyl-
5.531	1.51	918	918	1-Butanol, 3-methyl-, acetate
6.526	8.03	855	855	1-Butanol, 3-methyl-
8.093	1.71	800	828	ETHYL (S)-(-)LACTATE
8.186	0.33	878	878	1-Hexanol
8.440	0.08	907	907	1-Propanol, 3-ethoxy-
9.457	0.03	819	819	2H-Pyran, 3,4-dihydro-6-methyl-
10.080	0.06	752	952	1,2-Ethanediol, monoacetate
10.099	2.10	810	810	2,3-Butanediol, [R-(R*,R*)]-
11.087	0.50	917	917	Butanoic Acid, 4-hydroxy-
12.964	1.68	884	884	Hexanoic acid
13.292	0.16	894	894	L-Arginine, N2-[(phenylmethoxy)carbonyl]-
14.028	0.07	772	911	4H-Imidazol-4-one, 2-amino-1,5-dihydro-
14.211	0.37	945	945	2H-Pyran-2,6(3H)-dione
14.637	2.02	847	847	Butanedioic acid, hydroxy-, diethyl ester
11.523	0.49	833	850	Butanedioic acid, diethyl ester
17.903	0.12	813	813	S-Hydroxymethylfurfural
18.967	0.12	914	914	Ethanone, 1-(3-hydroxy-4-methoxyphenyl)-
19.106	0.39	799	814	Propan-2-one, I-(4-isopropoxy-3-methoxyphenyl)-
22.719	2.07	810	815	Homovanillic acid
22.892	0.13	897	970	1-Cyclooctene-1-acetic acid, à, à-dimethyl-

Peaks detected in Chardonnay were saved as a target library and the peaks detected in Merlot were matched against this list. The compounds common to both wines and unique to each wine can be sorted by the software with color coding (Fig. 2).

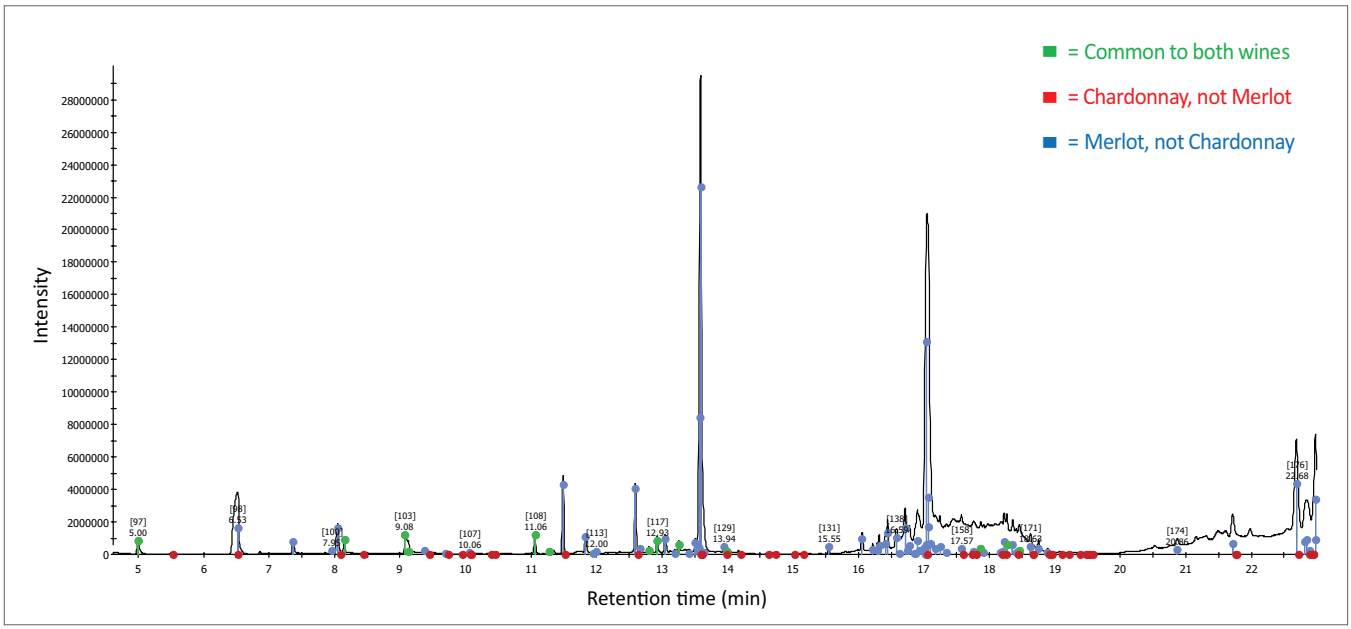

Figure 2. Peaks identified in Merlot were matched against compounds in Chardonnay. The compounds common to both wines are shown in green. The compounds exclusive to Merlot and Chardonnay are marked in blue and red color respectively.

A reference target list was generated to include peaks detected and identified in replicate samples of Merlot, Chardonnay and Rosé wine. Each of the replicate injections (n=6) was compared against this reference list and the data matrix generated was exported into Excel for PCA analysis by TIBCO Spotfire® software (Fig. 3). The PCA plot shows good separation of the grape varieties based on the six replicates analyzed for each sample. The loadings plot (Fig. 3) helped identify the chemical compounds that are unique to each of the wines.

For example, it was observed that diethyl malate, 2, 4-hexadienoic acid, and tryptophol are present at higher concentrations in Rosé compared to the other two wine types. The compounds hydroxy cinnamic acid ethyl ester, diethyl succinate and 3,5-dimethoxy-4-hydroxy benzoic acid contribute to the uniqueness of Merlot while ethyl lactate and 2-(2-Hydroxyethyl)phenol is higher in Chardonnay compared to the other two wines. Compounds mapped out in the center of the loadings graph are present in all three wine varieties at similar concentrations. The data of the loading graph for the compounds phenylethyl alcohol, ethyl lactate and dimethyl malate is displayed as bar charts in Fig. 4 further emphasizing the chemical difference between the wine varieties. The bar charts confirm the excellent reproducibility between replicate injections.

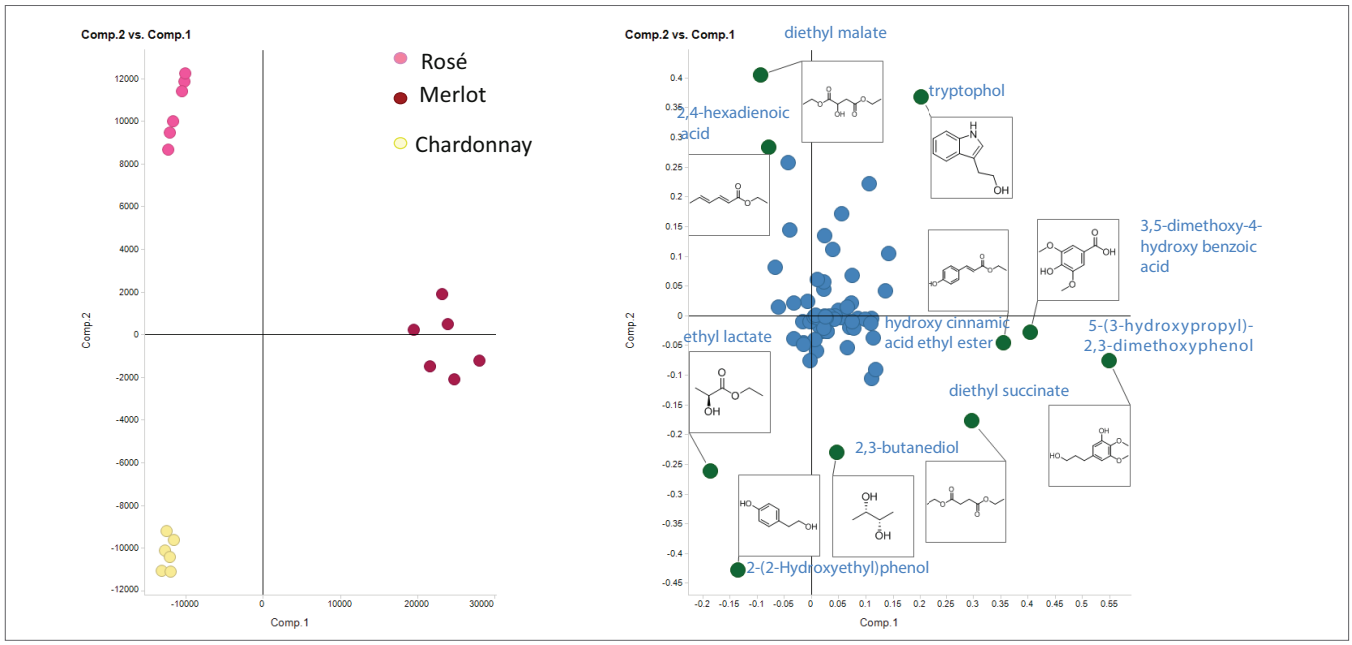

Figure 3. PCA analysis of wine samples using TIBCO Spotfire® software. The loadings graph on the right hand side maps the chemical space to the wine variety.

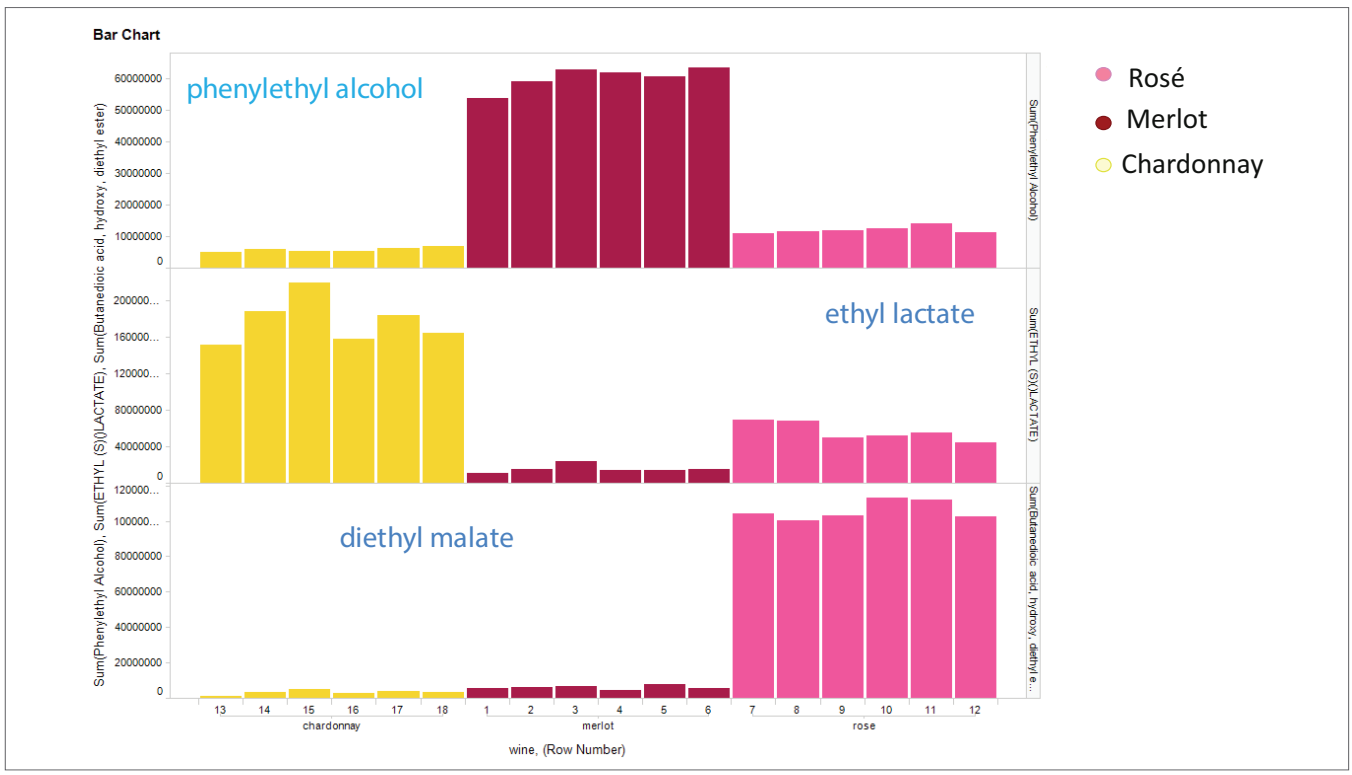

Figure 4. Intensities of phenylethyl alcohol, ethyl lactate and diethyl malate plotted for multiple injections of Chardonnay, Merlo and Rosé are shown as bar charts.

Discussion

The AxION iQT GC/MS/MS system in full scan mode can identify trace level analytes (low ppb) in a complex matrix such as wine. The eCipher™ peak deconvolution software in conjunction with the PerkinElmer PCA TIBCO Spotfire® software can be used to profile wine aromas and to identify differences between the wine varieties.

References

1. NIST/EPA/NIH Mass Spectral Library, NIST Standard Reference Database 1A, 2014.

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

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