

# An automated directional reflectance/transmittance analyser for coating analysis

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## Abstract

There is a growing need in the industry for motorized spectrophotometer accessories. Especially for measurements of directional reflectance and transmittance, which require many scans on the same sample at different angles of incidence, automation is beneficial. TNO TPD has developed a new motorised accessory for the measurement of directional reflectance and transmittance in the wavelength range between 250 and 2.500 nm. It is capable of making absolute measurements of the transmittance and reflectance of specular samples as well as performing BRDF measurements on diffuse samples. The accessory is a valuable tool in the optical characterisation of coatings and provides a means for analysis that yields the thickness and optical constants of the individual layers in multi-layer coatings, as well as other parameters that can be related to optical material properties.

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## 1. Introduction

In the past decade, considerable progress has been made in identifying and overcoming the sources of error present when making spectral optical measurements at oblique incidence [1]. This has led to the development and commercialisation of new spectrophotometer accessories for the measurement of reflectance and transmittance at oblique incidence. One of these accessories, a directional reflectance/transmittance accessory for manual use [2], is currently in use in over a dozen laboratories in Europe.

Related work on measurement of directional optical properties has been published by Roos, Chevalier and Olive [3], Nostel, Roos and Rönnow [4] and by Hutchins and Topping [5]. These articles discuss single beam instruments capable of absolute reflectance measurements, utilising an integrating sphere detector. The major difference between the two facilities lies in the type of instrument (respectively, a grating spectrophotometer [3,4] and a Fourier Transform spectrophotometer [5]). In spite of the significant difference between both these facilities and the set-up discussed in Ref. [2], reflectance and transmittance measurements on coated glass samples usually agree within 0.003 when the same sample is

measured with each of these facilities [6]. This demonstrates that accurate results of directional optical properties can be achieved with a spectrophotometer set-up, providing that the measurement problems (addressed below) have been successfully dealt with.

Although an efficient measurement procedure has been developed for the manual accessory, when a large number of scans are required for determining reflectance or transmittance at oblique incidence, these measurements are still relatively time-consuming. For example, if a coated glass sample has to be measured at (near-)normal and 4 oblique angles, it will require at least one scan at near-normal incidence and 16 scans at oblique incidence ( $2 \times 2$  scans per angle to take into account polarisation and angle calibration [2]). If these measurements have to be performed in transmittance and reflectance on both sides of the sample, the total number of scans to be performed on the same sample amounts to 51. Depending on the wavelength range and measurement interval, this can take up to 10 h. Between scans, angles have to be changed and, if necessary, alignment is adjusted. Avoiding mistakes requires the full attention of an experienced operator during the whole time.

This article discusses some of the major problems in measurement of directional optical properties and presents a new spectrophotometer accessory in which these measurements are automated.

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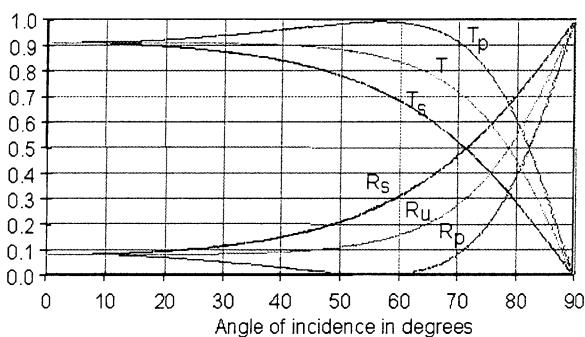


Fig. 1. Directional reflectance ( $R$ ) and transmittance ( $T$ ) of a 4 mm clear float glass at  $\lambda=500$  nm. The subscripts S, P and U refer to the polarisation state.

## 2. Measuring directional optical properties

### 2.1. Polarisation

One issue that must be dealt with when measurements are performed under oblique incidence is polarisation. Spectrophotometers use monochromatic radiation, which is strongly polarised. This polarisation varies with the wavelength. The directional optical properties of materials depend on polarization as illustrated by Fig. 1.

The so-called P and S polarisation states represent two extremes. The curves  $R_U$  and  $T_U$  in Fig. 1 represent the averages obtained for natural (unpolarised) daylight. For measurements at oblique incidence, we have to use polarizing elements, which enable us to perform separate measurements with P and S polarised radiation.

### 2.2. The importance of angular accuracy

A shortcoming of most commercially available accessories for directional measurements is that the setting of the angle of incidence is inaccurate. Especially for angles  $>45^\circ$ , where the angular dependency of optical properties is much greater than at normal incidence, can this lead to significant measurement errors. Most commercially available accessories for directional reflectance and transmittance measurements have accuracy in the angular setting in the order of 2–5° resulting in errors as large as several percent in the transmittance or reflectance.

A problem that has been discovered only a few years ago [7] is that the direction of the average energy of a grating spectrophotometer's light beam is slightly wavelength dependent. This was indicated by the observation that measurements performed under a positive angle  $+ \theta$  and a negative angle  $- \theta$  do not give the same results. Although the geometrical direction of the beam may be constant, a spectrophotometer's beam is non-parallel and the angular distribution of energy within the beam is not uniform. In order to quantify the effect,

the following experiment was performed. Using an accurate rotation stage, transmittance spectra were recorded on a 2 mm flat fused silica sample at positive and negative angles of incidence. During the measurements, the incident beam was P polarised and the wavelength range was 300–2500 nm. A transmittance spectrum was recorded at a positive angle of incidence  $\varphi_+ = +45.0^\circ$  and at several negative angles of incidence  $\varphi_- = -45.0^\circ + \Delta_i$ . By means of regression, the value of  $\Delta$  was determined for which the measurement result  $M(\varphi_+)$  equals the result  $M(\varphi_-)$ . If the angle of incidence  $\varphi$  indicated by the scale of the rotation stage, deviates from the true angle of incidence  $\theta$  by a systematic error of  $+ \delta$ , the negative and positive angles in this situation are  $\varphi_+ = \theta + \delta$  and  $\varphi_- = -\theta + \delta$ , respectively, and  $\Delta = 2\delta$ . The result obtained as a function of the wavelength is shown in Fig. 2. Similar experiments have been performed on the same instrument (Perkin–Elmer Lambda 900) with different detectors and also on an instrument that has a different design (Perkin–Elmer Lambda 19), except for the monochromator, which seems to be the cause of this effect. All results showed a linear increase of  $0.3^\circ$  in the effective angle of incidence when the instrument scans from 2500 to 250 nm.

An important result is that this error cannot be corrected by adjusting the rotation stage, unless the measurements are performed in a small wavelength interval. To obtain the correction for all wavelengths there are only two possibilities, (i) to vary the angle of the rotation stage during the scan or (ii) to perform two scans at positive and negative angles and take the average. The latter seems to be the most practical solution [2]. For example, if the positive and negative angular settings are respectively,  $+45^\circ$  and  $-45^\circ$  and the systematic error is  $-1.3^\circ$ , the true angles of incidence will be respectively,  $+43.7^\circ$  and  $-46.3^\circ$ . As a result, different values for the transmittance (or reflectance) are obtained. If the systematic error is not too

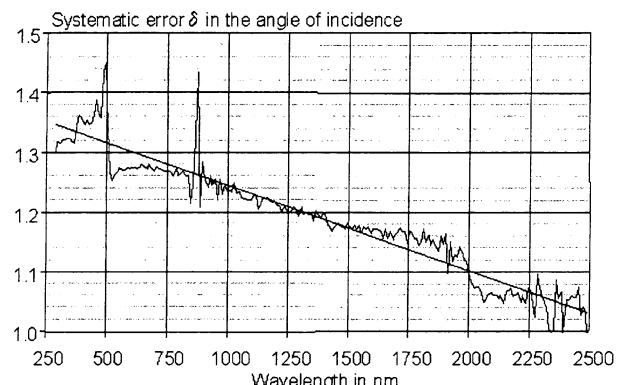


Fig. 2. Off-set in the angle of incidence as a function of the wavelength.

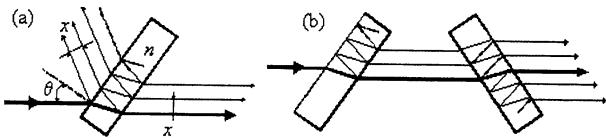


Fig. 3. Multiple shifted beams at oblique incidence: (a) Reflected and transmitted beams and (b) Use of a second sample to compensate the primary beam shift in transmittance.

large, the average of the two measurements will yield the transmittance (or reflectance) at 45.0°.

### 2.3. Proper detection

For measurements under oblique incidence, the secondary shifted beams due to multiple reflections inside the sample become more problematic. This is illustrated in Fig. 3. The lateral distance,  $x$ , between the secondary beams depends on the angle of incidence and is maximum at approximately 50° for which this distance becomes approximately 75% of the sample thickness [8]. The detector sphere must have a large enough entrance port to capture not only the primary reflected or transmitted beam, but also an adequate amount of those secondary beams. For example, assume that the beam width at the sample is 4 mm and the sample thickness is 8 mm and that the sample position is imaged 1:1 on the detector entrance port. In this case, the total width of the light spot at the entrance port taking into account only the primary beam and the first two secondary beams has a maximum value of  $4 + 2 \times 0.75 \times 8 = 20$  mm.

Some accessories for measuring directional transmittance utilise a second sample to put the transmitted primary beam back onto the optical axis (see also [8]). This situation is depicted in Fig. 3b. In this case, secondary beams occur on both sides of the optical axis, which can make matters worse.

## 3. The automated directional transmittance/reflectance accessory

The accessory is shown in Fig. 4. The sample is positioned on a motorised rotation stage in the centre (see Fig. 5) and the integrating sphere detector is either positioned behind the sample (at 180°) for transmittance measurements or in front of the sample for reflectance measurements (at twice the angle of incidence). A periscope is used to prevent the beam from being blocked by the detector sphere at small angles (see Fig. 5). The reference beam is guided through a mixed fiber bundle containing 50% UV/Vis fibers and 50% Vis/NIR fibers in order to obtain the whole UV/Vis/NIR range without the need for replacing the fiber bundle. The fiber bundle is mounted inside a flexible cable guide that allows



Fig. 4. Photograph showing the accessory with open cover.

bending only in the horizontal plane. The reference beam is coupled into the top of the integrating sphere using a 45° reflector. This top is allowed to rotate when the sphere's position is changed. Since bending the fibres to strong can result in a change in the transmittance, the minimum bending radius of the moving part is limited to approximately 120 mm. Tests have shown that the change in reference beam energy caused by this effect is negligible for wavelengths up to approximately 1500 nm and at higher wavelengths less than 0.2%. The measurement range of the analyzer is 300–2400 nm (limited by the range of the fiber bundle).

The integrating sphere detector is made from Spectralon and has a 30 mm wide and 17 mm high rectangular entrance port. The detectors, a photomultiplier for the UV/Vis range and a Peltier cooled PbS cel for the NIR range, are both screened from seeing directly the target positions of sample and reference beams. The integrating sphere is mounted on a large (320 mm diameter) ring that rotates in the horizontal plane along the same axis as the sample holder, driven by a second motorised rotation stage. The angular range is 15–345° (180° being the position directly behind the sample). The angular range for measurement of specular samples is 75°–85° for reflectance and 0–85° for transmittance (depending on sample type and size).

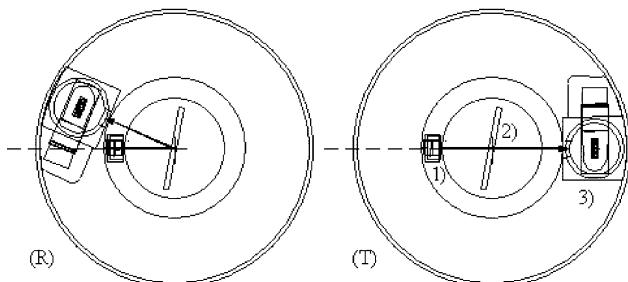


Fig. 5. Schematic drawing in top view of the optical path in reflectance (R) and transmittance (T). (1) Beam periscope; (2) Sample on rotation stage; (3) Detector sphere on ring shaped rotation stage.

The use of accurate stepper motor drive rotation stages (accuracy 0.023°) for the angular settings is an important improvement over other commercial accessories for directional measurements. Having the possibility for measuring at ‘positive’ and ‘negative’ angles makes it possible to compensate for systematic errors, by taking the average of these two types of measurements. This also results in an absolute calibration of the zero position of the angular setting.

The microcontroller that drives the rotation stages is built into the accessory and is connected by a cable to one of the serial COM ports of the measurement PC. The power supply for the controller and stepper motors is obtained from the spectrophotometer’s accessory connector. The accessory is equipped with a keyboard for manual control.

Measurements are performed as follows: The accessory user interface is programmed with a table of  $N$  angular settings, each row representing a measurement containing a specific setting for the sample and detector angles. The accessory is initialized and the rotation stages are set according to the first row in the table. UvWinlab (the spectrophotometer user interface) is instructed to perform  $N$  pairs of scans on the same sample with the polariser, respectively, in P and S state and to perform a so-called end-of-run application after each pair before continuing with the next pair of scans. The end-of-run application, in this case is only used as a flag that is detected by the accessory software, which upon detection changes the angular settings according to the next row in the table. When the accessory signals that the angles have been changed, the accessory user interface closes the end-of-run application after which UVWinLab continues with the next pair of scans. The whole procedure is repeated automatically until all measurements are performed.

#### 4. Determining optical material constants

In simulation of optical spectra, the interaction of electromagnetic radiation with matter is described by optical material constants such as the permittivity, the conductivity or the complex refractive index. In general, techniques for the determination of optical constants of materials can be divided into four categories [9]:

- i. photometry, where the optical constants are determined from reflectances and transmittances for S- and P-polarised radiation (or unpolarised radiation) at known angles of incidence;
- ii. polarimetry, where the phase changes on reflection of S- and P-polarised radiation are measured at one or more angles of incidence;
- iii. a combination of polarimetric and photometric methods;
- iv. ellipsometry, where plane polarised light becomes elliptically polarised by reflection at the surface of a

sample and the optical constants are determined from the shape and orientation of the ellipse.

The experimental methods for determining the optical constants, as discussed above, often require specialised equipment. However, an instrument, which is standard equipment in most laboratories where optical materials are being characterised, is the spectrophotometer. Before accurate methods for determining directional optical properties became available, it was advantageous to use a method by which the optical constants of a material could be derived from normal transmittance and (near) normal reflectance spectra, which are relatively easy to measure. A comparison of different methods is given by Arndt et al. [10]. Most of these methods determine a complex refractive index at one wavelength at a time, using the optical properties measured at this wavelength. This may cause problems, since in principle an infinite number of solutions will fit the equation when complex numbers are involved and more than one solution may seem physically plausible.

Nowadays, better methods in which the spectral material properties are described by complex dielectric functions that depend on a relatively small number of parameters are commercially available [11,12]. By using measured spectra of the optical properties, containing a large number of data points, the much smaller number of model parameters (layer thickness and dielectric function parameters) can be found by non-linear regression. A popular way of doing this is by using Variable Angle Spectral Ellipsometry [11] that requires an automated ellipsometer combined with a scanning monochromator. An alternative is to use directional transmittance and reflectance spectra obtained with the analyzer described in this article and to fit these spectra on a model using a commercial software application, e.g. CODE [12]. An example is given in the next section.

#### 5. Example

The manual directional RT accessory discussed in [2] requires a reference mirror for the reflectance measurements. A 50 × 100 mm<sup>2</sup> surface mirror was developed for this purpose. This mirror consists of a protected aluminium coating on the back of a 2 mm thick polished silica front plate, which is glued onto a glass back plate. The actual mirror is a vacuum deposited MgF<sub>2</sub>/Al/Cr/Al multi-layer. The MgF<sub>2</sub> layer is to enhance the adhesion of the coating on the silica surface, and acts as a barrier for oxygen from the SiO<sub>2</sub>. Its thickness is optimized to enhance the reflectance in the UV. The first (non-transparent) Al layer is the actual mirror. It is protected by a Cr barrier layer on top of which a second Al layer is deposited. This is a sacrificial layer, which together with the Cr layer protects the first Al layer

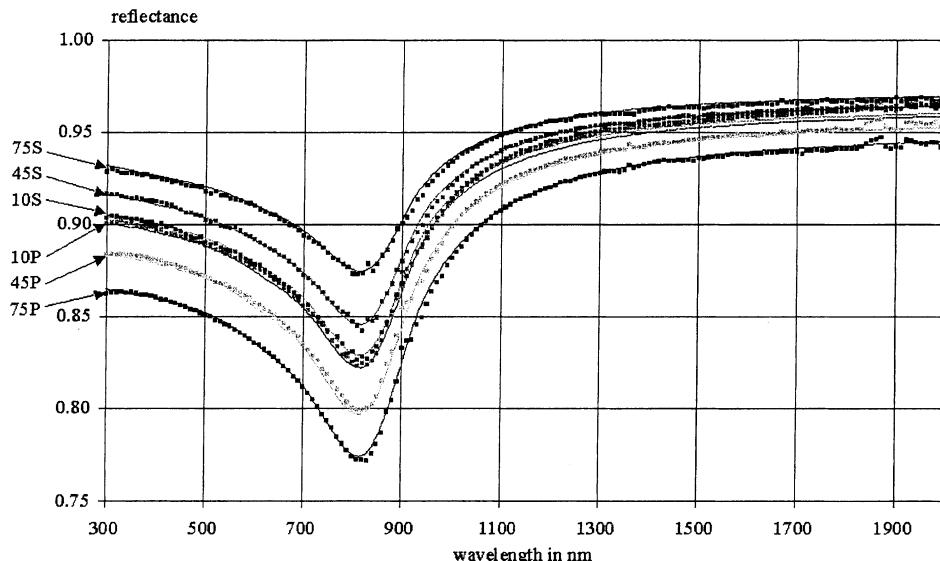


Fig. 6. Comparison of measurements (dots) and model calculations (lines).

when the freshly coated mirror is transferred from the vacuum chamber to the environment. A 3 mm back plate of soda-lime glass is glued to the back surface to provide mechanical stability and to protect the coating from being damaged from the back.

The analyser was used to characterise one of these mirrors. The purpose was to check the measurements for systematic errors, which generally shows as a disagreement between measured and calculated spectra. Measurements were performed at 10, 45 and 75° incidence and the software discussed in Ref. [12] was used for the analysis. The measurement reproducibility is better than 0.1% for wavelengths up to 1200 nm. For larger wavelengths the noise level is higher and this value increases. Typical values are 0.3% at 1500 nm and 0.5% at 2000 nm. The results were compared with data obtained on the same sample using the absolute directional VW reflectometer described in Ref. [1]. The results agreed well within the measurement uncertainty of the analyser. Fig. 6 shows a comparison between measured data and the data obtained by the model after completing the fit. The agreement is better than 0.1% for wavelengths up to 1000 nm, while the agreement at higher wavelengths is better than 0.2% at 45 and 75° and 0.6% at 10° incidence.

## 6. Conclusions

There is a growing need in the industry for motorized spectrophotometer accessories. Especially for directional optical measurements, which require many scans on the same sample, automation is beneficial.

The new motorised accessory presented in this article enables automated characterisation of the directional optical properties of a sample. Its use increases the

reliability of these measurements and significantly reduces the time required for the operator to be involved with the measurement. The accessory is controlled by a MS Windows application that allows the user to define a selection of angles for both detector and sample. The analyser can be used for coating analysis and also for the characterization of angle resolved scattering such as the BRDF (bi-directional reflection distribution function) of diffuse and translucent samples. The rectangular entrance port of the integrating detector sphere is equipped with an adjustable aperture, which enables adjusting the resolution in BRDF measurements.

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