Application note

Thermo Fisher SCIENTIFIC

Antaris II FT-NIR Analyzer

FT-NIR analysis of wine

Keywords
Antaris, Brix, density, ethanol, FT-NIR, pH, titratable acid, transmission, wine

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

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.

Near-infrared spectroscopy (NIRS) has recently 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 NIRS allow sampling through containers of glass and plastic, making NIRS an ideal QA/QC technique. NIRS 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.

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The Thermo Scientific™ Antaris™ II 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 a high signal-to-noise ratio, making it an ideal spectroscopic methodology for analyzing chemically complex media like wine. In addition, the precision engineering of the Antaris II 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 II FT-NIR Analyzer can be used successfully for the simultaneous quantitative analysis of multiple components of wine. NIRS can predict physical properties like density in addition to normal chemical parameters such as 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 (PLS) 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 II 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 an Antaris II FT-NIR Analyzer with temperature-controlled liquid transmission module (cell temperature 40°C). The scanned spectral range was 4,000–10,000 cm^{-1} with a precollection delay of 30 seconds.

One hundred co-averaged scans were collected at a resolution of 4 cm^{-1}. The InGaAs transmission detector was used for these measurements with a C attenuation screen, which attenuates the total beam energy to approximately 3% to prevent detector saturation.

Spectra were collected using validated Thermo Scientific RESULT™ Software. A simple workflow for the collection of calibration data was constructed in RESULT Integration, a method development package that allows anyone to run the same workflow with a simplified interface in RESULT Operation. A workflow for collecting, measuring, and reporting samples was created in RESULT Integration, but it was run in RESULT Operation for ease of use.

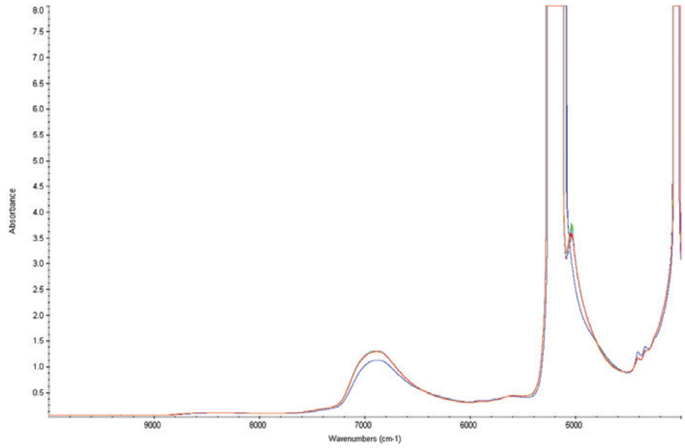

Figure 1: Example spectra of several wine standards.

Table 2 summarizes all quantitative methods developed in this study for the analysis of wine. These calibrations were developed using Thermo Scientific TQ Analyst™ Chemometric Software. All calibrations used the PLS 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, two types of spectral processing were used for different regions of the spectra. 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).

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/cm3	6	spectrum	0.9993	0.7×10^{-3}	0.8×10^{-3}
pH	1	5	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 II FT-NIR Analyzer.

Ethanol and density are two important parameters in wine analysis, so we will examine these chemometric models in depth. One hundred and twenty-four standards with concentrations between 4.23 and 27.63 % ethanol (v/v) were used for the model of ethanol in wine. TQ Analyst Software'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.

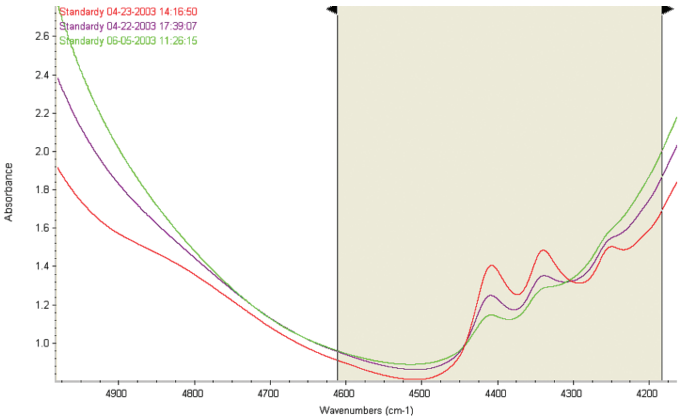

Figure 2a: Example of lower-frequency region.

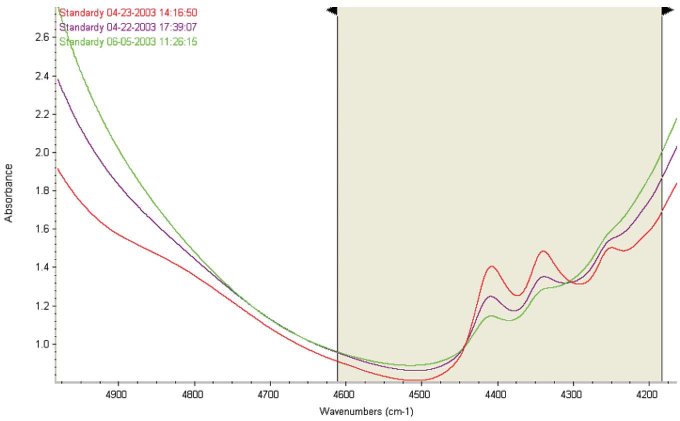

Figure 2b: Example of mid-frequency region.

Spectral processing for these regions consisted of a second derivative with no baseline correction. 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 II 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.

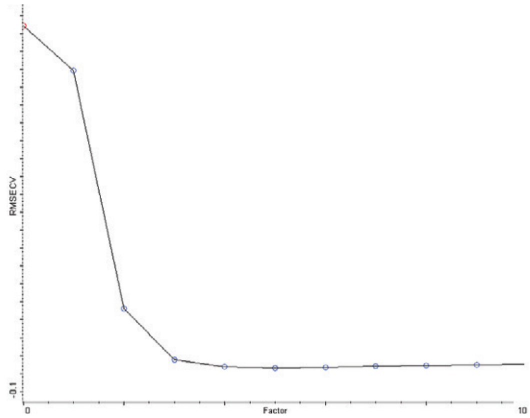

Figure 4a: PRESS plot for ethanol.

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.

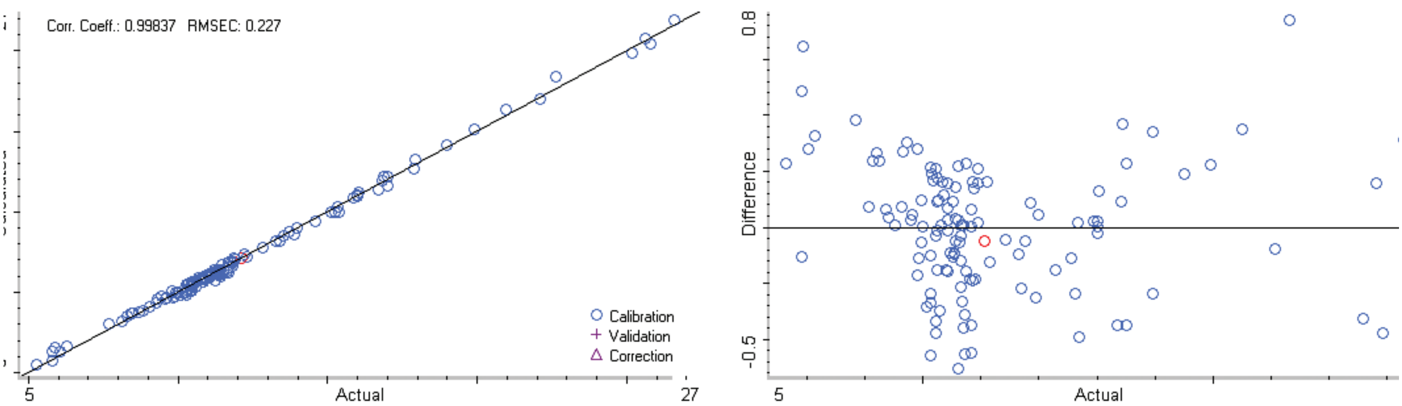

Figure 3: Calibration curve and residual for ethanol in wine.

The second method quantifies a physical parameter: density of wine. One hundred and thirty-three standards with densities between 0.987 and 1.076 g/cm3 were used. Two regions (4502–4829 cm^{-1} and 6038–6205 cm^{-1}) were chosen, where the correlation to density was the greatest as suggested by the statistical spectra tool in the TQ Analyst Software. The statistical spectra tool 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 correction with fixed location at 8,300 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. Six PLS factors were used for the calibration. Figure 6a and Figure 6b show the PRESS plot and associated statistics.

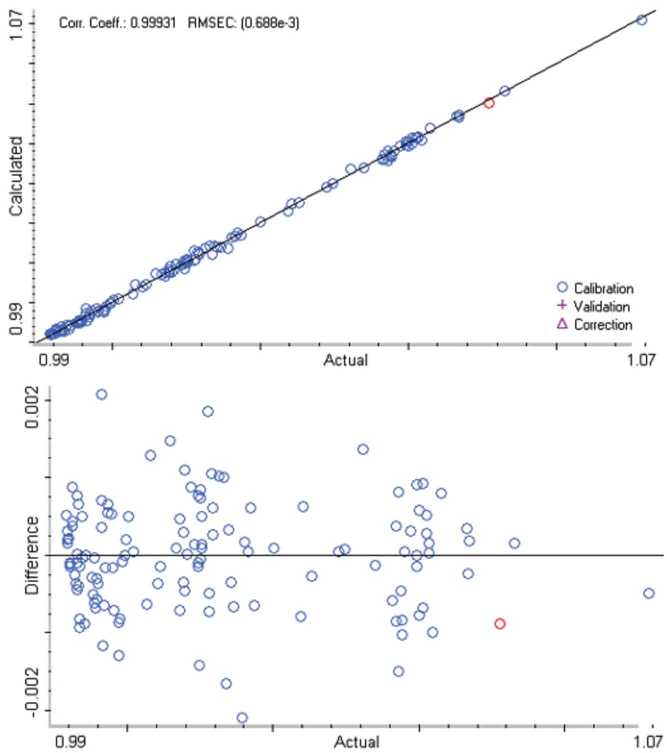

Figure 5: Calibration curve and residual for density in wine.

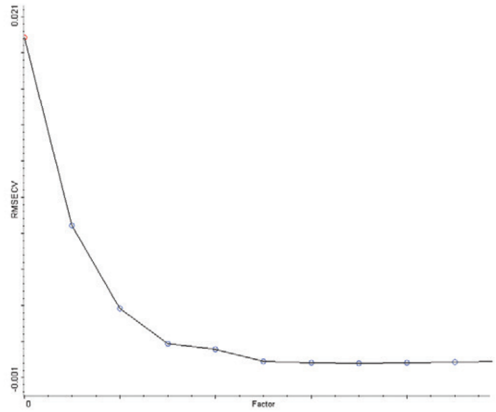

Figure 6a: PRESS plot for ethanol.

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.

Conclusions

The Antaris II FT-NIR Analyzer offers an excellent alternative to traditional methods for simultaneous determination of multiple parameters of wine. The unparalleled stability of the Antaris II FT-NIR 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.