ANALYSIS OF PORTUGUESE WINES BY FOURIER TRANSFORM INFRARED SPECTROMETRY (FTIR) *

ANÁLISE DE VINHOS PORTUGUESES POR ESPECTROMETRIA DE INFRAVERMELHO COM TRANSFORMADA DE FOURIER (FTIR)

J. L. Moreira, A. M. Marcos, P. Barros

Instituto da Vinha e do Vinho, Laboratório Vitivinícola, Unidade Laboratorial de Gaia, Rua Serpa Pinto, 571, 2.º, 4400-307 Vila Nova de Gaia, Portugal. E-mail: ulgaia@ivv.min-agricultura.pt

SUMMARY

The aim of this work is to present the results of the experimental optimisation of the essays with FTIR, supported by analytical data obtained by the methods that the laboratory routinely applies.

The use of FTIR in Enology - an emergent and very promising methodology - must be based on specific analytical calibrations established through the quantification by usual physical and chemical methods of the parameters to analyse.

The global calibration obtained for the analysis of wines allows good results for all parameters.

The specific calibration performed leads, in the case of the total sugars, to more adjusted results to the values given by the analytical methods in routine, being the use of a general or specific calibration indifferent for the remaining studied parameters

INTRODUCTION

Wine automatic analysers using FTIR methodology are routinely equipped with a general, robust calibration counting around a dozen of wine analytical parameters based on a varied group of samples from different countries which leads to reasonable results. However, it is to be expected that exactness will increase by creating specific calibrations for distinct subclasses of wines according to the matrix they represent.

The FTIR technique is an indirect analytical method (Patz *et al.*, 2000). The analytical calibrations for all parameters are created after the quantification of those parameters in the calibration samples using routine methods and the analytical results are used as a reference for the FTIR equipment calibration.

The analytical result is obtained applying an algorithm by which the interferences are compensated relatively to the direct relation with the wavelengths absorvances that are characteristic of the parameter to analyse. Therefore, it is necessary a measurement of multiple wavelengths (Dubernet, 1999). In order to compensate the interferences it is necessary to accomplish specific calibrations.

The selection of appropriate wavelengths for the quantification of each parameter is crucial in the development of new calibrations, for which a great diversity of wines is required. However, wines should present the same matrix effect as those that will be the object of analysis (Dubernet, 2000).

In order to calibrate the equipment, it is necessary to measure the infrared spectrum of a group of wine samples and the parameters to calibrate should be quantified in those wines by routine methods.

The equipment selects, for each parameter, n wavelengths that show higher statistical variation relatively to the analytical reference results. The calibration consists in calculating coefficients $(B_0, B_1, \dots, B_n)$ for each wavelength selected using a mathematical correlation.

The measurement of an infrared spectrum of wine sample and the significant absorvances $(A_1, A_2, \dots, A_n)$ allows the calculation of the FTIR result for that parameter:

$$\mathbf{FTIR_i = B_1 \cdot A_1 + B_2 \cdot A_2 + \dots + B_n \cdot A_n + B_0}$$

MATERIAL AND METHODS

Samples

A group of 897 wines divided in 4 subclasses: 425 (Red), 296 (White), 96 (Rosé) and 80 (Sparkling), was used in the essays.

The only sample preparation necessary was the degasification in an ultra sound bath for the wines that showed high CO_2 concentration, as in the case of the sparkling wines and some rosés.

Equipment

The equipment used was the Winescan FT 120 interferometer from FOSS that allows the scanning of the infrared spectrum from $926 - 5012$ cm^{-1} (Winescan FT120, 2000).

The equipment calculates the results using a PLS (Partial Least Squares) regression. The number of wavelengths selected for each parameter is 15.

All the parameters are analysed in duplicate, in the same analysis time (60 seconds) and using 20 mL of sample.

The zero set liquid (S-6060), the cleaning agent (S-470) and the FTIR equalizer were used. All products were provided by FOSS.

Analytical reference results

The parameters developed were: Density, Ethanol, Dry Extract, Total Sugars, Total Acid, Volatile Acid and Total SO_2.

The analytical methods used to obtain the reference results were the following:

TABLE I

Analytical reference methods
Métodos analíticos de referência

Parameters	Analytical reference methods
Density	Hydrometry*
Ethanol	Distillation + Hydrometry *
Dry Extract	Densimetry *
Total Sugars	Iodometry *
Total Acid	Titrimetry *
Volatile Acid	Distillation + Titrimetry *
Total SO₂	Iodometry *

* - (E.C. Regulation, 1990)

Calibrations

A global calibration for density, ethanol, dry extract, total sugars, total acidity, volatile acidity and total sulphur dioxide was obtained by using a group of 897 wines.

For the global calibration, all the samples were used to calibrate all the parameters, with the exception of total sugars. It was decided, in the case of total sugars, to divide all the samples into two different groups: one containing

the samples with total sugars lower or equal to 5 g/L and another one containing the samples with total sugars higher than 5 g/L. These groups of samples were used to produce two different calibrations for total sugars.

In order to improve the performance of the equipment, specific calibrations were developed dividing the samples in different subclasses (red, white, rosé and sparkling) and producing a total sugars calibration for each subgroup.

Quality Control

The quality control of the results was assured using a liquid "zero", an equalizer and a daily control sample (a wine divided in several bottles and stored in the refrigerator).

RESULTS AND DISCUSSION

A. Precision

In order to evaluate precision, repeatability (r), intermediate precision (IP) and reproducibility (R) were calculated for each parameter. The results are presented in Table II.

Reproducibility data were obtained by an interlaboratory essay of 6 Portuguese laboratories equipped with a Winescan FT 120. In this essay all the laboratories used the same calibration, the same samples and followed the same analysis procedure. A total of 3 samples were used to calculate the reproducibility.

TABLE II

Repeatability (r), intermediate precision (IP) and reproducibility (R) using the global calibration
Repetibilidade (r), precisão intermédia (IP) e reprodutibilidade (R) usando a calibração global

Parameter		r	IP	R	R (official methods)
Density	(g/mL)	0.00013	0.00022	0.00026	0.00037
Ethanol	(% vol.)	0.032	0.053	0.089	0.19
Dry extract	(g/L)	0.240	0.496	0.695	-
Total Sugars (≤ 5 g/L)	(g/L)	0.199	0.251	0.270	-
Total Sugars (> 5 g/L)	(g/L)	0.326	-	-	-
Total Acid	(g/L)	0.057	0.135	0.379	0.4
Volatile Acid	(g/L)	0.024	0.036	0.072	0.08
Total Sulphur Dioxide	(mg/L)	7.1	12.4	22.0	15

Comparing the results obtained with R data published in the European Official Methods, the FTIR provides better precision data for most of the parameters, similar results for total acid and volatile acid and poor results only for total sulphur dioxide.

B. Exactness

The exactness of the calibrations was measured by using the standard error (SE) and the Coefficient of Variation (CV(%)) using 75 samples (representative for the 4 subclasses, mainly red wines):

$$SE = \sqrt{\frac{\sum_{i=1}^{n}\left(Ref_i - FTIR_i\right)^2}{n}} \qquad CV(\%) = \frac{SE}{Ref_i} \times 100$$

FTIR$_i$ - Equipment result.
Ref$_i$ - Reference analysis results.
n   - Number of samples used to evaluate exactness.

The results concerning the global calibration are presented in Table III.

TABLE III

Standard-error (SE) and Coefficient of Variation (CV(%)) using the global calibration
Erro-padrão (SE) e Coeficiente de Variação (CV(%)) usando a calibração global

Parameter		SE	CV(%)
Density	(g/mL)	0.0011	0.107
Ethanol	(% vol.)	0.12	1.05
Dry extract	(g/L)	0.73	2.23
Total Sugars (≤ 5 g/L)	(g/L)	0.46	20.72
Total Sugars (> 5 g/L)	(g/L)	2.51	7.80
Total Acid	(g/L)	0.22	3.81
Volatile Acid	(g/L)	0.08	14.9
Total Sulphur Dioxide	(mg/L)	38.5	30.6

Another group of 125 samples have been used to compare the exactness of global calibration *vs.* specific calibration. All these samples were analysed by the equipment in both calibrations (global and specific) and the SE was calculated for each subclass. Improvements were only observed in the calibration of total sugars (Table IV).

TABLE IV

Standard-error for total sugars determination using global and specific calibration
Erro-padrão para a determinação dos açúcares totais usando a calibração global e a calibração específica

Samples		SE for Total Sugars (g/L)	
		Global calibration	Specific calibration
Subclass	Red	0.34	0.34
	White	0.94	0.52
	Rosé	1.46	0.84
	Sparkling	2.11	1.85
All samples (weighted average)		1.27	1.02

31

The specific calibration performed for total sugars leads to results more adjusted to those given by the analytical methods in routine, being the use of a general or specific calibration indifferent to the remaining studied parameters.

CONCLUSIONS

The global calibration allows excellent results concerning precision for almost all parameters. It was obtained and tested in different laboratories and provides a very good R for all parameters with the exception of total SO_2. However, a major improvement in the exactness results obtained with the specific calibration for total sugars was observed.

This workgroup is currently establishing specific calibrations for Portuguese wines with different geographic origins, which may lead to further improvement of the quality of the results obtained.

FTIR proves to be a very reliable methodology. It provides very reliable results for most wine analytical parameters if cautiously developed calibrations are applied.

RESUMO

Análise de vinhos portugueses por espectrometria de infravermelho com transformada de Fourier (FTIR)

O objectivo deste trabalho é apresentar os resultados da optimização das condições de ensaio em FTIR, suportada em calibrações analíticas baseadas nos métodos aplicados em rotina.

O uso de FTIR em Enologia - uma metodologia emergente e muito promissora - deve ser baseado em calibrações analíticas específicas estabelecidas através da quantificação dos parâmetros a analisar, por métodos físico-químicos usuais.

A calibração global desenvolvida para a análise de vinhos permite bons resultados para todos os parâmetros o que torna a metodologia FTIR de bastante confiança.

A calibração específica desenvolvida para a análise de açúcares totais conduz a resultados mais ajustados aos obtidos por métodos analíticos de rotina, sendo para os restantes parâmetros indiferente o uso de uma calibração global ou específica.

RÉSUMÉ

Analyse de vins portugais par spectrométrie d'infrarouge avec transformée de Fourier

Ce travail a comme but de présenter les résultats de l'optimisation expérimentale des conditions d'analyse avec FTIR, supporté par données analytiques obtenus par les méthodes que le laboratoire applique régulièrement.

L'usage de FTIR dans Oenologie - une méthodologie émergente et très prometteuse - doit être

basé sur des étalonnages analytiques spécifiques, établis à travers la quantification par des méthodes usuelles physico-chimiques, des paramètres d'analyser.

L'étalonnage global obtenu pour l'analyse des vins permet de bons résultats pour tous les paramètres.

L'étalonnage spécifique établi de cette façon permait, dans le cas des sucres totaux, d'obtenir résultats plus ajustés aux valeurs données par les méthodes analytiques dans routine étant indifférent pour les restants paramètres étudiés l'utilisation d'un étalonnage général ou spécifique.

REFERENCES

Patz, C-D *et al.*, 2000. Wine Analysis using FTIR, *In focus*, 24 (1), 16-18.

Dubernet, M., Dubernet, M. et Grasset F., 1999. Nouvelles applications de l'analyse infra-rouge dans les vins et les moûts, *Feuillet Vert OIV*, N.1089.

Dubernet, M., Dubernet, M., 2000. Utilisation de l'analyse infrarouge à transformée de Fourier pour l'analyse oenologique de routine, *Revue Française d'Oenologie*,181, 10-13.

WineScan FT120 - Reference Manual, Foss, 2000, August, Issue 4 GB.

E.C. Regulation N. 2676/90, dated 17/9/1990, *Official Journal of the European Communities* N. L272 of 3/10/1990.