Characterisation of wine vinegar by near infrared spectroscopy

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Introduction

Near infrared (NIR) spectroscopy is a non-destructive analytical technique to quantify, at the same time, different chemical-physical parameters in vinegar in a short period of time and assess the quality of the product. Total acids, non-volatile and volatile acids, organic acids, proline, dry extract, ash, chloride and pH were determined by the Spanish official methods or by other methods developed and validated in the laboratory to calibrate the NIR instrument. Several calibration equations and multivariate models were obtained.

Some of these parameters are part of the analyses included in the technical regulations for the safety of food products applied in the vinegar industry to test the quality of the product. An accurate monitoring and control of the acetification process and a complete examination of the final product to ensure it fulfils all the specifications required are common practices in the sector. NIR spectroscopy is a very useful tool that allows to control both parameters successfully without being time-consuming.

Experimental

Instrumentation

NIR spectra were collected for the 1100–2500 nm range with a Foss NIRSystem 5000 liquid analyser spectrometer (Foss NIRSystems, Silver Spring, MD 20904, USA) equipped with a flow cell. The instrument was controlled by a compatible PC using Vision 2.22 (Foss NIRSystems, Silver Spring, MD 20904, USA) for the acquisition of data.

For high performance liquid chromatography measurements, a modular apparatus composed of a complete HP 1100 Series System with a vacuum degasser, a quaternary pump, an autosampler, a thermostatic column compartment and a diode array detector was used. The separation was performed on an analytical Zorbax SB-C18 (i.d. 4.6×250 mm with 5 μm particle size). Detection was performed using a diode array detector. The detection wavelength was set at 210 nm and the slit-width was set at 2 nm.

For the regulatory analyses (*Reglamento Técnico Sanitario*), an oven (P Selecta), a furnace and a pH electrode (Crison, micropH 2002, Barcelona Spain) and a Cl⁻ Ion-selective electrode (Crison, Alella, Barcelona, Spain) were used.

Software

First and second derivatives, PLS calibrations and jack-knife technique to select variables were performed with Unscrambler v7.6[1] and PARVUS package.[2] Figures were produced in MATLAB 6.1.[3]

Samples

Genuine wine vinegar samples were taken directly from the fermentors of a vinegar producer and several dilutions were made in the laboratory to cover the whole range from the product just fermented (about 115-120 g L^{-1} of total acids expressed as acetic acid) to the commercial product (60 g L^{-1} expressed as acetic acid). The range was also extended below the lower limit to study and detect possible fraudulent dilutions. Spanish vinegar laws do not allow the vinegar industry to market wine vinegar bellow 60 g L^{-1} of total acids expressed as acetic acid. Besides, vinegar for industries which use it in their production processes, must have a richness of acetic acid between 80 and 110 g L^{-1}.[4,5]

Reagents

For organic acids and proline analyses, tartaric , malic , lactic , acetic , succinic, citric acid and proline of analytical-reagent grade were supplied by Merck (Darmstadt, Germany). For the preparation of the mobile phase, potassium di-hydrogen phosphate of analytical-reagent grade from Panreac (Barcelona. Spain), methanol of gradient grade and phosphoric acid 85% from Merck were used. Water purified using a Milli-Q system académic A10 (Millipore S.A., Molshlm France) was used. Standard and calibration solutions of the compounds were prepared in Milli-Q water. All the solutions were stored at 4ºC in the refrigerator.

For the regulatory analyses, sodium hydroxide from Prolabo (Fontenay, France), hydrogene peroxide 33% (110 vol) from Panreac (Barcelona, Spain) and phosphoric acid 85% from Merck were used.

Results and discussion

Near-infrared (NIR) spectroscopy is considered to be an alternative method for monitoring and analysing the acetification process in the vinegar industry. It allows to measure simultaneously multiple components with precision and accuracy. In addition, it can be easily adapted for on-line analyses using a fibre-optic probe with a simple cell configuration which allows non-invasive and non-destructive measurements became possible. It is also a useful tool for quality control in the industry as it allows to control the manipulation and characteristics of the product at each stage of the production and bottling processes. NIR spectroscopy has been commonly applied in feed industry and related fields for quality control analysis and the assessment and quantification of quality attributes[6, 7].

Total acids, volatile and non-volatile acids, dry extract, ash content and chloride were analysed following the official methods[8].

In the determination of the organic acids and proline all the standard solutions and vinegar samples were passed through a 0.7 μm glass microfibre GF/F from Whatman (Whatman International Ltd, Maidstone, UK), before injection into the HPLC System. A chromatographic method developed and optimised in the laboratory was used for the separation and quantification of these compounds.

The relationship between the NIR spectrum and the chemical composition or physical properties of vinegar can be established by a multivariate calibration technique[9]. Partial least square (PLS) regression was used to establish several models to quantify fifteen components. Finally, the calibration was used to predict concentrations of unknown samples, assuming that the unknowns are in the same sample population as samples used in the calibration set.

The spectra were recorded at 43ºC. The samples were heated up until this temperature before being introduced into the NIRSystem to take the NIR spectra. Each spectrum was an average of 32 scans at intervals of 2 nm within the wavelength range 1100–2500 nm. The original NIR spectra are

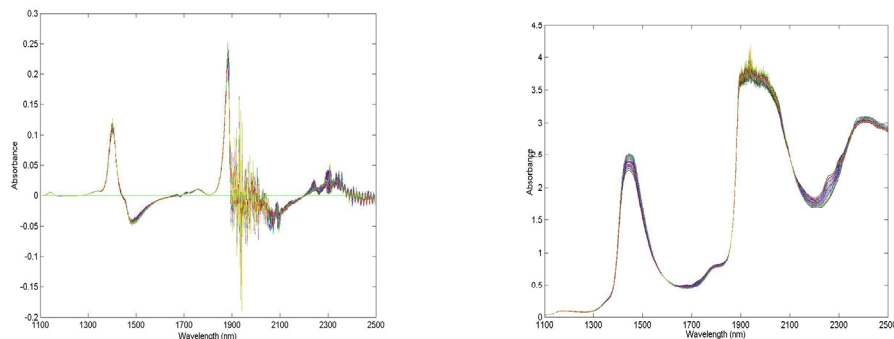shown in Figure 1 (first plot). Four replicas of each sample were taken and their mean value was calculated.

Figure 1. Original NIR spectra and Norris first derivative of the vinegar samples.
The spectral data were taken from the Vision software and treated with Unscrambler. Two segments of the spectrum were removed: the first one, from 1880 to 2080 nm, due to the saturation of the spectrum caused by the strong combination band of –OH from water (1950 nm), and the second one, from 2300 to 2500 nm, because of the low value of the signal/noise ratio. The mean values were centred and then divided by its standard deviation. Finally, the PLS models were calculated and jack-knife technique was applied to select variables.[10]

Table 1. PLS results. Calibration and prediction correlation coefficients of the calibration models.

Variable/ Units	Range	Original data		Norris first derivative		S.Golay first derivative		S. Golay second derivative	
		Corr. Calib.	Corr. Pred.	Corr. Calib.	Corr. Pred.	Corr. Calib.	Corr. Pred.	Corr. Calib.	Corr Pred.
Total acids (º)	11.817-0.485	0.997	0.997	0.999	0.998	0.998	0.988*	0.996*	0.994*
Non-volatile ac. (º)	0.206–0.003	0.967	0.964	0.971	0.966	0.973	0.967	0.974	0.960*
Volatile acids(º)	11.633–0.482	0.997	0.997	0.999	0.998	0.998	0.998	0.996*	0.994*
pH	3.220–2.348	0.936	0.907	0.982	0.947	0.992	0.891*	0.945	0.899*
Solids(g L^{-1})	17.95–0.83	0.997	0.997	0.996*	0.995*	0.996*	0.996*	0.997	0.996*
Ash(g L^{-1})	2.23–0.08	0.986	0.985	0.984*	0.982*	0.985*	0.983*	0.993	0.990
Cloride NaCl(g L^{-1})	0.444–0.011	0.954	0.931	0.954	0.931	0.975	0.926*	0.979	0.951
Proline (g L^{-1})	3.902–0.073	0.895	0.860	0.927	0.862	0.971	0.864	0.954	0.863
Tartaric ac. (g L^{-1})	1.494–0.061	0.997	0.997	0.999	0.998	0.998	0.998	0.995*	0.989*
L-malic ac. (g L^{-1})	0.629–0.026	0.997	0.997	0.998	0.998	0.998	0.998	0.995*	0.989*
Lactic ac. (g L^{-1})	0.890–0.023	0.958	0.934	0.951*	0.916*	0.990	0.931*	0.967	0.947
Acetic ac. (g L^{-1})	115.132–4.759	0.997	0.997	0.998	0.998	0.998	0.998	0.995*	0.989*
Citric ac. (g L^{-1})	1.277–0.048	0.994	0.992	0.993*	0.991*	0.993*	0.991*	0.994	0.991*
Succinic ac. (g L^{-1})	0.795–0.018	0.938	0.903	0.951	0.901*	0.977	0.956	0.954*	0.924*
D-malic ac. (g L^{-1})	0.046–0.002	0.993	0.991	0.992*	0.989*	0.991	0.989*	0.989*	0.984*

The principle of jack-knifing is used for estimating the standard errors of the regression coefficient estimates in the PLS model.

The percentage of explained variance in calibration and prediction, expressed as correlation coefficients, and the range of determination for each variable are shown in Table 1. One latent variable was used for each regression. In Figure 2, the predicted y compared to the measured y are plotted for six of the fifteen variables: acetic acid, dry extract, chloride, tartaric acid, ash and L-malic acid.

(a)   (b)

(c)   (d)

(e)   (f)
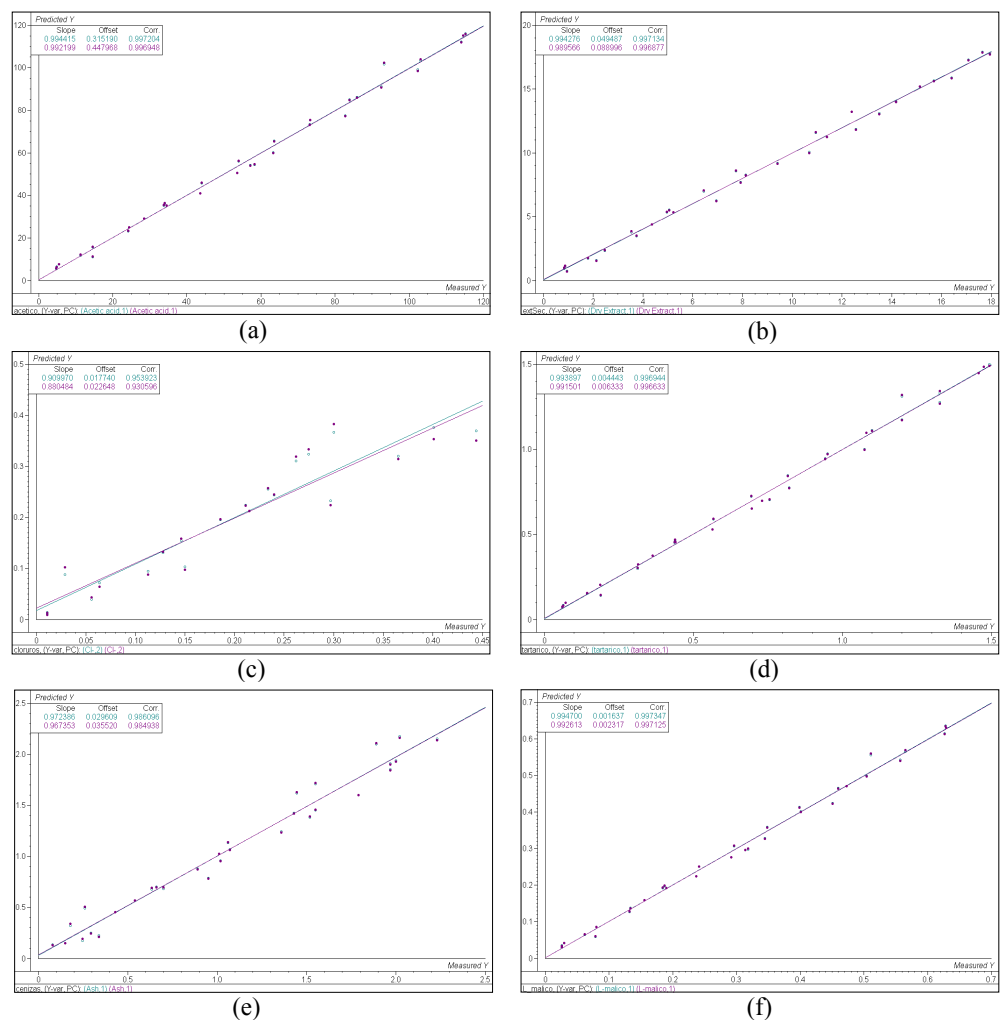
Figure 2. PLS1 calibration models for (a) acetic acid, (b) dry extract, (c) chloride, (d) tartaric acid (e) ash (e) and (f) L-malic acid.

The calibration model developed must be tested to ensure its validity. It was done splitting the whole sample set into several segments and systematic 123123123 cross-validation was performed.

Derivation is a usual treatment in NIR as it allows to correct spectral shifts. The first-derivative was performed by the Norris and Savitsky Golay's methods and the second-derivative by Savitsky Golay's method was also calculated. The spectra after applying Norris' first-derivative are shown in Figure 1 (second plot). All the spectra were derived and treated in the same way as the previous ones. Both the percentages of the explained variance in calibration and prediction are slightly increased by the derivative treatment as can be seen in Table 1, but in some cases they took the same values or even a bit lower (marked with an asterisk).

For most of the variables, the percentage of explained variance in prediction is very high and, taking into account that we are dealing with a real experimental system, the values are highly satisfactory.

Conclusions

NIR spectroscopy can be used to characterise wine vinegar and to quantify multiple parameters related with the quality of the product being at the same time a non-destructive and non-time consuming analytical method. This is quite an important tool in vinegar industry to assure the quality of the genuine products and to observe the required specifications in national and foreign markets where there is nowadays a highly competitive industry.

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