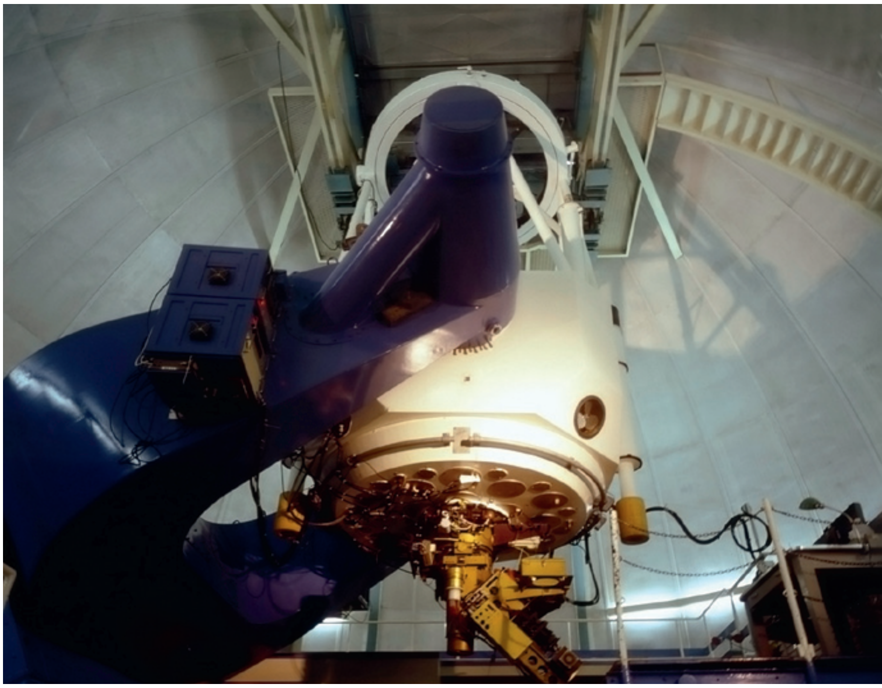

APPLICATION NOTE

FT-IR Spectroscopy

Authors

Dean H. Brown

Richard Spragg

PerkinElmer, Inc.
Shelton, CT 06484 USA

Instrumental Requirements for Accurate Analysis of Optical Components: A comparison of the PerkinElmer 983 Dispersive Spectrometer and the Frontier Optica FT-IR Spectrometer

Abstract

In the development of the Frontier™ Optica™, PerkinElmer has addressed the well known sources of error in the measurement of challenging optical materials with standard FT-IR instruments. The resulting improved performance over the previous standard of the optical industry is demonstrated by both the verification carried out internally, and also by that carried out by an external test laboratory.

Introduction

Measurements of optical components are some of the most challenging that can be made with an IR spectrometer (Figure 1). Since optical sensing systems can contain over 100 components, individual measurements require very high accuracy to minimize cumulative errors. The samples themselves present particular problems. Optical filters may themselves have 40 to 70 coating layers on a substrate with high refractive index. This affects the measurement by distorting the beam. They are often highly reflective, maximizing the potential errors from unwanted reflections.

For years the PerkinElmer® 983 double-beam dispersive IR spectrometer has been the standard for this industry. However dispersive instruments take longer to acquire a spectrum and do not benefit from the other advantages of FT-IR.[1]

PerkinElmer
For the Better

Whereas most analytical FT-IR applications are based on peak measurements relative to a baseline, performance of optical components is specified in terms of absolute transmittance and reflectance. Accurate measurement of these is critical in achieving and maintaining product specifications. As FT-IR spectrometers are single beam instruments, ordinate accuracy is more difficult to achieve due to changes in the baseline and other problems such as spectral artifacts and inaccurate transmittance values for such samples.[2] Despite attempts to make an FT-IR spectrometer for the optics market the PerkinElmer 983 has remained the standard for the industry.

In fact, over fifty sources of error have been reported in making accurate ordinate measurements by FT-IR.[2] Some of the problems that may be encountered include spurious reflections of beam involving source, interferometer, sample, windows and detector, distortion of beam at the detector by sample, signal digitisation errors, and detector and electronics linearity. For these reasons, an instrument would have to be designed specifically to overcome the challenges presented by the measurement of optical components using FT-IR.

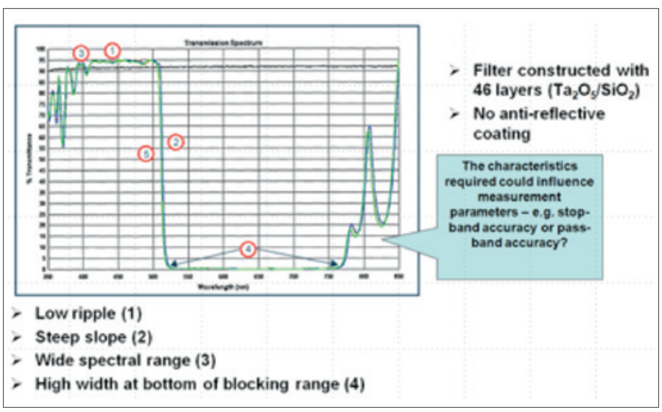

Figure 1. Typical optical filter spectrum.

Design

The Frontier Optica has been designed to eliminate inter-reflections involving the source, interferometer, sample, windows, and detector. There are baffles to block inter-reflections between the interferometer and the sample and source. All windows and the detector are angled to deflect reflections. To minimize the consequences of beam distortion by optically thick or wedged samples, the Optica has two variable apertures in the beam. These provide independent control of the size and of the convergence of the beam. The use of delta-sigma analog-to-digital conversion avoids the need for gain switching and ensures excellent linearity.[3] 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 the National Institute of Standards and Technology (NIST®) as a major source of error in FT-IR measurements of transmittance.[4] For that reason, lithium tantalate is used as the standard detector in the Optica.

Verifying performance

Verification of the performance also presents a challenge as there is no standard test for FT-IR ordinate accuracy in the mid-IR. Rotating sector mirrors were used to test dispersive IR spectrometers but they are not practical for FT-IR instruments because of the high modulation frequencies. In the absence of traceable high-refractive-index standards from national standards laboratories (e.g. NIST® or NPL) a common approach is to use %T values calculated from refractive indices that are known for high accuracy. Possible objections to this are that the bulk refractive index may not match that at the surface and that there may be scattering losses. A further issue is the influence of the sample on the beam geometry, defocusing or displacing the beam at the detector. A single test sample does not address the important practical issue of the sensitivity of the system to different sample thicknesses and to wedging.

The instrumental performance of the PerkinElmer Frontier Optica has been described by PerkinElmer[5] and some of the data is shown below. To further validate the performance of the instrument, it was tested by an independent laboratory that routinely measures optical components.

PerkinElmer Verification

Comparison with values calculated from refractive indices

For 1 mm thick germanium measured on several instruments, the results agree well with refractive index calculations between 4000 and 900 cm^{-1} (2.5 and 11 microns), but

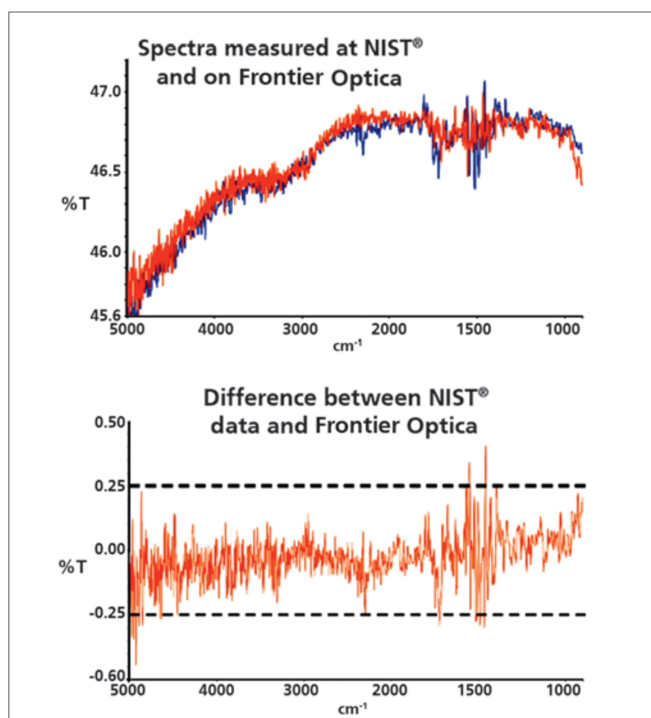

Figure 2. Comparison with NIST® measurements for germanium.

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. To address this inconsistency we had the samples measured at NIST®. The values measured at NIST® and at PerkinElmer differed by less than 0.1 %T over the range 5000 to 900 cm^{-1} (2 to 11 microns) (Figure 2).

Agreement between the transmittance values for the same sample measured on three different Optica spectrometers was generally better than ±0.1 %T outside regions of atmospheric absorption (Figure 3). The features seen between 1800 and 1300 cm^{-1} result from interaction between narrow water vapor lines and the channel spectra (fringes) of the sample.

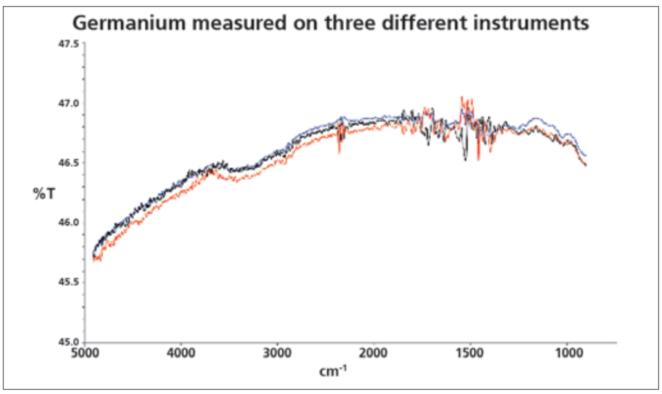

Figure 3. Germanium measured on three spectrometers.

The transmittance of germanium is about 47 %T. To test performance at other transmittance values, zinc selenide (70 %T) and calcium fluoride (94 %T) were measured. The results were compared 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.

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 Frontier 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 6.5 mm. Above 1000 cm^{-1} (10 microns), where absorption is negligible, the difference in transmittance is less than 0.2 %T for thicknesses up to 4 mm. A 6.5 mm thick sample shows similar values above 2000 cm^{-1} (5 microns) and appears to have increased absorption at longer wavelengths (Figure 4).

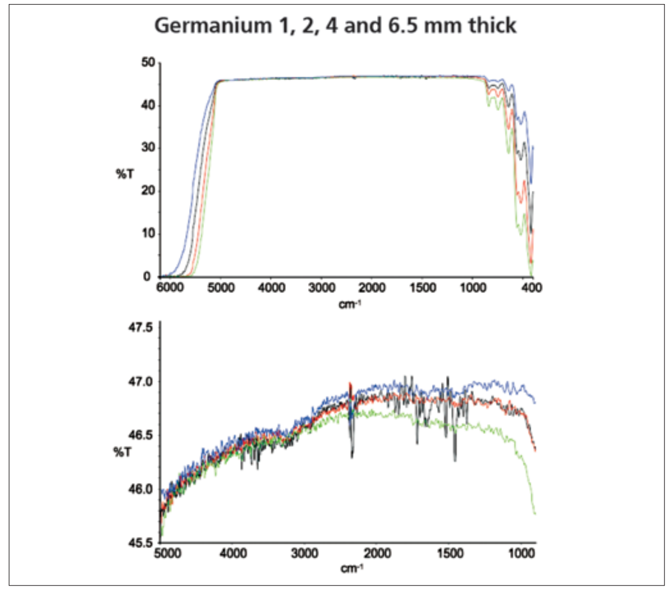

Figure 4. Germanium samples of different thickness.

Wedged samples

Optically thick samples where the faces are not parallel are often encountered in practice. They deflect the beam and can therefore give incorrect transmittance values. In Frontier 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 optimum optical alignment. Typical results for a sample with a 0.1 degree wedge show a maximum variation less than 0.25 %T (Figure 5).

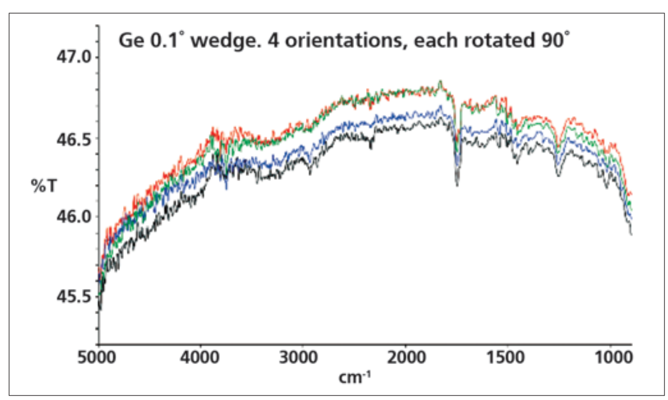

Figure 5. Germanium sample with 0.1 degree wedge.

Measurement of blocking regions

As a basic principle of operation, FT-IR spectrometers do not experience the stray light that can occur in instruments based on monochromators. However, unwanted reflections involving the interferometer produce artifacts where spectral features appear at double their true wavenumbers. The

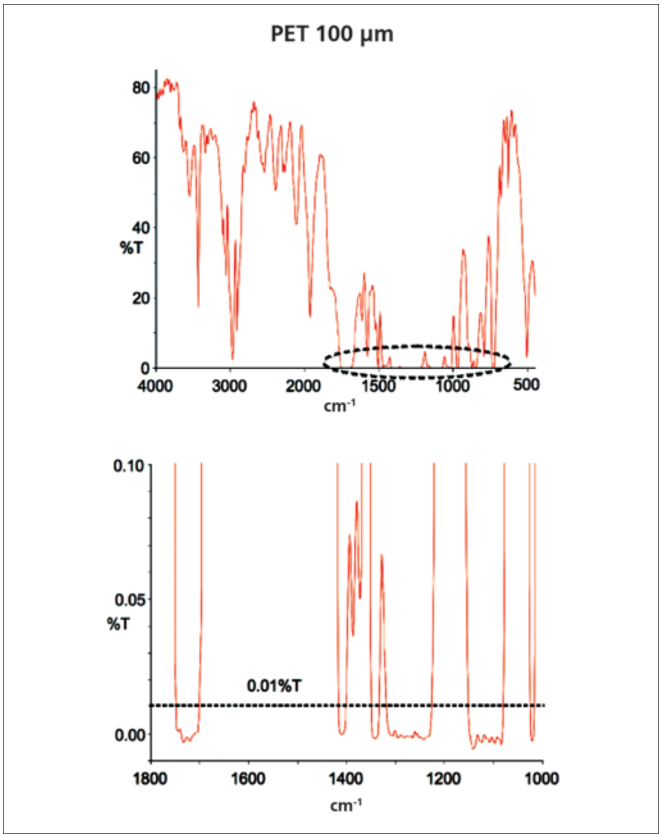

Figure 6. Totally absorbing bands of PET.

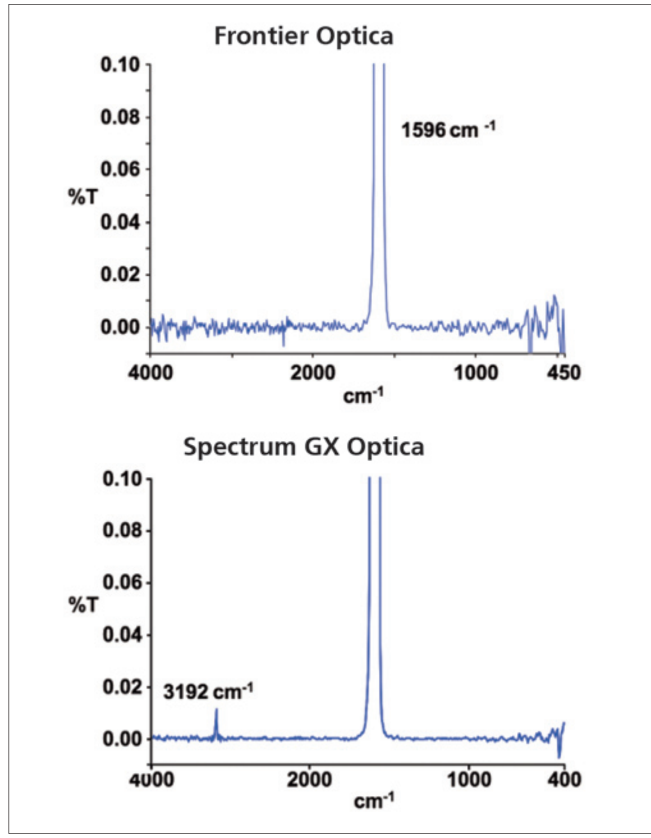

Figure 7. Narrow band pass filter, comparison with GX Optica.

dynamic range of the interferogram is another potential problem because all wavelengths are measured together. Any non-linearities in the electronics or digital processing lead to artifacts at multiples of the true wavenumbers. A recommended test for non-linearities is to measure totally absorbing bands in a film of polyethylene terephthalate[6] (Figure 6). 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.

The Frontier Optica has a lower level of such artifacts than has been demonstrated on previous systems.[7] 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 Frontier Optica any artifact is less than 0.005 %T (Figure 7).

Independent laboratory results

Optica 100 repeatability measurement

Because FT-IR instruments operate in a single beam mode, any drift between background and sample measurements would affect transmittance values. A germanium crystal was measured over a period of four hours to test the stability. The sample was removed from the instrument between measurements but the background was not renewed. The standard deviation of the measurements is shown in Figure 8. It is below 0.001 (0.1% T) for most of the range, increasing to about 0.25 %T at 2 µm (5000 cm^{-1}).

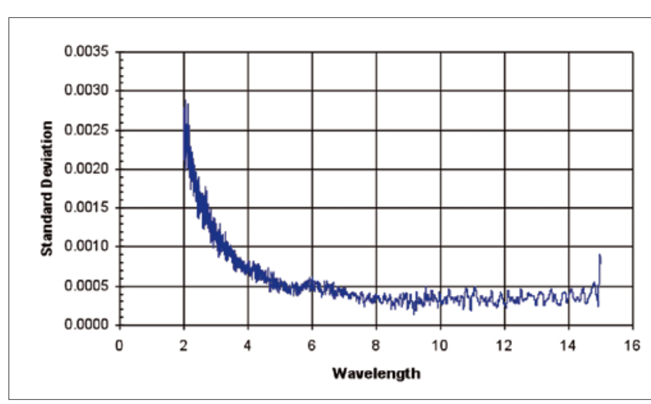

Figure 8. Standard deviation for transmittance measurements of germanium over four hours.

Optical 100 accuracy measurement

Accuracy was tested by measuring the reflectance of high refractive index samples designed so that reflection from the front surface was only detected. This avoids any problems associated with interference from back-surface reflection.

For silicon, the reflectance calculated from refractive index is close to 0.30 (30 %R). The observed values are about 0.1 %R lower than theoretical (Figure 9). The spectra show a small peak around 9.2 µm indicating the presence of silicon dioxide on the surface. The discrepancy between observed and calculated values is attributed to this. For zinc selenide, the observed and calculated values agree to better than 0.1 %R, essentially to within noise level (Figure 10).

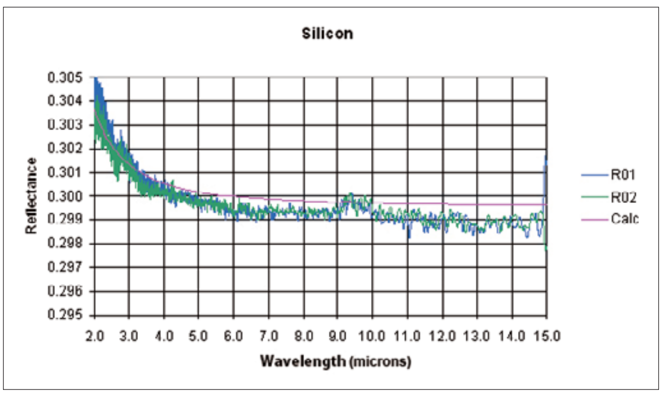

Figure 9. Comparison of theoretical and measured single-surface reflectance for silicon.

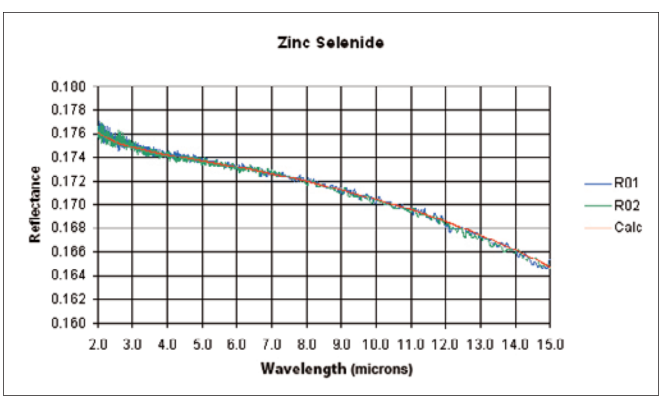

Figure 10. Comparison of calculated and measured single-surface reflectance for zinc selenide.

Summary

In the development of the Frontier 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 has proved that the highest levels of transmission accuracy are achievable with the Frontier Optica. The Frontier Optica outperforms the previous standard of the optical industry, the PerkinElmer Model 983.

References

1. P.R. Griffiths and J.A. de Haseth, *Fourier Transform Infrared Spectroscopy* (2nd edition), Wiley, 2007.
2. J.R. Birch and F.J.J. Clarke, *Anal. Chim. Acta* **380,** 369, (1999).
3. J.W. Brault, *Applied Optics* 35 (16), (1996).
4. S.G. Kaplan, L.M. Hanssen and R.U. Datla, *Applied Optics* 36 (34), 8896-8907 (1997).
5. PerkinElmer Technical Note 008136_02.
6. B.T. Bowie and P.R. Griffiths, *Applied Spectroscopy* 54(8), 1192-1202, (2000).
7. R. Hunneman, R. Sherwood, C. Deeley and R. Spragg, *Proceedings of the 11th International Conference on Fourier Transform Spectroscopy,* 435-438, 1998.

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

009527_01