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Use of Fourier transform infrared spectroscopy to create models forecasting the tartaric stability of wines

Mario Malacarne*, Luca Bergamo, Daniela Bertoldi, Giorgio Nicolini, Roberto Larcher

IASMA Fondazione Edmund Mach, Centro Trasferimento Tecnologico, Via E. Mach 1, 38010 San Michele all'Adige, Italy

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ABSTRACT

Tartaric instability of wines still represents a serious problem in terms of the commercial value of bottled wines, particularly whites, leading consumers to be suspicious as regards the effective healthiness or wholesomeness of products. The study, carried out on 536 Italian wines, investigated the potential of using Fourier Transform Infrared Spectroscopy, distinguishing between white and red/rosé wines, to create models predicting the instability of wines, assessed in comparison to two of the most widespread methods of reference: the "mini-contact test" (10 min, 0 °C, KHT) and the "cooling test" (5 days, −4 °C). The models proposed, constructed using 80% of the samples and based on Partial Least Squares-Regression and Artificial Neural Networks, were shown to work well in terms of correct classification (from 89% to 97%) of the external validation subset (20%). As regards the more problematical question of technical management of wines before bottling, in the worst cases only 4–6% of unstable samples were erroneously classified as stable.

1. Introduction

The main factors influencing the solubility of potassium bitartrate in wine are alcohol content and temperature, although pH and ionic force also have a significant role and have been the subject of studies [1,2]. However, the presence of colloids such as proteins, condensed tannins, glucose polymers and glycoproteins in solution may lead to a significant, albeit sometimes temporary inhibition of spontaneous phenomena in terms of the formation and growth of potassium bitartrate crystals, giving rise to the phenomenon of oversaturation [3–7]. While from the strictly oenological point of view this represents a positive aspect, leading to a greater abundance of salt and hence a richer flavour, at the same time it also represents a serious obstacle to correctly forecasting instability, particularly when this assessment is based exclusively on the application of models taking into consideration only the thermodynamic equilibrium of salt solubility.

While in wines of high quality, particularly red wines aged in wood barrels and conserved for several years in cellars, the natural lowering of the temperature in winter is enough to guarantee good stabilisation of tartaric precipitation, for *vins nouveaux*, young and fizzy wines, which must be sold rapidly, it is necessary to make use of stabilisation techniques such as refrigeration [8–10], ion exchange [11] or electrodialysis [12–15], also followed by the addition of crystallisation inhibitors such as metatartaric acid [16,17], mannoprotein extracted from yeast [18–20], gum Arabic or Carboxymethyl Cellulose (CMC) [21–24].

Models and mathematical algorithms based on knowledge of certain analytical parameters such as alcohol content, pH and the content of tartaric acid and potassium [25,26] or based on determination of the saturation temperature [3,27–29] have been proposed to assess the tartaric stability of wines. The former are often not particularly reliable, as they tend not to take into account the protective effect in relation to colloid precipitation, whereas the others are not a good indication of the real risks of tartaric precipitation in the bottle [30]. The so-called "mini-contact" [30,31] or "cooling" [32–34] methods are frequently used in laboratories and cellars. While technically more reliable than previous methods, these are relatively time-consuming.

In the last few years, infrared spectroscopy combined with multivariate statistical analysis of spectra information has increasingly established itself as an analytical technique, in the drinks sector in general and for wine in particular, as it can often supplement or even substitute traditional control techniques. Various studies have shown the suitability of these approaches for carrying out both basic analytical checks [35–38] and fine characterisation of commodities [39–43], often very rapidly and generally in a totally automated manner. Furthermore, use of IR spectroscopy to create models forecasting the colloidal stability (proteins and polysaccharides) of wines was also recently shown to be interesting [44]. The study, using information that can be extracted from the Near-Infrared (NIR) and Mid-Infrared (MIR)

* Corresponding author. Tel.: +39 0461 615260; fax: +39 0461 615288.
E-mail address: mario.malacarne@fmach.it (M. Malacarne).

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spectra of 111 Californian white wines, allowed creation of a model to predict colloidal instability which obtained a good correlation between the values expected and those measured ($R^2=0.80$) in a set of unknown samples.

As far as we know, in the current literature there is only a preliminary modellisation study regarding the application of IR spectroscopy to forecast the tartaric instability of wines [45], despite the fact that for the wine-making industry this represents one of the biggest problems linked to the sale of bottled wines. Any precipitation may indeed lead consumers to be suspicious about quality or, at the very least, to have doubts about the care taken in processing the product.

This work thus investigated the possibility of using FT-IR spectroscopy to create mathematical–statistical models using Partial Least Squares Regression (PLS-R) and Artificial Neural Networks (ANN), useful for forecasting the tartaric instability of wines, as compared to the information provided by the mini-contact test and the cooling test. The effectiveness of the models was assessed by applying them to an extensive external validation set.

2. Materials and methods

2.1. Set of samples

Five hundred and thirty-six wines, to which no oenological products for tartaric stabilisation were added, were collected at different private wineries and in the micro-vinification cellars of the Fondazione E. Mach. They came mostly from the Italian region of Trentino Alto Adige ($N=483$), although the set also including wines from other Italian regions—namely Campania (11), Umbria (30) and Sicily (12)—in order to extend the variability of the compositional profiles.

After having subdivided the samples into white wines (316) and red+rosé wines (220, hereafter referred to as reds), the calibration and validation sets were defined, containing respectively 80% and 20% of the samples. The validation sets (63 white wines, 44 red wines) were chosen in such as way as to be representative of the overall samples, according to the selection model already proposed by Versari et al. [44].

2.2. Valuation of instability

2.2.1. Mini-contact conductometric test

The mini-contact test was carried out using the TartarCheck instrument (Apparecchi Scientifici Ing. C. Bullio, Modena, Italy), calibrated with a standard conductivity solution 1413 μS/cm a 25 °C (HI 7031, Hanna Instruments, Italy) and a digital thermometer with PT 100 probe (TP9AP, DELTA OHM, Padova, Italy).

In the test, 25 mL of wine was stirred constantly at 0.0 ± 0.1 °C with the addition of 4 g/L KHT (60365, Fluka Analytical, US), for a period of 10 min. The result comes from the decrease in conductivity (ΔμS/cm) during the test. Indeed, the low temperature and presence of KHT crystals acting as crystallisation nuclei encourages tartaric precipitation in unstable wines; in these cases one can see a decrease in the ions in the solution and consequently a lowering of conductivity.

On the basis of reports in the literature [30,31,46] and the instructions of the equipment manufacturer [47], wines with values lower than 50 ΔμS/cm for white wines and 60 ΔμS/cm for red wines were classified as stable in terms of tartaric precipitation, and those with higher values as unstable.

2.2.2. Cooling test

In the past, the cooling test made it possible to carry out qualitative evaluation of tartaric stability, the eventual presence of crystals in the sample after the refrigeration treatment being estimated visually [30,33,48]. This was mainly due to the lack of rapid and automated analytical techniques to determine parameters which change in the event of tartaric precipitation (total acidity, tartaric acid, potassium etc.). Currently, the availability of the FT-IR technique makes it possible to determine these parameters simultaneously and very rapidly, before and after the cooling treatment, allowing quantitative estimation of the extent of precipitation.

In the cooling test proposed by us, the wine (50 mL), placed in a polypropylene conical tube and kept in a vertical position, was left alone for 5 days in a freezer at a temperature of −4 °C. The sample was analysed using a FT-IR WineScanTM Type 77310 (Foss Electric A/S Hillerød, Denmark) before treatment and after 5 days, after having been centrifuged at 4000 rpm for 5 min to remove any precipitation and brought back to a 20 °C. In a similar way to the mini-contact test, on the basis of the literature [10,34,46] the tartaric stability categories were determined on the basis of the decrease in total acidity, tartaric acid and potassium, expressed as potassium bitartrate (ΔKHT). The wine was classified as stable with ΔKHT values of less than 0.3 g/L and unstable in the case of higher values.

2.3. Obtaining FT-IR spectra

A FT-IR WineScanTM Type 77310 spectrometer (Foss Electric A/S Hillerød, Denmark), equipped with a Michelson interferometer and a pyroelectric detector was used to obtain the FT-IR spectra. The sample (30 mL) was placed in the autosampler (model 5027), filtered and introduced into a CaF_2 cuvette with 37 μm optical path length using a peristaltic pump, with temperature set to 40 °C. Two spectra of 40s each were obtained for each wine, in the frequency range of 926–5012 cm^{-1} (instrument manufacturer “pin numbers” 240–1299) at intervals of 4 cm^{-1}; however, only the 965–1543, 1717–2272 and 2434–2971 cm^{-1} spectra regions were taken into consideration in the statistical analysis. The 1543–1717 and 2971–3627 cm^{-1} regions were excluded because they are affected by the absorption of water, the 2272–2434 cm^{-1} zone because it is affected by the absorption of carbon dioxide, and the region beyond 3627 cm^{-1} because the manufacturer suggests that it provides little information [49].

All the samples were filtered using common filter paper (Albet) before the analysis, in order to eliminate any excess CO_2. The instrument was cleaned and zeroed using solutions supplied by the manufacturer (S-470 Cleaning Agent Solution and S-6060 Zero Liquid, Foss Electric) at the start of each day and subsequently at regular 60 min intervals. The removal of any polyphenolic deposits and other organic contaminants took place by washing with a 1% sodium hypochlorite solution, which was introduced and kept within the system for 15 min.

2.4. Basic analysis

The composition of the wines was characterised by considering 17 analytical parameters in the case of white wines and 18 for red wines (Table 1). A FT-IR WineScanTM was used in analytical mode, adopting calibrations implemented by our laboratory in relation to the official O.I.V method (Compendium of International Methods of Analysis, 2012) with evaluation of a database made up of more than 2000 Italian wines of different vintages and types.

2.5. Creation of models

2.5.1. Multivariate Partial Least Squares-Regression (PLS-R)

The FT-IR spectra of wines are extremely complex, due to the superimposing of bands of the different components; for this reason, chemiometric instruments must be used to carry out quantitative analysis. Using the software WineScan FT 120 v 2.2.2,

Table 1
Statistical distribution of the chemical–physical parameters for red and white wines (N=536).

	White wines (N=316)					Red wines (220)				
	Min	Lower quartile	Median	Upper quartile	Max	Min	Lower quartile	Median	Upper quartile	Max
Alcohol (% v/v)	10.42	12.05	12.50	13.04	14.69	9.79	12.29	12.65	13.19	16.59
Reducing sugars (g/L)	0.40	0.40	0.40	0.91	8.06	0.40	0.40	0.40	0.40	24.38
Relative density 20/20 °C	0.98893	0.99081	0.99143	0.99231	0.99566	0.98958	0.99260	0.99394	0.99462	1.00363
Total dry extract (g/L)	16.71	19.72	21.22	22.71	30.88	18.26	24.25	28.13	30.34	59.91
pH	3.01	3.26	3.35	3.45	3.91	3.10	3.47	3.62	3.79	4.03
Total acidity (g/L)	3.65	5.07	5.55	6.11	8.43	3.86	4.56	5.17	5.59	7.69
Volatile acidity (g/L)	0.05	0.16	0.22	0.27	0.50	0.05	0.19	0.27	0.36	0.79
Malic acid (g/L)	0.10	1.97	2.33	2.69	4.30	0.10	0.25	0.83	1.73	3.57
Lactic acid (g/L)	0.20	0.20	0.20	0.20	2.50	0.20	0.20	1.12	1.75	2.89
Tartaric acid (g/L)	1.00	1.82	2.13	2.47	3.49	0.79	1.51	1.78	2.08	3.27
Glycerol (g/L)	4.07	5.16	5.76	6.28	8.12	4.57	7.56	8.85	9.67	12.10
Methanol (mL % T.A.)	0.01	0.01	0.01	0.02	0.07	0.01	0.03	0.08	0.12	0.19
Potassium (g/L)	0.39	0.71	0.84	1.01	1.87	0.44	1.06	1.34	1.65	2.34
Ashes (g/L)	1.26	1.68	1.89	2.20	4.22	1.39	2.33	2.83	3.36	4.00
Total polyphenols (mg/L)	25	153	237	335	626	25	636	1469	1958	3862
Total anthocyanins (mg/L)	–	–	–	–	–	25	75	188	306	798
Total SO_2 (mg/L)	20	85	104	124	163	20	106	118	131	203
Concentration product KHT $\times 10^5$ (mol/L)^2	6.99	14.09	18.05	23.93	41.29	9.29	21.77	26.24	31.14	46.01

Table 2
Statistical distribution of the results of mini-contact and cooling reference tests and relative classification in the stable/unstable categories for red and white wines.

	Mini-contact (ΔμS/cm)						Cooling (ΔKHT g/L)					
	N.	Min	Lower quartile	Median	Upper quartile	Max	*N.*	Min	Lower quartile	Median	Upper quartile	Max
White wines												
Stable	62	12	32	38	43	50	123	0.05	0.05	0.05	0.09	0.28
Not stable	254	50	100	157	191	302	193	0.31	0.80	1.08	1.35	2.10
Red wines												
Stable	64	11	28	34	44	60	62	0.05	0.05	0.06	0.19	0.30
Not stable	156	61	113	144	176	314	158	0.32	0.70	0.98	1.22	1.83

four models to forecast instability were created: “mini-contact white wines”, “mini-contact red wines”, “cooling white wines” and “cooling red wines”. First of all individual frequencies or groups of consecutive frequencies (called filters) shown to be more closely correlated with the analytical parameters of the samples of reference measured with the mini-contact and cooling test were selected. Subsequently, the selected variables (filters) were compressed into PLS-R factors using Partial Least Squares Regression (PLS-R). Cross validation was carried out using the same software, by subdividing the calibration set into four subsets, each containing 25% of the total samples: on each occasion one subset was used to evaluate the effectiveness of the forecast on the basis of the other samples (75%), until all the subsets had been tested. This procedure made it possible to estimate in advance the behaviour that the calibration model adopted could have in relation to an independent set of samples. Finally, the minimum number of PLS-R factors was selected on the basis of the first local minima in the cross validation error (CVE) values, for each of the new parameters in the models, thus avoiding overfitting of the model and keeping the CVE low.

The performance of the models was evaluated using the three measurements provided by the software supplied with the instrument: correlation coefficient (R^2), standard error of calibration (SEC) and cross-validation error (CVE). The SEC, which indicates the accuracy with which the value of reference can be forecast for a calibration sample is defined as:

$$\mathrm{SEC} = \sqrt{\frac{\Sigma_{i=1}^{N}(y_i - x_i)^2}{N}} \tag{1}$$

where N is the number of samples, y_i is the reference value for sample i, and x_i is the value expected for sample i.

Estimation of CVE is instead represented by

$$\mathrm{CVE} = \sqrt{\frac{\Sigma_{s=1}^{S}\Sigma_{i=1}^{n}(y_{is} - x_{is})^2}{N}} \tag{2}$$

where S is the number of subsets, n is the number of samples in subset s, N is the number of samples, y_{is} is the value of reference of sample i in subset s, and x_{is} is the value expected for sample i in subset s.

The forecasting accuracy of calibration models was further validated through comparison of the expected values and values obtained with the methods of reference using an independent validation set.

2.5.2. *Artificial Neural Network (ANN)*

Processing was carried out using the application Automated Artificial Neural Network (SANN) of the software STATISTICA 9.1 (Statsoft Inc., Tulsa, OK), using all the spectra frequencies selected as above as input (or predictor variables) and the ΔμS/cm value obtained in the mini-contact test or the ΔKHT value in the cooling test as output (or predicted variables).

For the creation of the forecasting model (network architecture: multilayer perceptrons MLP; hidden units: max 20) the software uses a subset of samples (training data chosen casually, representing 70% of the total), while verification of the forecasting ability of the model is immediately and automatically observed in the verification data (15%) and the test data (15%).

In a similar way to the procedure stated for PLS-R analysis, the forecasting accuracy of the calibration models ("mini-contact white wines", "mini-contact red wines", "cooling white wines" and "cooling red wines") was further validated on an independent validation set.

3. Results and discussion

3.1. Reference values

The wines analysed showed wide variability in terms of their compositional parameters; the distribution in white and red wines is shown in Table 1. Assessed using Tukey HSD Test for Unequal Numbers, the white wines were significantly different ($p<0.05$) from the reds for all the parameters measured, with the exception of reducing sugars. Table 2 gives the results of tartaric stability measurements and the relative classification according to the criteria of "stable/unstable", as described in Section 2. When evaluated using the previously stated test, the white wines overall had significantly higher conductivity difference values in the mini-contact test as compared to red wines. As can be seen in the table, the two tests sometimes provided conflicting results in terms of stability. Indeed, 80% of white wines and 71% of red wines were unstable in the mini-contact test, whereas for the cooling test the percentages were 61% and 72% respectively. The percentages reflect the usual distribution of wines before the industrial processes of fining, stabilisation and bottling.

Table 3
Performance of PLS-R data for the calibration set of white wines ($N=253$) and reds ($N=176$). Optimum number of PLS-R factors (N. PLS factors), standard error of calibration (SEC), correlation coefficient (R^2), cross validation error (CVE).

Parameter	N. PLS Factors	SEC $\Delta\mu S/cm$	R^2	CVE $\Delta\mu S/cm$
Mini-contact (white wines)	11	22.4	0.89	24.1
Mini-contact (red wines)	13	23.8	0.88	25.7
		ΔKHT (g/L)		ΔKHT (g/L)
Cooling (white wines)	12	0.20	0.89	0.22
Cooling (red wines)	12	0.21	0.83	0.23

3.2. PLS-R models and validation

Table 3 gives the optimal number of PLS-R factors (from 11 to 13) necessary for the construction of forecasting models for the mini-contact and cooling tests. The SEC and CVE values were close together and higher for red wines as compared to white wines. As regards R^2, the values went from a minimum of 0.83 for the cooling red wines model, to a maximum of 0.89 for both the white wine models. These correlation coefficients are close to those observed for similar statistical approaches applied to FT-MIR determination of anthocyanins in wine [38].

The models created were tested on the external validation set in order to assess their capacity to forecast tartaric stability in unknown wines. All the correlations between the values obtained with the methods of reference and those forecast by the corresponding PLS-R models were statistically significant ($p<0.001$); the closest (R^2) were obtained for white wines as compared to reds

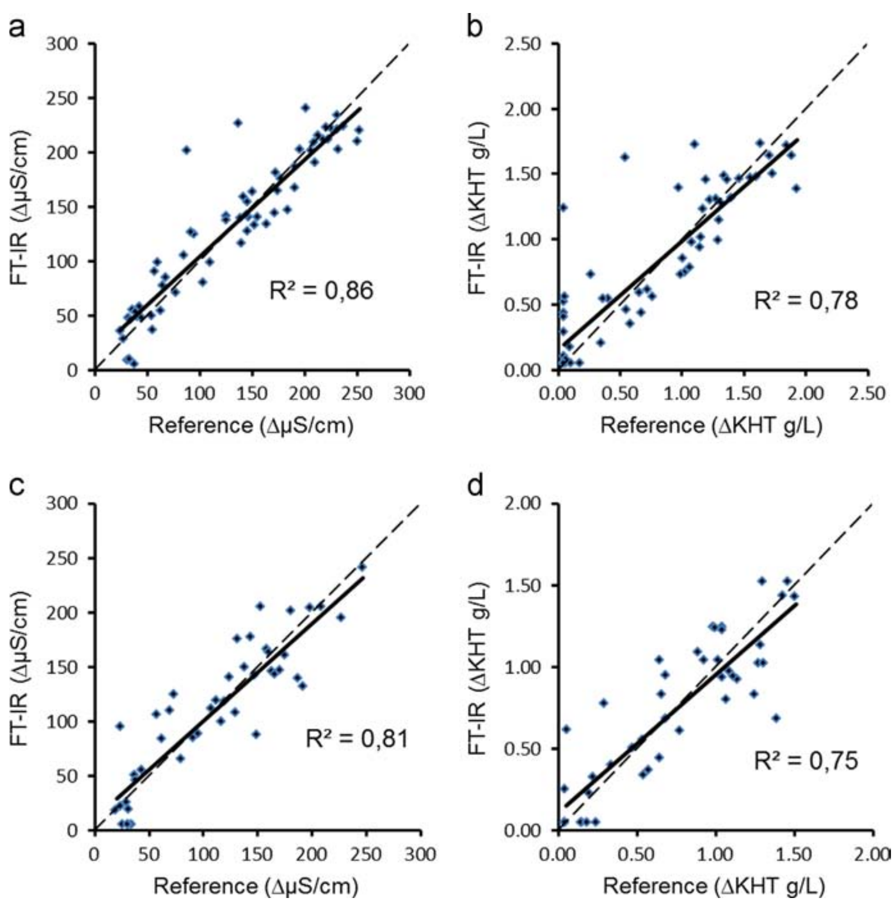

Fig. 1. Comparison between the reference values and the values forecast by the PLS-R models for the external validation sets. The theoretical trend (predicted value=reference value; dashed line) and the estimated functional relationship (solid line) are shown. (a) mini-contact white wines; (b) cooling white wines; (c) mini-contact red wines; and (d) cooling red wines.

Table 4
Application of PLS-R models to the external validation sets. Attribution matrix for stable/unstable categories for the mini-contact and cooling test and for white and red wines.

	White wines				Red wines			
	%[a]	Stable	Not stable	Total	%[a]	Stable	Not stable	Total
Mini-contact								
Stable	75	9	3	12	85	11	2	13
Not stable	96	2	49	51	100	0	31	31
Total	92	11	52	63	95	11	33	44
Cooling								
Stable	76	19	6	25	75	9	3	12
Not stable	97	1	37	38	100	0	32	32
Total	89	20	43	63	93	9	35	44

[a] Percentage correctly classified in the tartaric stability categories.

Table 5
Performance parameters for ANN data on the calibration set.

Parameter	Training performance	Verification performance	Test performance
Mini-contact (white wines)	0.99	0.91	0.92
Mini-contact (red wines)	0.91	0.93	0.89
Cooling (white wines)	0.96	0.93	0.93
Cooling (red wines)	0.96	0.84	0.85

and for the mini-contact test as compared to the cooling test (Fig. 1).

Table 4 shows the attribution performance of the proposed models, should the stability/instability categories proposed by the manufacturer and the literature be used as a reference – for the mini-contact and cooling tests respectively – in relation to technological cellar evaluation. The percentage of correct classification went from a minimum of 89% for the cooling white wine model to a maximum of 95% for the mini-contact red wine model. However, considering the fact that from a technological point of view the greatest risk lies in classifying an unstable product as stable, therefore not carrying out the necessary stabilisation procedures before bottling, the least effective model was surprisingly the mini-contact white wine model, which nevertheless saw only a 4% error. Similar results were also obtained for white wines in relation to the cooling test, whereas in the case of the reds, instable wines were correctly attributed in 100% of cases. This opens up interesting possibilities as regards the potential of the FT-IR technique for investigating the composition of wines, also in relation to the possible presence of natural molecules protecting from instability, in contrast with traditional thermodynamic approaches which are not particularly applicable in the case of red wines.

3.3. ANN models and validation

The forecasting models for the two types of wine and the two tests of reference constructed using Artificial Neural Networks provided training, verification and test performance data higher

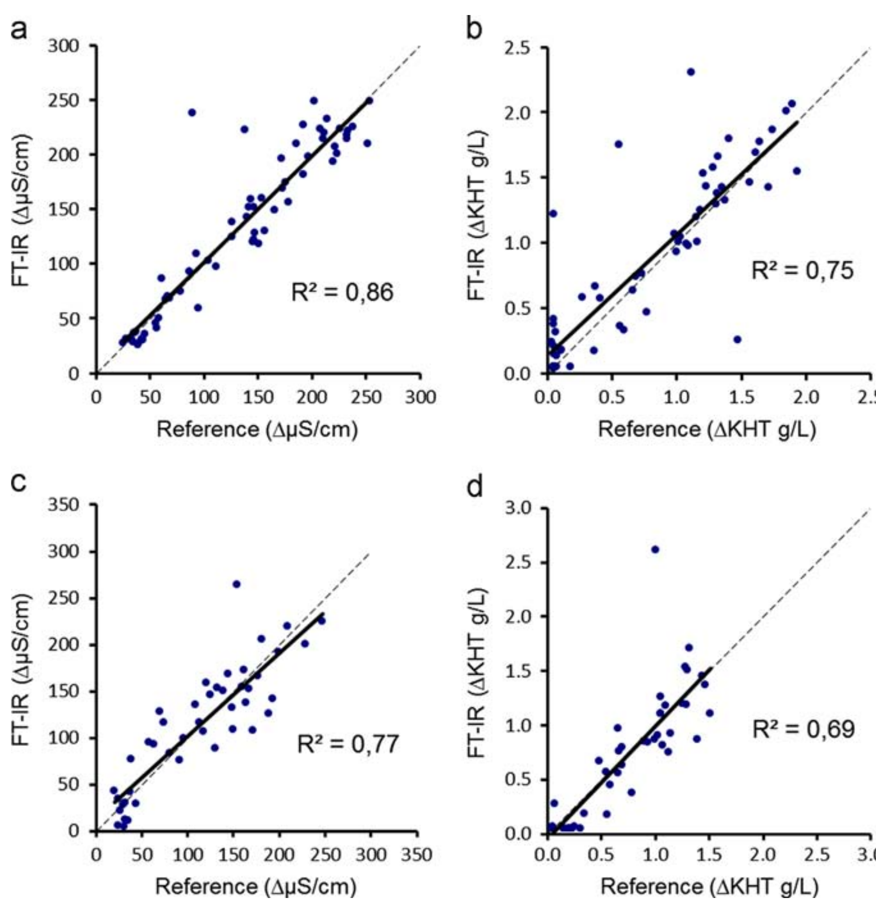

Fig. 2. Comparison between the reference values and the values forecast by the ANN models for the external validation sets. The theoretical trend (predicted value=reference value; dashed line) and the estimated functional relationship (solid line) are shown. (a) mini-contact white wines; (b) cooling white wines; (c) mini-contact red wines; (d) cooling red wines.

Table 6
Application of ANN models to the external validation sets. Attribution matrix for stable/unstable categories for the mini-contact and cooling test and for white and red wines.

	White wines				Red wines			
	%[a]	Stable	Not stable	Total	%[a]	Stable	Not stable	Total
Mini-contact								
Stable	100	12	0	12	85	11	2	13
Not stable	96	2	49	51	100	0	31	31
Total	97	14	49	63	95	11	33	44
Cooling								
Stable	80	20	5	25	100	12	0	12
Not stable	95	2	36	38	94	2	30	32
Total	89	22	41	63	95	14	30	44

[a] Percentage correctly classified in the tartaric stability categories.

than 0.9 for both the tests on white wines, whereas for red wines the results were between 0.84 and 0.96 (Table 5).

Application to external validation sets showed statistically significant correlation ($p<0.001$) between the results provided by the methods of reference and those forecast by the ANN models. The R^2 correlation coefficients confirm the results seen for the PLS-R analysis, with better values for white wines and the mini-contact test as compared to red wines and the cooling test (Fig. 2).

The attribution performance according to the categories of technological evaluation of instability for the models proposed is shown in Table 6. The percentage of correct classification went from 89% for the cooling white wine model to 97% for the mini-contact white wine model. The least effective model from the technological point of view, given the considerations stated above, was the cooling red wine model, with 6% of unstable samples classified as stable.

4. Conclusions

The joint use of the FT-IR technique and adequate statistical approaches for a substantial set of white and red wines without the addition of stabilisation products, and with a different degree of tartaric instability, made it possible to construct effective forecasting models in relation to the risk of crystalline precipitation in the bottle.

From the technological point of view, the performance of the models created using PLS-R and ANN analysis provided essentially equivalent results, limiting to 4–6% the risk of considering as stable a potentially unstable sample, which would therefore require stabilisation procedures before bottling.

The application of the forecasting models to certain specific types of wines (e.g. late-harvested, raisin or fortified wines) or to study the interference resulting from the use of stabilisation products, would undoubtedly be of interest.

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