INTRODUCTION

Wine quality is determined by an array of factors with grape quality as the fundamental element. Thus, the assessment of the grape quality potential is one of the priorities of the viticulturist and the oenologist interested in producing quality wines adapted to the market: the maturation has to be controlled, the optimum harvesting date set, the plots selected, the grapes paid according to their quality, the vinification protocol determined and planned, the traceability guaranteed from the vine to the consumer...

In the vineyard, this assessment is traditionally carried out by visual controls, samplings (samples of 200 berries and cluster fractions) and destructive laboratory analyses. The main difficulty of these controls lies in the large variability of the berries from one cluster and among the clusters from one plot. The grape sampling technique is essential and results strongly depend on the expertise of the sampler. Upon delivery at the winery, the harvest quality can also be assessed with must (generally filtered). Sampling conditions and sample preparation (temperature, sample handling…) can have a considerable influence on the values to be measured, especially with regards to acidity and polyphenols.

Near Infrared technology (NIRs*) allows to measure the entire fruit directly, by simple contact and at high speed (a few hundred milliseconds). In fact, in this spectral band light penetrates the product to depths, which can reach several centimetres. In other agricultural industries (meat, cereals, dairy products…), near infrared product assessment and selection methods are already widely implemented.

In 2002 and 2003, ITV, CEMAGREF, INRA and CTIFL have worked on the development and validation of a portable device, usable in the field and allowing to characterize grape quality regarding “sugar”, “acidity” and “polyphenols” by simple contact. The measure is based on visible and near infrared spectrophotometry. Below, we present the principal experimental results.

II PRINCIPLES OF INFRARED SPECTROSCOPY.

Spectroscopy can be defined as the study of light-matter interactions. The product to be studied is subjected to radiation, which can be partially and selectively absorbed. For every wavelength, the difference between the incoming and transmitted/reflected energy can be measured. An infrared spectrophotometer allows the recording of spectra consisting of hundreds or even thousands of data points.

Spectrophotometric methods are indirect methods and require a calibration. In the calibration phase, the values gathered in the spectrum are compared with the “true” values of the parameters to be measured for every product. A high number of calibration samples and mathematical data processing with statistical methods, such as PCA, PLS and neuronal
networks, allow to establish a predictive model. This model will then allow to convert “a spectrum” into the value of the parameter to be assessed.

III EQUIPMENT

Because of the heterogeneous ripening amongst clusters within one plot and between berries within one cluster, two prototype-probes have been developed:

- The first (Photo 1) has been adapted to the size of berries. It has the shape of a pair of tongs, which encloses the berry. It consists of a light source, fibre optics and photodetectors. The probe measures transmittance - the light passes through the entire berry. The information contained in the transmission spectrum is analysed.
- The second, named “tromblon” (“nozzle”, photo 2), has been tailored to the grape cluster. Measures are taken by touching the cluster with the probe, which works by diffuse reflection. Part of the light penetrating the berry is reflected. The reflection spectra are analysed.

Photo 1 : Probe specific for grape berries: “tongs”

PRINCIPLE OF TRANSMITTANCE

Part of the emitted light passes through the berry to the probe
Photo 2: Probe for entire grape clusters

PRINCIPLE OF REFLECTION

Part of the light is “reflected” and returns to the probe

IV EXPERIMENTAL METHODS

In order to establish a data base for the development of predictive models, the studies were carried out with clusters and berries of the most diverse maturities, varieties and origins. In parallel, validation collections of the models were established.

After two years of measurement, approximately 5 thousand berries (all varieties combined) had been analyzed by near infrared spectrophotometry. The study was focused on 4 wine grape varieties (Chardonnay, Grenache, Mourvedre, Carignan) and two table grape varieties (Muscat and Italia) coming from different terroirs and geographical origins over a period of two vintages. The measurements were carried out weekly, from veraison to harvest. More selective tests were realized with 15 other varieties. The reference analyses were obtained by refractometry and HPLC.

For the study with entire grape clusters, three varieties were used (Chardonnay, Grenache and Carignan). The reference analyses were carried out according to the usual methods.
V RESULTS WITH SINGLE BERRIES

Prediction of refractive indices

We tried to develop a global method for the prediction of berry sugar levels by near infrared, which could be used for all varieties (white or red grapes, wine or table grapes, regardless of the region and measuring date).

Of all the references obtained in 2002, 125 were retained as standard collection. A predictive model was established with this standard collection. The model was tested with all the other references. As visible in Figure 1, the model was appropriate for the estimation of the refractive index of berries.
The results of the 2002-2003 trials thus demonstrate the feasibility of the prediction of sugar levels in whole berries by near infrared spectrophotometry. The same prediction formula could be used for all the table and wine grape varieties. Thus, the quality of the results appears to be independent from the terroir and vintage factors. These excellent results are due to the quality of the database established and to the scientific advances in the field of chemometrics.

**Prediction of other quality parameters (acidity, polyphenols)**

Overall, the results were encouraging for total acidity and malic acid. The predictions of berry anthocyanin contents and total phenol indices (TPI) have not provided conclusive results (cp. Table 1). One of the difficulties was obtaining precise berry reference values.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Units</th>
<th>Number of references</th>
<th>$R^2$</th>
<th>Bias</th>
<th>Standard error of prediction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractometric index</td>
<td>°Brix</td>
<td>3635</td>
<td>0.96</td>
<td>-0.02</td>
<td>0.81</td>
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<tr>
<td>Total Acidity</td>
<td>g/l $\text{H}_2\text{SO}_4$</td>
<td>600</td>
<td>0.81</td>
<td>-0.01</td>
<td>1.62</td>
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<tr>
<td>Malic acid</td>
<td>g/l</td>
<td>150</td>
<td>0.78</td>
<td>-0.00</td>
<td>1.43</td>
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<tr>
<td>Tartaric acid</td>
<td>g/l</td>
<td>150</td>
<td>0.46</td>
<td>0</td>
<td>0.72</td>
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<tr>
<td>TPI</td>
<td>index</td>
<td>100</td>
<td>0.66</td>
<td>-0.05</td>
<td>9.4</td>
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</tbody>
</table>

Table 1: Prediction of grape berry quality parameters by near infrared.
VI RESULTS WITH WHOLE CLUSTERS

Prediction of refractive indices

The studies were carried out with 350 grape clusters (200 Carignan and 150 Grenache Blanc) and the model was calibrated with 35 of these references. Then, the model was tested with the verification collection, which consisted of 315 additional references.

The prediction of cluster sugar content was excellent in spite of the limited calibration collection (Figure 2). The results document the feasibility of predicting cluster sugar content with a model that can be used for all varieties, as found in the experiments with berries (see above).

Figure 2: Validation of the “sugars” model with 315 grape clusters
Axes: see Figure 1

![Figure 2: validation du modèle “sucré” sur 315 grappes](image)

R²=0.95
SEP=0.82

Prediction of other grape cluster quality parameters (acidity, polyphenols)

The first results obtained for the parameters “acidity” and “colour” were very promising. It appears to be possible to “measure” or rather predict the total acidity and anthocyanin concentration of a cluster with sufficient precision by simply touching it with the probe. These first results certainly display room for improvement, especially regarding the standard error of the prediction.

<table>
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<th>Bias</th>
<th>Standard error of prediction</th>
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<tbody>
<tr>
<td>Refractometric index</td>
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<td>315</td>
<td>0.95</td>
<td>0.03</td>
<td>0.82</td>
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<tr>
<td>Total Acidity</td>
<td>g/l H₂SO₄</td>
<td>305</td>
<td>0.84</td>
<td>0</td>
<td>1.44</td>
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<td>Anthocyanins</td>
<td>mg/kg</td>
<td>100</td>
<td>0.79</td>
<td>-13.13</td>
<td>150.9</td>
</tr>
</tbody>
</table>

Table 2: Prediction of grape cluster quality parameters by near infrared.
VII CONCLUSIONS

The feasibility of predicting sugar levels of berries and clusters by simple contact with a near infrared probe has been established. The method performance and specifically the robustness are good since the quality of the output was shown to be independent from the variety, the terroir and the vintage. For the prediction of the two other essential grape quality parameters, i.e. the acidity and grape colour (anthocyanins), the feasibility was also demonstrated with clusters. However, the quality of this prediction can still be improved with more thorough trials and additional references.

The prototype “tongs” probe developed for berries could be applied in research centres or service laboratories, where ripening heterogeneity remains a poorly studied parameter because of the absence of rapid methods.

Regarding the utilization of the “nozzle” probe with grape clusters, the overall results show that it is possible to develop a portable device capable of measuring the average quality of a vineyard by simple and non-destructive contact allowing to assess the sugar, total acidity and anthocyanin contents. Further studies in collaboration with industry should allow to develop this prototype into a useful tool.

** NIR s : Near Infra Red Spectrophotometry

Bibliography


