THE COMPLEX REFRACTIVE INDEX AND REFLECTOMETRY VERSUS ELLIPSOMETRY

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1.   INTRODUCTION

Refractive index (RI) is a complex number comprising a real refractive index and an imaginary part: the absorption (or extinction) coefficient. The analysis of refractive index by the Surfoptic Imaging Reflectometer yields an approximation to the real part of the refractive index. The well established technique of ellipsometry, by contrast, can determine both the real refractive index and the extinction coefficient.

This note provides some background on the complex refractive index, presents comparative data from ellipsometry and reflectometry, and discusses the merits and limitations of the two techniques. (Note that the term "reflectometry" is used here in the context of the Surfoptic Imaging Reflectometer – the terminology is not standardised and various kinds of Reflectometer exist, often performing quite different measurements.)

2.   COMPLEX REFRACTIVE INDEX

Refractive index is a complex number describing how electromagnetic radiation is refracted and absorbed by a material. In general, it may be written

$$n = n' - i n'' \tag{1}$$

Where n' is the real refractive index and n'' the extinction (absorption) coefficient. Note that various conventions exist for the expression of (1) and there is no standard form.

The real part of the refractive index describes how the speed of light changes as it enters the material. The extinction coefficient describes how light is absorbed (or scattered). In a transparent material, absorption is zero and $n = n'$.

The reflectivity of an absorbing material depends on both parts of the complex refractive index, and, in fact a highly absorbing material will in general be much more reflective than a corresponding transparent material (fig 1). This is why metals, for instance, make such good mirrors – the refractive index of aluminium is 1.21 - 6.92 i.
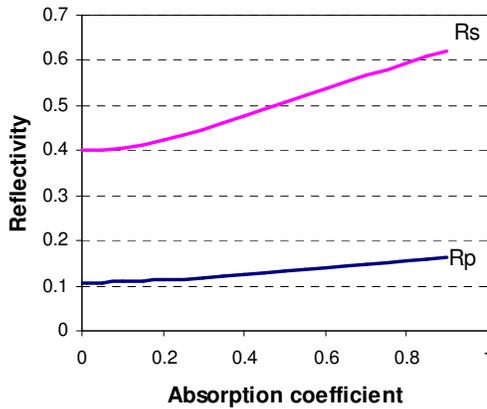
Figure 2.1   Variation of Rs and Rp with absorption coefficient at an angle of 75° (n' = 1.5)

Linearly polarised light can be thought of as having two perpendicular electric field components, denoted r_p and r_s, oscillating in phase. When linearly polarised light is reflected from a surface, in general the amplitudes r_p and r_s change and so does the phase between them. The light becomes elliptically polarised (Figures 2.2 and 2.2). If the substrate is non-absorbing, the phase change is zero and linear polarisation is preserved.
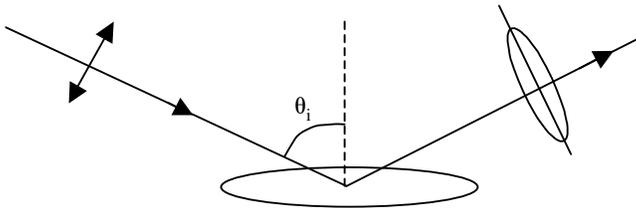

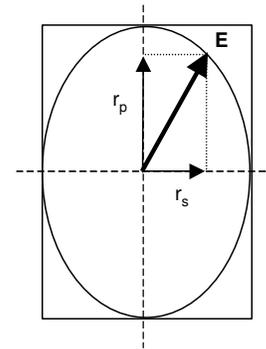**Figure 2.2** – in general linearly polarised light reflected from a surface becomes elliptically polarised.

Figure 2.3 – In plane polarised light, rp and rs oscillate in phase. In elliptically polarisedlight, there is a phase lag (Δ) between them, such that the electric field rotates and changes amplitude in time describing an ellipse.

Ellipsometry is a well established experimental method for analysing the phase and amplitude of reflected polarised light in order to extract information about the surface (see for example Tompkins & McGahan, 1999 or many other textbooks). Various types of ellipsometer exist, but a common form is the rotating polariser. In this design, linearly polarised light is incident on the sample surface, as illustrated in Figure 2.2, but the polariser is rotated, so that the plane of polarisation rotates about the axis of the incident light. On the detector side, the (generally) elliptically polarised light is passed through a fixed analyser. The intensity of light on the detector oscillates with rotation of the incident polariser according to the amplitude and phase change at the specimen.

The following quantities are defined:

Δ The phase change between r_p and r_s upon reflection

$$\tan \Psi = \left| R_p \right| / \left| R_s \right|$$ Where Ψ is the angle whose tangent is the ratio of the intensity of the Rp and Rs components.

The fundamental equation of ellipsometry is

$$\rho_e = \tan \Psi e^{i\Delta}$$

In the case of reflection from a simple substrate, Ψ and Δ can be inverted directly to give the real refractive index and extinction coefficient (e.g. Tompkins & McGahan, 1999). In any other situation, e.g. in the presence of one or more thin films, surface roughness, interface roughness etc., it is necessary to start from a model of the surface and to fit the measured values of Ψ and Δ to the model to obtain a best fit.

For a non-absorbing substrate, $\Delta = 0$, and ρ_e is real. But in general, if absorption is present, ρ_e is a complex number.

Reflectometry (as implemented in the Surfoptic Imaging Reflectometer) is a related technique. However, in this case, the surface is illuminated with s and p polarised light. The reflected intensities of the p and s polarised components are measured (Rp and Rs). But the phase information is lost. In this case we define (beware of confusing ρ and ρ_e)

$$\rho = \sqrt{Rp / Rs} \qquad (2)$$

In the reflectometry measurement, the measured Rp and Rs intensities are used to calculate a refractive index using the form of the Fresnel equations for a transparent substrate:

$$n_R = \sin \theta_i \left[1 + \left(\frac{1-\rho}{1+\rho} \right)^2 \tan^2 \theta_i \right]^{1/2} \qquad (3)$$

The important point here is that the reflectometry analysis *assumes* that the material is non-absorbing. If the material truly is non-absorbing, then reflectometry will return the correct real refractive index. If the material is absorbing, then reflectometry will return an approximation to the real refractive index.

This approach is a trade-off between absolute accuracy for refractive index on one hand and a desire for speed of operation and the ability to measure several other parameters (such as roughness) at the same time. For the types of material that reflectometry is aimed at, the simplified measurement of refractive index generally works very well, as will be shown in subsequent sections of this note. At 75° angle of incidence, and for materials with a real refractive index around 1.5 to 1.6, it can be shown theoretically that the ratio Rp/Rs is almost independent of the extinction coefficient (so long as the extinction is not too great) (Preston & Gate, 2004). For materials like coated and printed paper, by measuring at 75°, the reflectometry method is expected to return a close approximation of the real refractive index.

Note that, in principle, if the *absolute* values of Rp and Rs are known, it is possible to solve the reflection equations for both n' and n'' (Azzam, 1979, 1994). However, if the surface is rough, the reflected light will be scattered over a range of angles making the analysis extremely difficult. The problem is avoided by using the ratio Rp/Rs, but with the limitation that only the approximation to n' can be determined as described above.

3.   INSTRUMENTATION AND SAMPLES

The ellipsometer used was a Horiba Jobin Yvon MM-16. This instrument is a spectroscopic ellipsometer covering the spectral range 430 – 850 nm and using liquid crystals to modulate the polarisation. Reflectometer data were obtained using Surfoptic's own development Imaging Reflectometer (SIRS75). Measurement time for ellipsometry depended upon sample roughness (and the light intensity reaching the detectors), but ranged between 10 and 60 seconds. Measurement area on the specimen was an ellipse roughly 1 x 4 mm. Measurement time for the Reflectometer was about 0.8 seconds and spot size on the surface about 3 x 12 mm. Wherever possible all samples were measured 8 – 10 times to obtain averages over the surface.

A wide range of coated and printed paper samples were used. These included a range of ground calcium carbonate coated papers at different pigment particle sizes, two ranges of clay coatings, a range of coatings of other pigments including precipitated calcium carbonate, plastic pigment and titanium dioxide. Some of these ranges of paper coatings were available at various calendering conditions. A wide range of printed papers were also measured: these included commercial prints on coated and uncoated paper and laboratory prints on coatings calendered to various degrees. Print colours covered a broad spectrum.

4.   REFRACTIVE INDEX BY ELLIPSOMETRY VS. REFLECTOMETRY

The following graphs summarise the main points of comparison. Figure 4.1 shows the correlation between ellipsometry real refractive index and the Reflectometer effective RI.
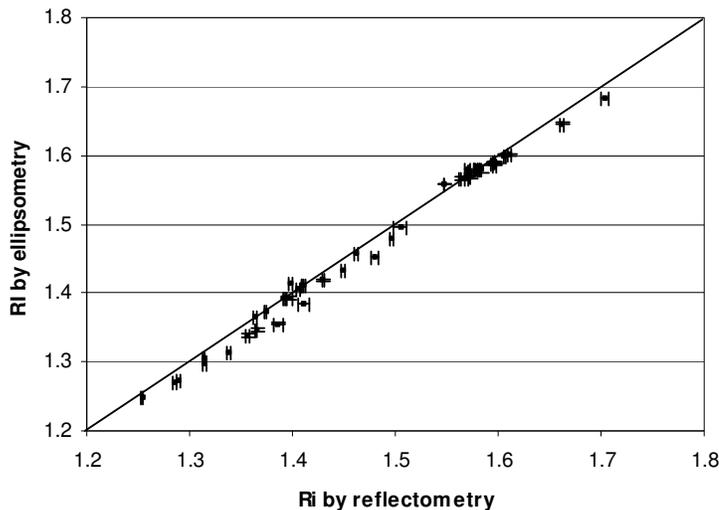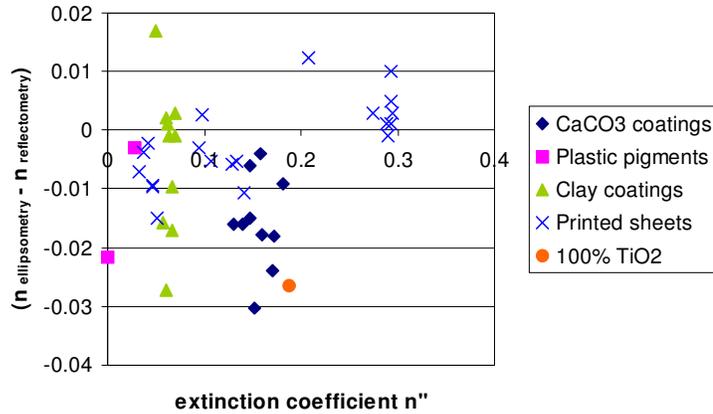

Figure 4.1

RI by ellipsometry vs Reflectometry for a wide range of coated and printed paper, plus some special pigments (plastic pigment and 100% Ti02).

The correlation between RI by ellipsometry and reflectometry illustrated by Figure 4.1 is reasonably good. The Reflectometer is calibrated using a glass standard and all Rp and Rs measurements are referred to the calibration intensities. In addition, The measured refractive index is adjusted by a "factory" calibration made using a series of glass standards of different RI – this adjustment is to compensate for internal polarisation losses and deviation from ideal geometry.

The difference between the refractive indices by ellipsometry and reflectometry is sample dependent in a systematic way. This is illustrated in Figure 4.2 which shows the difference in RI as a function of extinction coefficient for the various classes of surface.

Figure 4.2

Difference in RI between reflectometry and ellipsometry vs. extinction coefficient *n"*

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Generally, the printed surfaces give better agreement between the two methods, while the pigmented surfaces (clay and CaCO$_3$) show greater variability. As noted in section 2, at 75° incidence, the value of *n* obtained from Rp/Rs ratio is approximately the real part of the refractive index for n'~1.5 and moderate-low values of extinction (Preston & Gate, 2004). However, this approximation is generally not as good as the precision of the measurements (which is typically around ± 0.001). Correcting for the small effect of extinction reduces the systematic deviation between the ellipsometry and reflectometry results by almost half. The adjustment is particularly significant for the CaCO$_3$ samples which have relatively low *n'* but significant *n''*. The remaining deviation is then within calibration and other systematic alignment errors of the two instruments.

Appendix I provides further illustration of the scope and limitations of the assumption of zero extinction on reflectometry measurements.

5.   EXTINCTION COEFFICIENT

As shown in figure 4.2, the various coated papers all exhibit some non-zero extinction coefficient. The clays and GCCs fall into two distinct groups with the clays coatings having n'' ~ 0.05 – 0.07 while the GCCs have n'' in the range 0.13 – 0.19.

The extinction coefficient for bulk calcite is effectively zero over the wavelength ranges studied here (e.g. Thompson *et al.*, 1998). For bulk crystalline (thin film) TiO2, n'' < 0.02 over the wavelengths used here (Madare & Hones, 1999). Therefore, the measured extinction does not arise from the intrinsic absorption properties of the coating pigments, but rather from the way the coatings scatter light.

For a surface of given absorption properties, it is expected that the presence of microroughness should lead to a rise in extinction coefficient (and decrease in refractive index) (e.g. Ohlidal & Lukes, 1979). It obviously does not make sense to compare extinction coefficient across both printed and unprinted surfaces, because the printed surfaces will show strong absorption according to the ink colour. Figure 5.1 shows microroughness plotted against extinction for the unprinted sheets. There appears to be a weak correlation of decreasing extinction with increasing microroughness, which is contrary to expectation. It is unlikely that microroughness is the only factor contributing to the observed extinction: the detailed coating structure determined by particle size, distribution and packing is likely to be of overriding significance in determining extinction by multiple scattering. More detailed analysis shows trends of extinction coefficient with both particle size and calendering conditions, but it appears very difficult to use the extinction coefficient directly to derive practical information about the surface structure: there are too many contributing factors to be disentangled.
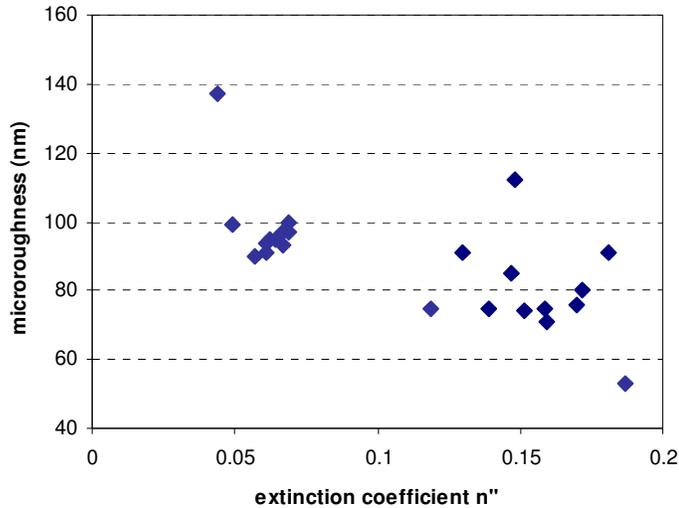
Figure 5.1

microroughness vs. extinction coefficient *n"* for unprinted coated papers.

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6.　　WAVELENGTH DEPENDENCE

One potentially useful feature of spectroscopic ellipsometry is the ability to report real refractive index and extinction coefficient over a range of wavelengths. Some representative data are shown in figures 6.1 - 6.4. The 100% Ti02 sample shows the greatest variation in n", while other coatings show little change with wavelength.. The 100% TiO2 coatings also shows the greatest changes in n' with wavelength. Thin film data (Madare & Hones, 1999) indicate that n' for crystalline Ti02 is expected to decrease monotonically from around 2.7 to 2.4 over the wavelength range 450 – 850 nm, while n" < 0.02 over the same interval. The trends observed in figures 6.1 and 6.2 are therefore not due to dispersion properties of TiO2, but must rather be related to the complex reflectance behaviour in the rough, particulate coating. The observed behaviour is interesting, but difficult to interpret.
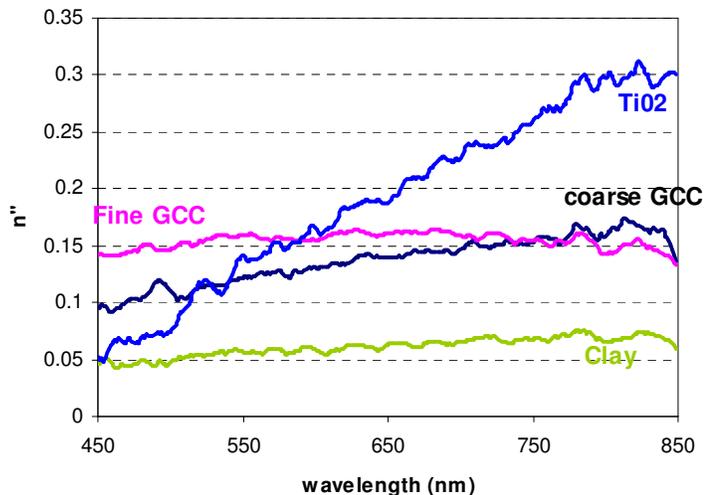

Figure 6.1

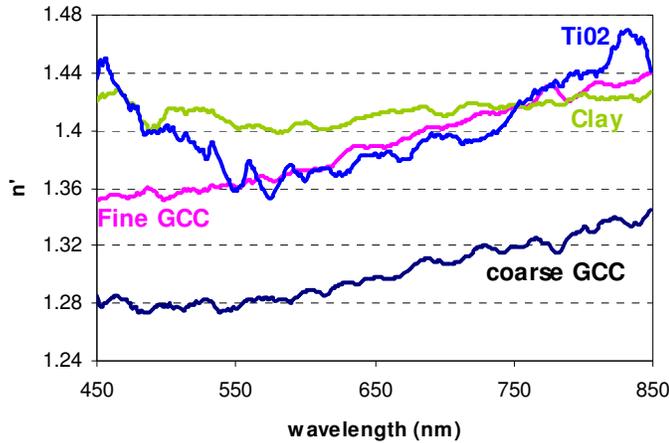extinction coefficient *n"* versus wavelength for several coatings.

Figure 6.2

Refractive index versus wavelength for various coatings.

Figures 6.3 and 6.4 show n' and n'' versus wavelength for solid cyan prints on a clay coating – corresponding curves for the unprinted coating are shown for comparison. The dependence observed is due to the colour of the print – being cyan, absorption peaks towards the red end of the spectrum. Notice that the behaviour of refractive index and extinction coefficient with wavelength for this print seems related (the wavelength curve for n'' resembles a derivative of the n' curve.) In fact, for many materials the wavelength behaviour of n' and n'' is not independent - this topic is far beyond the scope of this note, but further information can be found in most ellipsometry textbooks.

It is not clear what the practical use the information on the wavelength dependence of refractive index might be. A measure of spectral response could be obtained by standard diffuse reflectance colour measurement. A knowledge of how n' and n'' vary with wavelength could be helpful in calculating the wavelength response of specular reflection, but surface microroughness would also be a very significant factor, and would require additional measurements.
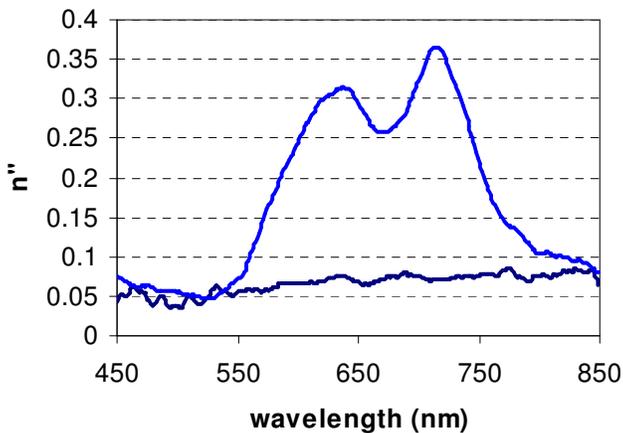

Figure 6.3

extinction coefficient *n''* as a function of wavelength for the clay coatings and cyan prints.
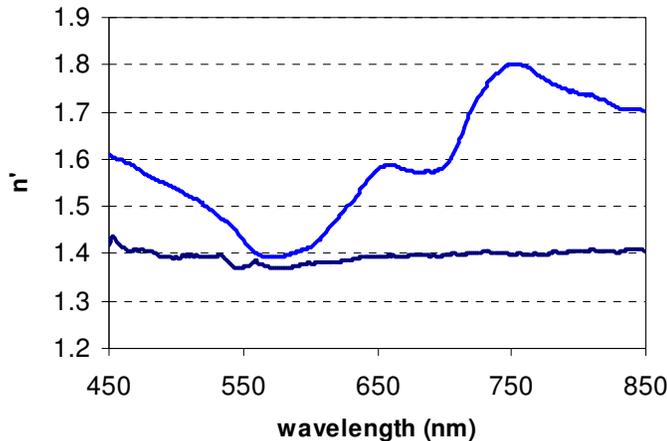
Figure 6.4

Refractive index *n* as a function of wavelength for the clay coatings and cyan prints.

7.   ELLIPSOMETRY VERSUS REFLECTOMETRY

Ellipsometry and Reflectometry (as implemented in the Imaging Reflectometer) are related techniques with rather different aims.

Ellipsometers are normally used for the analysis of very smooth substrates, thin films, adsorption processes or layer growth, often for the opto-electronics industries. With a suitable model of the surface, ellipsometry is a powerful technique for obtaining information on refractive index, extinction and film thickness. As shown here and elsewhere (e.g. Bakker et al,), ellipsometry can be applied successfully to relatively rough surfaces like coated and printed paper, but measurement times can be fairly long (10 – 60 seconds per point). Measurement area on the sample is about 3 mm^2.

The Imaging Reflectometer was designed specifically for measuring coated and printed papers and related materials such as paints and plastics. It determines an approximate real refractive index, which is typically accurate to about 0.01 which is probably of the same order as systematic instrumental errors due to alignment and calibration. The Imaging Reflectometer also measures macroroughness, microroughness and various gloss values. Measurement time is about 0.8 seconds per point and measurement area is about 28 mm^2. The approximations in the determination of refractive index mean the Imaging Reflectometer cannot provide meaningful refractive index or microroughness results for metals or thin transparent films (although macroroughness and gloss are still valid).

The extinction coefficient appears to be related in a rather complicated way to the scattering efficiency of the surface layers (related to pigment type, particle size, distribution and packing) and their microroughness. It is not clear whether practical information can be extracted directly from the extinction coefficient. Similarly, it is not clear whether practical information can be obtained form the wavelength behaviour of n' and n''. Significant further work would be required to assess the possibilities and limitations properly. It has been shown previously, that the real refractive index correlates rather well with surface porosity (Elton & Preston, 2005 - see also Surfoptic Applications Note AN4). It would be interesting to compare n'' with porosity data to see whether any trends emerge.

Both techniques have merits and limitations: although closely related, they do not ultimately do the same thing. If a choice is needed between the two methods, it must depend on the end applications.

ACKNOWLEDGMENTS

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APPENDIX 1 – REALM OF VALIDITY OF IMAGING REFLECTOMETER MEASUREMENTS OF REFRACTIVE INDEX

Figure 1 shows the expected deviation of the effective refractive index obtained by Reflectometer from the true real refractive index as a function of both n' and n".
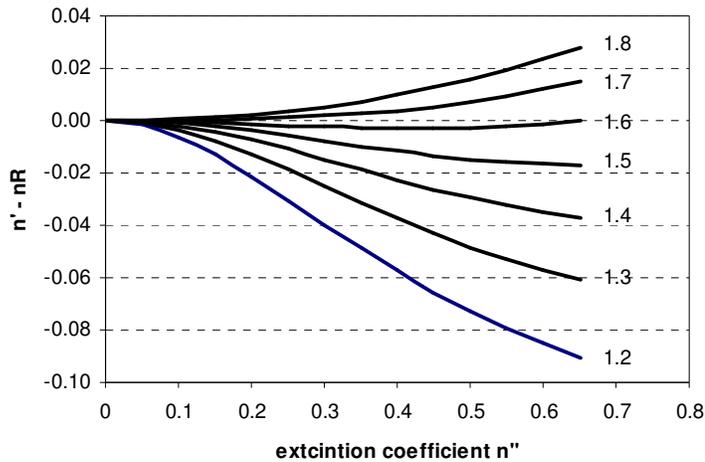

Figure A1
Difference between true real refractive index n' and the reflectometry result n_R with extinction coefficient for various n' at 75° incidence.

Table A1 gives some illustrative values of n' and n'' for a range of materials, along with an indication of how successfully the refractive index may be measured using the Imaging Reflectometer.

The method appears satisfactory for the intended applications area of printed and coated paper, paints, plastics and related industrial materials. Use of the Imaging Reflectometer for analysis of metals or any material with very high extinction is ill-advised.

As a rule of thumb, Reflectometry is appropriate for materials with n' ⩽ 3.7 and n'' ⩽ 0.5. (n.b. the method may be applied to materials of n' > 3.7 and n'' ⩽ 0.5 with a modification to the signs in equation (3) – section 2)

Material	n'	n''		n_R	n' - n_R
Coated paper	1.3 – 1.5	0 – 0.2	√		< 0.01
Printed paper	1.4 – 1.7	0.2 – 0.3	√		<0.01
glasses	1.5 – 1.8	0	√		<0.005
Unfilled & mineral filled plastics	1.4 – 1.6	~0	√		<0.01
Al_2O_3	1.77	0	√	1.770	0.00
TiN	1.39	1.76	√	1.366	0.02
TiO_2	2.2	0	√	2.200	0.00
Si_3N_4	2.021	0	√	2.021	0.00
$WSi_{2.2}$	4.25	1.37	X	2.632	1.62

CoSi$_2$	2.15	1.45	X	1.873	0.28
TiSi$_2$	2.85	2.7	X	1.766	1.08
W	3.41	2.63	X	1.936	1.47
Ni	2.01	3.75	X	1.287	0.72
Al	1.21	6.92	X	0.997	0.21
Au	0.16	3.21	X	0.969	-0.81
Poly Si*	4	0.035	X	3.482	0.52
amorphous Si*	4.3	0.192	X	3.224	1.08

* good results may be obtained if a modified form of the usual equation is used.