FT-NIR Analysis of Wine

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Introduction

Although the art of winemaking has been practiced for centuries, the science of wine manufacture is relatively new. The use of chemical methods in wine analysis allows for monitoring of such critical parameters as Degrees Brix (°B), the total amount of sugar in unfermented juice, ethanol (a parameter that not only influences aroma and taste but also the rate of taxation), total and volatile acids, and pH. Table 1 shows a list of many different chemicals and characteristics that need to be monitored in wine manufacture to ensure quality. All of these quality variables have associated chemical, chromatographic or, in some cases, spectroscopic methods that are designed for determination of only one species. For example, the determination of ethanol content in wine can be achieved by ebulliometry, hydrometric analysis or dichromate oxidation while the acetaldehyde content can be determined by enzymatic analysis.

The use of spectroscopic methods for the determination of critical quality parameters in wine has met with some success, but usually only when the analyte in question is elemental (e.g. potassium, calcium, or iron). In the last five years Near-infrared (NIR) spectroscopy has presented itself as a rapid, accurate, and precise alternative to traditional chemical, physical, and chromatographic methods for many different types of wine analysis. In addition, the long pathlengths in near-infrared spectroscopy allow sampling through containers of glass and plastic making near-infrared an ideal QA/QC technique. Near-infrared also has the ability to monitor multiple species at the same time, using a single spectrum for identification or quantification of many crucial chemical or physical variables germane to wine production.

Acetaldehyde
Ethanol
Degrees Brix
Titratable Acids
Density
pH
Total Acids
Volatile Acids
Sulfur Dioxide
Mold
Glycerol
Methanol
Fusel Oils
Malic Acid
Carbohydrates
Phenols
Sorbic Acid
Benzoic Acid
Tartaric Acid
Conductivity

Table 1

The Thermo Scientific Antaris™ FT-NIR analyzer, makes use of Fourier transform (FT) technology which has significant advantages over older near-infrared instrumentation including fewer moving parts and the ability to sample all wavelengths simultaneously. Other advantages of FT-NIR technology include wavelength accuracy, high throughput, and high signal-to-noise making it an ideal spectroscopic methodology for analyzing chemically complex media like wine. In addition, the precision engineering of the Antaris FT-NIR analyzer includes pinned-in-place optics, consistent beampath, and a dynamically aligned interferometer resulting in exceptional scan-to-scan repeatability, stability, and method transfer characteristics.

In this report we demonstrate that the Antaris FT-NIR analyzer can be used successfully for the simultaneous quantitative analysis of multiple components of wine. NIR can predict physical properties like density in addition to normal chemical parameters like ethanol content or Degrees Brix. We also describe the prediction of nine quality parameters involved in wine analysis. Table 2 shows the names of the analyte and the statistical correlations achieved from the near-infrared calibration plots. Partial Least Squares methods for ethanol content (chemical parameter) and wine density (physical parameter) are described in detail.

Traditional chemical or physical techniques were not fast enough for these analyses because they could not quickly determine all the necessary parameters required. In this case, we show how the Antaris FT-NIR analyzer achieves rapid, accurate analysis where traditional chemical or physical methods fail.

Experimental

The samples of wine were degassed (if necessary) and pre-heated to 40 °C in 1 mm glass cuvettes in an external heater. Samples were collected on a Antaris liquid analyzer in cuvettes placed in a three-position, heated-cuvette holder (cell temperature 40 °C). The scanned spectral range was 4000 to 10000 cm^{-1} with a pre-collection delay of 30 seconds. 100 co-averaged scans were collected at a resolution of 4 cm^{-1} (the maximum resolution on the Antaris FT-NIR analyzer is 2 cm^{-1}). The InGaAs transmission detector was used for these measurements with a C attenuation screen.

Spectra were collected using validated RESULT™ software. A simple workflow for the collection of calibration data was constructed in RESULT Integration, allowing anyone (no spectroscopy experience necessary) to run the same workflow with a simplified interface in RESULT Operation. After the calibration, a workflow for collection, measuring, and reporting of samples was created in RESULT Integration, but it was run in RESULT Operation for ease of use.

Data Analysis and Results

Figure 1 shows example absorption spectra of several wine standards. The totally absorbing water peaks of irregular shape were not used in the current methods. The regions suitable for quantitative calibration are 4100 – 4600 cm^{-1}, 5700 – 6000 cm^{-1}, and 6450 – 7700 cm^{-1} (although water interferences may be present in this final region). The first two of these regions are shown in Figures 2a and 2b. Ethanol peaks are readily observable around 4400 cm^{-1}.
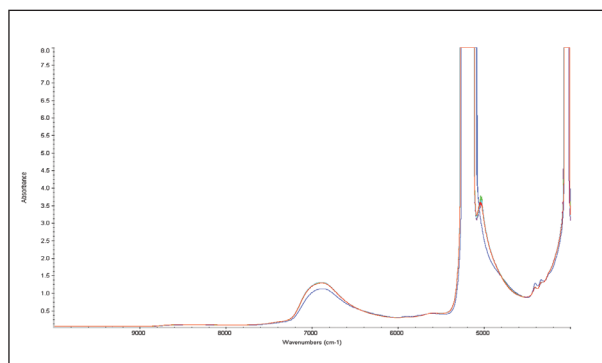

Figure 1: Example spectra of several wine standards

Table 2 summarizes all quantitative methods developed in this study for the analysis of wine. These calibrations were done using TQ Analyst™, our chemometric software package. All calibrations used the Partial Least Squares algorithm due to its ability to account for overlapping and broad peaks. For some of the calibrations listed, such as total acids or Brix refraction, there are two types of spectral processing listed indicating different regions of the spectra were processed differently. Other columns in Table 2 show standard chemometric parameters for Near IR method development like Root Mean Square Error of Cross Validation (RMSECV) and correlation coefficient (R).

Ethanol and density are two important parameters in wine analysis, so we will examine these chemometric models in depth. 124 standards with concentrations between 4.23 and 27.63 % ethanol (v/v) were used for the model of ethanol in wine. TQ Analyst's Automatic Region Selection Expert feature suggested two regions that performed well. As the regions were narrowed slightly, the performance of the method improved even more. Figures 2a and 2b show the regions used.
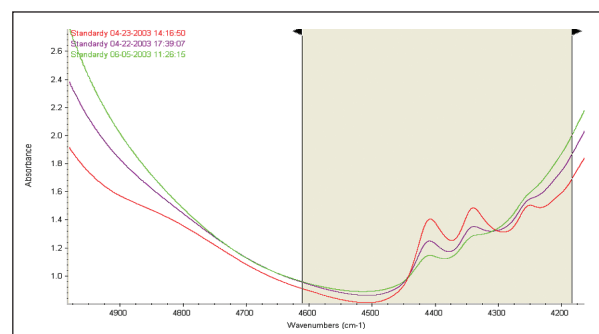

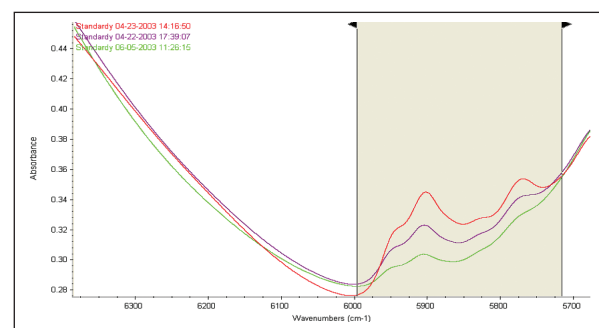Figure 2a: Example of lower-frequency region

Figure 2b: Example of mid-frequency region

Parameter	Unit	Nr. of PLS Factors	Spectral Processing	Correlation Coefficient	RMSEC	RMSECV
Ethanol	%	4	2nd der.	0.9984	0.23	0.26
Total sugars, lower values	g/l	8	spectrum	0.9968	1.5	1.7
Total sugars, higher values	g/l	6	spectrum	0.9995	1.2	1.5
Sugar-free extract	g/l	7	spectrum and 2nd der.	0.9869	0.5	0.8
Total acids	g/l	5	spectrum and 2nd der.	0.9872	0.3	0.4
Volatile acids	g/l	6	spectrum and 2nd der.	0.9788	0.04	0.06
Density	g/cm^3	6	spectrum	0.9993	0.7x10^{-3}	0.8x10^{-3}
pH		1	spectrum	0.9505	0.05	0.08
Brix refraction	°Brix	6	spectrum and 2nd der.	0.9998	0.04	0.08

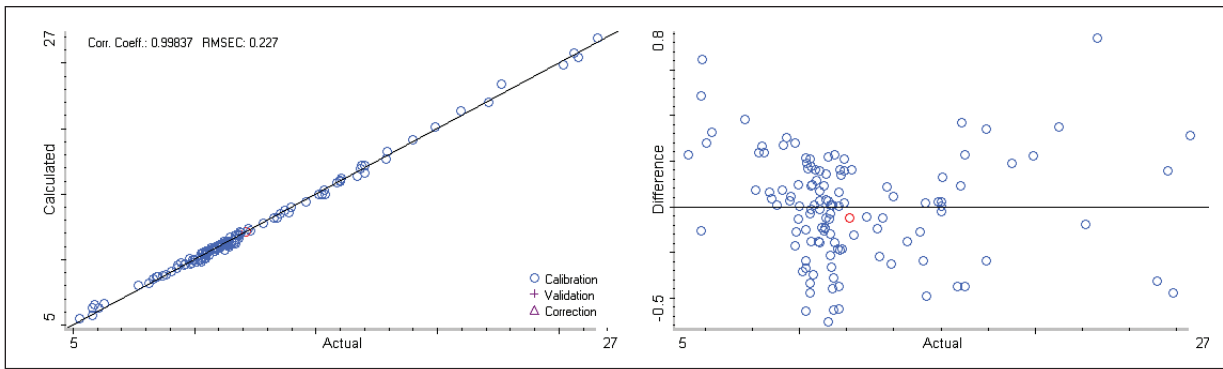Table 2: Statistical summary of components in wine analyzed with the Antaris FT-NIR analyzer

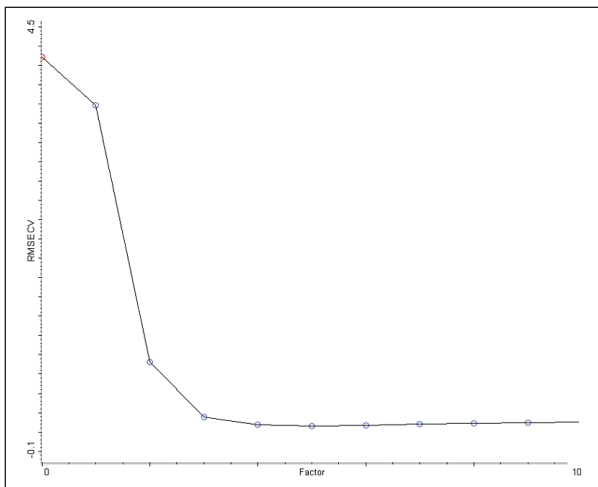Figure 3: Calibration curve and residual for ethanol in wine

Figure 4a: PRESS plot for ethanol

Factor	PRESS	RMSECV
0	2,068.99536	4.08478
1	1,597.24365	3.58901
2	106.01149	0.92463
3	15.52398	0.35383
4	9.63308	0.27872
5	8.50854	0.26195
6	8.89775	0.26787
7	10.01419	0.28418
8	10.32760	0.28860
9	10.97542	0.29751
10	11.65864	0.30663

Figure 4b: PRESS statistics
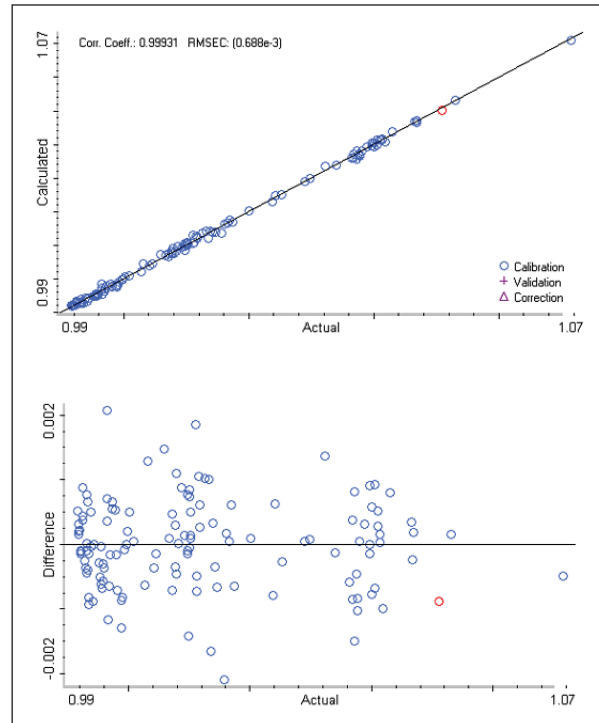
Figure 5: Calibration curve and residual for density in wine

Spectral processing parameters for these regions consisted of a second derivative with no baseline. Figure 3 shows the correlation plot between the known concentration of ethanol and that predicted by the TQ Analyst software from the data acquired on the Antaris FT-NIR analyzer. The shape of the Predicted Error Sum of Squares or PRESS plot (Figures 4a and 4b) was excellent with a true minimum occurring on the fifth PLS factor. The TQ Analyst software suggested a calibration with 4 factors which was subsequently used to avoid overfitting.
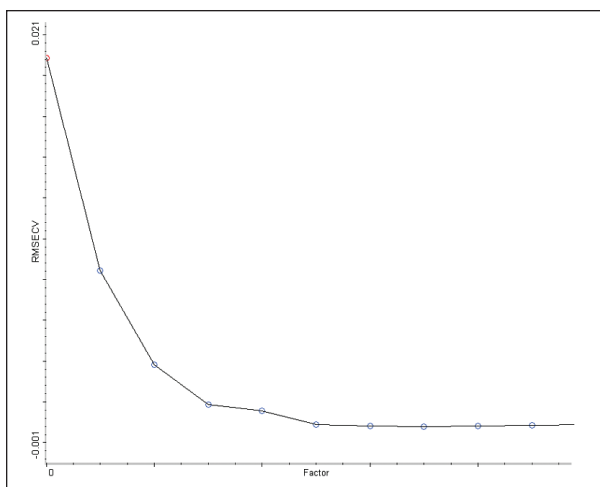
Figure 6a: PRESS plot for density in wine

Factor	PRESS	RMSECV
0	0.04726	0.01885
1	0.00948	0.00844
2	0.00196	0.00384
3	0.00046	0.00187
4	0.00033	0.00158
5	0.00011	0.00090
6	0.00009	0.00084
7	0.00008	0.00079
8	0.00009	0.00082
9	0.00009	0.00084
10	0.00011	0.00090

Figure 6b: PRESS statistics

The second method quantifies a physical parameter – density of wine. 133 standards of densities between 0.987 and 1.076 g/cm^3 were used. Two regions (4502 cm^{-1} - 4829 cm^{-1} and 6038 cm^{-1} - 6205 cm^{-1}) were chosen where the correlation according to statistical spectra tool was the greatest. The statistical spectra tool in the TQ Analyst software allows the user to see the correlation between spectral data and primary numbers before any calibration is performed, streamlining the process of making a robust, effective calibration. A one-point baseline with the fixed location at 8300 cm^{-1} was used for both regions. Figure 5 shows the correlation plot for wine density with a correlation coefficient of 0.99931. In addition, the RMSECV value for this component was only 14% higher than the original RMSEC, implying a stable method. Again, the shape of the PRESS plot is excellent and suggests using either 5 or 6 factors. 6 PLS factors were used for the calibration. Figure 6a and Figure 6b show the PRESS plot and associated statistics.

Conclusions

The Antaris FT-NIR analyzer offers an excellent alternative to traditional methods for determination of multiple parameters of wine simultaneously. The unparalleled stability of the Antaris analyzer coupled with easy-to-use RESULT software demonstrates the ability to affect significant change in QA/QC of foods and beverages. Analyses that would traditionally have taken hours can now be done in seconds without sacrificing accuracy or precision. In this case study, the user was able to obtain the data quickly to allow for the analysis of wine in an acceptable timeframe.

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