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# Analysis of Volatile Profiles of Fermenting Grape Must by Headspace Solid-Phase Dynamic Extraction Coupled with Gas Chromatography−Mass Spectrometry (HS-SPDE GC-MS): Novel Application To Investigate Problem Fermentations

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The occurrence of stuck and sluggish wine fermentations is a persisting problem in the wine industry worldwide. This study illustrates the suitability of headspace solid-phase dynamic extraction coupled with gas chromatography−mass spectrometry (HS-SPDE GC-MS) for wine analysis and the subsequent application to discriminate between control and problem fermentations using partial least-squares discriminant analysis (PLS-DA) models. The specific analytical technique is relatively new and has not yet to the authors' knowledge been evaluated for the analysis of wine within this context of problem fermentations. HS-SPDE GC-MS was used to determine 68 volatile compounds (higher alcohols, fatty acids, esters, and carbonyl compounds) in 94 monovarietal fermenting must samples consisting of 56 red and 38 white cultivars. PLS-DA models showed the potential to discriminate between control and problem fermentations using corrected peak area headspace data for the 68 analytes. This possibility to discriminate between problem and control fermentations with only the headspace data could possibly be applied for the prediction of problem fermentations in future studies and to better understand the chemical causes of problem fermentations.

**KEYWORDS: HS-SPDE GC-MS; headspace analysis; wine; discrimination; problem fermentations**

## INTRODUCTION

The ultimate goal during the winemaking process is the successful completion of fermentation, resulting in a final product of high quality without the presence of any off-flavors. This is often a challenge due to a number of factors that can potentially influence fermentation onset and successful completion (defined as having $< 5$ g/L residual sugar, depending on the wine style). Stuck and sluggish fermentations refer to premature fermentation arrest and fermentations with a sluggish or slow rate of sugar consumption by the yeast, respectively (*1*). For the purpose of this study, control fermentations refer to fermentations for which the mentioned stuck and sluggish fermentation characteristics are absent. Extensive research has been conducted to understand stuck and sluggish fermentations (referred to as "problem fermentations" in the text), and several causative factors have been identified (reviewed in refs (*1*−*5*)). Some of these factors, such as yeast strain used (*6*, *7*), fermentation conditions such as pH of the must or wine, content and type of nitrogen available, initial sugar concentration and glucose to fructose ratio, fermentation temperature, and aeration (*8*−*10*) could, in addition to their effect on fermentation efficiency, also influence the wine volatile composition.

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Volatile compounds play an important role in the sensory characteristics and quality of wines and belong to heterogeneous chemical groups such as monoterpenes, alcohols, aldehydes, ketones, esters, organic acids, and fatty acids. Some of these compounds originate from grapes, and others are formed during fermentation processes or wine aging (*10*−*12*). Apart from information related to the aroma of wine, the volatile composition could also provide information that can be interpreted in terms of the microbiological status of fermentations. Problem fermentations could potentially have a different volatile profile from control wine fermentations due the presence, absence, or influence of certain wine parameters and their effect on yeast metabolism. Compounds such as amino acids, originating from grapes, are typical of a specific variety, and the amino acid profile could therefore be related to the aroma profile of the wine (*12*). Deficiencies in several amino acids would therefore result in changes in the yeast efficiency and subsequent aroma profile. Monitoring the quantities of these volatiles during fermentation is important in understanding their synthesis from yeast and the factors affecting their production. However, the analysis of the volatile fraction of wine is extremely challenging due to the complex nature of the wine matrix. The great variety of volatile compounds, with different polarities, volatilities, and a wide range of concentrations, contributes to the complexity of wine

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and the challenges associated with the analytical measurements of these compounds.

Sample preparation, especially extraction and concentration of aroma compounds, remains a critically important stage in aroma volatile analysis. The majority of extraction and concentration techniques such as solvent extraction (*10*), static headspace (*13*), purge and trap (*14*), solid-phase extraction (*15*), simultaneous extraction and distillation (*16*), supercritical fluid extraction (*17*), liquid−liquid microextraction (*18*), ultrasonic-assisted extraction (*19*), microwave extraction (*20*), and stir bar sorptive extraction (*21*) have several disadvantages, including extensive equipment requirements, significant quantities of expensive and toxic organic solvents, multiple-step procedures prone to analyte loss, and time-consuming and labor-intensive procedures.

Solid-phase dynamic extraction (SPDE) is an alternative enrichment method that provides high analytical efficiency for sorption and solvent-free extraction followed by gas chromatography−mass spectrometry (GC-MS) analysis (*22*). The principles of this method are based on the solid-phase microextraction (SPME) technique developed by Pawliszyn and co-workers (*23*). For SPDE, an internally coated steel needle (*24*, *25*) is used for the extraction and preconcentration from the solution headspace (HS). A dynamic extraction is performed by repeated aspiration and dispension of the syringe volume compared to the static extraction of SPME. Consequently, analytes present in the sample are adsorbed onto the sorbent inside the needle. Analyte desorption into the GC injector port is induced by the rapid heating of the metal needle followed by GC-MS analysis. SPDE is generally not as widely applied as SPME, and reference to the use of this technique is limited (*22*, *26*, *27*).

The application of the SPDE technique has not yet to the authors' knowledge been evaluated for the analysis of wine or the application to wine-related problems. However, SPME works on a similar principle, and references to the use of this technique for wine and food analysis are numerous (*28*−*31*). The principal aims of the present work were to evaluate the suitability of this novel technique to discriminate between control and problem fermentations by using the "headspace fingerprint" profiles by constructing multivariate models.

## MATERIALS AND METHODS

**Fermenting Grape Must Samples.** This study formed part of a larger industry-wide assessment of problem fermentations with various industrial cellars form different regions in South Africa participating in the project. A total of 94 actively fermenting grape must samples (500 mL quantities) were collected from large-scale fermentation tanks in various South African commercial wineries participating in the project during the 2005 and 2006 harvest seasons. Control and problem fermentation samples were obtained from the fermentation tanks after the plastic sampling bottle had been rinsed with the wine. In this study, problem fermentation samples refer to samples acquired from either stuck or sluggish fermentations. These were collected upon notification from winemakers and were, in the majority of cases, after midalcoholic fermentation. Control samples refer to samples obtained from fermentations lacking stuck or sluggish characteristics, and samples were collected at different stages throughout the alcoholic fermentation for different cultivars from different cellars (some additional data relating to the distribution in sugar concentration are given in the Supporting Information, Figure 12). The sample taps of these commercial fermentation tanks (12000, 25000, 33000 L) were situated either a third from the bottom on the side of the tank or at the top of the tank in the case of 100000 L tanks. The samples were subjected to headspace SPDE GC-MS analysis. Samples were stored at −20 °C prior to analysis. The cultivar distribution of the samples was as follows: Cabernet Sauvignon (6), Chardonnay (14), Chenin blanc (2), Malbec (4), Merlot (13), Pinot Noir (7), Pinotage (9), Sauvignon blanc (19), Shiraz (13), Barbera (1), Viognier (1), Mouverdre (1), Shiraz Rosé (1), and Petit Verdot (1). The red cultivars ($n = 56$) consist of 46 problem and 10 control fermentation samples, whereas the white cultivars ($n = 38$) comprise 14 problem and 24 control fermentation samples.

**Headspace Solid-Phase Dynamic Extraction (HS-SPDE) Procedure.** HS-SPDE was performed to avoid direct contact between the sample matrix and the needle for extended needle lifetime and to focus the aroma compounds present in samples. The volatile wine compounds were extracted after optimization of the major parameters influencing the extraction process: time and temperature of adsorption and ionic strength. Samples were defrosted, and for each SPDE extraction, 10 mL of wine was transferred to a 20 mL headspace glass vial (La-Pha Pack, Langerwehe, Germany) containing 1.00 g of sodium chloride (Saarchem, Merck, Gauteng, South Africa) and a small magnetic stir bar. The addition of NaCl facilitates increased amounts of volatiles in the headspace by rendering water molecules less available for solubility of volatile compounds. Internal standard solution (100 $\mu$L) of 2-octanol in absolute ethanol (both from Sigma-Aldrich, Germany) was added, giving a final concentration of 2.0 mg/L in the vial. The vials were tightly sealed with screw-caps fitted with PTFE-Teflon septa (La-Pha-Pack, Langerwehe, Germany). A 10 min pre-equilibration step was sufficient for the sample and headspace to equilibrate completely (data not shown). For the extraction procedure, a 74 mm PDMS/AC (90% polydimethylsiloxane and 10% activated carbon) coated needle (Chromsys, Alexandria, VA), connected to a 2.5 mL gastight syringe, performed 50 aspirations of 1000 $\mu$L each at 70 $\mu$L/s (total 23:48), whereas the sample was continuously agitated by the magnet at 750 rpm (bidirectional). The needle was then removed from the sample vial and immediately inserted into the "gas station" port of the SPDE system where 500 $\mu$L of helium carrier gas was pulled into the syringe. Desorption was achieved in the GC inlet (heated to 230 °C, splitless mode) by pumping the helium through the needle into the inlet at 15 $\mu$L/s. Postdesorption bake-out of the needle at 270 °C for 10 min ensured full desorption of all analytes from the needle coating, thus avoiding carry-over between injections (data not shown).

**Gas Chromatography−Mass Spectroscopy Conditions.** GC-MS analysis was performed using a gas chromatograph (Agilent Technologies 6890N, Network GC system) coupled to a mass selective detector (Agilent Technologies, model 5973 *inert*) and Enhanced Chemstation version D.01.02.16 software (both from Agilent technologies, Little Falls, Wilmington, DE). The GC was fitted with a CTC CombiPal autosampler (CTC Analytics, Switzerland) in SPDE mode. Compounds were separated on a J&W DB-Wax capillary column (Agilent Technologies, Little Falls, Wilmington, DE) with dimensions of 30 m × 0.25 mm inside diameter and 0.5 $\mu$m film thickness. Splitless injection mode was used with the split vent closed for 2 min. The initial oven temperature was 35 °C, held for 2 min, then increased to 220 at 5 °C/min, and held for 6 min. Postrun time was 2 min at 220 °C. The injector temperature was 230 °C, and the transfer line was held at 240 °C. The carrier gas was 0.8 mL/min, constant flow. The mass spectrometer was set in electron-impact (EI) mode at 70 eV covering a mass-to-charge ratio range ($m/z$) from 29 to 280 atomic mass units (amu). The ion source and quadrupole temperatures were set to 230 and 150 °C, respectively. Peak identification of the volatile components was achieved by comparison of mass spectra and confirmation with GC retention indices of standards (Sigma-Aldrich, Germany, and Merck, Gauteng, South Africa) and with mass spectral data from the Wiley 7th and NIST 98 libraries. Separate ions for each component, usually the most prominent in the mass spectrum, were used for component integration. Components' ion chromatogram peak areas were measured and divided by the peak area of the internal standard to obtain the corrected peak areas. These corrected peak areas and not the actual concentrations were used for further data analysis.

**Chemometrics and Data Analysis.** *Data Processing*. The chemical data, consisting of corrected peak areas (peak area/internal standard area), obtained from the SPDE GC-MS analysis were imported into The Unscrambler software (version 9.2, Camo ASA, Norway) for the purpose of principal component analysis (PCA) and partial least-squares (PLS) regression. The objects were fermenting must samples from various cultivars and stages of fermentation. The data matrix with rows representing must samples (objects) and columns corresponding to volatile aroma compounds (variables) was used for multivariate analysis. PCA and PLS techniques were applied to the scaled corrected peak areas of the volatile

compounds. Scaling was performed as follows: the individual peak area for a specific compound was divided by the average peak area for that compound. The whole data matrix comprised 94 objects and 68 volatile variables.

*Principal Component Analysis (PCA).* PCA is an unsupervised technique frequently used to reduce the dimensionality and complexity of the original data matrix while retaining the maximum amount of variability (*32*−*35*). The projection of the samples in a multidimensional space allows for the identification of the main directions of variance, depicted by a principal component (PC). The number of PCs for a specific model is selected as the number of PCs that explains the maximum amount of variance. It is therefore possible to interpret the relationships between various samples in the score plot defined by the PCs and to study the relationship between variables and objects in the loadings plot. Samples with similar aroma compositions sharing high loadings for some compounds in the loadings plot cluster together, and PCA allows for these possible sample groupings to be identified. Similarly, PCA also allows for discrimination between samples that differ in aroma composition. In addition, variables that contribute the most to differences between samples could be identified and variables that are highly correlated with each other could also be identified.

*Partial Least Squares Discriminant Analysis (PLS-DA).* The purpose of constructing these regression models was to investigate the potential of the models to differentiate between problem and control fermentations using only headspace analysis. PLS-DA models were constructed by using a no-metric dummy variable (*Y* variable) as a reference value (*35*). This dummy variable is an arbitrary number for a sample belonging to a particular group or class. The PLS-DA model was developed by regression of the HS-SPDE GC-MS data (*X* variables/matrix) against the assigned reference value (dummy variable). The ability of a model to discriminate between control and problem fermentations was tested by assigning a dummy variable, signified by −1 for problem samples and +1 for control fermentations, to the samples.

## RESULTS AND DISCUSSION

**GC-MS Method Optimization.** Experimental conditions including extraction temperature and time, ionic strength, and ethanol content of the sample matrix as well as the settings and oven program for the GC-MS analysis were developed and optimized prior to the analysis of the 94 samples (a selection of the results are summarized in **Table 1** and some additional data relating to method development and validation are given in the Supporting Information, Figures 1−7). The optimum conditions were chosen on the basis of the following criteria: peak shape and intensity and sensitivity. Some parameters, extraction temperature and injection type, were optimized on the basis of peak shape and overall chromatographic quality and not purely maximum sensitivity. A PDMS/AC coated needle was used to analyze fermentation products such as esters, higher alcohols, and organic and fatty acids. A list of the compounds analyzed for is given in **Table 2** along with a number for easier identification on the graphs. The repeatability of the wine aroma volatiles measured with this method was acceptable with only the repeatability for some long-chain compounds (octanoic acid, decanoic acid, hexanoic acid, β-phenethyl alcohol, diethyl succinate, and isobutyl decanoate) being in excess of 10% relative standard deviation (% RSD).

It was also shown that the peak areas obtained with the SPDE technique for a white wine sample correlate well with the actual concentrations of the analytes as determined using a calibrated solvent extraction GC-FID method (**Figure 1**). Because this method has been validated in the classical appropriate analytical chemistry, it is of great interest that there is such a good relative relationship between the two techniques, which shows that the SPDE technique has merit for use in wine analysis.

Although method development is an ongoing process, it was found that this technique is suitable for wine analysis with excellent repeatability and lots of promise for future use because a wealth of information is determined with this technique.

**Table 1.** Parameters Tested during HS-SPDE GC-MS Method Development and Final Parameters Used

| parameter | specific parameters tested | final parameters used |
|---|---|---|
| extraction temperature | 30, 50, 70 °C | 40 °C |
| no. of aspirations | 10, 25, 50, 75 | 50 |
| aspiration/injection plunger speed | 30, 50, 70, 100 μL/s | 70 μL/s |
| type of salt | NaCl, $Na_2SO_4$ | NaCl |
| helium desorption volume | 500, 1000, 2500 μL | 500 μL |
| desorption speed | 10, 20, 40 μL/s | 20 μL/s |
| injection mode | split/splitless | splitless |

**Pattern Recognition To Discriminate between Control and Problem Fermentations.** On the basis of the wealth of information captured in the headspace analysis (compound list shown in **Table 2**), it was of interest to investigate whether differentiation between control and problem fermentations within a cultivar was possible. For this reason the most abundant cultivars, Chardonnay ($n = 14$) and Sauvignon blanc ($n = 14$), were chosen. PCA on the headspace analysis of these cultivars was implemented to investigate the stated objective (**Figure 2**). Differentiation between control and problem fermentations was achieved for Chardonnay and Sauvignon blanc samples, respectively. Control fermentation samples were collected throughout the fermentation (fermentation progress indicated by the arrow in both cases in **Figure 2**), and it appeared that fermentation problems occurred from the middle of fermentation onward for both cultivars in this sample set.

Headspace data were also used to investigate the feasibility of using these data to discriminate between control and problem fermentations by constructing a PLS-DA regression model. The initial model included all of the samples, both white and red cultivars, and partial discrimination between control and problem fermentations was observed (data not shown). Subsequently, more generic PLS-DA models to discriminate between control and problem fermentations were constructed for red and white cultivars, respectively (see **Figure 3**). It is clear from these data that separation along the first principal component reflects a differentiation between two groups of samples, namely, problem fermentation samples (indicated by the letter P on the score plot) and control fermentation samples (indicated by the letter C). This observation was made for both red (**Figure 3A**) and white (**Figure 3C**) cultivars, respectively. Principal component 1 (PC1) explains 14% of the *X* variance (chemical composition) and 67% of the *Y* variance (the ability to discriminate problem and control fermentations) for the red cultivars. Similarly, for the white cultivars 28% of the *X* variance and 62% of the *Y* variance is explained by PC1 (**Figure 3C**). The small percentage of *X* variance used to explain a larger percentage of *Y* variance is an indication that relevant information to discriminate between problem and control fermentations for both red and white cultivars is captured by the headspace data.

To identify which variables contribute most to this discrimination, the loading weights plots for red cultivars (**Figure 3B**) and for white cultivars (**Figure 3D**) were interpreted. Variables with high loading weights are positioned on the far left- and right-hand sides of the loading weights plot away form the origin of the graph and contribute significantly to the observed data structure. The dummy variable (*Y* variable) used in this supervised technique for discriminating between problem and control fermentations is shown in **Figure 3B**,**D** with the symbol ■. In both the red (**Figure 3B**) and white (**Figure 3D**) cultivars, variables that are more correlated with problem fermentations are situated toward

**Table 2.** Compounds Identified with HS-SPDE GC-MS, Ion Used for Integration, Percentage Relative Standard Deviation, and Number Used for Identification in Figures

| no. | compound | ion | % RSD | no. | compound | ion | % RSD |
|---|---|---|---|---|---|---|---|
| 1 | ethyl acetate | 43 | 3.86 | 35 | 1-octen-3-ol | 57 | 2.70 |
| 2 | isobutyl acetate | 43 | 1.55 | 36 | acetic acid | 60 | 10.04 |
| 3 | ethyl butyrate | 41 | 1.95 | 37 | isoamyl hexanoate | 70 | 4.03 |
| 4 | ethyl 2-methylbutyrate | 102 | 3.19 | 38 | octyl acetate | 43 | |
| 5 | *n*-propanol | 31 | 9.37 | 39 | propyl octanoate | 145 | 4.19 |
| 6 | ethyl 3-methylbutyrate | 88 | 3.08 | 40 | benzaldehyde | 106 | 1.35 |
| 7 | hexanal | 31 | nd[a] | 41 | ethyl nonanoate | 88 | 4.51 |
| 8 | isobutanol | 43 | 7.05 | 42 | vitispirane | 192 | 3.57 |
| 9 | isoamyl acetate | 70 | 0.69 | 43 | linalool | 93 | nd |
| 10 | ethyl pentanoate | 88 | 8.23 | 44 | isobutyl octanoate | 57 | 1.27 |
| 11 | *n*-butanol | 56 | 2.40 | 45 | 1-octanol | 56 | 4.09 |
| 12 | ethyl 2-butenoate | 69 | 1.09 | 46 | isobutyric acid | 43 | |
| 13 | pentyl acetate | 43 | 6.28 | 47 | methyl decanoate | 74 | 2.27 |
| 14 | methyl hexanoate | 74 | 3.46 | 48 | *n*-butyric acid | 60 | |
| 15 | active and isoamyl alcohols | 51 | 1.24 | 49 | ethyl decanoate | 88 | 4.56 |
| 16 | ethyl hexanoate | 99 | 0.99 | 50 | isoamyl octanoate | 70 | 6.29 |
| 17 | isoamyl butyrate | 70 | 2.32 | 51 | ethyl benzoate | 105 | nd |
| 18 | hexyl acetate | 56 | 1.13 | 52 | diethyl succinate | 101 | 13.36 |
| 19 | acetoin | 45 | 8.29 | 53 | ethyl 9-decenoate | 55 | 1.01 |
| 20 | ethyl 3/4-hexenoate | 68 | 2.05 | 54 | α-terpineol | 93 | nd |
| 21 | hexenyl acetate (cis/trans) | 67 | 1.09 | 55 | propyl decanoate | 61 | 2.26 |
| 22 | hexenyl acetate (cis/trans) | 67 | nd | 56 | 1,1,6-trimethyl-1,2-dihydronaphthalene | 157 | 8.53 |
| 23 | propyl hexanoate | 117 | nd | 57 | methyl salicylate | 120 | nd |
| 24 | 4-methylpentanol | 56 | 7.86 | 58 | β-phenethyl acetate | 104 | 4.99 |
| 25 | ethyl heptanoate | 88 | 2.39 | 59 | β-damascenone | 69 | 6.73 |
| 26 | ethyl 2-hexenoate | 97 | 1.78 | 60 | ethyl dodecanoate | 88 | 9.77 |
| 27 | ethyl lactate | 45 | 6.58 | 61 | hexanoic acid | 60 | 16.99 |
| 28 | isobutyl hexanoate | 99 | 1.27 | 62 | isoamyl decanoate | 70 | 3.48 |
| 29 | *n*-hexanol | 56 | 1.19 | 63 | benzyl alcohol | 108 | 6.45 |
| 30 | *cis*-3-hexen-1-ol | 67 | 3.48 | 64 | unknown succinate ester | 129 | 13.06 |
| 31 | heptyl acetate | 43 | 6.54 | 65 | β-phenethyl alcohol | 91 | 23.98 |
| 32 | *trans*-3-hexen-1-ol | 67 | 1.96 | 66 | nerolidol | 69 | nd |
| 33 | methyl octanoate | 74 | 8.75 | 67 | octanoic acid | 60 | 20.90 |
| 34 | ethyl octanoate | 88 | 2.40 | 68 | decanoic acid | 60 | 21.64 |

[a] nd, not detected.

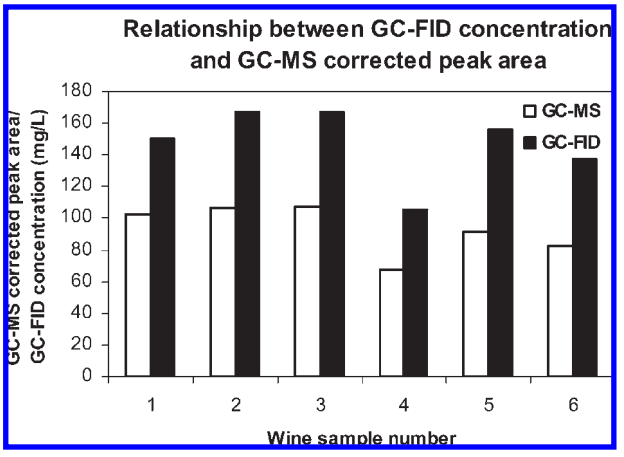


**Figure 1.** Peak areas for isoamyl alcohol obtained with SPDE for a white wine correlate well with the actual concentrations of the analytes as determined using an internal standard calibrated solvent extraction GC-FID method. (Additional data for other compounds are given in the Supporting Information, Figures 8−11).

the left of the loading weights plot and variables more correlated with control fermentations are positioned toward the right-hand side of the graph. Variables are shown as numbers for easier visualization of the graphs. The list of chemical compounds with corresponding numbers is shown in **Table 2**. In our study, variables that had high loading weights and made a significant contribution to the separation between problem and control fermentations include, among others, acetic acid, isobutyric acid, butyric acid, isobutanol, ethyl acetate, ethyl butyrate, and ethyl lactate. These variables could possibly be associated with the occurrence of problem fermentations in this study and for these specific samples; however, further investigation is needed. The association of these mentioned compounds with problem fermentations are briefly discussed.

Acetic acid has previously been associated with stuck and sluggish fermentations (*1*−*5*) whether it is as a causative factor or as a result of already existing fermentation problems, possibly indicating growth of acetic acid bacteria (AAB) or lactic acid bacteria (LAB). The presence of both acetic acid and ethyl acetate at high concentrations in wine could result in high volatile acidity levels and consequent wine spoilage.

The presence of LAB during alcoholic fermentation could lead to the formation of the observed ethyl lactate. Ethyl lactate is formed by the esterification of ethanol with lactic acid, the latter being the result of malic acid degradation by LAB. The presence of ethyl lactate could be an indicator of bacterial growth during alcoholic fermentation, and this microbial coexistence of yeast and bacteria could result in decreased nutrient availability and the production of toxic compounds, resulting in sluggish or stuck fermentations (*1*−*5*).

Isobutyric acid, butyric acid, isobutanol, and ethyl butyrate also had high loading weights, indicating a significant contribution to the observed discrimination between problem and control fermentations. These compounds are linked to the yeast

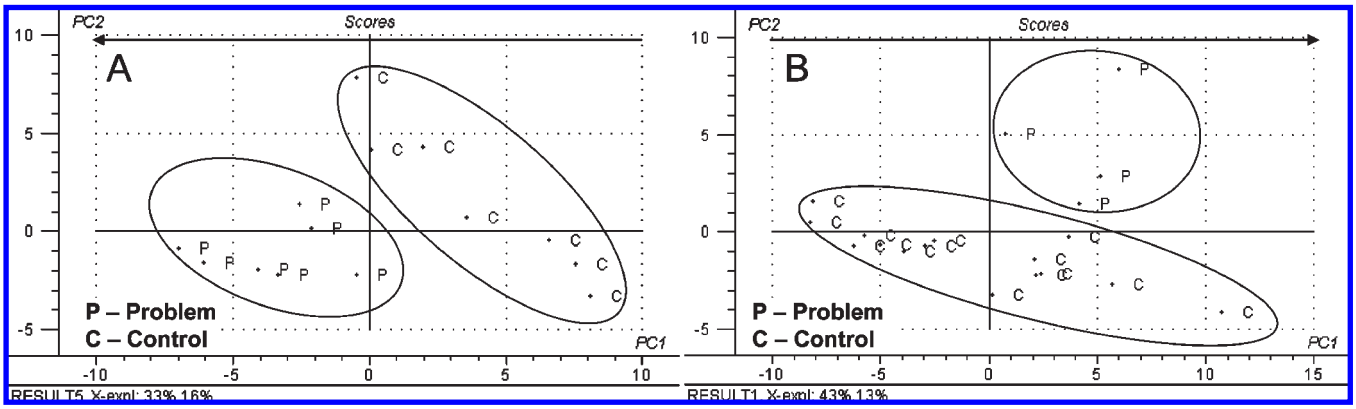


**Figure 2.** PCA performed on the headspace volatile compounds of (**A**) Chardonnay ($n$ = 14) and (**B**) Sauvignon blanc ($n$ = 19) shows the possibility of differentiation between control and problem fermentations (indicated by C and P, respectively). Fermentation progress is indicated by the arrow in both figures.

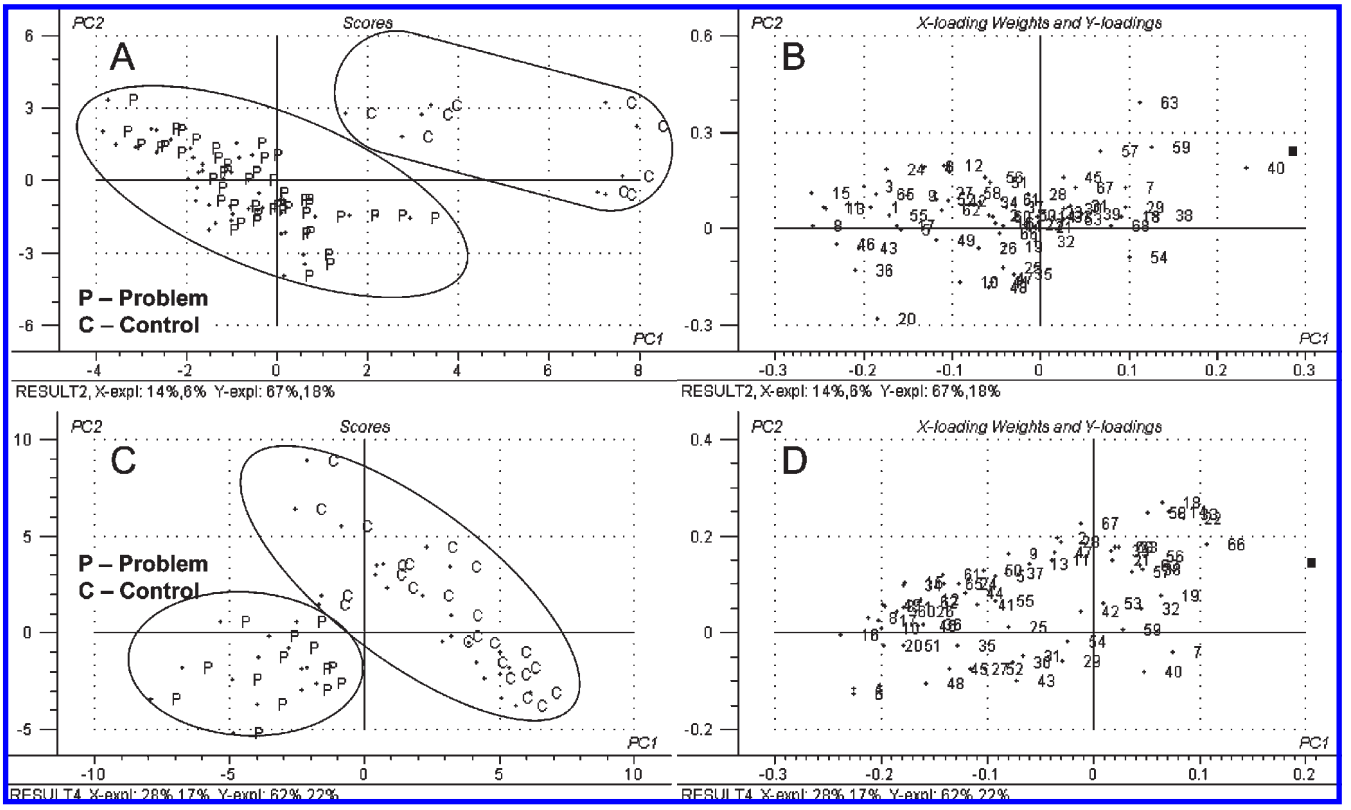


**Figure 3.** Differentiation between problem and control fermentations for red (**A**) and white (**C**) cultivars, respectively. The loading weights plots shown in **B** for the red cultivars and in **D** for the white cultivars indicate which variables contribute significantly to the observed differentiation. Discrimination between problem and control fermentation samples are indicated by the letters P and C, respectively. Variables to the far left of the graph correlate with problem fermentations and those to the far right with control fermentations. Compounds (listed in **Table 2**) are represented by numbers for visualization purposes. The symbol ■ represents the $Y$ variable used in the PLS-DA model.

metabolism and could possibly be used as stress indicators. However, this matter needs further investigation.

PLS discriminant models (data not shown) for Sauvignon blanc ($R^2$ = 0.990) and Chardonnay ($R^2$ = 0.998) also showed successful discrimination between control and problem fermentations with acceptable correlation coefficients. Similar variables made a contribution to the discrimination between problem and control fermentations in these models; however, ethyl 2-methylbutyrate, ethyl 3-methylbutyrate, and hexanoic and octanoic acids also had high loadings in these specific models. These medium-chain fatty acids have also been associated with stuck and sluggish fermentations (*1*−*5*) as a result of their possible toxicity to yeast.

Headspace analysis with the use of the SPDE technique coupled to GC-MS is an effective analytical method to generate a wealth of information regarding the volatile composition of fermenting must and wine samples. The data were successfully implemented for multivariate data analysis and showed that this technique is suitable for differentiating between different types of wine samples. Satisfactory differentiation between problem and control fermentations was achieved with headspace volatile component data.

Although the individual cultivar sample set sizes were relatively small, the constructed models were still powerful enough to illustrate the possibilities of discrimination as set out by the objectives. These initial models are therefore crucial to identify and critically evaluate possible applications of this analytical technique combined with chemometrics for future research work.

**Supporting Information Available:** Additional data for other compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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