

Truth lies in the must

Must content as wine quality indicator – FTIR-Spectroscopy

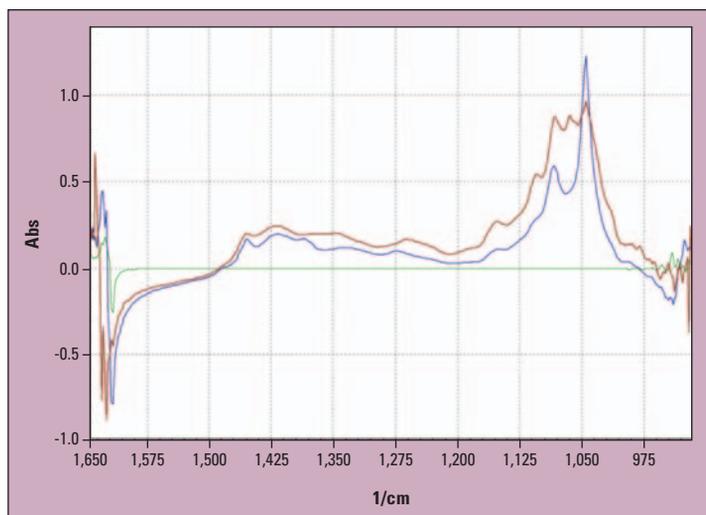


Figure 1: Infrared spectra of liquids after subtraction of the reference (water) where green = water difference, blue = wine and red = must. The fingerprint region is shown.

Wine is one of the oldest cultural products in human history. Vines have been cultivated for over 8000 years. The oldest known archaeological evidence of wine-making is an 8000-year old wine- and fruit press found near Damascus. Awareness of the medicinal effects of wine also date back to this time. Hippocrates (460 – 377 B.C.) recommended wine diluted with water as a remedy against headaches and digestive disorders.

Winemaking is a rather simple process: freshly harvested grapes are crushed and the resulting juice (must) is collected. The must contains fermentable sugars and natural yeasts which, either by themselves or with the help of additional yeast cultures, start the fermentation process in which mainly ethyl alcohol and carbon dioxide are formed. The latter is a gas and escapes. The fermentation process comes to a halt when all of the sugars are fermented or the alcohol concentration becomes too high and kills off the yeasts.

At this point the must has turned into wine.

Spectroscopic methods for quality assurance

A meticulous quality control procedure is essential, and during each stage of the production process spectroscopic methods such as FTIR spectroscopy are applied for quality assurance or for product characterization, for example the determination of must content in grapes. Must is the juice collected from grapes after crushing or pressing, before the process of fermentation has begun.

This application note describes the determination of must content of different types of grapes from the Trieste region in Italy according to the Brix method. The Brix value [% Brix] is measured using a refractometer and is a percentage indication of the general must value or sugar content of the grapes. This value, in turn, indicates the potential alcohol content of the future wine. In Germany this determination is usually measured in degrees Oechsle (°OE) and in other European regions in KMW (Klosterneuburger Mostwaage, where 1 KMW = 5 °OE), Babo, KMN and Baumé. The must weight is an important classification criterion for the quality of a wine.

This article will present FTIR as a suitable analytical technique for very rapid measurement of must

content based on acquisition of infrared spectra.

FTIR – fast analysis of IR-active compounds

FTIR spectroscopy is a fast analytical technique for the identification and quantification of IR-active compounds, for instance those present in must and wine. Both samples consist mainly of water, sugar, acids and other ingredients whereby the crucial distinction is the alcohol present in the wine.

In IR spectroscopy it is well known that water present in the samples strongly influences the infrared spectra. Nevertheless, a measurable region was found in the fingerprint where the IR-bands of the must ingredients and of the wine are clearly visible (Figure 1).

As mentioned before, both the must and the wine differ with respect to their sugar (must) and alcohol (wine) content as indicated in the spectral range of 1200 up to 1000 cm^{-1} . This is also the case in other wavelength ranges. As both substances can be identified in the water background, these wavelength ranges can also be used for quantification.

Measurement

Measurement was carried out using a Shimadzu IRPrestige-21 FTIR spectrophotometer in the

Standard	Spectrum	Must content (% Bx)
1	most_sample4	32.0
2	most_sample2	27.2
3	most_sample3F	16.9
4	most_sample2_1	26.0
5	most_sample1F	16.5

Table 1: List of the standards used

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conventional transmission mode using a flow cell with a layer thickness of 50 μm . The cell is equipped with water-resistant CaF_2 windows. As infrared radiation is also a form of heat radiation, the cell was thermostatted in order to maintain a constant temperature in the sample. Variation of temperature of the analytical system during spectral acquisition can lead to high measuring errors in the quantification of liquid samples and errors as high as 0.0125 Abs per 1 $^\circ\text{C}$ have been reported.

The accuracy of the FTIR system with respect to the baseline can be specified to within 0.005 Abs with water serving as reference as well as sample. In comparison, for refractometers an error range of 0.1 up to 0.5 % Bx is reported, depending on the measuring range. The temperature stability of the cell is achieved with an error of ± 1 $^\circ\text{C}$. In this measurement set-up, the water spectrum was used as reference and measured against the sample.

Quantification

In this case, as an indicator of the early stages during wine production, the must content and its determination according to Brix is considered to be a one-component system. Using mathematical quantification models, the Brix parameter can be correlated to the absorption of a spectrum.

Although the “must content” characteristic property is considered here, the conventional calibration method – plotting the concentration of one component against a discrete analytical wavelength – does not lead to a suitable quantification model. When taking into account the character-

istics reflected in the must content, a multivariate model spanning the entire spectrum or parts of it will be a more suitable tool for tackling this quantification issue.

The infrared spectrum represents all ingredients and their corresponding characteristics. The PLS (Partial Least Square) method was therefore used for this application. In PLS, a factor set is sought after which represents the standard spectral set and its components. Based on the established factors, the content of a certain component (in this case must) can be determined in a sample.

For this model, 5 must samples (Table 1) were determined in 10-fold using an autosampler. 48 measuring values were acquired in the calibration (Table 2). In order to test the calibration model, a sample was created from must standards 2 and 1. The result is listed in Table 3.

The deviation of the Brix mean value of five measurements with 0.0138 % Bx lies below the error that can result from a false reading of 0.2 % Bx on the refractometer scale. Each single measurement lies in turn below the reading error.

Evaluation

This limited standard model was meant to illustrate that a calibration of must with the aid of infrared spectroscopy is possible. The quality of calibration models is obviously dependent on the quality of the standards and reference methods used. This model can be further improved by using more standards, enabling in turn more accurate calibration. It is also important to use a reliable

Report of PLS Calibration	
Algorithm	PLS I
Number of components	1
Number of references	48
Range [1]	2432.60 – 3000.60
Range [2]	1122.59 – 1558.41
Centered data	Yes
Components	Must content
Number of factors	3
Correlation coefficient	0.99905
MSEP	0.00186
SEP	0.04319

Table 2: Calibration model of the must application

No.	Sample	Must content (% Bx)
1	most_sampleF1and2_003	22.3893
2	most_sampleF1and2_002	22.4411
3	most_sampleF1and2_001	22.4413
4	most_sampleF1and2_004	22.3474
5	most_sampleF1and2_005	22.3119
	Mean value	22.3862
	Difference in terms of the mean value	0.0138

Table 3: Testing the model using a sample representing a must content of 22,4 % Bx

reference method, fast processing of the standards – as these are not stable over time – and temperature control as the measurements are strongly influenced by temperature variations.

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We will gladly send you further information. Please note the appropriate number on your reply card. **Info 318**