ASSESSING MACRO-ELEMENTS CONTENTS IN VINE LEAVES AND GRAPE BERRIES OF VITIS VINIFERA USING NEAR-INFRARED SPECTROSCOPY COUPLED WITH CHEMOMETRICS

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Abstract:

Context and purpose of the study - The cultivated vine (*Vitis vinifera*) is the main species cultivated in the world to make wine. In 2017, the world wine market represents 29 billion euros in exports, and France contributes 8.2 billion (28%) to this trade, making it a traditional market of strategic importance. Viticulture is therefore a key sector of the French agricultural economy. It is in this context that the nutritional diagnosis of the vine is of real strategic interest to winegrowers. Indeed, the fertilization of the vine is a tool for the winegrower that allows him to influence and regulate the quality of the wine. Nowadays, nutrition analysis is made with CHNS analyzer for elemental particles, and mass-spectroscopy for macro and microelements. Such methods are destructive and time consuming, then results could be obsolete for the vine grower. Near-infrared spectroscopy coupled with chemometrics tools allows to developed models of prediction that can provide accurate information about nutrition status of the vine in the field. In this study, we concentrate on the relative amount of Carbon [C], Hydrogen [H], Nitrogen [N], Sulphur [S] in dry matter (DM) and the C:N ratio.

Material and methods - 252 samples of different organs (leaves blade, leaves petioles, pea sized berries and berries at véraison) of 4 varieties (Muscat, Chasselas, Négrette and Sauvignon blanc) were analyzed. Spectrum were taken on both fresh material and dried ones with a reflectance spectrometer. The spectra were pre-processed using multiple scatter correction (MSC) and 1st and 2nd order Savitsky-Golay derivative (D1 and D2), before developing the cross-validation models using partial least square (PLS) regression and test it on a prediction set.

Results - The coefficient of determination in prediction (r^2), the roots mean square error of prediction (RMSEP) and the ratio of performance of prediction (RPD) were obtained for C (0.49, 14.6% of DM and 1.33 on fresh material with MSC, 0.45, 15.4% of DM and 1.26 on dry material with MSC), H (0.56, 1.71% of DM and 1.45 on fresh material with D1, 0.49, 1.88% of DM and 1.32 on dry material with D1), N (0.91, 1.12% of DM, 3.32 on fresh material with raw spectra, 0.95, 0.84% of DM and 4.39 on dry material with MSC), S (0.47, 0.319% of DM and 1.31 on fresh material with MSC, 0.46, 0.322% of DM and 1.30 on dry material with D2) and C:N ratio (0.85, 8.20 and 2.58 on fresh material with raw spectra, 0.87, 7.55 and 2.80 on dry material with D2). Results show that the near-infrared reflectance spectroscopy can be used to assessing the level of nitrogen nutrition in vine and the C:N ratio. All model performance could be improved by increasing the number of samples.

Keywords: Infrared, Spectroscopy, Elemental analysis, *Vitis vinifera*

1. Introduction.

Assessing macro-elements contents in vine leaves and grape berries of *vitis vinifera* using near-infrared spectroscopy and chemometrics

Vitis vinifera is the foremost cultivated vine species in the world for making vine. This production is also a key sector in French agriculture sector. Nutrition diagnosis of the vine is very strategic for vine growers, mainly because that allows them to adjust fertilization. Those adjustments is a tool to influence and regulate the quality of their wine. Nowadays, nutritional analysis is done by sampling in field, and destructive methods are used, an organic element analyzer for C, H, N and S, and mass spectroscopy to detect macro and micro elements. Such methods are destructive and time consuming, to the point that results could be obsolete for the winegrowers. Another approach is to used spectroscopy coupled with chemometrics tool. In the present work, we coupled near infrared (NIR) spectroscopy, which could provide a rapid and *in-situ* diagnosis.

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Materials and methods

4 different grape varieties, representative of Fronton and Moissac vineyard were analyzed: Chasselas, Muscat, Négrette and Sauvignon Blanc. 252 samples were collected in 2017, 63 for each organ (leaves blades, leaves petioles, pea-sized berries and veraison berries).

The MicroNIR spectrometer (Viavi, USA) was used in reflectance mode to acquire reflectance spectra over the spectral range 908-1676nm. For fresh material, spectra were acquired directly in contact with each organ, whereas for dry grounded sample (powder), it was done through a quartz glass.

Then, the spectra were preprocessed to reduce the noise stemming from spectral acquisition, and enhance the difference between each spectra, for example, by highlighting peak in spectra. The mathematical preprocessed methods used were the multiple scatter correction (MSC), and the Savitzky-Golay first and second order derivative.

All the samples were analyzed by using a Flash 2000 CHNS analyzer (Organic Element Analyzer, Thermo Scientific). Results obtained correspond to the relative amount of the given element (C, H, N and S) in the dry matter (% of DM). Also, the C:N ratio was calculated.

The preprocess spectra were associated to the reference analysis stemming from the CHNS analyzer. Then, partial least square (PLS) models were developed. This regression is a parametric and linear method. The performance criterion used to select the best PLS model is the ratio RPD. The higher is the RPD, the more accurate is the model. In fact, a RPD > 2 is commonly considered to justify the use of the model for prediction in routine analyses to quantify a component. For RPD between 1.4 and 2, classification models are preferred.

All statistical analysis was done by using Matlab 2018.a (Mathworks, Natick, MA, USA) installed with the SAISIR Toolbox (Cordella and Bertrand, 2014).

Results

The spectra of the samples from the 63 plots were averaged per organ collected to obtain four mean spectra (petiole, leaf blade, berry peas, veraison berries). Figure 1 shows the raw and pre-processed spectra from the different fresh vine organs.

This representation allows us to visualize the spectral profile of each vine organ and effect of pre-processing.

Table 1 reference all the RPD obtain for the different prediction models, both on fresh and dry material and for all the different pre-processing methods apply. For each couple pre-processing method / fresh or dry material, the best RPD are bolded.

For N and C:N ratio models show the best results, with RPD > 2. Developed models can be used to predict N in vine organs.

For H, the best model (on fresh material), have a RPD > 1.4, so it presents possibility to create a classification model based on excess / normal / deficiency model.

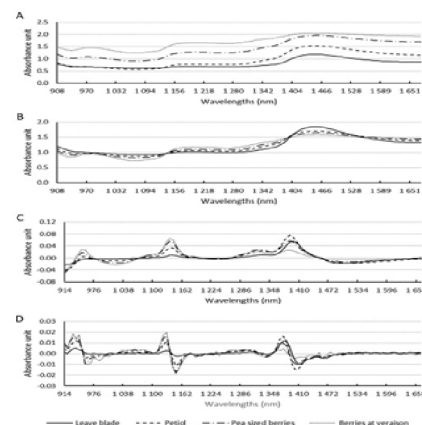For C and S, RPD are too low (< 1.4), so models need to be enhanced by adding new spectra and sample.

Figure 1: Average infrared absorbance spectra of the organs of the 63 vine plots (leaves, petioles, berries, small pea stage, berry veraison stage) taken from fresh material: (A) raw spectrum, (B) multiple scatter correction pretreatment, (C) first derivative (D) second derivative.

Validation set = 187, prediction set = 64, based on spectra from leaf blades, petioles, pea-sized berries, and berries at veraison					
Preprocessing and sample preparation	RPD for C (% DM)	RPD for H (% DM)	RPD for N (% DM)	RPD for S (% DM)	RPD for C:N ratio
Raw - fresh	1.28	1.30	**3.32**	1.29	**2.58**
Raw - dry	1.23	1.27	3.89	1.21	2.56
MSC - fresh	**1.33**	1.31	3.25	**1.31**	2.42
MSC - dry	**1.26**	1.17	**4.39**	1.27	2.61
D1 - fresh	1.19	**1.45**	2.84	1.27	2.40
D1 - dry	1.23	**1.32**	3.34	1.24	2.59
D2 - fresh	1.13	1.20	2.40	1.25	2.16
D2 - dry	1.25	1.24	3.41	**1.30**	**2.80**

Table 1: For each element and CN ratio, RPD for infrared model obtained from PLS regression for each preprocessing method [MSC, first and second derivative (D1, D2)] and for both fresh and dry material (berries and leaves) gathered in a single database, also the best RPD for each model is bold

Conclusion and perspectives

This study assesses the feasibility of using near-infrared spectroscopy to assess the macro-element content (C, H, N, and S) in the various vine organs (berries and leaves) of vitis vinifera. The next step in this work is to add more samples from different years and locations in order to include climatic effects on matter accumulation in the different organs. Furthermore, incorporating the analysis of the micronutrients (Ca, P, K, Mg, etc.) could lead to the development of a multi-analysis tool.