

Infrared Spectroscopy



Demonstrating the Accuracy of Transmittance Measurements for High Refractive Index Materials

Background

The PerkinElmer Spectrum 3 Optica* has been developed to provide accurate transmittance measurements on high refractive index materials.

There are several well known sources of error in standard FT-IR instruments that lead to spectral artifacts and inaccurate transmittance values for such samples¹. These have been addressed in the Spectrum 3 Optica. Interreflections involving the source, interferometer, sample and detector have all been eliminated. The use of delta-sigma analog-to-digital conversion avoids the need for gain switching and ensures excellent linearity². Although the linearity of DTGS detectors is widely thought to be well established, the presence of a sample changes the detector temperature, with a consequent change in responsivity. This was identified by NIST as a major source of error in FT-IR measurements of transmittance¹. For that reason, lithium tantalate is used as the standard detector in the Spectrum 3 Optica.

A further issue is the influence of the sample on the beam geometry, defocusing or displacing the beam at the detector. The Spectrum 3 Optica has two variable apertures in the beam path, allowing independent control of the size and the convergence of the beam at the sample. This reduces the sensitivity of the system to different sample thicknesses and to wedging.

*The Spectrum 3 Optica supercedes the Frontier Optica and the Spectrum 100 Optica system

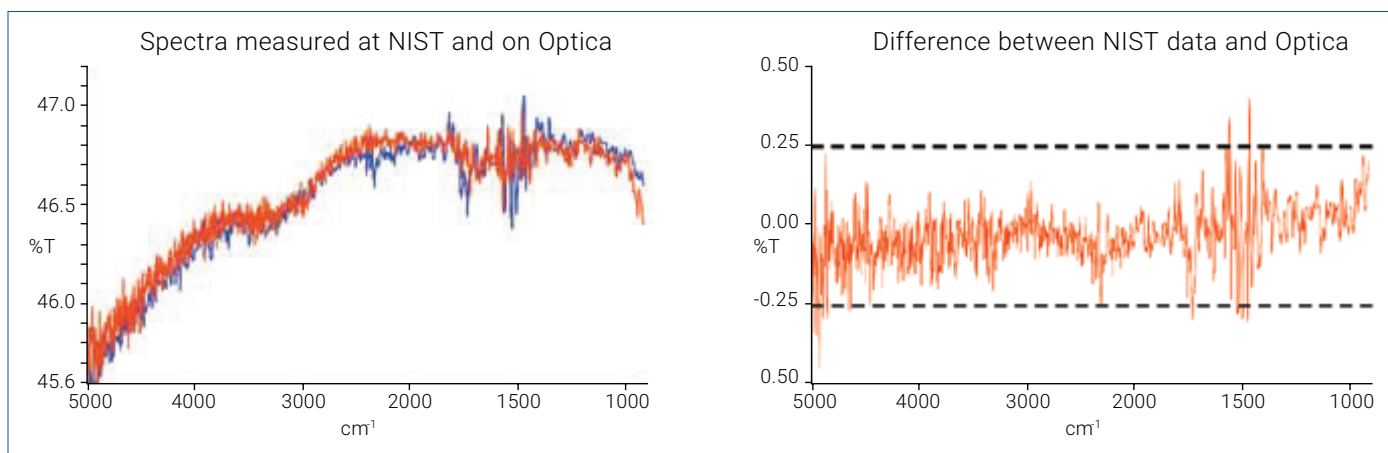


Figure 1a and 1b: Germanium measured on Optica and at NIST

Testing Transmittance Accuracy

The time-honored approaches used to test the ordinate accuracy of dispersive spectrometers, rotating sector discs and double apertures, are not practicable for FT-IR spectrometers³. There are two alternative methods available. One is to rely on transmittance calculated from refractive index values that are often known to very high accuracy. The other is to use traceable standards from suppliers such as NIST or NPL, but such standards are not currently available for the mid-IR region.

Transmittance values derived from refractive index are subject to the uncertainty that the surface reflection may not be adequately described by the bulk refractive index.

However, we have adopted this approach using germanium windows and have confirmed the transmittance values by having the samples measured at NIST.

Germanium

For 1 mm thick germanium measured on several instruments, the results agree well with refractive index calculations except between 4000 and 900 cm^{-1} (2.5 and 11 microns), but between 5000 and 4000 cm^{-1} (2 and 2.5 microns) the measured values are consistently lower than calculated by more than 0.1 %T. Measurements on the same samples at NIST are essentially identical with those on Spectrum 3 Optica, the differences being less than 0.1 %T over the range 5000 to 900 cm^{-1} (2 to 11 microns.) See Figure 1.

Other Materials

To test performance at other transmittance values we have measured zinc selenide (70%T) and calcium fluoride (94 %T) and compared the results with calculations from the refractive indices. In both cases, the agreement between measured and calculated transmittance is within ± 0.1 %T in the regions where absorption is negligible. See Figures 2 and 3.

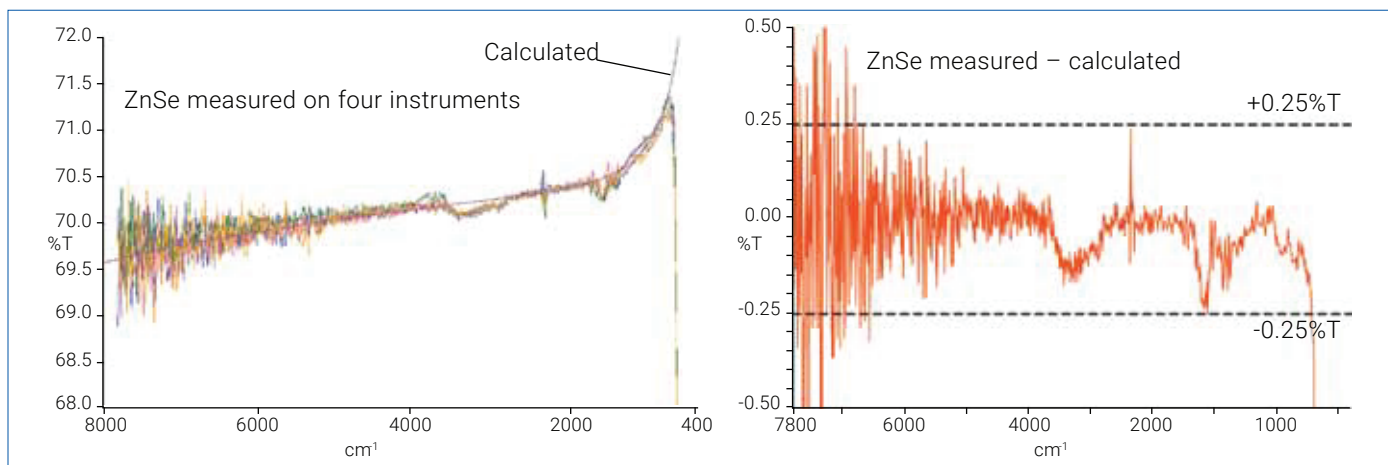


Figure 2a and 2b: Zinc selenide measured and calculated

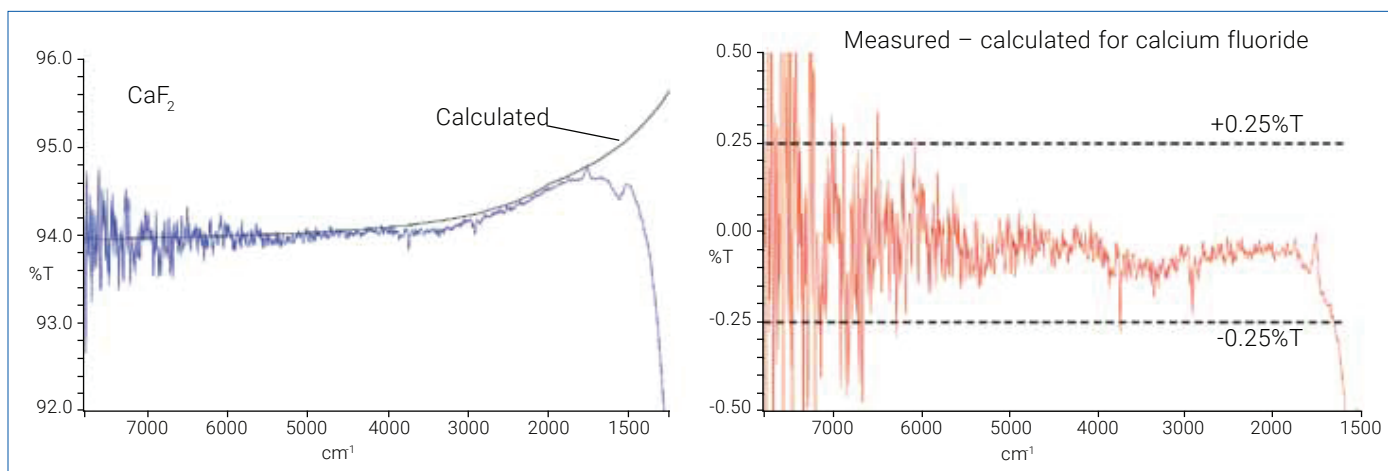


Figure 3a and 3b: Calcium fluoride measured and calculated

Instrument to Instrument Variation

In the absence of standard sample with known transmittance values, it has been a common practice to compare values for the same sample on different instruments. When we have tried this with Spectrum 3 Optica, the agreement is typically to better than $\pm 0.1\%$ T outside regions of atmospheric absorption. The example in Figure 4 is for germanium on three instruments.

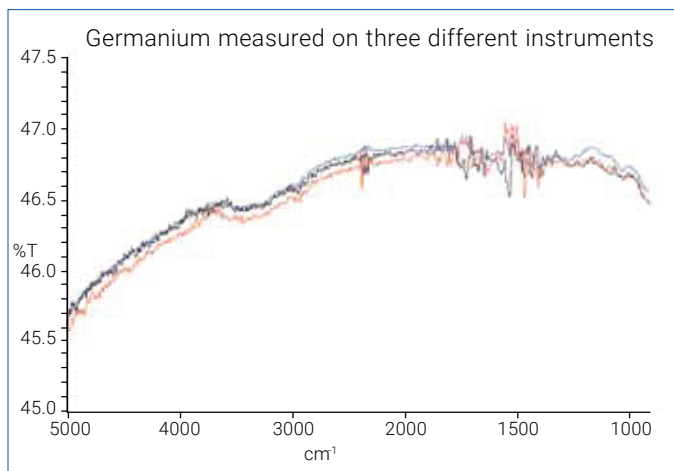


Figure 4: Germanium measured on three different Optica instruments

Effects of Sample Thickness

A known problem is that optically thick samples change the focusing of the beam at the detector, with the potential effect of reducing the apparent transmittance. In the Spectrum 3 Optica, the magnitude of this effect is controlled by using the variable apertures to limit the convergence of the beam at the sample.

This has been tested using germanium windows varying in thickness from 1 to 4 mm. For these thicknesses, the difference in transmittance is less than 0.2 %T above 1000 cm^{-1} (10 microns), where absorption is negligible. See Figure 5.

Wedged Samples

Optically thick samples where the faces are not parallel deflect the beam and can therefore give incorrect transmittance values. In the Spectrum 3 Optica, we have addressed this problem by a combination of conservative design and careful optical alignment. Each spectrometer is factory tested using a wedged germanium sample in different orientations to ensure correct optical alignment. Typical results for a sample with an 0.1 degree wedge are seen in Figure 6.

Measurement of Blocking Regions

FT-IR spectrometers, unlike those based on monochromators, do not suffer from 'stray light'. However because all wavelengths are measured together, the dynamic range of the interferogram is a potential problem. Any non-linearities in the electronics or digital processing lead to artifacts at multiples of the true wavenumbers. The Spectrum 3 Optica has a lower level of such artifacts than has been demonstrated on previous systems⁴. The transmission of the narrow band filter shown below is about 40% at 1596 cm^{-1} . With the Spectrum GX Optica there was an artifact at about 0.01%T at 3192 cm^{-1} , but with Spectrum 3 Optica any artifact is less than 0.005 %T. See Figure 7.

The freedom from artifacts means that measurements on blocking filters are limited only by resolution and noise level. A recommended test for FT-IR spectrometers is to measure totally absorbing bands in a film of polyethylene terephthalate⁵. At 4 cm^{-1} resolution, the strong bands can be seen to have transmittance well below 0.01 %T, 4 absorbance. This can be contrasted with dispersive IR spectrometers such as the PerkinElmer 983 where stray light is typically around 0.1 %T. See Figure 8. Spectral range

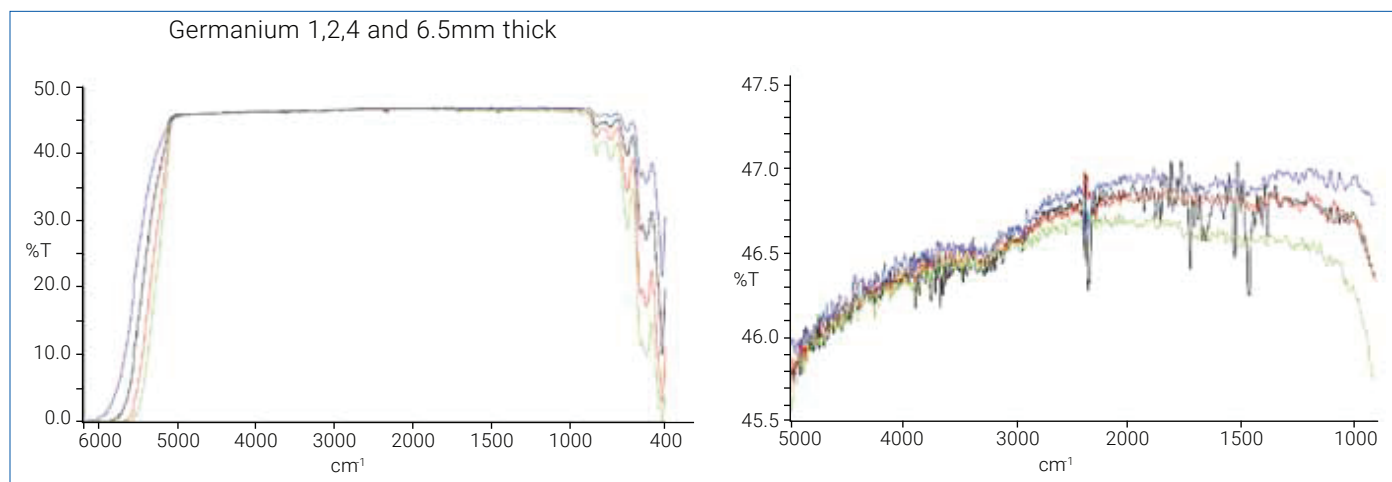


Figure 5: Transmittance of germanium windows of different thickness

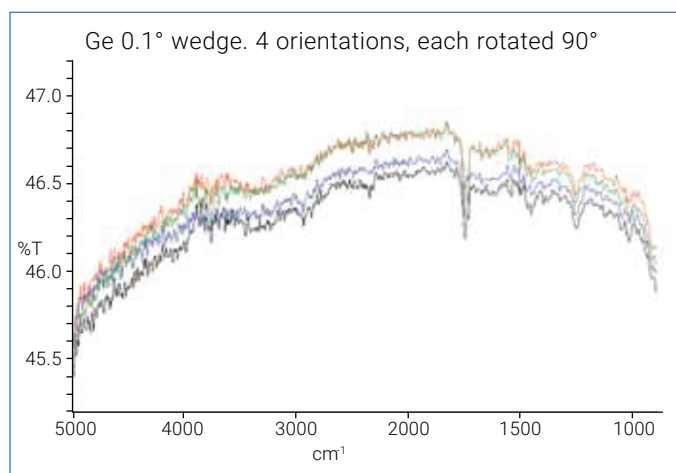


Figure 6: Measured transmission of wedged sample at different orientations

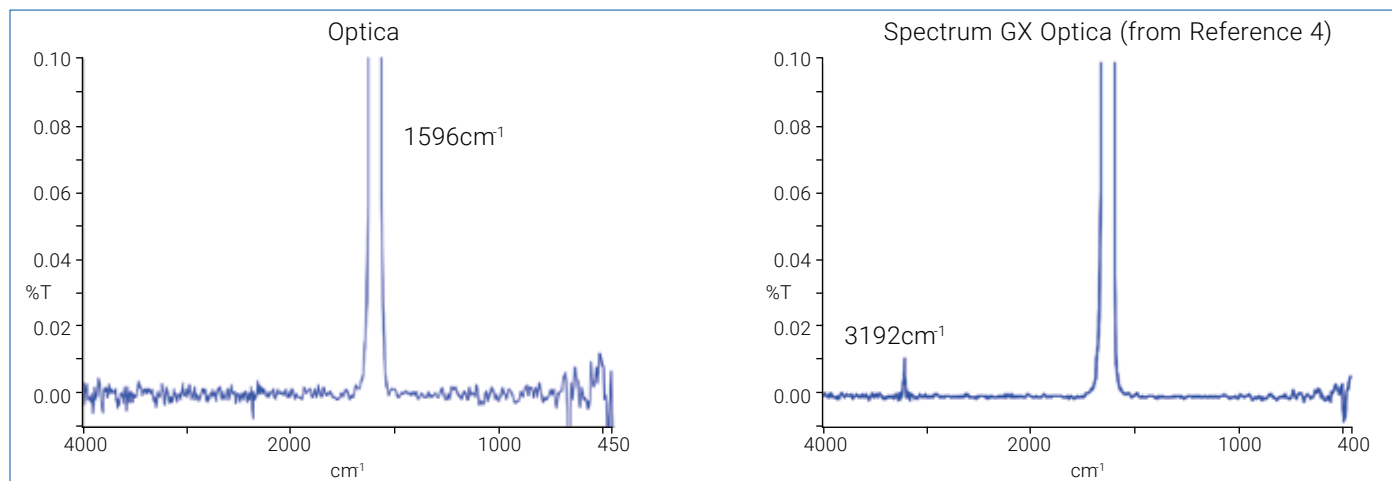


Figure 7: Measurement of a band pass filter with Spectrum GX Optica4 and with Spectrum 3 Optica

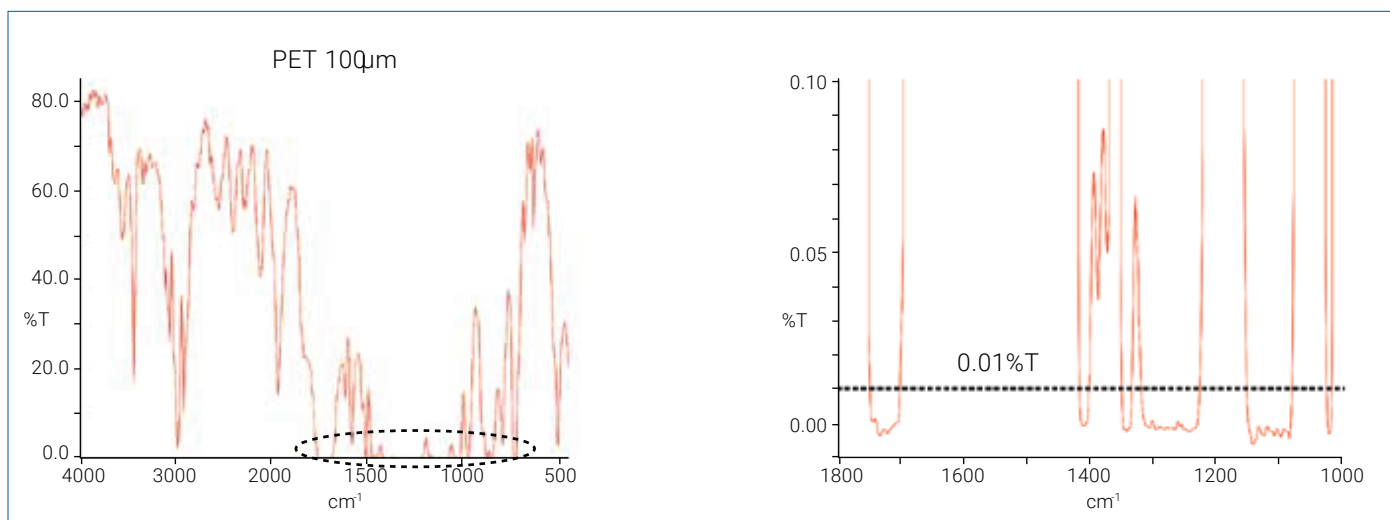


Figure 8: Totally absorbing bands of PET

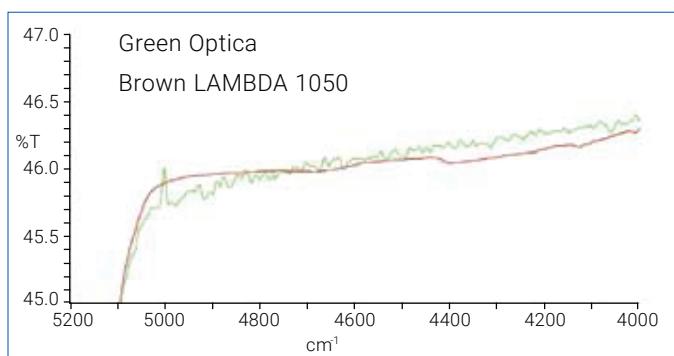


Figure 9: Comparison of Spectrum 3 Optica and LAMBDA 1050+ measurements of the same sample.

Spectral range

The accuracy specification is quoted for a range up to 5000 cm^{-1} (2.0 μm .) Spectra can be measured to 7800 cm^{-1} but there is a significant increase in noise at shorter wavelengths because of the low source output. The range extends well outside the traditional mid-IR region and overlaps with the PerkinElmer® LAMBDA 1050+ UV/Vis/NIR spectrophotometer. This instrument is the established standard for optical measurements and so can be used to verify the performance of the Spectrum 3 Optica in the NIR. As an example of the agreement between the two systems, the spectra of germanium in Figure 9 agree to within 0.1 %T.

Summary

In the development of the Spectrum 3 Optica, PerkinElmer has addressed the well known sources of error in the measurement of high refractive index materials with standard FT-IR instruments. In addition, a series of tests have proved that the highest levels of transmission accuracy are achievable with the Spectrum 3 Optica.

References

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4. R. Hunneman, R. Sherwood, C. Deeley and R. Spragg, Proceedings of the 11th International Conference on Fourier Transform Spectroscopy, 435-438, 1998.
5. P.R. Griffiths and J.A. de Haseth, Fourier Transform Infrared Spectroscopy (2nd edition), Wiley 2007.