EFFECTS OF CROP LEVEL ON CHEMICAL COMPOSITION AND HEADSPACE VOLATILES OF LODI ZINFANDEL GRAPES AND WINES

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ABSTRACT

A method is given for quantitative analysis of wine headspace. The reproducibility of the method, for 24 identified peaks, is ±10-15% if internal standards are chosen correctly. Unidentified peaks of lesser intensity generally have larger coefficients of variation. Variations in headspace analysis between field replications were too large for the data to be pooled. All calculations were done on individual field replicates. Stepwise discriminant analysis was used to show that the wines could be correctly sorted on the basis of analysis of either must, wine, or headspace. Selective must, wine, and headspace data were correlated linearly with crop levels.

For prediction of the effects of various vineyard treatments on wine quality it is beneficial to determine which chemical compounds in the grape or in the wine can be related to the vineyard treatment. The composition of grapes determines, in part, the ultimate quality of the wine.

Common applications of gas chromatography to wine flavor research have been identification of trace volatile of wine components (3,4,23) and study of the effects of time and production variables on selected volatile components of wine (5,12,18,19,20).

General support for the use of headspace analysis in flavor studies has been given by Jennings and Filsoof (9), Jennings et al. (11), Heatherbell et al. (8), and Nawar and Fagerson (15). Weurman (24) reviewed early techniques of direct headspace injection and cold-trap concentration.

The best alternative in many cases has been the enrichment of headspace components by trapping on adsorbents followed by desorption of water and ethanol (9,11). Volatiles have been eluted from the adsorbents by solvent extraction and by thermal desorption. The former suffers from the same disadvantage mentioned for direct solvent extraction. Thermal desorption has been affected by artifacts resulting from bleeding of the adsorbent and from pyrolysis of the volatiles (16). Volatiles have been lost through irreversible adsorption (16).

Tenax-GC has been shown to have excellent thermal stability (16,17,21) and very low retention volumes for water and lower alcohols relative to the majority of headspace components (9). The lower alcohols make Tenax-GC ideal for headspace sampling of alcoholic beverages.

The principal effect of overcropping is a delay in maturation of the fruit (2,14). Loinger and Safran (13), found that overcropped vines produced inferior wines but that undercropped vines did not always produce the best wines.

This report summarizes a one-year investigation of a crop-level vineyard experiment. Data were gathered to determine whether chemical responses in either grapes or wine could be correlated satisfactorily with the field treatments.

EXPERIMENTAL

Viticultural: The vineyard trial was set up on mature head-trained spur-pruned Zinfandel vines at the J. Fry vineyard in Lodi, California. The vineyard was divided into 30 segments to accommodate five treatments with six replications each. Each segment consisted of five vines, adjacent to each other and in the same row. Each segment was labeled to designate the treatment (A-E) and the replication (1-6). The five treatments were: A) pruned to 12 spurs, not thinned; B) pruned to 12 spurs, hand-thinned; C) pruned to 8 spurs,

not thinned; D) pruned to 8 spurs, gibberellic-acid-thinned; and E) pruned to 8 spurs, hand-thinned.

Maturity effects were eliminated as much as possible by harvesting each treatment separately at 22.0° Brix. The harvest dates of the five treatments were: D) September 18; B, E) September 30; and A, C) October 8.

The 1975 growing season in Lodi was relatively cool. Unseasonable storms brought 0.8 inch of precipitation in August. These factors led to considerable bunch rot. Rotten clusters and portions of clusters were separated from the sound fruit.

Enological: The wines were made by standard experimental practices at the University of California at Davis. Sulfur dioxide was added to a concentration of 75 mg/l. One percent by volume of a yeast starter culture (*Saccharomyces cerevisiae,* strain Montrachet) was added.

Chemical analysis: The must samples were analyzed for total soluble solids, pH, total acidity, total nitrogen, proline, and arginine. Wine samples were analyzed for ethanol, pH, total acidity, total phenols and color.

Arginine was determined as described by Gilboe and Williams (7). The other determinations were done as described by Amerine and Ough (1).

Gas collection and handling: Headspace volatiles were trapped on an adsorbent porous polymer, thermally desorbed, and condensed in glass tubes chilled in dry ice by a modification of the procedure described by Jennings and Filsoof (9).

The adsorbent was Tenax-GC, 60/80-mesh (Applied Science Laboratories, Inc.). The Tenax-GC trap was prepared by a 3-ml-ID glass tube with the adsorbent. The trap was 63 cm long.

The temperature of the trap was regulated with two ovens constructed from 8-mm-ID copper tubing wrapped with heating tape and insulated with fiberglass. Two variable output transformers (Powerstat type 3PN116B) were used to set the temperatures of the two ovens. One oven was set at 35.0°C for the trapping and developing operations (described below). The second oven was set at 125°C for the backflushing and reconditioning operations (described below).

Water-pumped nitrogen (Liquid Carbonic Corp.) cleaned with Carbosieve 5X was used throughout. Flow rate, regulated with a heated and insulated micro-needle valve (Whitey No. SS-22RSH), was set at 25.0 ml/min immediately before the trapping operation.

Gas chromatography of essence: The collected headspace essence (about 3 μl) was analyzed on a 0.25-mm-ID x 50-m Wall Coated Open Tubular (WCOT) glass capillary column using Carbowax 20M as the liquid phase.

The gas chromatograph was a Hewlett-Packard 5720A fitted with a glass annular ring splitter. The inlet-to-split ratio was set at 20 to 1. The instrument was equipped with a flame ionization detector.

Peak areas were determined with a Varian CDS 101 digital integrator.

Statistics: All analyses of variance were calculated by hand. Stepwise regression analysis (SRA) and stepwise discriminant analysis (SDA) were run on a Burroughs 6700 computer using programs from the BMD manual (6).

Two criteria were established for selecting the cut-off point for equations generated by SRA and SDA. The first was to accept a maximum of five independent variables in any single equation. The second criterion was to reject the first equation which did not improve the efficiency of the equation in the previous step. For SRA, that meant rejecting the first equation which did not increase the multiple correlation coefficient (R) or did not decrease the standard error of the estimate (s_e). For SDA, that meant rejecting the first equation which did not increase the number of samples correctly sorted in the previous step.

All variables were converted to Z values prior to SRA and SDA. Z values were obtained from the following equation:

$$\frac{X_i - \overline{X}}{s} = Z_i$$

where X_i is the observed or actual value, $\overline{X}$ is the mean and s is the standard deviation.

RESULTS AND DISCUSSION

Table 1 summarizes crop-level values and the chemical must and wine analysis by treatments. The crop levels were significantly different. The LSD (P = 0.05) was 5.5 lb/vine. The criterion set for equal maturity (°Brix at harvest) was not met. Treatments B and E had a significantly higher °Brix at harvest than did the other three treatments. The LSD (P = 0.05) was 0.70 °Brix. The other data show some rather large variations. The nitrogen-related measurements show increases with decreased crop load. The differences, except for D, in the total acidity and pH are probably closely related to the maturity differences already noted.

Table 2 gives chemical analysis of the wines by treatment. The ethanol increases verify the maturity differences. The total phenols and color data reflect the greater maturity of B and E, and perhaps some crop level effect as well. Treatment D was notably low in these values, causing some question as to the use of gibberellic acid.

Headspace measurements of the volatiles yielded chromatograms of the type shown in Fig. 1. The peak codes given in that figure are referred to throughout the paper. Some of the peaks are identified in Table 3. For the purpose of this study their identities are not important.

Reproducibility of the headspace analysis was determined from three consecutive runs on samples taken from a single one-gallon bottle of wine typical of the wines used for headspace analysis and sensory evaluation. The samples were taken through a glass siphon using nitrogen gas for pressure and to prevent

exposure of the wine to air.

All peaks from these three runs were initially normalized on each of the two internal standards, 3-pentanol and 1-octanol, respectively coded as IS-1 and IS-2 in Fig. 1. Peaks were normalized by dividing the area of individual peaks with the area of an internal-standard peak. The reproducibility of any single peak was markedly affected by the internal standard chosen for normalizing that peak. That is shown in Table 4. Peaks A through T-1 had substantially smaller coefficients of variation when normalized on IS-1. Similarly peaks U-1 through Z had better reproducibility when normalized on IS-2. Therefore, for the purposes of data reporting and statistical analysis, peaks A through T-1 were normalized on IS-1 and peaks T-2 through Z were normalized on IS-2.

Because of poor reproducibility, peaks A, B, and D were not considered in any further statistical analyses. The overall reproducibility for the remainder of the peaks is estimated to be ±10 to 15%.

Except in the reproducibility study, only one analysis was made per sample

Table 1. Summary of the must analyses.

Analysis	Treatments					
	Mean ± coefficient of variation					
	A[a]	B[a]	C[a]	D[b]	E[a]	All[c]
Crop level (lbs/vine)	40.8 ± 14.1%	33.4 ± 10.0%	35.5 ± 14.7%	22.5 ± 19.9%	29.1 ± 12.4%	32.6 ± 22.8%
Soluble solids (°Brix)	21.8 ± 3.2%	24.1 ± 1.0%	22.4 ± 4.0%	22.2 ± 0.8%	24.6 ± 2.4%	23.0 ± 5.5%
pH	3.46 ± 1.6%	3.42 ± 1.6%	3.49 ± 2.4%	3.40 ± 1.5%	3.40 ± 1.1%	3.43 ± 1.9%
Total acidity (g/100 ml)	0.93 ± 6.7%	0.80 ± 4.7%	0.89 ± 9.3%	0.98 ± 2.8%	0.83 ± 4.2%	0.88 ± 9.4%
Total nitrogen (mg/l)	756 ± 13.3%	799 ± 6.7%	699 ± 7.1%	838 ± 11.8%	840 ± 6.1%	784 ± 11.1%
Proline (mg/l)	2017 ± 13.8%	2715 ± 15.5%	2305 ± 13.1%	2682 ± 10.6%	2793 ± 8.9%	2496 ± 16.8%
Arginine (mg/l)	788 ± 12.6%	862 ± 6.2%	773 ± 7.2%	941 ± 8.7%	1066 ± 7.1%	884 ± 14.8%

[a] n = 6.

[b] n = 5, sample D5 not included.

[c] n = 29.

Table 2. Summary of the wine analyses.

Analysis	Treatments					
	Mean ± coefficient of variation					
	A[a]	B[a]	C[a]	D[b]	E[a]	All[c]
Ethanol (vol %)	13.5 ± 6.2%	14.4 ± 1.3%	13.6 ± 5.0%	13.2 ± 4.8%	14.2 ± 3.6%	13.8 ± 5.2%
pH	3.46 ± 1.9%	3.56 ± 1.4%	3.47 ± 3.2%	3.45 ± 2.0%	3.57 ± 2.7%	3.50 ± 2.6%
Total acidity (g/100 ml)	0.74 ± 1.9%	0.75 ± 2.2%	0.75 ± 5.9%	0.85 ± 2.5%	0.79 ± 4.4%	0.77 ± 6.4%
Total phenols (mg/l)	1462 ± 7.7%	1552 ± 5.7%	1350 ± 4.2%	1110 ± 5.3%	1552 ± 5.4%	1415 ± 12.6%
Absorbance at 420 nm (l-cm cell)	130 ± 11.2%	141 ± 10.8%	122 ± 5.7%	109 ± 7.2%	146 ± 10.3%	130 ± 13.5%
Absorbance at .540 nm (1-cm cell)	177 ± 10.4%	182 ± 10.3%	164 ± 6.1%	137 ± 6.4%	187 ± 10.6%	170 ± 13.4%

[a] n = 6.

[b] n = 5, sample D5 not included.

[c] n = 29.

Table 3. Identification of gas-chromatographic peaks.

Peak[a]	Compound[b]
A	Acetaldehyde
B	Methyl acetate
C	Ethyl acetate
D	Ethanol
E	Ethyl propanoate
F	Ethyl 2-methyl propanoate
G	1-Propyl acetate
H	2-Methyl-l-propyl acetate
I	1-Propanol
J-1	Ethyl butanoate
K	Ethyl 2-methyl-butanoate
L	Ethyl 3-methyl-butanoate
M-1	2-Methyl-l-propanol
N-1	3-Methyl-l-butyl acetate
O-1	2-Methyl-l-butanol + 3-Methyl-l-butanol
P-1	Ethyl hexanoate
Q-1	1-Hexyl acetate
R-1	Ethyl lactate
S-1	1-Hexanol
T-1	Methyl octanoate
U-1	Ethyl octanoate
V-1	Ethyl nonanoate
W-1	Ethyl decanoate
X-1	Ethyl 9-decenoate
Y	Ethyl dodecanoate
Z	2-Phenylethanol
IS-1	3-Pentanol
IS-2	1-Octanol

[a] Peak codes correspond to those used in Fig. 1.

[b] Tentative identification based on the work of Sinton and Ough (22).

Table 5 summarizes the headspace data gathered from the 29 analyses of the individual replicates by treatments for the 52 peaks monitored. The variation among the replicates is quite large, as demonstrated by the coefficients of variations. These variations are accumulated by differences in individual samples, fermentations, and handling as well as the included sampling variations. Difficulties in meaningfully relating the average values to the imposed treatment variables are considerable.

The individual replicate values of the data were further investigated by the use of discriminant analysis. This method is designed to investigate unrelated variables. Use of the technique is somewhat unjustified in this case since some of these variables are significantly correlated and also the data sets are small. Nevertheless, the analyses were made as a preliminary step.

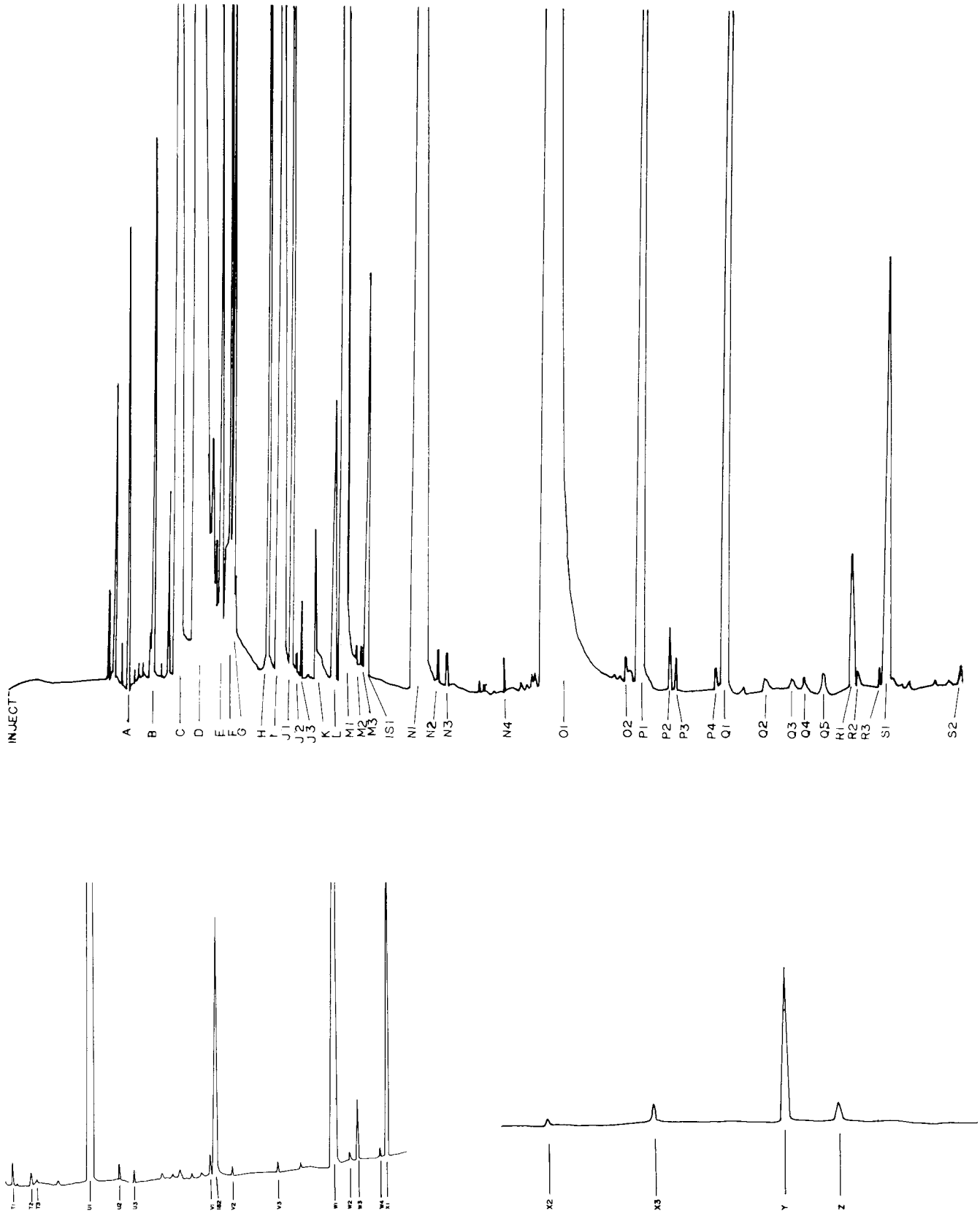

Fig. 1. A typical chromatogram.

The four variables of the musts (°Brix, arginine, total acidity, and pH) were capable of correctly sorting out 27 of the 29 samples. With the wine-analysis data, 24 of the 29 samples could be correctly sorted out. Lastly, with the headspace data of 52 variables, four peaks correctly selected out 24 of the 29 samples.

Table 4. Reproducibility of the gas-chromatographic headspace analysis.

Peak[a]	Coefficient of variation[b] (%) for peaks normalized on:	
	IS-1 (3-pentanol)	IS-2 (1-octanol)
A	59.0	67.2
B	36.8	54.4
C	12.7	27.3
D	17.4	42.7
E	14.5	26.6
F	13.1	29.4
G	14.2	35.3
H	14.6	31.4
I	8.0	35.9
J-1	7.7	35.6
K	8.7	38.3
L	8.9	32.3
M-1	7.7	32.5
N-1	8.8	31.3
O-1	13.8	26.4
P-1	9.4	31.7
Q-1	9.4	36.0
R-1	11.2	52.4
S-1	15.3	28.4
T-1	4.0	45.2
U-1	28.0	9.0
V-1	33.2	9.2
W-1	37.1	11.1
X-1	15.7	7.9
Y	21.7	11.0
Z	23.0	10.4

[a] Peak codes correspond to Fig. 1.

[b] n = 3.

Table 5. Summary of mean normalized peak areas ± coefficient of variation.

Peak[a]	Treatments					
	A[b]	B[b]	C[b]	D[c]	E[b]	All[d]
C	313 ± 26.7%	450 ± 23.3%	362 ± 27.3%	449 ± 22.2%	402 ± 28.2%	393 ± 27.3%
E	1.77 ± 13.5%	1.76 ± 10.1%	1.84 ± 13.1%	1.97 ± 15.2%	1.53 ± 18.7%	1.76 ± 15.4%
F	3.37 ± 9.2%	3.12 ± 11.8%	3.29 ± 18.4%	2.97 ± 10.6%	2.46 ± 17.5%	3.05 ± 16.9%
G	1.19 ± 23.2%	1.79 ± 17.7%	1.84 ± 23.7%	1.97 ± 25.4%	1.53 ± 28.7%	1.76 ± 30.4%
H	5.34 ± 23.6%	6.11 ± 23.0%	4.72 ± 53.8%	6.22 ± 14.0%	5.38 ± 24.7%	5.72 ± 21.1%
I	13.5 ± 27.0%	16.0 ± 16.9%	10.9 ± 36.1%	18.7 ± 16.3%	12.1 ± 27.9%	14.4 ± 25.6%
J-1	5.84 ± 19.7%	6.59 ± 18.1%	6.19 ± 10.2%	5.86 ± 11.9%	5.56 ± 19.5%	6.02 ± 16.4%
J-2	0.125 ± 30.3%	0.111 ± 75.2%	1.742 ± 208.5%	0.121 ± 51.0%	0.084 ± 54.2%	0.447 ± 374.8%
J-3	0.153 ± 20.4%	0.122 ± 40.3%	1.150 ± 73.7%	0.181 ± 11.1%	0.138 ± 18.5%	0.365 ± 148.8%
K	0.925 ± 14.8%	0.788 ± 27.8%	0.947 ± 25.2%	0.669 ± 35.7%	0.613 ± 33.2%	0.792 ± 29.9%
L	0.900 ± 12.7%	0.720 ± 9.1%	0.760 ± 34.7%	0.895 ± 19.5%	0.716 ± 19.4%	0.829 ± 18.7%
M-1	51.8 ± 7.7%	52.2 ± 19.1%	53.9 ± 12.3%	50.7 ± 9.3%	42.7 ± 23.0%	50.2 ± 16.1%
M-2	0.0111 ± 55.9%	0.0232 ± 39.9%	0.0126 ± 69.1%	0.0268 ± 53.8%	0.0474 ± 50.5%	0.0241 ± 77.6%
M-3	0.0732 ± 26.3%	0.0549 ± 67.1%	0.0874 ± 25.1%	0.0549 ± 17.7%	0.0853 ± 42.1%	0.0717 ± 40.5%
N-1	216 ± 20.7%	264 ± 26.0%	252 ± 20.8%	236 ± 11.5%	217 ± 23.2%	237 ± 21.7%
N-2	0.0678 ± 13.6%	0.0740 ± 14.7%	0.0631 ± 51.0%	0.0835 ± 22.5%	0.0798 ± 20.9%	0.0750 ± 19.1%
N-3	0.119 ± 15.8%	0.115 ± 19.7%	0.131 ± 20.6%	0.135 ± 17.1%	0.106 ± 20.5%	0.120 ± 19.7%
N-4	0.103 ± 35.1%	0.118 ± 25.5%	0.114 ± 40.8%	0.132 ± 24.5%	0.126 ± 13.7%	0.118 ± 27.9%
O-1	302 ± 11.2%	290 ± 27.6%	345 ± 14.8%	258 ± 12.1%	223 ± 21.5%	284 ± 22.7%
O-2	0.119 ± 25.8%	0.143 ± 37.4%	0.170 ± 20.3%	0.124 ± 30.6%	0.134 ± 22.9%	0.138 ± 29.0%
P-1	21.5 ± 13.1%	21.0 ± 19.4%	22.7 ± 9.3%	20.0 ± 13.0%	17.5 ± 16.3%	20.5 ± 16.1%
P-2	0.164 ± 20.8%	0.229 ± 51.9%	0.161 ± 17.3%	0.364 ± 40.1%	0.177 ± 61.3%	0.214 ± 54.3%
P-3	0.0243 ± 30.7%	0.0209 ± 40.4%	0.0256 ± 45.8%	0.0637 ± 33.0%	0.0123 ± 25.9%	0.0285 ± 70.0%
P-4	0.0553 ± 11.1%	0.0490 ± 34.5%	0.0589 ± 25.0%	0.0774 ± 50.7%	0.0811 ± 41.5%	0.0639 ± 40.9%
Q-1	6.43 ± 14.3%	5.61 ± 26.0%	6.98 ± 23.9%	6.70 ± 16.3%	5.08 ± 22.2%	6.14 ± 22.8%
Q-2	0.0788 ± 36.8%	0.0443 ± 35.8%	0.0644 ± 14.3%	0.0955 ± 20.5%	0.0433 ± 47.9%	0.0642 ± 42.4%
Q-3	0.1242 ± 39.5%	0.0552 ± 29.6%	0.0866 ± 31.9%	0.0569 ± 38.2%	0.0408 ± 38.6%	0.0732 ± 55.6%
Q-4	0.0993 ± 36.4%	0.0449 ± 49.1%	0.0656 ± 31.8%	0.0695 ± 32.8%	0.0474 ± 30.2%	0.0651 ± 46.4%
Q-5	0.190 ± 24.7%	0.147 ± 20.0%	0.186 ± 20.0%	0.176 ± 10.0%	0.112 ± 17.1%	0.162 ± 26.4%
R-1	0.332 ± 12.0%	0.343 ± 13.0%	0.329 ± 34.3%	0.516 ± 29.8%	0.298 ± 20.6%	0.356 ± 31.5%
R-2	0.0318 ± 66.0%	0.0403 ± 45.0%	0.0397 ± 26.7%	0.0648 ± 22.7%	0.0513 ± 32.5%	0.0449 ± 42.5%
R-3	0.0743 ± 44.5%	0.0742 ± 42.1%	0.0992 ± 25.7%	0.1026 ± 29.7%	0.0884 ± 36.7%	0.0872 ± 35.4%
S-1	2.20 ± 29.4%	1.33 ± 32.0%	2.31 ± 13.7%	1.79 ± 9.1%	1.12 ± 30.0%	1.75 ± 35.5%
S-2	0.0507 ± 19.7%	0.0495 ± 18.6%	0.076 ± 43.5%	0.0853 ± 5.3%	0.0464 ± 17.3%	0.0606 ± 36.5%
T-1	0.227 ± 25.5%	0.279 ± 28.7%	0.323 ± 12.2%	0.263 ± 15.8%	0.201 ± 32.0%	0.258 ± 27.1%
T-2	0.0483 ± 23.8%	0.0695 ± 23.3%	0.0634 ± 27.1%	0.0467 ± 28.4%	0.0489 ± 22.2%	0.0556 ± 28.9%
T-3	0.0322 ± 41.8%	0.0454 ± 28.3%	0.0445 ± 54.0%	0.0362 ± 29.7%	0.0318 ± 52.8%	0.0380 ± 59.9%
U-1	21.5 ± 12.2%	26.9 ± 16.8%	20.5 ± 17.8%	17.3 ± 29.7%	22.2 ± 13.9%	21.8 ± 21.5%

Table 5 (continued)

Peak[a]	A[b]	B[b]	C[b]	D[c]	E[b]	All[d]
U-2	0.0668 ± 56.7%	0.0655 ± 36.4%	0.0962 ± 33.1%	0.0592 ± 40.0%	0.0653 ± 19.4%	0.0772 ± 34.2%
U-3	0.0476 ± 28.7%	0.0608 ± 18.7%	0.0589 ± 44.9%	0.0382 ± 29.9%	0.0553 ± 20.9%	0.0526 ± 32.4%
V-1	0.0521 ± 23.1%	0.0459 ± 35.9%	0.0515 ± 44.5%	0.0292 ± 51.0%	0.0589 ± 21.0%	0.0514 ± 32.1%
V-2	0.0387 ± 14.2%	0.0240 ± 37.0%	0.0408 ± 65.9%	0.0276 ± 31.0%	0.0233 ± 11.1%	0.0310 ± 47.7%
V-3	0.0350 ± 10.4%	0.0309 ± 31.1%	0.0388 ± 37.8%	0.0292 ± 51.1%	0.0315 ± 16.5%	0.0332 ± 31.0%
W-1	14.5 ± 21.3%	20.5 ± 13.2%	15.1 ± 21.4%	14.0 ± 28.5%	17.6 ± 19.5%	16.4 ± 23.8%
W-2	0.0297 ± 30.0%	0.0425 ± 41.6%	0.0256 ± 50.9%	0.0282 ± 58.6%	0.0337 ± 42.4%	0.0321 ± 45.5%
W-3	0.251 ± 60.0%	0.273 ± 27.5%	0.346 ± 23.7%	0.214 ± 39.4%	0.253 ± 25.7%	0.276 ± 33.7%
W-4	0.0306 ± 76.3%	0.0446 ± 28.4%	0.0323 ± 27.7%	0.0255 ± 24.5%	0.0298 ± 42.7%	0.0349 ± 35.3%
X1	0.801 ± 30.4%	0.540 ± 48.9%	0.768 ± 21.1%	1.170 ± 24.5%	0.838 ± 21.1%	0.880 ± 29.1%
X-2	0.0212 ± 245.0%	0.1070 ± 157.9%	0.0000 ± 0.0%	0.0624 ± 27.6%	0.0355 ± 181.2%	0.0449 ± 205.4%
X-3	0.151 ± 35.4%	0.169 ± 59.1%	0.160 ± 32.2%	0.076 ± 43.7%	0.115 ± 17.8%	0.136 ± 47.3%
Y	0.552 ± 32.1%	0.767 ± 48.3%	0.523 ± 63.5%	0.673 ± 38.3%	0.657 ± 45.1%	0.743 ± 45.2%
Z	0.208 ± 38.1%	0.227 ± 84.1%	0.749 ± 39.9%	0.429 ± 56.3%	0.175 ± 26.4%	0.262 ± 65.8%

[a] Peak codes correspond to those used in Fig. 1.

[b] n = 6.

[c] n = 5, sample D5 not included.

[d] n = 29.

The interrelation between the data (must, wine, and headspace analysis) were determined by running correlation coefficients. The values with significant correlation coefficients are tabulated in Table 7, along with their coefficients. The arginine was correlated with total nitrogen, and the phenols with color. Both of these correlations are expected. Some of the negative correlations of the arginine (and nitrogen) with several peaks of the headspace analysis are interesting. The phenols and color reading had no correlation (over 0.5) with any of the headspace peaks. Many of the headspace peaks had excellent correlation with other headspace volatiles.

Table 6. Stepwire discriminant analysis of data from must, wine, and headspace analysis.

Step	Variable entered	F-to-remove (df[a])	U-statistic (df[a])	Number of lots sorted correctly[b]
Must data				
1	Soluble solids	25.8 (4, 24)***	0.189 (1, 4, 24)***	19
2	Arginine	8.81 (4, 23)***	0.075 (2, 4, 24)***	21
3	Total acidity	4.32 (4, 22)**	0.042 (3, 4, 24)***	24
4	pH	4.26 (4, 21)*	0.023 (4, 4, 24)***	27
Wine data				
1	Total phenols	26.0 (4, 24)***	0.188 (1, 4, 24)***	16
2	Total acidity	7.36 (4, 23)***	0.082 (2, 4, 24)***	21
3	pH	7.55 (4, 22)***	0.035 (3, 4, 24)***	24
Headspace data				
1	Peak P-3[3]	17.1 (4, 24)***	0.260 (1, 4, 24)***	16
2	Peak J-3	9.38 (4, 23)***	0.099 (2, 4, 24)***	20
3	Peak Q-3	8.09 (4, 22)***	0.040 (3, 4, 24)***	23
4	Peak Q-4	3.75 (4, 21)*	0.023 (4, 4, 24)***	25

[a] Degrees of freedom.

[b] Out of a total of 29 lots.

*** Significant at p = 0.001.

** Significant at p = 0.01.

* Significant at P = 0.05.

Table 8 lists the compounds, or headspace peaks which had correlation coefficients above 0.5 for regression between crop level. Three of the measurements were from the must analysis, one from the wine analysis, and four from the headspace analysis. All are negatively correlated with crop level.

Variation among the treatment replicates made difficult any substantial correlation of treatments to the analysis. However, treatment of the individual replicate samples did allow reasonable differentiation by use of the analytical data.

Further detailed studies (22) will comment on the cultural effects on composition changes.

Table 7. Highly significant correlation coefficients between all the analytical data.

		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1.	Arginine	1.00	0.77	0.11	0.32	0.13	0.40	0.56	0.14	−0.72	−0.60	−0.06	−0.76	−0.44	−0.25	−0.33
2.	Total nitrogen		1.00	0.10	0.31	0.12	0.56	0.72	0.42	−0.61	−0.32	0.17	−0.57	−0.15	0.01	−0.10
3.	Total phenols			1.00	0.85	0.88	0.06	−0.07	−0.02	0.06	−0.02	0.16	−0.01	0.04	−0.26	−0.04
4.	Color (420 nm)				1.00	0.96	0.31	0.22	0.29	−0.13	0.03	0.33	−0.09	0.10	−0.08	0.07
5.	Color (540 nm)					1.00	0.15	0.00	0.17	0.02	0.09	0.27	0.05	0.16	−0.08	0.10
6.	Peak c[a]						1.00	0.91	0.86	−0.23	0.02	0.73	−0.22	0.37	0.41	0.38
7.	Peak G							1.00	0.73	−0.35	−0.05	0.54	−0.34	0.20	0.27	0.23
8.	Peak H								1.00	−0.05	0.37	0.88	0.09	0.62	0.68	0.54
9.	Peak K									1.00	0.72	0.19	0.81	0.46	0.30	0.47
10.	Peak M-1										1.00	0.50	0.89	0.68	0.52	0.71
11.	Peak N-1											1.00	0.39	0.80	0.75	0.78
12.	Peak O-1												1.00	0.69	0.48	0.70
13.	Peak P-1													1.00	0.81	0.80
14.	Peak Q-1														1.00	0.71
15.	Peak T-1															1.00

[a] Peak codes correspond to those used in Fig. 1.

Table 8. Correlation and determination coefficients for regressions between crop level and other chemical and headspace data where r>0.5.

Variable	Correlation coefficient r (27 df[a])	Determination coefficient R^b
Peak G[b]	−0.654***	42.8%
Arginine	−0.583***	34.0%
Proline	−0.581***	33.8%
Peak M-2[b]	−0.570***	32.5%
Peak N-4[b]	−0.567**	32.1%
Total acidity[c]	−0.561**	31.5%
Total nitrogen	−0.541**	29.3%
Peak R-2[b]	−0.526**	27.7%

[a] Degrees of freedom.

[b] Peak codes correspond to those used in Fig. 1.

[c] Determined in the wine samples.

*** Significant at p = 0.001.

** Significant at p = 0.01.

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