Analysis of Volatile Organic Compounds in Wine by Purge and Trap Concentration and Gas Chromatography/ Mass Spectrometry (GC/MS)

Introduction

Many of the flavors and fragrances which make up a wine's profile consist of volatile organic compounds (VOCs). These chemicals, even at small concentrations can affect the flavor and aroma of a wine. Many subjective descriptors are used such as buttery, a hint of oak, peppery, vanilla, and so on. Wine flavors and aromas can be organized into three primary groups: fruit; floral; and herbal, spice, and earth.[1] VOCs are produced at different times in the winemaking process. For instance, VOCs accumulate in the grape as the grape seed matures and as the fruit ripens by binding to other molecules such as sugars and amino acids. Winemakers release these compounds by breaking the bonds: both physically by crushing the grapes and chemically during fermentation with grape and yeast enzymes.[2] Traditionally, the detection of VOCs has been accomplished by the oenologist through taste and smell. There is growing interest in using chemical analysis to identify and quantitate the VOCs in the various stages of the winemaking process. For example, esters can add fruit and flower notes; terpenes can add piney, rose, and lavender notes; and organic acids can add sour, vinegary notes.[1]

The use of GC/MS may lead to identification of previously unknown VOCs in wine as well as help winemakers make adjustments to the growing and winemaking techniques based upon scientific data.

Many VOCs can be analyzed by purge and trap concentration and detection by GC/MS. A variety of wines were analyzed by this technique. A calibration was run using commercially available compounds and a library search was performed on peaks not identified by the calibration method, i.e., tentatively identified compounds (TICs).

Eclipse 4760 P&T and 4100 Autosampler

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Experimental

The instrumentation used for sample concentration was the OI Analytical 4760 Purge and Trap (P&T) along with a 4100 Sample Processor. An Agilent 7890A/5975C GC/MS was used for chromatographic separation and detection. EPA Method 8260 was used for analysis. Please see Table 1 for instrument parameters.

An initial screening of samples was performed to determine the most significant compounds that may be in a variety of wines. These standards were obtained and a calibration was analyzed at varying concentrations according to how well the compounds purge. For example it was necessary to run the alcohol standards at higher concentrations because of their solubility in water. Increasing the purge temperature above 45° C did not significantly improve the alcohol response; therefore, in order to keep the water transferred to the GC/MS minimized, 45° C was used. The P&T bake and GC final hold time were increased to help the GC/MS recover from the percent Ethanol concentration contained in the samples. Samples were also run in the soil mode, i.e. purged in a 40 mL VOA vial, to further assist with water management and prevent sample foaming.

A variety of samples were obtained for under $20 a bottle. For this initial study the interest was variety instead of expense. Samples were run at a 2x dilution and then diluted further to get compounds that were over-calibration within range (20-100x).

Table 1. Instrument Parameters

Purge-and-Trap	Eclipse 4760 P&T Sample Concentrator
Trap	#10 trap; Tenax® / Silica gel / CMS
Purge Gas	Zero grade Helium at 40 mL/min
Purge Time	11 min
Sparge Mount Temperature	45 °C
Sample Temperature (purge)	45 °C
Sample Temperature (bake)	45 °C
Desorb Time	0.5 min
Bake Time	5 min
OI #10 Trap Temperature	Ambient during purge 180 °C during desorb pre-heat 190 °C during desorb 210 °C during bake
Water Management	120 °C during purge Ambient during desorb 240 °C during bake
Transfer Line Temperature	140 °C
Six-port Valve Temperature	140 °C
Autosampler	**4100 Water/Soil Sample Processor**
System Gas	Zero grade nitrogen
Purge Gas	Zero grade helium
LV20 Pressure	8.0 psi
Loop-based Time Settings	Default
Rinse Water	80 °C
Soil Sample Transfer	150 °C
Soil Oven	150 °C
Soil Life Station	45 °C
Gas Chromatograph	**Agilent 7890A**
Column	Restek Rtx – VMS 30 meter, 0.25 mm ID, 1.4 µm
Carrier Gas	Zero grade helium
Inlet Temperature	240 °C
Inlet Liner	Agilent Ultra Inert, 1 mm straight taper
Column Flow Rate	0.8 mL/min
Split Ratio	150:1
Oven Program	Hold at 40 °C for 1.5 min 16 °C/minute to 180 °C 40 °C/minute to 220 °C Hold at 220 °C for 4.25 min Total GC Run is 15.5 min
Mass Spectrometer	**Agilent 5975C**
Mode	Scan 35-300 amu
Scans/Second	5.19
Solvent Delay	1.60 min
Transfer Line Temperature	240 °C
Source Temperature	300 °C
Quadrupole Temperature	200 °C
Draw Out Plate	6 mm

Results and Discussion

A seven point calibration was analyzed. For compounds which had a %RSD</= 15%, the average response was used and linear regression was used for the others.

Please see Table 2 for calibration data.

Table 2. Calibration Data

Analyte	Compound	Calibration Range (ppm)	Retention Time (min)	Avg Responce Factor	% RSD/Coeff Of Det
1	Pentafluorobenzene (IS)	N/A	5.066	N/A	N/A
2	n-Propanol	1-100	4.217	0.003	11.98
3	Ethyl acetate	0.02-2	4.687	0.599	11.35
4	Dibromofluoromethane (SS)	0.05	4.754	0.591	2.03
5	Isobutanol	0.2-20	5.143	0.022	8.61
6	1,4 – Difluorobenzene (IS)	N/A	5.468	N/A	N/A
7	1,2 – Dichloroethane – d4 (SS)	0.05	5.147	0.053	3.94
8	Chlorobenzene – d5 (IS)	N/A	7.719	N/A	N/A
9	Toluene – d8 (SS)	0.05	6.484	1.386	0.98
10	Isoamyl alcohol	0.2-20	6.606	0.014	13.03
11	Isoamyl acetate	0.01-1	8.143	0.762	0.999
12	1,4 – Dichlorobenzene – d4 (IS)	N/A	9.751	N/A	N/A
13	4 – Bromofluorobenzene (SS)	0.05	8.744	0.944	1.52
14	Ethyl hexanoate	0.01-1	9.442	0.463	0.999
15	Ethyl caprylate	0.01-1	11.297	0.528	0.999
16	Ethyl caprate	0.01-1	12.815	0.528	14.30

Samples were quantitated for the target compounds and a library search was performed for unknown compounds or TICs. Sample results are presented in the results table from lightest color to darkest. The compounds found, for the most part, contributed to sweet alcohol, fruit, and floral bouquets in the form of alcohols and esters.

The TICs found were Sulfur dioxide and Ethyl butanoate. Sulfur dioxide is used as a preservative in wine at various concentrations and also occurs naturally during fermentation. The U.S. requires labelling for wines containing over 10ppm sulfites.[3] The TIC results for the compound can only be considered a broad estimate since the compound was not calibrated for due to standard availability and price. It is also very volatile and will not remain stable in samples.

Each compound found has a specific effect on the wine. One compound of interest is Ethyl acetate. The sensory threshold is between 90-150 mg/L. Lower levels can give the wine a sweeter, "younger" taste whereas higher levels may impart aromas of acetone and be considered a fault in the wine.[5] Another compound found in significant concentrations is Isoamyl alcohol which can be associated with the fruitiness of the wine. The compounds at lower concentrations, such as Ethyl caprylate, can impart floral fragrance. Please see Table 3 for Sample Results.

Table 3. Sample Results

LB = Light bodied MB = Medium bodied FB = Full bodied

Sample	Description	ppm n-Propanol (sweet alcohol)	ppm Ethyl acetate (fruit, pear)	ppm Isobutanol (sweet, alcohol)	ppm Isoamyl alcohol (fruit, banana oil)	ppm Isoamyl acetate (banana oil, pear)	ppm Ethyl hexanoate (apple, aniseed)	ppm Ethyl caprylate (fruit, flowers)	ppm Ethyl caprate (fruit, pineapple)	ppm Sulfur dioxide*	ppm Ethyl butanoate(fruit, citrus, pineapple)*	Labelled % Alcohol
Chardonnay A	MB to FB; citrus; pomaceous and tropical fruits;oak/unoaked	20.4	107	25.3	162	0.43	0.55	0.68	0.2	0.21	0.12	13.5
Chardonnay B	MB to FB; citrus; pomaceous and tropical fruits;oak/unoaked	33	80.1	19.4	110	2.33	0.88	1.48	0.37	0.46	0.16	13.5
Pinot Grigio A	LB; delicate citrus; pomaceous fruits; floral notes; cheese	29.6	63.3	15.2	88.1	2.45	1.17	1.35	0.25	1.13	0.22	13.5
Pinot Grigio B	LB; delicate citrus; pomaceous fruits; floral notes; cheese	17.2	64.5	15.5	108	1	0.91	1.4	0.31	0.52	0.15	13.5
Sauvignon Blanc	LB to MB; citrus; tart; exotic fruits; herbaceous	15.5	54.8	8.99	103	0.69	0.86	1.33	0.29	0.72	0.12	13.5
Moscato	LB; sweet and fruity; floral and perfume profile	18.4	38.4	13.8	88.4	0.86	0.42	0.47	0.06	0.86	0.12	10
Pink Moscato	LB; sweet and fruity; floral and perfume profile	17	40.7	14.5	86.4	0.56	0.36	0.31	0.01	0.56	0.1	10
Sweet Red	LB; sweet and fruity mix of red wines; jammy; cherry and berry	23.3	49.2	21	119	1.08	0.44	0.52	0.08	0.31	0.11	12.5
Beaujolais	LB; similar to Pinot, but lighter, juicier, more floral and less complex	28.1	67.4	39.7	200	0.84	0.36	0.46	0.09	<0.01	0.12	13
Pinot Noir	LB; very red fruited; rose; vegetal notes; soft tannin	37.6	153	74.7	153	0.17	0.26	0.21	0.04	<0.01	0.07	14
Merlot	MB; similar to Cab, but fruitier flavor and less tannins	35	70.6	26.6	162	0.65	0.33	0.4	0.12	<0.01	0.08	13.5
Cabernet A	FB; black cherry and currant; spice; oaky; bold tannins	17	154	36.4	271	0.28	0.2	0.16	0.04	<0.01	0.06	13.5
Cabernet B	FB; black cherry and currant; spice; oaky; bold tannins	22.6	126	46.1	299	0.36	0.2	0.15	0.03	<0.01	0.07	15.5
Malbec A	FB; similar to Syrah, but more black fruited and oaky and less meaty	13.8	118	40.9	241	0.22	0.17	0.17	0.02	<0.01	0.05	13.5
Malbec B	FB; similar to Syrah, but more black fruited and oaky and less meaty	15.8	153	41.7	258	0.26	0.17	0.17	0.03	<0.01	0.06	13.5
Syrah	FB; blueberry; plum; tobacco; meat; black pepper; mid tanins	24	131	31.8	244	0.36	0.19	0.14	0.02	<0.01	0.06	13.5

It had been noted by some OI Analytical customers that, after running the instrument for an extended period of time, a contamination peak at ~3-4.5 ms formed after the hydrocarbon emission at ~1-3 ms. Various tests were run at OI to duplicate this.

Build-up varied according to injections made and concentration. If high concentrations of >1 ppm were run successively over a two day period, the contamination was fairly significant. Some decrease over time was observed because of the self-cleaning properties of the combustion zone. Replacing the combustor, baking out the system, and performing inlet maintenance helped somewhat but the only action that completely removes the contamination is clipping the column at the detector end. Installing a guard column at the detector end may help extend column life. Setting the Tin gate after the contamination will ensure that it does not interfere with the analysis.

Figure 1. Standard

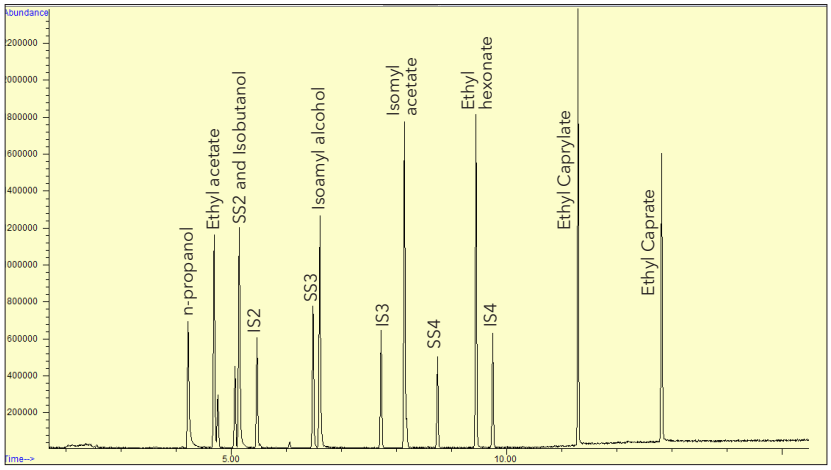


Figure 2. Chardonnay A

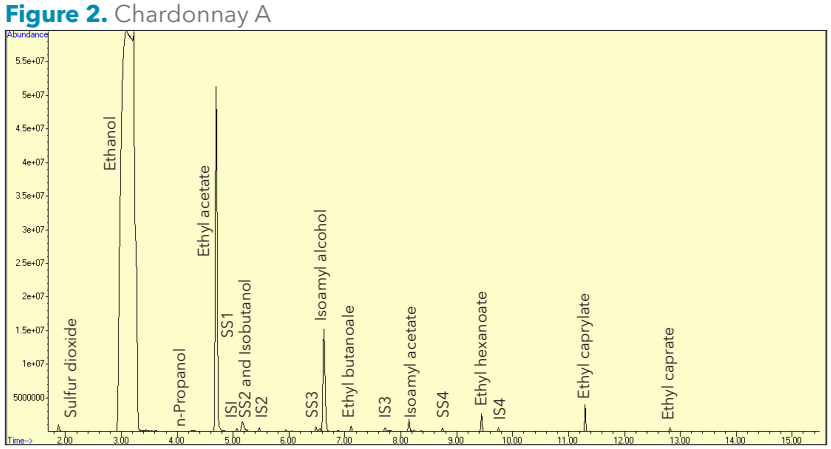
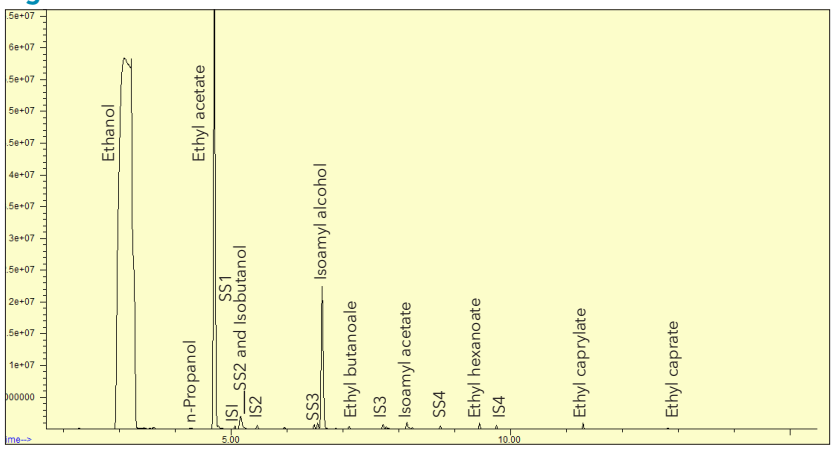


Figure 3. Cabernet A



Conclusions

While all flavor and fragrance compounds are not suitable for purge and trap analysis, purge and trap is a viable option for the analysis of volatile flavors and fragrances in wine. Small differences in volatile components can greatly affect the taste and bouquet of the wine. The data presented here is of interest because it shows quantifiable reasons for differences in wine rather than the subjective qualitative differences attributed to taste and smell.

References

1. "Where Wine Flavors Come From: the Science of Wine Aromas" WineFolly, January 7, 2015.

2. "The Why Behind a Wine's Bouquet" NBC News Technology and Science, February 9, 2006.

3. "The Bottom Line on Sulfites in Wine" WineFolly, January 15, 2014.

4. "Common Types of Wine (the Top Varieties) WineFolly, May 18, 2015.

5. "Wine Fault" Wikipedia, Rev January 2018.

6. USEPA Method 8260B Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) Revision 2, December 1996.

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