Accurate measurement of absorption spectra and refractive index of glass by Spectrophotometry

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Abstract

The experimental methods for determining optical constants like refractive index and absorption coefficient often require specialized equipment. An instrument that is standard equipment in most laboratories where optical materials are being characterized is the spectrophotometer. This type of instrument is widely used for the measurement of reflectance and transmittance spectra at wavelengths ranging from 200 nm up to 50,000 nm. The paper aims to present a state-of-the-art overview of methods for determination of the optical constants of glass by Spectrophotometry. Examples are given for various types of glasses and applications under room temperature as well as elevated temperatures.

Introduction

Many applications for glass in devices such as interference filters, optical fibers, optical instruments, coated glazing for windows and solar energy collectors, require an accurate knowledge about the refractive index and absorption of glass over wide ranges of wavelengths. Furthermore, there is an increasing need for these properties at forming and melting temperatures to improve the radiation heat transfer calculations in glass process modelling.

An instrument, which is standard equipment in most laboratories where optical materials are being characterised, is the spectrophotometer. This type of instrument is widely used for the measurement of reflectance and transmittance spectra at wavelengths ranging from 200 nm up to 50,000 nm, mostly by irradiation at (near-)

normal incidence. It is therefore advantageous to use a method by which the optical constants of a material can be derived from its normal transmittance and (near) normal reflectance spectra, which are relatively easy to measure. After a short discussion of the optical constants of glass and their relation with reflection and transmission spectra, a state-of-the-art overview is given of the various methods.

Interaction of electromagnetic waves with glass

The interaction of electromagnetic waves with matter causes a mutual displacement of the positive and negative charges within a neutral atom or molecule. In the linear approximation this results in a dipole moment per unit volume, proportional to the electric field intensity by a dimensionless constant χ_e known as the electric susceptibility. The electric flux density is also proportional to the electric field intensity by a dimensionless constant ε_r known as the relative permittivity (or dielectric function). Between these two material constants exists the relation $\varepsilon_r \equiv 1+\chi_r$ [1]. The permittivity and susceptibility are in fact wavelength dependent functions representing electron transitions, optical vibrations, and other electric and magnetic effects. The relative permittivity is a complex variable $\tilde{\varepsilon}_r = \varepsilon_1 - i\,\varepsilon_2$, which for a nonmagnetic material like glass is related to the complex refractive index $\tilde{n} = n - i\,\kappa$ by the definition $\tilde{n} = \sqrt{\tilde{\varepsilon}_r}$ [1]. The real and imaginary parts of the complex refractive index of a material are commonly referred to as its optical constants.

For non-crystalline solids, the dispersion model by Efimov [2]

$$\tilde{\varepsilon}_r(\omega) = \varepsilon_\infty + \sum_j \left\{ \frac{S_j}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \frac{\exp\left\{-(x-\omega_j)^2/2\sigma_j^2\right\}}{x^2-\omega^2-i\gamma_j\omega} dx \right\} \quad , \qquad (1)$$

based on the convolution of Lorentzian and Gaussian functions has proven to give an adequate description of the wavelength dependency of the optical constants in terms of the various vibrational excitations. In Eq.(2), x is the variable oscillator frequency, S_j and ω_j respectively the strength and the central frequency for the j-th oscillator distribution, and σ_j is the standard deviation for this distribution.

Reflectance and transmittance

The reflectance of electromagnetic radiation at an interface between two media is determined by Fresnel's equations and depends on the refractive indices of the two media, the angle of incidence and the polarisation state of the incident radiation. A typical measurement situation for spectrophotometry of glass samples is normal incidence, for which the power reflectance R at the glass - interface is related to the amplitude reflectance r and the optical constants through [1]:

$$R = |\tilde{r}|^2 = |\frac{\tilde{n} - n_a}{\tilde{n} + n_a}|^2 = \frac{(n - n_a)^2 + \kappa^2}{(n + n_a)^2 + \kappa^2} \quad , \tag{2}$$

in which n_a is the constant refractive index of air, assumed to be real, and ñ the complex refractive index of the medium.

The power transmission coefficient T of a planar sample with a thickness that is large as compared to the coherence length can be given in terms of its internal power transmittance τ and the power reflection coefficient R (according to Eq.(2)) at its surface, by the formula [3]

$$T = (1 - R)[\tau + R^2\tau^3 + R^4\tau^5 + \ldots](1 - R) = \frac{(1 - R)^2\tau}{1 - R^2\tau^2} \quad , \tag{3}$$

in which (1 - R) is the power transmittance through the air - sample interface and where the terms between square brackets represent the total internal power transmittance, taking into account multiple internal reflections. In a similar manner, the total power reflection coefficient R_{tot} can be derived, resulting in

$$R_{tot} = R + (1 - R)[\tau + R^2\tau^3 + R^4\tau^5 + \ldots]R\tau(1 - R) = R(1 + \tau T) \quad . \quad , \tag{4}$$

in which the internal transmittance τ of a glass sample of a given thickness d is a function of the absorption coefficient K according to

$$\tau = \exp\{-Kd\} \quad . \tag{5}$$

The absorption coefficient is related to the imaginary part of the complex refractive index according to $K = 4\pi\kappa/\lambda$, where λ is the wavelength.

Measurement of the refractive index of transparent samples

By inverting (2) we obtain a simple equation for the calculation of the refractive index from the air - glass interfacial reflection:

$$\frac{n}{n_a} = \frac{1+R}{1-R} + \sqrt{\left(\frac{1+R}{1-R}\right)^2 - 1 - \left(\frac{\kappa}{n_a}\right)^2} \approx \frac{\sqrt{R}-1}{\sqrt{R}+1} \quad . \tag{6}$$

The approximation is valid for sufficiently low values of κ, resulting in an uncertainty in the refractive index

$$\delta n = \frac{(n+1)^3}{n-1}\frac{\delta R}{4} + \frac{n\kappa^2}{n^2-1} + n\,\delta n_a \quad , \tag{7}$$

in which δR and δn_a are the uncertainties in the measured reflectance and the refractive index of air. For values of the absorption index κ <0.01 (transparent range) and n_a = 1.00030 $\pm$ 0.0003 [4], the first term is dominant. For a relative uncertainty $\delta R/R$ = 0.5%, the relative uncertainty $\delta n/n$ is < 0.2% for n < 1.8.

For this type of measurement it is really important to make sure that reflected radiation from the back reflectance of the sample does not reach the detector. The best way to guarantee that is make a sample with a sufficiently tilted back surface. A simply roughened or black painted back surface will still cause some stray radiation into the detector.

Figure 1 shows a result obtained by this method on Chalcogenide glass of the composition Te20As30Se50. A cylindrically shaped sample of this glass was cut in a plane along the axis and polished in this plane. The cylindrical back surface causes the reflectance from this surface to be scattered and dispersed so that only the reflectance of the flat polished front surface is measured. A smooth curve for n was obtained by fitting a 3-term Sellmeier equation. Data obtained in the Visible range (not shown in figure 1) was also included in the fit. The error band in the graph was determined using Eq.(7).

The triangles mark the values obtained by Aio, Efimov and Kokorina on glass of the same composition, using the more accurate classical method of measuring the angle of minimum deviation in a prism [5]. The curve obtained with the reflection method agrees within 0.007, which is well within the uncertainties. Although the reflection method is not as accurate as the minimum deviation method, its advantage lies in its simplicity and its ability to obtain the refractive index over a wide wavelength range.

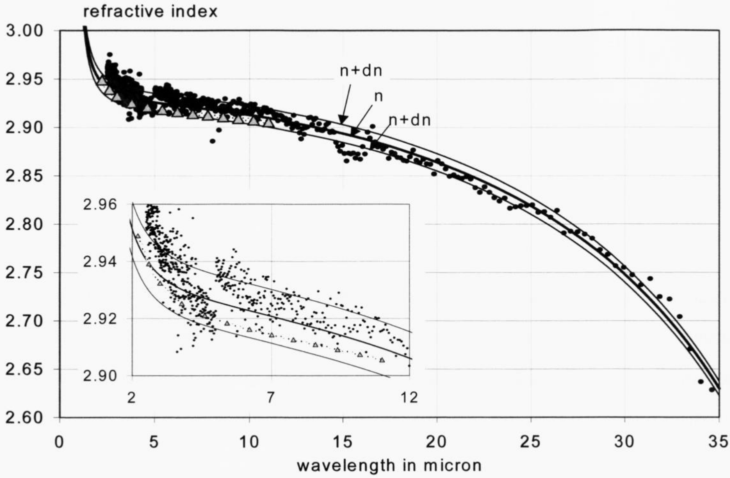

Figure 1. Refractive index determined from reflectance measurements of glass of the composition $Te_{20}As_{30}Se_{50}$. The dots represent the raw measurement data.

Although the refractive index and absorption coefficient can be determined simultaneously from the reflectance and transmittance, this usually results in larger systematic errors due to the limited accuracy in the total reflectance, which is more difficult to measure than the interfacial reflectance.

A high accuracy (< 0.01%) seems possible with a relatively new refractive index method that is discussed in [6]. This method is based on measuring the interference fringes in the transmittance spectrum a thin planparalel sample, obtained using a high resolution Fourier Transform spectrophotometer. The accuracy with this method is restricted mainly by the accuracy in the thickness measurement of the sample.

Measurement of the Refractive index of strong absorbing samples

For determining the optical constants of glass in the ranges of the fundamental excitations, for which κ is to large for using the reflection method described above, the two methods described in this section are known to give reliable results:

Dispersion Analysis is a technique based on a model for the dielectric function (for example Eq.(1)), from which the values of the band parameters are determined by nonlinear regression. This procedure yields a set of parameter values that minimises the mean square difference between measured and calculated reflectance spectra. An example for results obtained on a soda lime glass is shown in Figure 2 below. The model that was used in the fit contained 10 oscillators and a Sellmeier term [1] to represent the contributions from the high frequency bands outside the region of interest. The resulting optical constants are shown in figure 3.

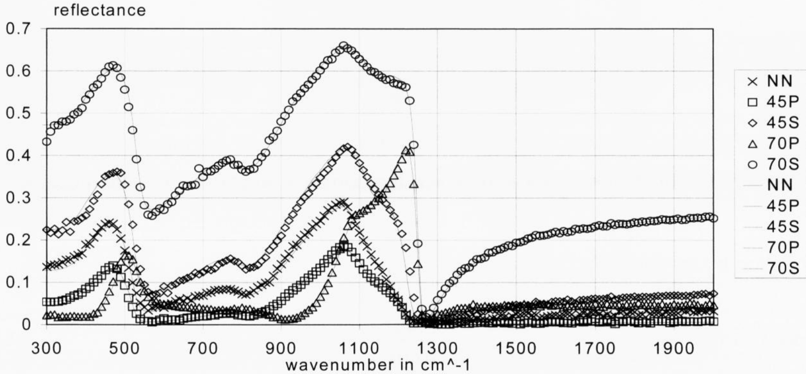

Figure 2 Comparison of measured data (markers) with calculated reflectance at near-normal incidence and 45 and 70 degrees for P and S polarisation.

The uncertainties in the optical constants determined by this method generally lie in the range of 0.004 – 0.04, depending on the value. For accurate determination a single reflectance spectrum is sufficient but it requires expert knowledge to avoid starting values that lead to a local minimum in the mean square difference function of the regression procedure. More information from multiple spectra determined at different angles of incidence and polarisation makes the regression procedure less dependent on the choice of starting values to converge to the correct solution (global minimum of the mean square difference).

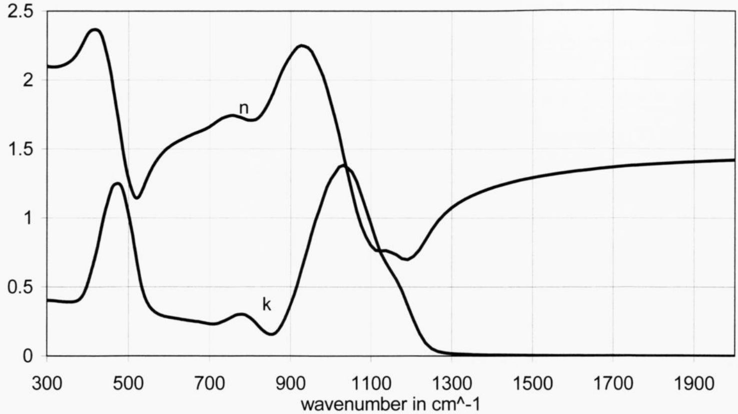

Figure 3 Real and imaginary parts of the complex refractive index of soda lime glass obtained by dispersion analysis.

Kramers-Kronig analysis is a technique that makes use of the interfacial reflectance measured at normal incidence, of which the complex amplitude reflection coefficient $\tilde{r} = R^{1/2}\exp\{i\phi\}$ is related to the optical constants through Eq.(2). We obtain this relation by inverting Eq.(2), resulting in

$$n(\omega) - i\kappa(\omega) = n_a \frac{1 - R(\omega) + 2i\sqrt{R(\omega)}\sin(\phi(\omega))}{1 + R(\omega) - 2\sqrt{R(\omega)}\cos(\phi(\omega))} \quad . \tag{8}$$

In order to determine both n and κ, we can make use of the following Kramers-Kronig relation that generates the spectral argument $\phi(\omega)$ of the amplitude reflectance (also referred to as the phase spectrum) from the measured reflectance through [7]:

$$\phi(\omega_j) = -\frac{\omega_j}{\pi} P \int_0^\infty \frac{\ln(R(\omega))}{\omega^2 - \omega_j^2} d\omega \quad . \tag{9}$$

By dividing the integration domain into two ranges, integrating the high frequency part with respect to the wavelength λ and the low frequency part with respect to the frequency, we obtain two finite integration domains [8]. An advantage of this method is that it uses a relatively simple computational procedure. Another advantage is that it does not require a physical model for the dielectric function.

A disadvantage of the method is that it requires extrapolation to fill in the missing regions at both ends of the spectrum. Therefore, modified Kramers-Kronig equations have been derived which, compared to Eq.(9), are much less sensitive for errors in the extrapolated regions where $\omega^2 >> \omega_j^2$. These relations, given by [8]

$$\phi(\omega_j) \equiv \frac{\omega_j}{\omega_h}\phi(\omega_h) + \frac{\omega_j(\omega_j^2 - \omega_h^2)}{\pi} P\int_0^\infty \frac{\ln(R(\omega)) - \ln(R(\omega_j))}{(\omega^2 - \omega_j^2)(\omega^2 - \omega_h^2)} d\omega \ , \qquad (10a)$$

$$\phi(\omega_j) = \frac{\omega_j}{\omega_h}\phi(\omega_h) + \frac{\omega_j(\omega_j^2 - \omega_h^2)}{\pi} P\int_0^\infty \frac{\ln(R(\omega)) - \ln(R(\omega_h))}{(\omega^2 - \omega_j^2)(\omega^2 - \omega_h^2)} d\omega \ , \qquad (10b)$$

use an expansion around a point in the transparent region in which the function ϕ is known for $\omega=\omega_h$. In the work described in [8], these integrals were used in combination with an IR extrapolation formula for dielectrics and a phase correction that takes proper care of the systematic errors in the extrapolated regions. The result is a reliable Kramers-Kronig analysis procedure for determining optical constants of glass in the infrared with uncertainties in n and κ similar to those obtained by dispersion analysis. A thorough evaluation of all uncertainties involved is given in [8]. A comparison of Dispersion analysis and Kramers-Kronig analysis can be found in [9].

Measurement of the Absorption coefficient in the transparent region

The general procedure for determining the absorption coefficient of glass is based on calculation from the internal transmittance determined from the measured total transmittance of a glass sample, by correcting for glass - air interfacial reflection losses. Inverting Eq.(3) results in:

$$K = -\frac{1}{d}\ln|\tau| = -\frac{1}{d}\ln\left|\sqrt{\left(\frac{1-R}{R}\right)^4 \frac{1}{4T^2} + \frac{1}{R^2}} - \left(\frac{1-R}{R}\right)^2 \frac{1}{2T}\right| \ . \qquad (11)$$

Substituting Eq.(2) yields

$$K = -\frac{1}{d}\ln\left|\left(\sqrt{1 + \frac{T^2}{64}\left(\frac{n^2 - n_a^2}{n\, n_a}\right)^4} - 1\right)\frac{8n^2 n_a^2}{T(n - n_a)^4}\right| \ . \qquad (12)$$

The uncertainty in K can be determined from the uncertainties in n, T and d by

$$\delta K = \left|\frac{K(T, n+\Delta n) - K(T, n-\Delta n)}{2\Delta n}\right|\delta n + \left|\frac{K(T+\Delta T, n) - K(T-\Delta T, n)}{2\Delta T}\right|\delta T + \frac{K}{d}\delta d \qquad (13)$$

in which the partial (central) differences are determined with Eq.(12) by introducing a small change Δn in the refractive index or ΔT in the transmittance. Figure 4 shows a plot of the relative uncertainty in K, calculated using Eq.(13).

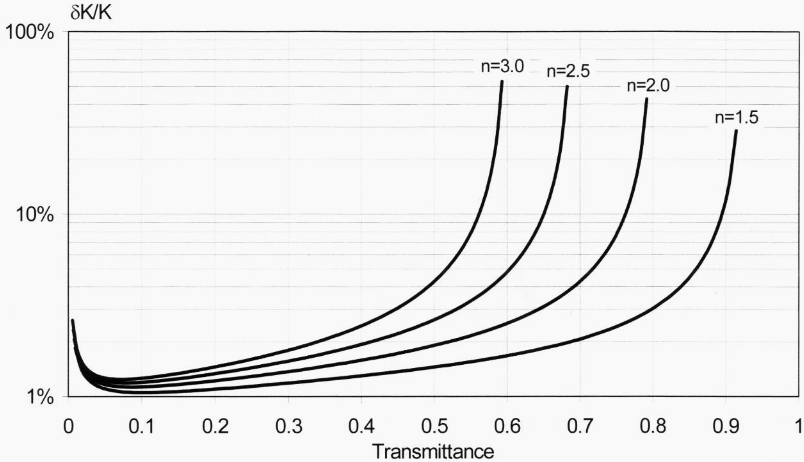

Figure 4. Relative uncertainty in K calculated using Eq.(13) with a relative uncertainty of 0.5% in the refractive index and sample thickness and an uncertainty in the measured transmittance given by the function $\delta T = 0.005 + 0.006\, T(1-T)$ [10].

For accurate determination of K (or κ) from a transmittance measurement, a sample is necessary with sufficient thickness. This poses a problem for low absorbing samples since in this case a large thickness may be required which introduces a significant distortion in the image (spot size and shape) on the detector by the change in optical path length. The solution to this problem is to use an integrating sphere as detector [11].

Another problem that occurs with highly transparent glass samples is that the absorption is extremely low and the reflection losses dominate the transmittance. Due to systematic errors and noise, the internal transmittance determined from the measured transmittance of such a glass can be even greater than one, resulting in negative values for K.

In this case, systematic errors can be reduced significantly by using a method based on the ratio of transmittance measured on samples of different thickness d_1 and d_2. The spectral absorption coefficient K(λ) is then calculated by iteration using [11]

$$K_1 = \frac{1}{d_2 - d_1} \ln\left|\frac{T_1}{T_2}\right| \tag{14}$$

for the first estimate, and

$$K_i = \frac{1}{d_2 - d_1}\left[\ln\left|\frac{T_1}{T_2}\right| + \ln\left|\frac{1 - R^2 \exp\{-2K_{i-1}d_1\}}{1 - R^2 \exp\{-2K_{i-1}d_2\}}\right|\right] \tag{15}$$

for the final iteration steps. The single surface reflectance R is measured or calculated with Eq.(2) using known or estimated values for the refractive index. Since the influence of R in the value of K according to Eq.(15) is small, a relative uncertainty of 1% in n is usually more than sufficient to calculate R.

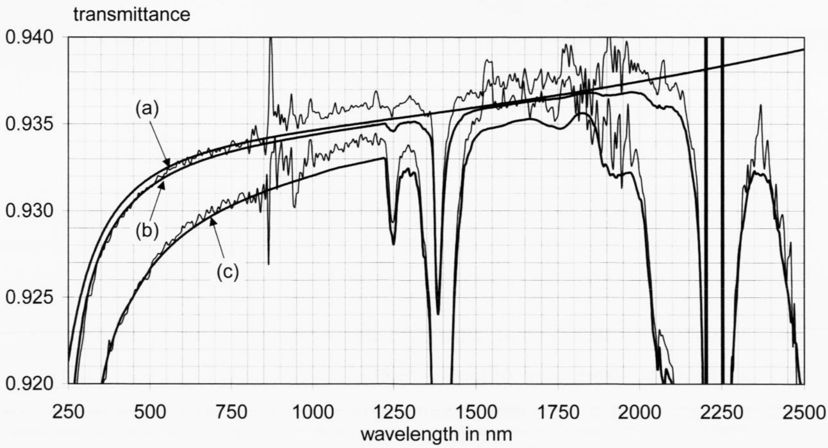

Figure 5 Corrected transmittance spectra (smooth lines) for fused silica samples with respectively approaching zero thickness (a), $d_1 \equiv 6.00$ mm (b) and $d_2 \equiv 59.7$ mm (c). The measured transmittance spectra T_1 and T_2 corresponding with d_1 and d_2 are also shown (noisy lines). [11]

The power of this method in reducing systematic errors is illustrated by figure 5. After removing the noise in the absorption spectrum that was obtained by the transmittance ratio method, the corrected spectra in this graph were calculated. Figure 5 clearly shows that the systematic error resulting in a “step” in the measured spectra for wavelengths above 860 nm, is not present in the corrected spectra.

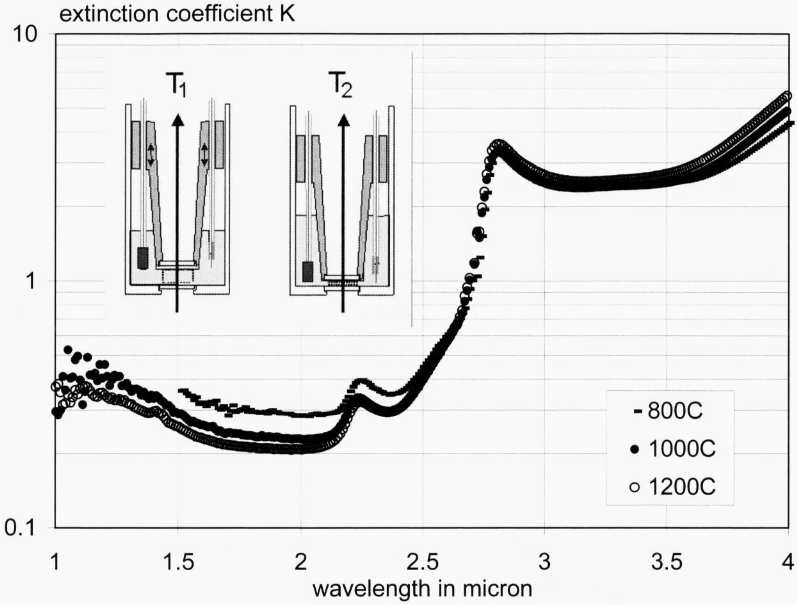

Figure 6 High temperature spectral absorption coefficient of clear float glass, obtained with the transmittance ratio method. The schematical drawing shows the sample holder in the two transmission positions.

The transmittance ratio method proved to be particular useful in determining the spectral absorption coefficient of glass melts [11,12]. Figure 6 shows results, which were obtained using a high temperature variable optical path sample holder. This sample holder was specially designed to measure the transmittance through a volume of molten glass between two sapphire windows. The distance between the windows can be varied to obtain different optical path lengths in the molten glass.

An advantage of using the transmittance ratio method is that errors in the transmittance and reflectance of the sapphire windows and the effect of deterioration of the sapphire-glass interface are mostly cancelled out [12]. Even a common systematic error in the measurement of d_1 and d_2 is compensated (Eq's.(14) and (15) require only an accurate value for the difference between d_1 and d_2).

A high accuracy (<1%) in the absorption coefficient can be obtained by applying the transmittance ratio method on an optical fiber. In this application, The transmittance of a long fiber with sufficient absorption is measured first. Then the fiber is cut to obtain a short sample with the same reflectance losses.

Conclusion

A state-of-the-art overview was given of different techniques that are currently available for determining the refractive index and absorption coefficient over a wide range of wavelengths using reflectance and transmittance spectrophotometry. It was shown that the optimal choice of methodology depends on the level of absorption in the available sample.

With the presently available instrumentation, the absorption coefficient can be determined with a relative uncertainty in the range 2% - 10% for higher values and as high as 30% - 80% for the extreme low values. An exception is optical fiber measurements, for which higher accuracy (< 1%) is possible. The transmittance ratio method used in [10-12] significantly reduces the influence of systematic errors.

Generally, although reflectance measurements are more difficult and have a higher uncertainty than transmittance measurements, the refractive index can be determined with an accuracy in he range of 0.1% - 2% using single surface reflection measurements.

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