Technical Note: 50782

Method Transfer through Superior Engineering: Analysis of Variance Related to User-replaceable Components

Key Words

- **FT-NIR**
- **Laser**
- **Method Transfer**
- **Source**
- **Wavelength Precision**

Abstract

The effect of replacing laser and source on the reproducibility of spectral data is discussed. The change in peak locations after replacing the laser and source are presented. The effect of replacing the source on line shape and band intensity is examined.

Introduction

The increasing popularity of Fourier transform near-infrared (FT-NIR) spectroscopy is primarily due to the fundamental advantages of this technology for developing chemometric methods. Since creating and validating chemometric methods requires a substantial investment of both time and money, reproducibility of spectral data is essential. This required reproducibility allows a method developed on one analyzer to be transferred to another. Because of the substantial effort involved in developing and validating a method, it is also essential that the method can be used for many years. This requires that results remain accurate and repeatable after servicing the system or replacing consumables. Two components that may be replaced by the user are the source and the laser.

Because any near-infrared source has a finite lifetime, it is important that it be long lasting and easy to replace (Figure 1). The source is a critical optical component in the instrument. Slight changes in its location could cause wavelength and intensity shifts in the spectral data. If these shifts are large enough, the instrument may need to be recalibrated after each source change. Recalibrating could require a physical alignment procedure or a software adjustment of the spectrum response and often requires extensive revalidation to reestablish confidence that the procedure is unchanged.

Figure 1. Changing the source assembly on a Thermo Scientific Antaris FT-NIR analyzer

The source assembly in the Thermo Scientific Antaris™ FT-NIR analyzer has been specifically designed for rapid replacement and precise positioning. The source assembly is pin mounted into the precision cast baseplate ensuring on-axis and concentric alignment with the optical path of the spectrometer. The precision mounting system also includes automatic power contacts. It is easily accessible from the side of the analyzer. This design, illustrated in Figure 1, results in a source assembly that can be replaced in less than a minute without opening the cover of the instrument.

The helium neon (HeNe) laser is the master clock of the system that ensures the inherent stability and wavelength accuracy of FT-NIR. The laser assembly was designed to be easily replaceable by a user, while maintaining its accuracy. The laser is pre-aligned and pinned-in-place.

Experimental

Six sources were used for the first wavelength reproducibility experiment. Three sources, three lasers, and two instruments were used for the second. Reference spectra with six different sources were obtained from a National Institute of Standards and Technology's (NIST) Near-infrared Reflectance Wavelength Standard: SRM 1920a. The analyzers were operated in a normal laboratory environment without purge or desiccant, and no attempt was made to control the temperature during these measurements. No software adjustment of the spectrum was employed.

All spectra were acquired at 2 cm^{-1} resolution with an Antaris FT-NIR Method Development Sampling system. Thermo Scientific TQ Analyst™ software was used to analyze the data. Variance spectra were also calculated using TQ Analyst software. The location of the peaks was determined by Lagrangian interpolation.

Results and Discussion

Because of the design of the Antaris analyzer, effects of changing a source or a laser on wavelength precision are small. Subtle changes in the sample or sample position can easily overwhelm the small shifts in peak location caused by component replacement. Therefore, the peak locations of water vapor in the single beam were used for these experiments. Ratioed spectra were not used because the water peaks are very weak and cannot be seen in most spectra. High resolution (2 cm^{-1}) was selected so very small shifts in the peak locations caused by replacing components could be accurately measured.

The first experiment used the Integrating Sphere module to evaluate component swapping on diffuse reflectance measurements. After replacing the source, a two-minute delay was used before collecting the spectrum of the internal gold flag of the Integrating Sphere module. Table 1 reports the peak values calculated for two water vapor peaks with the Thermo Scientific RESULT™ software used by the Antaris analyzer. The average peak location and the standard deviation were also calculated for each peak.

SOURCE #	PEAK 1 (CM^{-1})	PEAK 2 (CM^{-1})
S5	7299.03	5307.22
S4	7299.03	5307.22
S3	7299.01	5307.20
S0	7299.02	5307.21
S1	7299.01	5307.20
S2	7299.04	5307.22
Average	7299.02	5307.21
Std Dev.	0.012	0.010

Table 1: Peak values calculated for two water vapor peaks with the RESULT software used by the Antaris analyzer

To evaluate the effect of replacing components, an experiment was designed with two different analyzers, three lasers, and three sources. After each component swap, the analyzer was allowed to stabilize for twenty minutes and a single beam using the main transmission detector was acquired. The results for the 7299 cm^{-1} peak are summarized in Table 2. The results for other water vapor peak locations gave similar results.

	SYSTEM I		SYSTEM II	
	LASER	SOURCE	LASER	SOURCE
Min	7299.04	7299.03	7299.01	7299.01
Max	7299.06	7299.05	7299.03	7299.02
Average	7299.04	7299.04	7299.02	7299.01
Std. Dev	0.009	0.006	0.010	0.002

Table 2: Results for the 7299 cm^{-1} peak

Note that the standard deviation is two orders of magnitude better than the 2 cm^{-1} resolution used to acquire the spectra. This result clearly indicates that no significant peak shifts occurred when changing the source or the laser in the Antaris analyzers. This conclusion is also confirmed by viewing the spectra from which the above results were calculated. Figure 2 shows the ~7299 cm^{-1} water vapor peak for System I (System II gave similar results). The spectra are presented in single beam format. There is clearly little difference between the spectra.

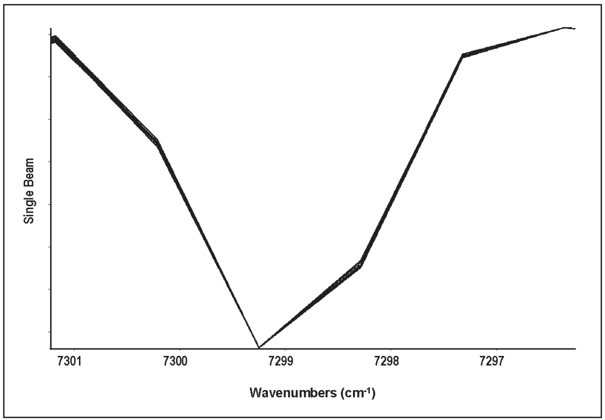

Figure 2: Overlay of six single beam spectra obtained in first experiment

A second concern related to source replacement is the effect on the intensity and line shapes of the spectral peaks. NIST's SRM 1920a is a suitable sample for these types of studies because it is a certified standard and has excellent spectroscopic properties. As a standard reference material developed and certified by NIST, the SRM 1920a is well characterized. The standard is a powdered mixture sealed in a holder with a sapphire window that can be placed directly on the window of the Integrating Sphere module. The standard is also spectroscopically rich with numerous, well-defined spectral peaks varying from less than 0.01 to greater than 0.5 absorbance units throughout the region from 11000 cm^{-1} to 4000 cm^{-1} (Figure 3).

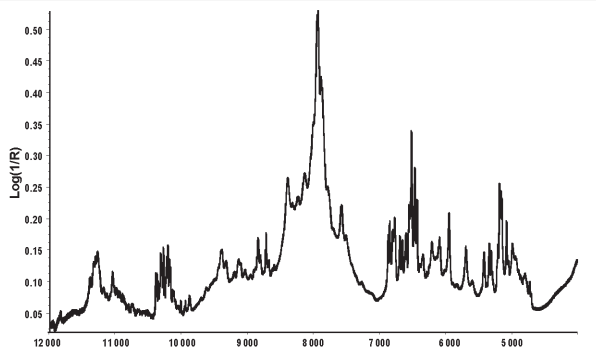

Figure 3: Overlay of spectra obtained with six different sources on the Antaris analyzer Integrating Sphere module

To minimize the effects of sampling variance, the standard was not moved during the source replacements. After replacing the source, a two-minute delay was used before collecting the spectrum of the internal gold flag as a background and then collecting a diffuse reflectance spectrum of the SRM 1920a.

As can be seen in Figure 3, there is very little difference in the spectra acquired with the six different sources. A more sensitive analysis of spectral differences uses what is known as a variance spectrum that calculates the standard deviation at each spectral data point. The advantage of using standard deviation is that the y-axis has the same units as the original spectra and subtle differences can be clearly seen. The variance spectrum calculated from the six spectra can be seen in Figure 4. The variance spectrum is relatively flat with residual peaks less than 0.001 log(1/R) units. Note that when dealing with real samples (even ideal samples like the SRM 1920a) and examining differences as small as those reported here, there is a question whether the sample or the analyzer is the source of the variation.

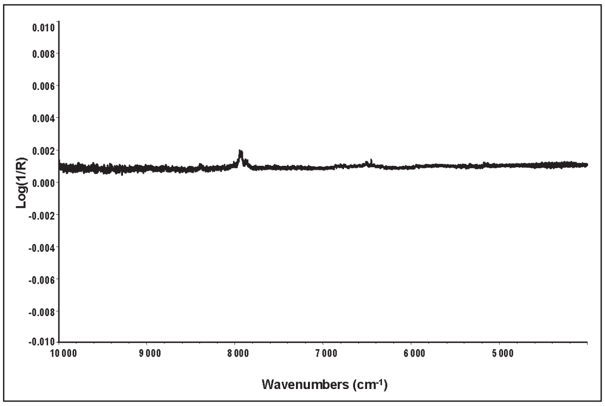

Figure 4: The variance spectrum computed from the spectra acquired with six different sources

Conclusion

The effects of changing user-replaceable components on band shape, position, and intensity have been studied. Wavelength precision should be ten times better than resolution to ensure method stability and transferability. Results obtained from the Antaris analyzer are orders of magnitude better than required. The results show that no significant peak shifts occurred when changing the source or the laser of Antaris analyzers. Even without controlling temperature or moisture and using high resolution, the results showed that deviations were several orders of magnitude better than required for method transfer and long term stability. These results indicate that it is not necessary to rely on uncertain algorithms to remove differences between individual instruments if all components are designed and manufactured to the same high standards.

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