Early detection of undesirable deviations in must fermentation using a portable FTIR-ATR device and multivariate analysis

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Summary

A portable FTIR-ATR spectrometer was used to monitor small-scale must fermentations (microvinifications) with the aims to describe the process and to early detect problematic fermentations. Twenty fermentations at normal operation conditions (NOC) and 3 fermentations that were intentionally deviated from NOC (yeast assimilable nitrogen deficiency - YAN) were monitored. FTIR-ATR spectra were registered after a minimum sample pretreatment during the fermentation process. In addition, density, sugars (glucose and fructose) and acetic acid contents were determined by traditional methods. Different multivariate analysis strategies (global and local models) were applied to the spectroscopic data to describe the evolution of the NOC fermentation and to early detect the abnormal fermentations. Global models based on principal component analysi (PCA) and partial least squares discriminant analysis (PLS-DA) allowed to describe the fermentations evolution in time and to correctly classify NOC and YAN fermentations. Abnormal deviations were successfully detected by developing one model for each sampling time. YAN experiments could be identified 49 hours after the beginning of the fermentations by means of Hotelling T^2 and residual F statistics. In conclusion, ATR-FTIR coupled to multivariate analysis showed great potential as afast and simple at-line analysis tool to monitor wine fermentation and to early detect fermentation problems

Key words: ATR-FTIR, fermentation monitoring,, multivariate analysis, wine

Introduction

In the winemaking industry, the control of the whole production chain, from harvest to bottling, is essential to obtain high-quality wines. One of the crucial phases in wine production is certainly the must fermentation, which is the biological transformation of grape juice into wine. Whereas it comprises many biochemical reactions, the most important change is the conversion of sugars into ethanol and CO_2. Nevertheless, the secondary reactions that take place during must fermentation have a substantial impact on the quality, flavor and character of the final wine.[1]

Must fermentation requires, therefore, a thorough monitoring: failing to achieve a successful process control at this stage may result in stuck or sluggish fermentations that could throw away a whole vintage or lead to low quality wines.[2]

Several routine measurements such as density, temperature and pH, are usually carried out throughout the fermentation process in wine cellars. However, additional measurements (e.g. total and volatile acidity, sugars, SO_2, assimilable nitrogen) which are often costly, time-consuming and require specific equipment and personnel, are commonly performed to gain more information.[3]

In 2004 the United States Food and Drug Administration introduced the concept of 'Process Analytical Technologies' (PAT), aiming at implementing a real-time monitoring system through the production chain. This would replace final product testing as quality is controlled during the production process, giving the possibility to 'readjust' a process before the product is made and thus minimizing rejects.[4]

Over the last decades, infrared spectroscopy, in combination with multivariate analysis, has proven to be a powerful tool for food analyses and, specifically, for wine analyses. Partial Least Squares Regression (PLSR) has been the most used calibration algorithm to predict chemical or physical parameters in wine from spectroscopic data.[5]

As reviewed by dos Santos et al., it has been shown that Near Infrared Spectroscopy (NIR) and Mid Infrared Spectroscopy (MIR) are both suitable techniques to predict several quality control parameters in grape juice, must and wine at different production stages, including total sugars (mainly glucose and fructose), ethanol, glycerol, total phenolics, anthocyanins or acetic acid, among other compounds.[6] The potential of NIR and MIR to monitor and model alcoholic fermentations was also investigated, demonstrating the usefulness of these techniques to monitor the evolution of the fermentation process.[7-10]

Regmi et al used MIR in the transmission mode with PLSR to predict the concentration of several acids in wine. They obtained good calibration results for citric, malic, tartaric, acetic, succinic, and lactic acids.[11] Moreover, MIR spectroscopy with PLS regression was also used for the quantification of reducing sugars, titrable acidity, total soluble solids, pH, and some phenolic compounds (see the review by Dambergs et al and references therein[12])

Among the different vibrational spectroscopic modes, the attenuated total reflectance MIR (ATR-MIR) mode is particularly advantageous over traditional transmission MIR modes because it requires little or even no sample pretreatment and it is faster and simpler to use. Moreover, as the infrared beam only penetrates the samples a few microns, so typical spectra saturation due to the high-water absorption band does not occur.[13]

ATR-MIR was successfully employed to determine the total soluble solids (°Brix), pH, total phenolics, ammonia, free amino nitrogen, and yeast assimilable nitrogen (YAN) in grape juice samples.[14] Kim *et al*. were able to predict alcohol, reducing sugars and titratable acidity in fermenting samples of Makgeolli rice wine using ATR-MIR, thus proving the suitability of this technique to monitor the fermentation process.[15] Wu et al used ATR-MIR to successfully monitor the course of Chinese rice wine fermentation.[16]

The researchers were capable to predict total sugar, ethanol, titratable acidity, and amino nitrogen by applying different calibration models. Previously, Cozzolino et al had also investigated the suitability of ATR-MIR to predict the time course of fermentation in samples at different days of fermentation using PLS discriminant analysis (PLS-DA) models. They obtained promising results, with low standard errors of prediction.[17]

Portable FTIR instruments are rapidly gaining popularity across the food industry sector. They are cheaper, simpler to use, and faster than traditional instruments and allow sample analysis to be performed directly on the field: for these reasons, they could be considered powerful tools to rapidly perform quality control test and process monitoring especially when coupled with multivariate analysis. Portable FTIR instruments have been used for multiple purposes in foodstuff analysis, including, eg, the prediction of fatty acid content in marine oil, quantification of acrylamide in potato chips, or quantification of trans-fat content in fat and oil samples.[18-20] To our knowledge, this is the first time that a portable ATR-FTIR device is used for the analysis of must and wine fermenting samples.

The aim of this research was to develop a strategy to monitor the must fermentation and to early detect deviation from the typical fermentation using a portable ATR-FTIR instrument coupled with multivariate analysis. The first step of the study concerned the investigation of the suitability of the instrument to the scope. Twenty-three must fermentations were carried out, and data were recorded during the whole process after a minimum sample pretreatment. Different multivariate approaches were applied for modeling the typical fermentation process, thus describing the normal operation conditions (NOC), and to early predict deviation from the NOC, in particular for a fermentation run with deficiency of assimilable nitrogen. The choice of the chemometric strategy was driven by the idea to give to winemakers a quite easy to understand process control model, which coupled with a portable device resulted in a process control

methodology cheap and easy to implement.

Material and methods

Samples

Concentrated white natural must was obtained from "Concentrats Pallejà" (Riudoms, Spain). This was diluted 1:4 with distilled water to give an initial sugar (glucose and fructose) concentration of about 200 g/L (to emulate the concentration of sugars found in a must coming from optimal mature grapes) and supplemented with 0.3 g/L of actimaxbio*(Agrovin) to ensure a YAN source. Table 1 summarizes the chemical parameters of must once diluted and supplemented.

209 g/L glucose + fructose
228 g/L yeast assimilable nitrogen
pH = 3.94
Total Acidity = 7.0 g Tartaric acid/L
Density = 1.0865 g/mL
Malic acid = 2.12 g/L

Table 1. Chemical Parameters of diluted must

The microvinifications were conducted in 500 mL Erlenmeyer flasks containing 350 mL of diluted must and under constant temperature of 18°C. Twenty microvinifications were carried out without manipulating them or varying any parameter (NOC). Moreover, three microvinifications were intentionally altered to promote nitrogen deficiency: they were run without the addition of the YAN source.

Yeast and nutrients

The alcoholic fermentations were carried out by *Saccharomyces cerevisiae* yeast, and the inoculation was done asfollows: 3.15 g of active dry yeast "VitilevureDV10" (Danstar

Ferment AG, Denmark) was rehydrated in 60 mL of milliQ water, and 2 mL of yeast solution was added to the 23 Erlenmeyer flasks containing 350 mL of must, to reach a final concentration of 0.3 g/L in each flask.

ATR-FTIR spectroscopic analysis

Data acquisition was performed using a portable 4100 ExoScan FTIR instrument (Agilent, California, USA), equipped with an interchangeable spherical ATR sampling interface, consisting on a diamond crystal window.

A total of 17 sampling points (times) were analyzed before the end of fermentation. Samples were randomly collected twice a day (every 12 hours approximately), centrifuged at 10 000 rpm for 10 minutes so that the supernatant could be collected using a micropipette. A drop of the supernatant was placed on top of the crystal using a Pasteur pipette, ensuring that the surface was completely covered with the sample, and the spectrum was recorded immediately afterwards. All spectra were recorded in the region of 3999 to 649 cm, with 32 scans and 8 cm^{-1}resolution. An air background was collected after every triplicate, that is, one background per sample. After each measurement, the crystal was carefully cleaned using deionized water and cotton wipes. Spectra were examined using the Microlab PC software (Agilent, California, USA), and data were saved as.spc files.

Absorbance data were used for the chemometric calculation. The mean of the sample replicates was calculated, and different preprocessing (smoothing and normalization) methods were tested in order to remove unwanted variations not due to changes in chemical compounds during fermentation, such as baseline drifts and noise observed in the raw spectra.

The final data was a three-way array containing the spectroscopic signals of 23 samples (20 NOC and three YAN) with 899 wavelengths recorded for 17 times covering a total of 258 hours of fermentation.

Quality Control Parameters

Reference analyses were carried out every 24 hours to monitor the fermentation process. Density was measured using an Densito 30PX electronic densimeter (Mettler Toledo), whereas sugars (glucose and fructose) and acetic acid were determined using a Y15 Analyser (Biosystems, Barcelona, Spain). All the analyses were performed right after sample collection.

Multivariate Analysis

The collected data consisted of a three-way structure containing spectra (J = 899), batches or samples (I = 23), and sampling times (K = 17). Depending on the information we want to obtain, this data matrix can be treated as a multiway structure, unfolded into a two-way structure or divided into several matrices, usually one for each sampling time. Unfolding can be performed in several ways, depending on the mode that is kept in common. If unfolding is performed sample-wise, the final matrix has dimensions (I×KJ), with each row containing the spectra of a given sample at the different time points. If the spectral mode is common, then the final unfolded matrix has dimensions (J×IK). In this last matrix, each row contains a spectrum of sample i at time point k. Finally, if unfolding is performed timewise, the final matrix has dimensions (K×JI), where each row contains the spectra of all samples at time point k. Once unfolded, the matrix structure can be processed also in different ways. Global approaches can be applied, which means that all the data collected throughout the process are used in a global model. Alternatively, local approaches refer to the use of data separately from each sampling time to build independent models.[21] Principal component analysis (PCA), partial least squares

regression (PLSR), and PLS-DA were used to process the data. The strategies used in this work are described in the following section.

All the models were cross-validated with random subsets (10 splits and five iterations). In PLSR and in PLSDA, the root mean square error of cross-validation (RMSECV) error was used to estimate the optimum number of latent variables to be used in prediction.

All multivariate data analyses were performed using the PLS Toolbox v8.6.1 (Eigenvector Research Inc., Eaglerock, USA) with MATLAB R2015b (The MathWorks, Natick, USA).

Results and discussion

Spectroscopic Data

Firstly, the signal quality was investigated. Several combinations of spectral resolution and number of acquisition scans were tested. An increase in the resolution (8-4-2 cm^{-1} was tested) did not add any relevant information to the spectra: peaks were well described, and this was confirmed by the chemometric modeling, which did not change in performances when using spectra recorded at higher resolution values. Regarding data acquisition, scan numbers from 32 to 512 were tested, but the final models did not change relevantly in their performances. For this reason, a more rapid solution (32 scans) was preferred as it allowed reaching satisfactory results.

The evolution of the ATR-FTIR spectra throughout the whole fermentation process is shown in Figure 1. Due to the high absorbance of the O-H bond of water in the mid-infrared region and the high amount of overlapping vibrational modes in similar molecules, single molecules peak assignment is quite difficult. The main changes in the spectra are found between 950-1500 cm^{-1} and 3000-3500 cm^{-1}. The bonds in the 950-1500 cm^{-1} region could be associated with sugars and organic acids. Peaks between 1500

and 1200 cm^{-1} correspond mainly to deformations of $–CH_2$, deformations of C–C–H and H–C–O. On the other hand, peaks between 1200 and 950 cm^{-1} could be related to stretching modes of C–C and C–O. The broad band between 3000 and 3500 cm^{-1} could be ascribed to water and ethanol O-H stretching vibrations These results are in agreement with the literature, both in ATR and transmission IR modes[22].

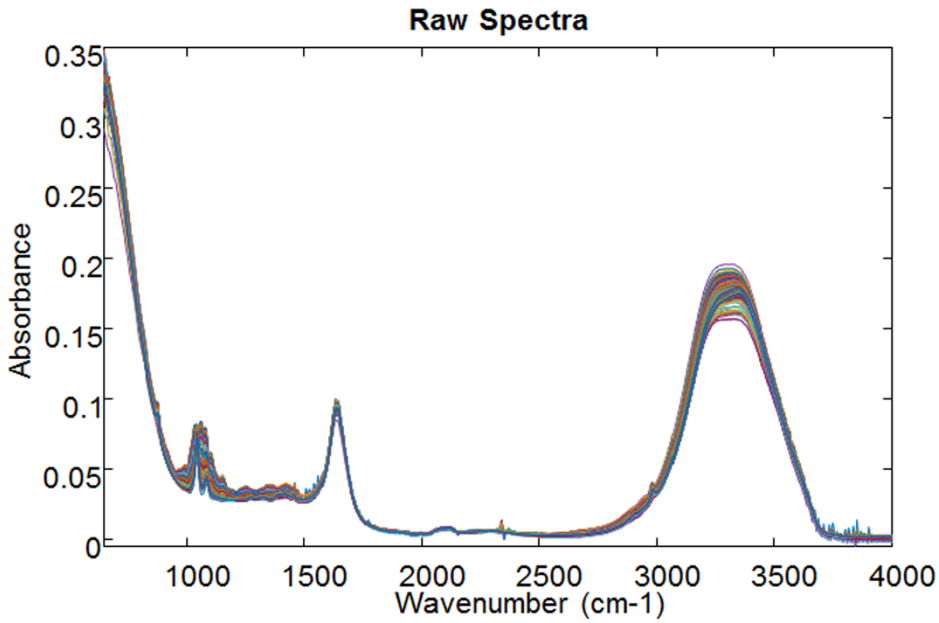

Figure 1. FTIR full spectra for all the fermenting samples (including all time points).

Data preprocessing

After calculation of the mean of the sample replicates, different preprocessing methods were tested to overcome baseline drifts and noise observed in the raw spectra. The following combination of preprocessing methods gave the best results:

- Smoothing (Savitzky-Golay) filter: window size 11pts, polynomial order 2.
- Standard Normal Variate (SNV) normalization
- Mean Centering

Because the objective of the work was to detect deviations from the NOC, the average trajectory of each variable was subtracted in the batches. In this way, models focused the attention on the variability around these trajectories.

Fermentation control parameters

Density, sugars (glucose and fructose) and acetic acid values during fermentation are depicted in Figure 2, in which NOC samples are described by circles and YAN samples are indicated with stars. Density vary between 1,09 g/mL at the beginning of the fermentation and 0,99 at the end of the process, showing typical values for white wine fermentations. NOC samples reached sugar depletion sooner than nitrogen-deficient samples. This behaviour could be explained considering that a lack of nutrients causes a decrease in yeast's enzymatic activity, which results in sluggish fermentations[2]. A higher production of acetic acid could be observed in the nutrient deficient samples. Acetic acid

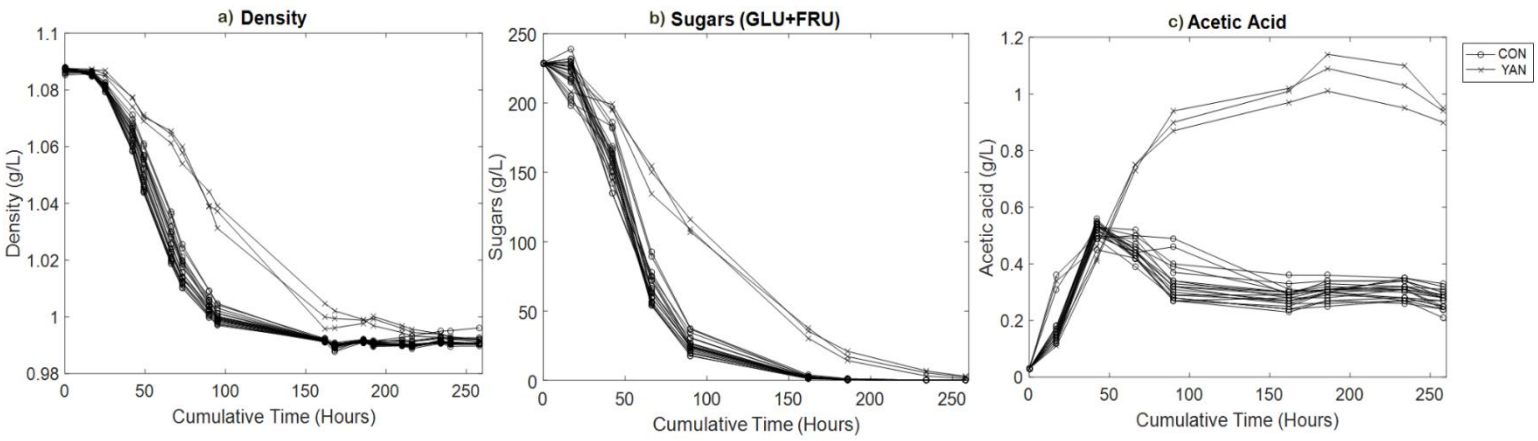

Figure 2. Evolution of chemical parameters: A: Density; B: Sugars (Glucose+Fructose); and C: Acetic acid.

is a by-product of yeast metabolism, which is generated from acetyl-coenzyme A derived from oxidative decarboxylation of pyruvate[23]. An increase of its values could be often observed in stuck fermentations, where conditions for yeast development are not optimal.[24]

Global PCA model

First, we decided to explore the whole data set following a global approach. Data collected from NOC experiments were arranged in a two-way unfolded matrix with samples × times in the rows and spectra (wavenumbers) in the columns, with the aim to

study the sample evolution throughout the fermentation process. The final matrix had size 391 × 899. The score plot for the first two PCs (90.16% of the total variance) is reported in Figure 3. A trend in the samples position clearly emerges from the graph: samples are located along the first PC, from positive to negative values, according to the sampling time. All the NOC experiments and the YAN experiments showed a similar trend. While the PC1 accounted for the spectra variation in time, the second PC seemed to account for an experimental variability that could be possibly related to small differences between the evolving of samples during the fermentation process. Focusing the attention on PC1, the scores showed a tendency very similar to the one described for density and sugar values, confirming that this component mainly explains the fermentation evolution in time. Moreover, it is possible to distinguish the NOC and YAN fermentations that show a similar but not identical behavior. This model was able to detect the main changes in the samples at the different sampling times. This first promising result motivated us to further investigate the possibility to use the portable ATR-FTIR instrument to monitor the wine fermentation process.

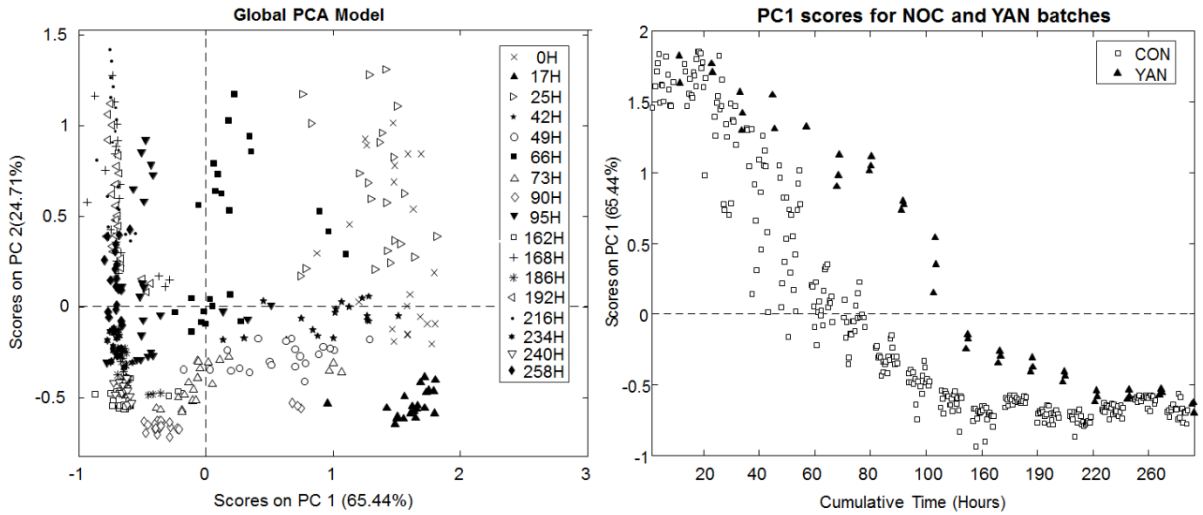

Figure 3. Scores plot for the global PCA model (left), samples are marked according to their sampling time. PC1 scores for NOC and YAN batches (right).

A partial least squares (PLS) regression model was then built on the same unfolded data matrix to predict the total sugars (glucose and fructose) concentration values from the recorded ATR-FTIR spectra along the fermentation. The values obtained with the reference analytical method were used as the Y data. The aim of this model was to prove the suitability of the portable ATR-FTIR spectrometer to monitor the wine fermentation through the prediction of one of the most important parameters, that is, the change in the total sugar content along fermentation. The statistical parameters of the regression model (two factors accounting the 98.68% of the Y variability) were RMSEC = 10.6 g/L, RMESCV = 10.9 g/L, R^2 = 0.987, and bias = −0.02 g/L

Figure 4 shows the measured vs PLSR predicted total sugar. There is a good agreement between measured and predicted values, confirming that coupling ATR-FTIR portable spectroscopy and multivariate analysis allowed to successfully monitor one of the major changes in fermenting wine samples and possibly the whole fermentation process.

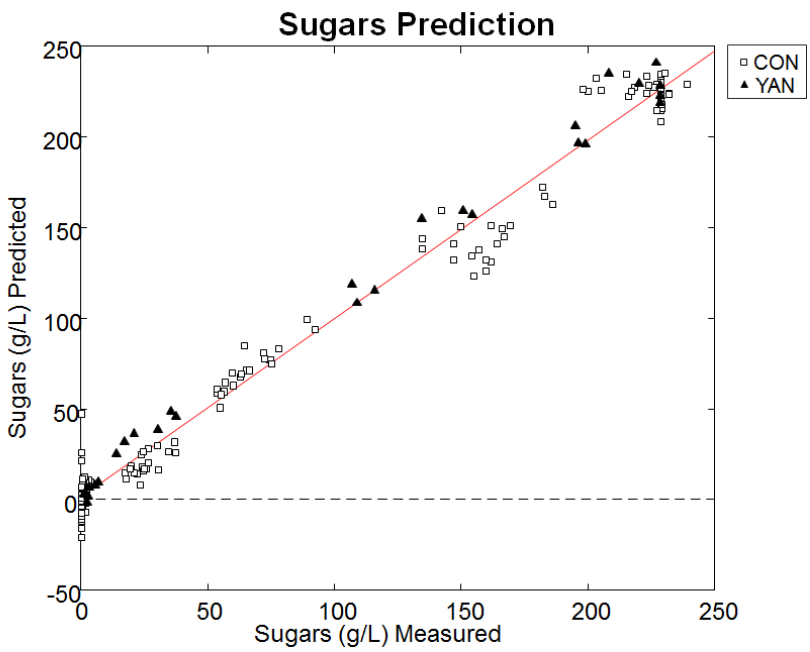

Figure 4. Measured vs Predicted concentrations of sugars (glucose+fructose).

Global PLS-DA model

The global data analysis strategy was then employed with the aim of evaluate the possibility to distinguish NOC fermentation from YAN fermentation using the spectra collected with the portable device during the whole fermentation process. In this case, the original three-way data matrix was unfolded in a time-wise manner so that sample direction was maintained. The unfolded matrix size was 23x15283 (23 samples x (899 variables x 17 time points)). A PLS-DA strategy was chosen due to the small number of samples and a PLS-DA model was built in order to classify fermentation experiments in NOC and YAN classes (in the Y vector, zeros were attributed to the NOC class samples, and ones were attributed to YAN class samples)

Figure 5 depicts the classification between normal and nitrogen deficient fermentations. As emerged from the graph, the two classes are well separated and no overlapping between them could be observed. The threshold used to discriminate between the classes was calculated as the value that best splits the classes with the least probability of both false positives and false negatives (assuming that the predicted values for each class are approximately normally distributed). The algorithm is implemented in the PLS-Toolbox. Even if the number of YAN fermentation experiments is quite small with respect to the NOC fermentation, these results are really promising, showing the possibility to distinguish the different types of fermentation when spectra collected along all the fermentation process are available.

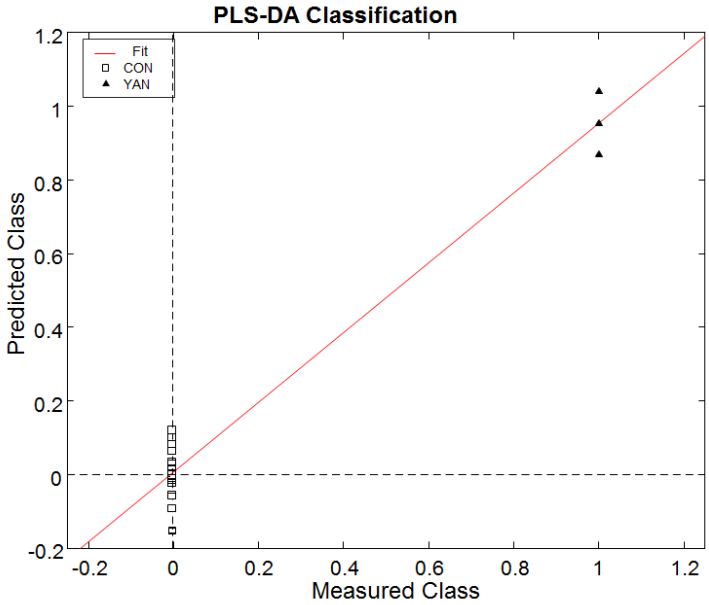

Figure 5. PLS-DA model for control (CON) and nutrient deficient samples (YAN). Zero was assigned to CON samples whereas ones was used for YAN samples.

k-PCA (Local Models)

A local strategy to early predict deviations from NOC was then developed. Local k-PCA models were built using the two-way matrices (samples × wavelengths [23 × 899]) obtained separately for each sampling time collected (a total of 17 data matrices, one for each time). A very satisfactory result was obtained, as the model built with spectra recorded after 49 hours (time point 4) was able to distinguish between NOC and YAN fermentations processes. Figure 6 shows the influence plot for PC1. The same result was obtained with the PLS-DA modeling strategy as expected. Several PLS-DA models were built, one for each sampling time. The PLS-DA model built after 49 hours (time point 4) gave the 100% of correct classification with no overlap between the classes (0 was attributed to NOC class, 1 was attributed to YAN class).

Using a moving window approach (see the article by Camacho et al and references therein[21]) to try to perform an earlier prediction of the deviation from NOC did not provide better results. A possible explanation to this behavior could be the quite small number of sampling points analyzed at the beginning of the fermentation, which is

clearly the moment of the whole process in which the main changes (especially in abnormal fermentations) occurred. For this reason, any other evolving modeling approach was not considered in this first step of the research project

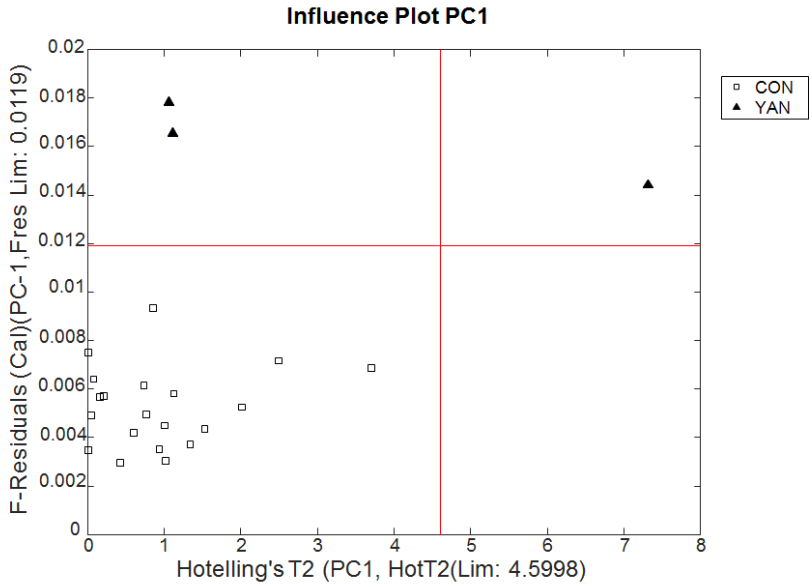

Figure 6. Influence plot for the k-PCA model at time point 4.

Biological process time

To monitor the evolution of the abnormal YAN fermentation, the approach developed by Jørgensen et al. was applied[25]. The reasoning behind the method is that each fermentation, starting similar initial conditions, can evolve slower or faster, and this different behavior can be detected. The idea is that spectra of the NOC samples can be modelled against the evolving time, but if this relationship is different for the abnormal batches then it means the fermentation has a different speed or has followed another direction. The method operates as follows:

1) The original data structure is unfolded keeping as common the spectral mode. Then, the relative times of all fermentations of all NOC samples are calculated, as the real time at time point *k* divided by the total time of the fermentation:

$$\text{Rel time}_{ferm\,i} = \frac{\text{Actual time}_{ferm\,i}}{\text{Total time}_{ferm\,i}}$$

The final time of a fermentation is assumed to have a relative time of 1, and the rest of relative times take values within 0 and 1. The relative time is also the % of evolution of the fermentation (relative time 0.6 means the fermentation is at 60%). Finally, a PLS regression model is built between the spectra of all NOC samples against the relative times. At this point, it is important to decide what the total time of a fermentation is. We decided to use the time where the sugar value was around the detection limit of the instrument, what coincided with the usual glucose value of a wine at the end of the fermentation process.

2) The spectra of all NOC samples at all fermentation times are regressed onto the previous PLS model to estimate what is called the "biological" process time. This is done because the assumption is that the difference between relative and biological time is due to the fermentation process.
3) A second PLS model is built between the NOC spectra and the "biological" time, that is, the predicted time of the first PLS model.
4) From this second PLS model, the resulting scores are used to build control charts for future batches. In these control charts (one for each PLS factor) confidence limits are calculated from the NOC training set (±2 and 3± standard deviation curves) and represented *vs* "biological" time (see Fig 7).
5) Finally, to monitor future batches, their spectra are used in the second PLS model to predict the scores and the biological process time. Both predicted biological process time and scores are used in the control chart evaluations (see Fig 7). This allows on-line monitoring of batch evolution.

The approach was applied to monitor both normal control samples (NOC) and the YAN abnormal samples. Results areshown in Figure 7. It can be seen that YAN samples evolve

in a substantially slower way, but the relationship betweenthe spectra and time works. The prediction of the biological time for the YAN sample confirms that, when the NOC samples are 100% fermented, YAN samples are about 60% fermented.

Conclusions

Monitoring the fermentation process is a crucial step in order to obtain high-quality wines and avoid materials and money waste. Several analytical techniques measuring a variety of analytes and properties fit for the purpose and give good performances, but often they need intensive sample preparation, or highly specialized instruments and operators, besides costly and time-consuming analyses. This work was focused on the use of a portable, easy-to-use ATR-MIR device, coupled with multivariate analysis, as a rapid and economical strategy to monitor fermentation processes and to detect deviation from NOC. The results obtained were very satisfactory. The prediction of the sugar content in fermenting samples from the beginning to the end of fermentation was performed, demonstrating the possibility to use this portable device to rapidly monitor fermentations running under normal operation condition. Moreover, slower fermentations (YAN) could be detected at an early stage of fermentation (when NOC are well described), giving the possibility to the winemaker to eventually correct the process and to obtain a good quality product.

Future work will be done increasing the number of samples both in NOC and in abnormal operation conditions, especially at the beginning of the fermentation, as it emerged from the models that the first 50 hours of fermentation are possibly the crucial ones to detect deviations from NOC conditions. We will take advantage of other strategies (eg, time evolving and moving average) to develop multivariate models. Moreover, a chemometric strategy will be developed to compare fermentations running in different times, for

different wine types and including other problems that may occur during the fermentation process.

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