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NIST–NPL comparison of mid-infrared regular transmittance and reflectance

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Abstract

The National Institute of Standards and Technology (NIST) and the National Physical Laboratory (NPL) realize independent scales for regular transmittance and near-normal regular reflectance in the mid-infrared part of the spectrum. Comparisons of these scales have recently been completed and the results are reported here. The agreement was excellent, lying within the quadrature combined uncertainties for the great majority of values measured and within the simple sum of uncertainties in all cases, demonstrating the level of equivalence of the NIST and NPL scales.

1. Introduction

The mutual recognition arrangement (MRA) requires that the metrological equivalence of national measurement standards be based on the results of comparisons which follow the guidelines established by the BIPM [1]. Comparisons of regular transmittance and regular reflectance in the mid-infrared part of the spectrum satisfying these guidelines have recently been completed between the National Institute of Standards and Technology (NIST) and the National Physical Laboratory (NPL). These comparisons are the first of their kind in the mid-infrared and the results are reported here.

2. Measurement techniques

Major differences exist between the techniques used at NIST and NPL to realize these scales [2]. NIST uses Fourier transform (FT) spectrometers, whereas NPL has so far used grating spectrometers. Secondly, NIST uses an improved integrating sphere system [3, 4] for both transmittance and reflectance measurements, whereas NPL uses focusing optical systems with no diffusing components [5, 6].

The comparisons addressed the standard manner in which NIST and NPL disseminate their scales. The NIST technique is a direct absolute technique, and therefore each artefact is independently calibrated. NPL calibrates an artefact relative to in-house reference standards that have been previously calibrated absolutely. There is a very small degradation in uncertainty, but since the reference standards are similar to the artefacts, a like-with-like measurement is carried out which relaxes most of the stringent experimental conditions required for absolute calibrations.

The NIST primary scales and measurement facility is based on a Bio-Rad[3] FTS-60A FT-IR spectrometer with a custom-built external integrating sphere assembly where corrections are applied for sphere non-ideality [3, 4].

The NPL primary scales are established using modified Perkin–Elmer PE580B and PE983G grating IR spectrometers. These instruments are also used to calibrate the NPL reference standards as well as customer artefacts. For regular reflectance, a VW reflectometer technique is used to establish an absolute calibration, and relative calibrations are made using a V-only substitution technique [5, 6].

3. The comparison

The measurement sequence was NPL–NIST–NPL. Measurements were carried out between 2.5 μm (4000 cm^{-1}) and 18 μm (550 cm^{-1}), the spectral range common to both laboratories. The comparison of regular reflectance was limited to near-normal incidence, as large angles introduce further complications which may be addressed in future.

3.1. Description of artefacts

3.1.1. Transmittance artefact. An NPL transmittance transfer and QA standard was used. This consists of an optically worked filter of Schott NG11 optical glass, a material

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[3] The identification of any commercial product or trade name does not imply endorsement or recommendation by NIST.

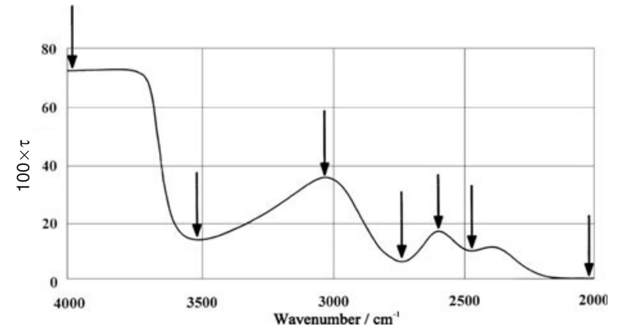

Figure 1. Typical transmittance spectrum of 1 mm of Schott NG11 glass.

known from some 50 years' work in visible region standards to be very stable for transmittance, provided that it is not cleaned repeatedly using fluids. (These can slowly leach out the metal oxide constituents, leaving a silica-rich residual surface layer of reduced refractive index.) The thickness is nominally 1 mm, which gives a very useful selection of transmittance levels at portions of the spectrum with zero gradient and low enough second derivative to eliminate significant influence from wavenumber error or inadequate resolution. As a consequence stray light (grating) or apodization fall-off (FT) are not likely to be critical or even need correction. These levels are at about 73%, 36%, 17%, 14%, 10%, 6% and just above 0% as shown in figure 1. The standard therefore samples enough values to reveal any problems with non-linearity of response, zero-offset error or scaling error due to imperfect substitution with respect to the reference readings. The 1 mm thickness is thin enough, in conjunction with the refractive index of only 1.45, to minimize problems of beam shift, beam size or focal shift, yet it is thick enough to eliminate problems of interference fringing at all but the highest resolutions possible on normal analytical instruments. In addition, it has the useful property of being insensitive to multiple modulation effects in FT instruments caused by interreflections between sample and interferometer.

3.1.2. Reflectance artefacts. Three flat samples were used—a non-overcoated aluminized glass mirror, a NiCr coating on a glass substrate and an uncoated plate of 6 mm thick Schott BK7 optical glass. The first sample has a very high reflectance (about 98% to 99%), the second has a progressive change of reflectance from about 84% to about 92%, while the third has a more complex spectrum including a long flat low-reflectance region with a narrow peak of about 40% and variable values at the low-wavenumber end. These three samples therefore cover a large range of reflectance values, as shown in figure 2. They also have zero or very low transmittance, and therefore no reflected component from the back surface. BK7 does suffer from this drawback from 4000 cm^{-1} to 3600 cm^{-1}, so while measurements were generally made from 4000 cm^{-1} to 550 cm^{-1} at intervals of 10 cm^{-1}, measurements for BK7 were only made from 3600 cm^{-1}.

3.2. Results for transmittance comparison

3.2.1. Results. The NIST measurements were carried out at $f/6$ with 8° incidence at 23.5 °C, and at 8 cm^{-1} and 16 cm^{-1} spectral bandwidths. The NPL measurements were carried out at $f/6.5$ with 5° incidence at 27 °C. The NPL reference standard was calibrated on two different instruments with bandwidths varying from 9.5 cm^{-1} to 5.5 cm^{-1}, and from 17.5 cm^{-1} to 6.5 cm^{-1}, going from high to low wavenumber. Neither laboratory observed significant differences due to bandwidth. The reported uncertainties are given in table 1.

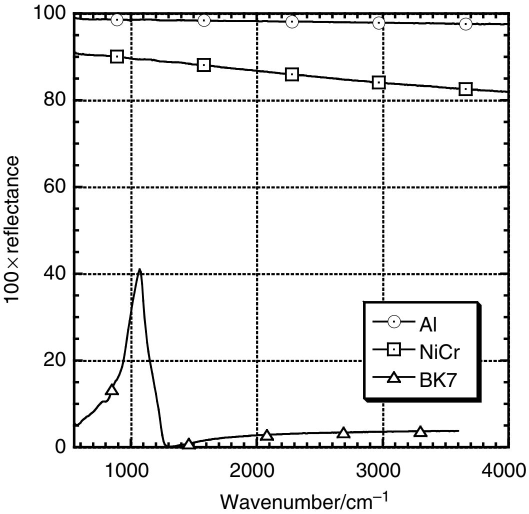

Figure 2. Reflectance curves of the three artefacts (NIST measurements).

The measured values were corrected to a common basis of 0° incidence and 26 °C for randomly polarized incident light. The difference in correction between $f/6$ and $f/6.5$ is negligible. For the NPL measurements, corrections were done from a state of 5° incidence and 29 °C, which were the conditions under which the reference standard (a 1 mm Schott NG11 glass filter NPL no 7) had been calibrated. The polarization bias of the NPL spectrometers was measured, while the NIST measurements were taken to be as for random polarization.

In order to facilitate these corrections NPL made a reassessment of the corrections for tilt, solid angle and polarization that are valid for the Schott NG11 glass transfer standards. These corrections are discussed in [5, 7] and use the same equations as Mielenz and Mavrodineanu [8]. The uncertainties ($k = 1$) due to the temperature correction were 0.008% transmittance for both laboratories, except at 2010 cm^{-1} where it was 0.000%. The uncertainties for the tilt correction (including polarization in the case of NPL) came to 0.005% for both laboratories, except at 2010 cm^{-1} where it was

Table 1. Uncertainties for NIST and NPL measurements.

Wavenumber/ cm^{-1}	100 × Expanded combined uncertainty ($k = 2$)	
	NPL mean	NIST
3990	0.151	0.150
3512	0.055	0.042
3031	0.107	0.072
2739	0.041	0.029
2598	0.070	0.039
2473	0.048	0.029
2010	0.009	0.018

Table 2. Summary of results for transmittance comparison after inclusion of thermochromism and tilt corrections and their uncertainties.

Wavenumber/ cm^{-1}	100 × Transmittance NPL mean: 2000, 2001	100 × Transmittance NIST: 2000	100 × Expanded combined uncertainty ($k = 2$) NPL mean	100 × Expanded combined uncertainty ($k = 2$) NIST	100 × Quadrature sum of uncertainties: NPL mean, NIST	100 × Simple sum of uncertainties: NPL mean, NIST	100 × Difference of values: NPL mean minus NIST
3990	72.925	72.79	0.152	0.151	0.215	0.303	0.135
3512	14.40	14.315	0.058	0.046	0.074	0.104	0.085
3031	35.68	35.57	0.109	0.074	0.132	0.183	0.110
2739	6.35	6.29	0.045	0.035	0.057	0.080	0.060
2598	16.855	16.835	0.072	0.043	0.084	0.116	0.020
2473	9.985	9.94	0.052	0.035	0.062	0.086	0.045
2010	0.0114	0.0160	0.009	0.018	0.020	0.027	−0.004

Table 3. NIST uncertainty budget for NG11 glass measurement at 35% transmittance peak, showing standard uncertainty components and combined expanded ($k = 2$) uncertainty.

Source of uncertainty	100 × u_i
Type B standard uncertainty component	
Interreflections	0.004
Detector non-linearity	0.015
Atmospheric absorption variation	0.007
Inequivalent sample/reference beam geometry	0.018
Retroreflected light lost from entrance port	0.007
Sample port overfill	0.004
Beam geometry, polarization	0.011
Phase errors	0.018
Quadrature sum	**0.033**
Type A standard uncertainty component	0.015
Thermochromism correction to 26 °C	0.008
Correction from 8° angle to 0°	0.005
Expanded uncertainty ($k = 2$)	**0.074**

Table 4. NPL uncertainty budget for 35% transmittance peak of NG11 glass, showing standard uncertainty components and combined expanded ($k = 2$) uncertainty.

Source of uncertainty	Absolute calibration of reference artefact 100 × u_i	Relative calibration of comparison artefact 100 × u_i
Repeatability (std. dev. of mean) [Type A]	0.010	0.019
Effect of off-axis angle (beam displacement)	0.022	0.005
Uncertainty of angle	0.003	0.001
Non-flatness, non-parallelism	0.007	0.020
Instrument non-linearity	0.035	0.001
Zero offset correction not fully valid	0.003	0.000
Residual ordinate scaling error	0.007	0.010
Uncertainty of temperature	0.007	0.002
Thermochromic correction	0.005	0.001
Residual sample interreflections at 5° angle	0.018	0.012
Residual interreflections through sample position	0.016	0.000
Wavenumber error	0.014	0.002
Combined uncertainty (relative value scaling)		**0.032**
Combined uncertainty (absolute scaling)		0.012
Uncertainty of reference standard (absolute scaling)		0.052
Correction from 5° angle to 0°, including polarization		0.005
Correction to 26 °C		0.008
Combined uncertainty (absolute scaling)	**0.052**	**0.054**
Expanded uncertainty (absolute scaling) ($k = 2$)	**0.104**	**0.109**

0.001%. Table 2 summarizes the results of the transmittance comparison after these corrections and their uncertainties have been included.

3.2.2. Uncertainties. Table 3 lists the significant uncertainty components for the NIST transmittance measurement, with values for the 35% transmittance peak given as an example. Other potentially important sources of error in the measurement, such as interreflections, non-source emission, sample non-uniformity and scattering, were not significant for this measurement. The type A component is evaluated from the standard uncertainty in the mean of repeated measurements.

The uncertainties in the NPL measurements arise from two processes: (i) calibration of the reference artefact; (ii) relative measurement of the comparison artefact. Table 4 gives the uncertainty budget for the 35% transmittance level as an example.

In table 2, mean NPL values are used to evaluate the comparison in order to make use of all the measurements. Type B uncertainties dominate, and the overall $k = 2$ uncertainties for the first and second NPL measurements are at most 0.001% transmittance units greater than the uncertainty for the NPL mean.

3.2.3. Analysis. The measurements of all but two of the features lie well within the quadrature combined uncertainties of the two laboratories, while the remaining two measurements, at 3512 cm^{-1} and 2739 cm^{-1}, lie within the simple combined uncertainty. This may be due to a small bias between the laboratories, since the NPL values are generally larger than those of NIST. However, there is no evidence that the uncertainties have been understated by either laboratory.

3.3. Results for reflectance comparison

3.3.1. Results. The NIST measurements were carried out at $f/6$ with 8° incidence at 23.5 °C. Random polarization was assumed. In order to obtain values at integer wavenumber, cubic-spline fitting was applied to the data in order to calculate

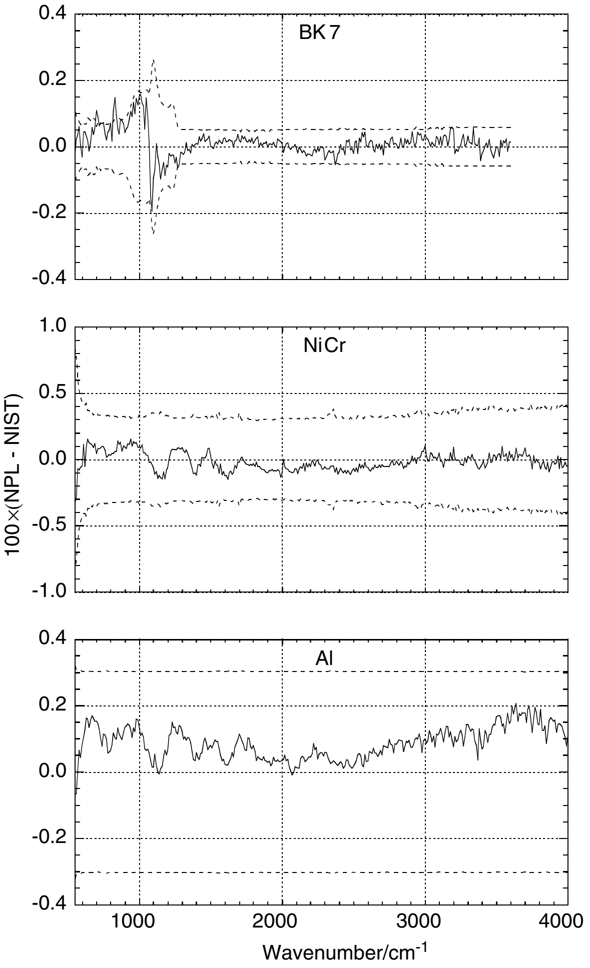

Figure 3. Spectra comparing the results and uncertainties of the reflectance measurements. In each plot, the full curve is the difference between the NPL and NIST results; the dotted curves are the combined uncertainties of the two measurements.

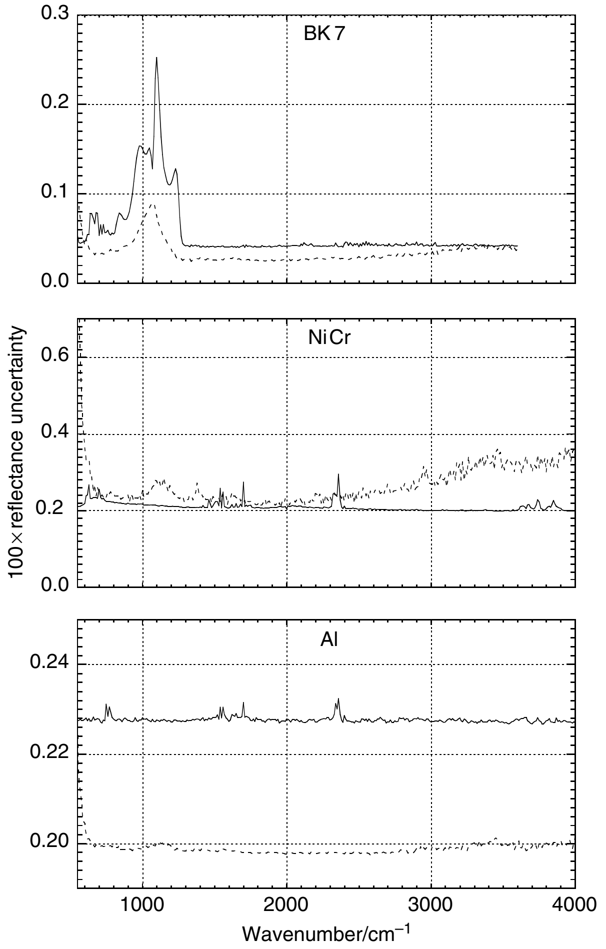

Figure 4. Uncertainties ($k = 2$) for NIST (· · · · · ·) and NPL (——) reflectance measurements.

Table 5. NIST uncertainty budget for BK7 glass measurement at the 40% reflectance peak.

Source of uncertainty	$100 \times u_i$
Type B standard uncertainty component	
Interreflections	0.013
Detector non-linearity	0.011
Atmospheric absorption variation	0.004
Beam flip	0.010
Inequivalent sample/reference beam alignment	0.030
Retroreflected light lost from entrance port	0.012
Entrance port overfill	0.005
Sample port overfill	0.004
Beam geometry, polarization	0.020
Phase errors	0.006
Quadrature sum	**0.044**
Type A standard uncertainty component	0.015
Expanded uncertainty ($k = 2$)	**0.093**

interpolated values at 10 cm^{-1} intervals from the original data, which had a wavenumber spacing of 7.7 cm^{-1}.

The NPL measurements were carried out at $f/5.9$ with 10° incidence at 27 °C. The reference standard used was reference mirror OG65, which has an approximately uniform spectral reflectance of 98% to 99%. Corrections for polarization bias were derived from supplementary investigations, and the values were corrected to a common basis for randomly polarized incident light, for which the differences in reflectances between 8° and 10° are negligible.

No temperature corrections were applied as there was no evidence of significant thermochromism for these samples, and no thermochromic coefficients were known of.

The results of the reflectance comparison are shown in figure 3. In each figure the full curve shows the difference between the NPL mean and NIST, while the dotted curves denote the range of the quadrature sum of uncertainties. Figure 4 shows the expanded ($k = 2$) uncertainties for NIST and NPL.

3.3.2. Uncertainties. Table 5 lists the uncertainty components for the NIST reflectance measurements, with example values from the 40% reflectance peak in the BK7 spectrum. Two additional potential sources of error not present in the transmittance measurement are beam flip due to the reflection from the sample and entrance port overfill. The relative uncertainty values for the other two samples are similar. The NPL uncertainties have absolute and relative calibration components as for transmittance, and table 6 gives

Table 6. NPL uncertainty budget for BK7 glass measurement at the 40% reflectance peak.

Source of uncertainty	Absolute calibration of reference artefact $100 \times u_{\mathrm{i}}$	Relative calibration of comparison artefact $100 \times u_{\mathrm{i}}$
Repeatability	0.013	0.014
Imperfect alignment of VW mirror and sample aperture, and the spectrophotometer with the reflectometer	0.097	0.020
Instrument non-linearity	0.002	0.036
Zero offset correction not fully valid	0.001	0.012
Residual ordinate scaling error	0.019	0.008
Possible residual interreflections across sample position	0.001	0.016
Wavenumber error	0.001	0.000
Combined uncertainty (relative scaling)		**0.049**
Combined uncertainty (absolute scaling)		0.048
Uncertainty of reference standard (absolute scaling)		0.100
Polarization bias correction		0.013
Combined uncertainty (absolute scaling)	**0.100**	**0.112**
Expanded uncertainty (absolute scaling) ($k = 2$)	**0.200**	**0.224**

the uncertainty budget for the 40% reflectance level as an example.

3.3.3. Analysis. For the aluminized mirror and the NiCr coating there are no differences that exceed the quadrature sum of the expanded uncertainties of each laboratory's measurements, and hence there is excellent agreement between the laboratories.

For the uncoated BK7 glass there is also excellent agreement over most of the spectrum. However, there are three short regions of the spectrum, from 1280 cm^{-1} to 1270 cm^{-1}, from 840 cm^{-1} to 800 cm^{-1} and from 750 cm^{-1} to 700 cm^{-1}, where the difference between NIST and NPL exceeds the quadrature sum but not the simple sum of uncertainites. In addition, at 830 cm^{-1} and at 700 cm^{-1} the difference exceeds the simple sum of uncertainties by 0.03 percentage reflectance units.

These discrepancies arise in spectral regions with appreciable spectral gradients of reflectance, and hence wavenumber error, resolution or lineshape may be responsible. Extra tests with additional ammonia absorption lines in these regions have suggested that the problem does not arise from wavenumber scale errors. The NIST measurements were made at 8 cm^{-1} and 16 cm^{-1} bandwidths, and no appreciable differences were found. The bandwidth for the NPL measurements was approximately 3.4 cm^{-1} to 4.2 cm^{-1} in the three spectral regions concerned.

The number of data points where the quadrature sum of uncertainties is exceeded is 13 out of a total of 306, or under 5%, which is consistent with the 95% level of uncertainty used.

4. Conclusions

A comparison of regular transmittance and near-normal reflectance scales in the mid-infrared spectral region has been carried out between NIST and NPL. Three front-surface reflectance artefacts and one transmittance artefact, covering three decades of dynamic range on the ordinate scale, were measured under ambient conditions. No evidence of systematic discrepancies outside the combined uncertainty limits was found in comparing the measurement results from the two laboratories.

Despite the large differences in experimental apparatus and measurement approach between the two laboratories, the good agreement tends to support their stated uncertainties, and to demonstrate the applicability of high-quality standard artefacts for quality assurance checking of mid-infrared spectrophotometers.

Acknowledgments

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References

[1] Quinn T J 1999 *Guidelines for Key Comparisons Carried out by Consultative Committees* (Sèvres: BIPM)

[2] Clarke F J J 2002 *Handbook of Vibrational Spectroscopy* ed J M Chalmers and P R Griffiths (Chichester: Wiley) pp 891–8

[3] Kaplan S G and Hanssen L M 1999 *Anal. Chim. Acta* **380** 303–10

[4] Hanssen L M 2001 *Appl. Opt.* **40** 3196–204

[5] Clarke F J J 1999 *Anal. Chim. Acta* **380** 127–41

[6] Clarke F J J 1996 *Proc. SPIE* **2776** 184–95

[7] Chunnilall C J, Clarke F J J and Rowell N L 2003 *Proc. SPIE* **4826** to be published

[8] Mielenz K D and Mavrodineanu R 1973 *J. Res. NBS.* **77A** 699–703