

# The promise of Fourier transform near infrared: universal calibrations

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## Introduction

Fourier transform infrared (FT-IR) is well known for its sensitivity and wavelength precision in mid-infrared applications. Alignment control and optical stability, traditional weaknesses of FT-IR when used in near infrared (NIR) applications, have been overcome by a new patented optical interferometer design and scanning mechanism employed in our FT-NIR spectrometers.

With these FT-NIRs absorbance spectra are highly reproducible over an indefinite period when repeatedly measured with the same spectrometer. This feature has led to the development of factory and field service alignment procedures that also ensure a high level of absorbance reproducibility from spectrometer to spectrometer.

Deviations in absorbance spectra of repeat measurements of a sample influence the quantitative results of analysis. This influence varies greatly and depends on the available spectral response due to the parameters to be quantified as well as the extent to which the set of reference spectra represent instrument variations.

Testing procedures and acceptance criteria for stability over time and reproducibility from unit to unit have been established and are presented. Based on these reproducibility and stability characteristics, several calibrations have been developed and thoroughly tested. We believe these to be "Universal Calibrations" for their applications because they have provided analysis results

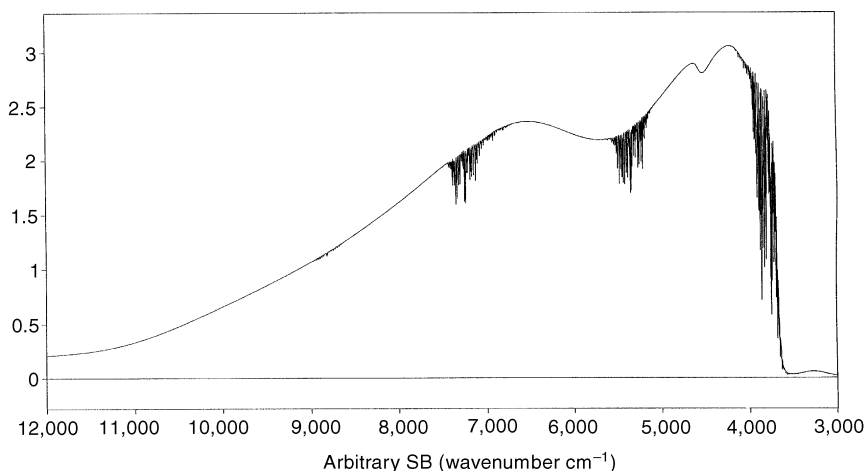


Figure 1. Typical spectral response for FT-NIR.

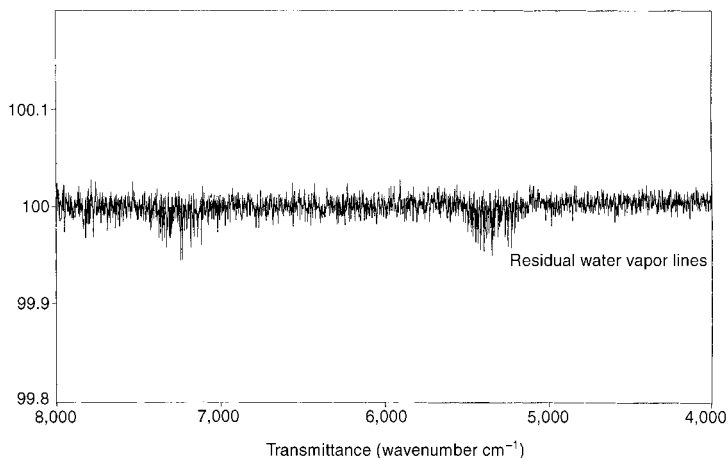


Figure 2. Typical 100% line for FT-NIR.

within their specifications without requiring any adjustment with time or when transferred to other spectrometers.

## Instrument stability and repeatability tests

A common test of FT-IR instrument stability is the “100% line” test. It consists of repeatedly measuring the spectral response when transmitting maximum intensity to the detector: with no sample present in transmittance mode the ratio of the repeat measurements should give a straight line at 100%. Figures 1 and 2 show typical spectral response and 100% lines, respectively. These tests are done only over short time intervals between repeats. It is expected that even the finest spectral details will ratio correctly. It is not expected that the spectral response of an FT-IR instrument will stay constant over a long time: the 100% line may drift slowly. This establishes the need for regular renewal of the spectral response, or reference spectrum, or means for correcting for drift.

The ratio of instrument response between two spectrometers is not a straight line at 100% because of substantial variation in source intensity distribution, optics transmission and detector response. It is not useful for comparing instruments.

In quantitative IR analysis the absorbance spectrum of the sample is used for analysis. This consists of the logarithm of a sample spectrum ratioed against a recent reference. By this means it is immune to variations and drifts in spectral response. Figure 3 shows a typical absorbance spectrum of toluene. This leads to the importance of the repeatability of absorbance spectra of stable samples.

It is desirable to do system verification with some standard sample, representative of the samples to be analysed. For a particular analysis application, the “standard sample” should be one or several check samples belonging to the calibration for the application. Conformance of the analysis values to accepted values constitutes acceptable operation of the analyzer.

For the manufacturer of spectrometers it is desirable to utilize a standard sample that may provide a broader verification of spectrometer conformance that will ensure that many different calibrations will remain constant and may be used interchangeably on different spectrometers.

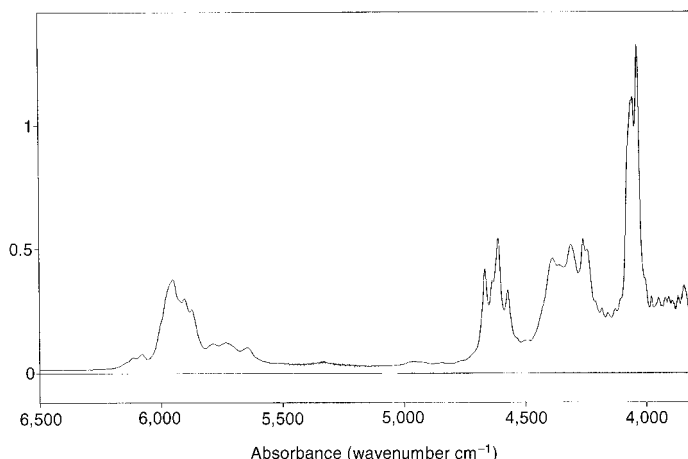


Figure 3. Typical absorbance spectrum of toluene in 0.5 mm liquid cell at 28°C.

### The toluene test

Clear liquid analysis by transmission shows the least variability of sampling, suggesting that this is the preferred sampling technique for instrument validation. In this light toluene in a liquid cell with a pathlength of about 0.5 mm appears a good candidate for a standard sample. Toluene can be obtained in high purity and has a stable absorbance spectrum when temperature controlled. Figure 4 shows the variations in absorbance with temperature.

For more than one year we have initiated testing of all manufactured FT-NIRs by means of the absorbance spectrum of toluene, in addition to other standard performance tests. At first, the spectra recorded on different instruments showed variations of as much as  $\pm 2\%$  of typical absorbance band heights. Improvements in signal processing and particularly improvements in input and output optics alignment have reduced differences down to less than  $\pm 0.1\%$ .

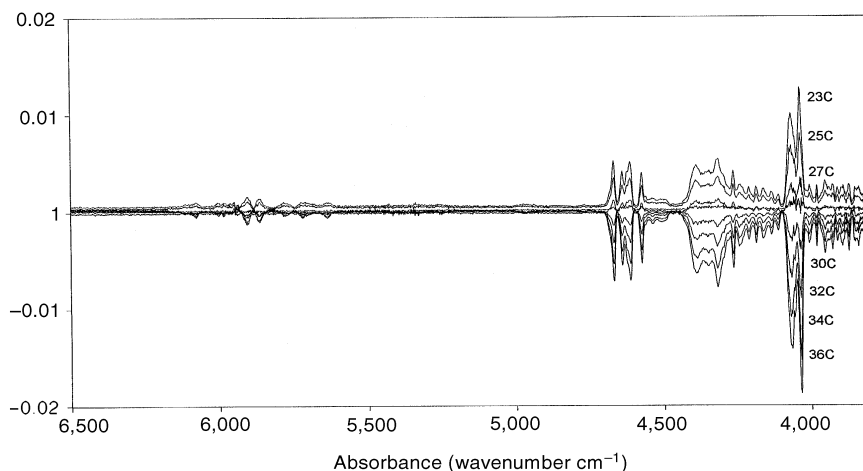


Figure 4. Temperature effect on toluene absorbance.

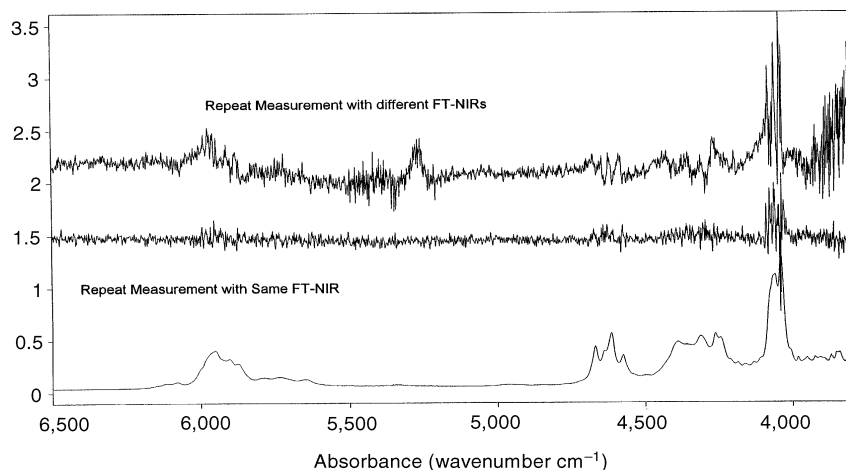


Figure 5. Repeat measurement with different FT-NIRs (top) and same FT-NIR (bottom).

Figure 5 shows typical differences of toluene absorbance spectra for successive measurements on a single spectrometer and for measurements on different spectrometers. At the random noise levels typically achieved in a short measurement period with an FT-NIR, the residual error in absorbance between different spectrometers is about three times higher than the reproducibility of a single spectrometer.

## Analysis performance of calibrations

How do we relate the stability and reproducibility performance of FT-NIR spectrometers to the analysis performance of a calibration for a given application?

In developing a calibration for an application, we work with reference samples that have been characterized by a reference method. For a calibration model, the deviation from the linear regression between actual reference values and NIR predicted values of the parameters of interest, provides an indication of the combined random errors in the reference method and the NIR method. Outliers can usually be spotted and removed.

The accuracy of a NIR analysis method compared with the reference method derives from the general agreement between results obtained by both. High measurement precision, long term stability of an analyzer and repeatability from analyzer to analyzer are very useful characteristics for continued validation for accuracy.

The precision of measurement for the reference method and the NIR method can be determined individually by repeat analysis of a single sample by these methods. If by repeat analysis of a single sample, or several samples spanning the calibration range, it is seen that the NIR analysis deviation is less than for the reference method deviation, we can say that the NIR analysis has suitable precision for the application. If the NIR analysis deviation is greater, its precision is unsuitable for the application.

There are several scenarios of precision or repeatability: (i) short-term repeatability, which is the precision and agreement achieved in a series of analyses done sequentially; (ii) long-term repeatability, which is the precision and agreement achieved in a series of analyses spread out over a long time; and (iii) analyzer to analyzer repeatability and agreement.

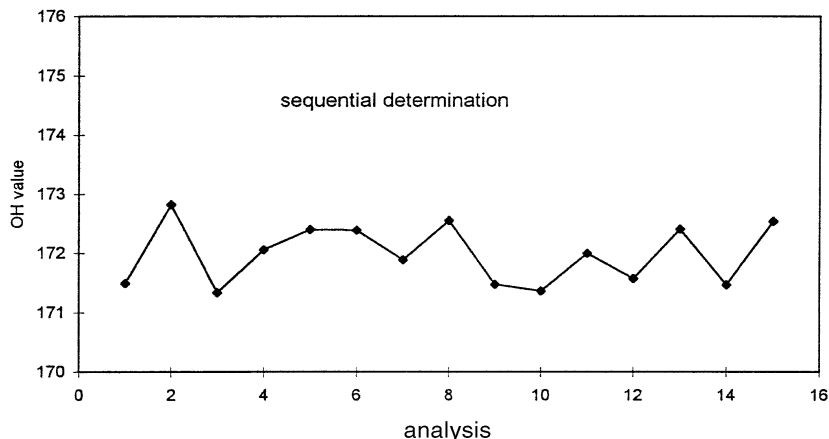


Figure 6. OH value for check sample—sequential determination.

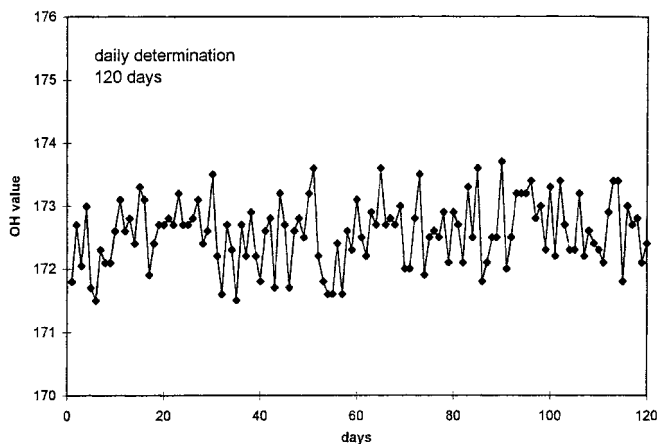


Figure 7. OH value of check sample—daily determination (120 days).

When the precision and agreement of an NIR analysis is within the precision of the reference method for all three cases above, there is no further need to tune or repeat the calibration after its first development. In this case the calibration is universal for this application.

Figure 6 shows the sequential repeat analysis of the OH value for a check sample of an ethoxylated fatty alcohol. From this we determine a short-term precision of 0.51 rms. This was considerably better than the estimated precision of the chemical method of about 1 rms. Figure 7 shows the trend of daily analysis of a check sample for 120 days. Here the standard deviation is 0.52 rms which is nearly equal to the short-term precision. There was no systematic drift.

The same calibration was installed on four different analyzers. The short-term precision was the same as in Figure 5 on each analyzer. The mean values for 10 repeat analyses on each analyzer was 172.1, 172.6, 172.7 and 172.4. The variations in mean values could be seen as offsets from analyzer to analyzer but their values lie within the statistics of the analysis and would need more measurements on each analyzer to confirm the presence of an offset.

## Conclusions

We have found that with a well-designed FT-NIR spectrometer we can achieve consistency of analysis precision for short-term precision and long-term precision without any evidence of drift for a period of at least 120 days of operation. Furthermore, by means of rigorous manufacturing techniques including testing for reproducibility of the absorbance spectrum of a standard toluene sample, we can achieve consistent analysis performance on different FT-NIR analyzers using a single calibration. This development leads to applications where the calibration is only developed once and need not be tuned or repeated. We consider this a universal calibration for such applications.