Helsinki University of Technology
Department of Electrical and Communications Engineering
Espoo 2004

CHARACTERIZATION OF MATERIALS AND COMPONENTS USING ACCURATE SPECTROPHOTOMETRIC MEASUREMENTS AND MATHEMATICAL MODELING

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Dissertation for the degree of Doctor of Science in Technology to be presented with due permission of the Department of Electrical and Communications Engineering, Helsinki University of Technology, for public examination and debate in Auditorium S4 at Helsinki University of Technology (Espoo, Finland) on the 15th of October, 2004, at 12 o'clock noon.

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ISBN 951-22-7333-0

Picaset Oy
Helsinki 2004

Abstract

This thesis considers metrological application of spectrophotometric measurements in characterization of optical thin-film coatings, diffuse reflectance standards, and filter-radiometer components.

For the optical metrology of thin films, various systematic errors in the measurements were studied in order to understand their effect on the determined optical parameters of thin films. The analysis was done based on computer simulations. Experimental results for several coated samples are also presented. The results demonstrate the importance of accurate spectrophotometric measurements for reliable characterization of thin films. It is shown that when the characterization is done based on measurements at oblique angles of incidence, significant errors may be introduced due to certain systematic effects. Thus the use of ordinary commercial spectrophotometers may restrict the accuracy of the characterization. The experimental data obtained with the high-accuracy spectrophotometer at HUT demonstrates consistency among the derived thin-film parameters at both normal and oblique angles of incidence.

For the calibration of diffuse reflectance standards, a gonioreflectometer-based absolute scale of spectral diffuse reflectance has been established at HUT and is presented in the thesis. The newly established absolute scale of spectral diffuse reflectance is at the present moment the second in the world, where the hemispherical reflectance factors are derived without the use of integrating spheres. The gonioreflectometer setup, measurement and characterization procedures, as well as uncertainty analysis and results of test measurements are summarized in the thesis.

For the characterization of filter radiometers (FRs), which is needed for the realization of the primary spectral irradiance scale at HUT, the thesis includes a comprehensive overview of the developed measurement methods, modeling and rigorous uncertainty-analysis procedures. An intercomparison of the characterization techniques in the UV spectral region adopted at HUT and at several other National Metrology Institutes is also presented. For the first time, effects of correlations in the FR signals originating through the characterization of the FRs were studied. This has led to a method of optimizing the selection of FR wavelengths and a practical range of uncertainties in the case of correlations in input parameters.

Preface

The research work presented in this thesis has been carried out at the Metrology Research Institute, Department of Electrical and Communications Engineering of the Helsinki University of Technology, during the years 2000 – 2004.

I wish to express my gratitude to Professor Pekka Wallin, the Head of the Department of Electrical and Communications Engineering, for providing me the opportunity to study and work in this interesting field.

I am most grateful to my supervisor Professor Erkki Ikonen for his continuous guidance, encouragement and valuable support throughout these years.

My special thanks to my senior colleague Farshid Manoocheri who has been my closest adviser and discussion partner in all the stages of the research work.

I am indebted to the coauthors of my publications and past and present employees at the Metrology Research Institute. In particular, I would like to thank Petri Kärhä, Toomas Kübarsepp, Atte Haapalinna, and Arto Niemelä for their share of work in the research and publications. I acknowledge Seppo Metsälä for his excellent work done in machining all the fine-mechanical parts used in the projects.

I would also like to thank Professor Alexander Tikhonravov for useful discussions and contributions to the publications.

Funding of the work has been provided by several sources. I appreciate the financial support by the Centre for Metrology and Accreditation (MIKES), National Technology Agency (TEKES), National Graduate School of Electronics Manufacturing and Graduate School of Electrical and Communications Engineering.

My warmest thanks to friends and colleagues Kęstutis Grigoras, Farshid Manoocheri and Mart Noorma for their fruitful team work in tennis courts that has brightened the long days spent in the laboratory rooms.

Finally, I am grateful to my wife Aušra and my son Bartas for their love, patience and support that they have given me during all these years.

Espoo, October 2004

Saulius Nevas

List of publications

The thesis consists of an overview and the following selection of the author's publications.

I. S. Nevas, F. Manoocheri, and E. Ikonen, "Determination of thin-film parameters from high accuracy measurements of spectral regular transmittance," *Metrologia* **40**, S200-S203 (2003).

II. S. Nevas, F. Manoocheri, E. Ikonen, A. Tikhonravov, M. Kokarev, and M. Trubetskov, "Optical metrology of thin films using high-accuracy spectrophotometric measurements with oblique angles of incidence," in *Advances in Optical Thin Films*, C. Amra, N. Kaiser, H. A. Macleod, eds., *Proc. SPIE* **5250**, 234-242 (2004).

III. A. Haapalinna, S. Nevas, F. Manoocheri and E. Ikonen, "Precision spectrometer for measurement of specular reflectance," *Rev. Sci. Instrum.* **73**, 2237-2241 (2002).

IV. S. Nevas, F. Manoocheri, and E. Ikonen, "Gonioreflectometer for measuring spectral diffuse reflectance," Accepted for publication in *Applied Optics*.

V. T. Kübarsepp, P. Kärhä, F. Manoocheri, S. Nevas, L. Ylianttila, and E. Ikonen, "Spectral irradiance measurements of tungsten lamps with filter radiometers in the spectral range 290 nm to 900 nm," *Metrologia* **37**, 305-312 (2000).

VI. P. Kärhä, N. J. Harrison, S. Nevas, W. S. Hartree, and I. Abu-Kassem, "Intercomparison of characterisation techniques of filter radiometers in the ultraviolet region," *Metrologia* **40**, S50-S54 (2003).

VII. S. Nevas, E. Ikonen, P. Kärhä, and T. Kübarsepp, "Effect of correlations in fitting spectral irradiance data," *Metrologia* **41**, 246-250 (2004).

Author's contributions

The research work presented in this thesis has been conducted at the Metrology Research Institute of the Helsinki University of Technology. All publications included are the results of a fruitful team work of the contributing researchers, where the author had a well-defined role.

For Publ. I, the author developed the analysis procedures, studied the effect of the systematic errors in the measurements on the thin-film parameters, measured the transmittance of the samples, analyzed the measurement results, and prepared the manuscript. Both the modeling and the results of the oblique-incidence transmittance measurements as well as analysis of the results in Publ. II are the author's contribution. The manuscript for Publ. II was also prepared by the author.

For Publ. III, the author did a part of the experimental work and contributed to the uncertainty analysis. The author had major responsibility for the design of the gonioreflectometer, developed the alignment, characterization and measurement procedures, determined the instrumental parameters, did the uncertainty analysis, performed the test measurements, and wrote the manuscript for Publ. IV.

For Publ. V, the author contributed to the characterization of filter-radiometer components and the analysis of uncertainties due to the characterization measurements. The author was responsible for the HUT part of the filter-radiometer responsivity measurements in the intercomparison of the characterization techniques of Publ. VI. He planned and carried out the measurements as well as determined the uncertainty estimates for the values measured at HUT.

For Publ. VII, the author did the analysis to estimate the correlations in the filter-radiometer responsivity data, implemented procedures for studying the propagation of uncertainties and correlations through fitting the measurement data, determined the effect of the correlations, and prepared the manuscript.

List of abbreviations

CCPR	Consultative Committee for Photometry and Radiometry
CIE	International Commission on Illumination
BNM-INM	Bureau National de Metrologie - Institut National de Metrologie, France
HUT	Helsinki University of Technology, Finland
NMI	National Metrology Institute
NIST	National Institute of Standards and Technology, USA
NRC	National Research Council, Canada
NPL	National Physical Laboratory, UK
OIC	Optical Interference Coatings
PTB	Physikalisch-Technische Bundesanstalt, Germany

BRDF	bidirectional reflectance distribution function
DVM	digital voltage meter
FR	filter radiometer
FWHM	full-width at half-maximum
NIR	near infrared wavelength region
VIS	visible wavelength region
UV	ultraviolet wavelength region
WDM	wavelength division multiplexing

List of symbols

σ	electric conductivity
ε	electric permittivity
ψ	ellipsometric parameter related to the magnitude of the ratio of the two eigen-polarization reflection coefficients
Δ	ellipsometric parameter related to the phase difference between the two eigen-polarization reflection coefficients
κ	wave number (=$2\pi/\lambda$)
λ	wavelength in vacuum
Al_2O_3	aluminum sesquioxide coating
c	speed of light in vacuum (=2.99792458×10^8 m/s)
$\overline{E}$	electric field vector
$\overline{H}$	magnetic field vector
i	imaginary unit (=$\sqrt{-1}$)
$k(\lambda)$	extinction coefficient
$n(\lambda)$	refractive index
$N(\lambda)$	complex index of refraction {= $n(\lambda) - ik(\lambda)$}
p-polarization	polarization plane parallel to the plane of incidence
SiO_2	silicon dioxide coating
s-polarization	polarization plane perpendicular to the plane of incidence
$v(\lambda)$	phase velocity of light in material {= $c/n(\lambda)$}
β	radiance factor
ρ	reflectance
$\Phi(\lambda)$	spectral radiant flux
R	reflectance factor
$\varepsilon'(\lambda)$	effective emissivity in the model for spectral irradiance of lamps
$\tau(\lambda)$	spectral transmittance of a band-pass filter
A	area of an aperture
B	auxiliary factor in the model for spectral irradiance of lamps
c_1	first radiation constant in Planck's law ($\approx 3.7418 \times 10^{-16}$ W m^2)
c_2	second radiation constant in Planck's law ($\approx 1.4388 \times 10^{-16}$ m K)
$E_c(\lambda)$	spectral irradiance of lamps modeled by a modified Planck's law
i_c	photocurrent
$R(\lambda)$	spectral responsivity of a photodetector
T	absolute temperature

Contents

Abstract **3**
Preface **4**
List of publications **5**
Author's contributions **6**
List of abbreviations **7**
List of symbols **8**
Contents **9**
1. Introduction **10**
1.1. Background 10
1.2. Progress in this work 13
2. Characterization of optical thin-film coatings **16**
2.1. Optical parameters of thin films 16
2.2. Characterization methods 18
2.3. Inverse synthesis 21
2.4. Effect of systematic errors in spectrophotometric measurements 22
2.5. Systematic effects in oblique-incidence measurements 25
3. Characterization of diffuse reflectance standards **29**
3.1. Definitions 29
3.2. Diffuse reflectance scales 30
3.3. Gonioreflectometric determination of hemispherical reflectance factors 31
3.4. Results of intercomparison 33
4. Characterization of filter radiometers **34**
4.1. Principle of filter radiometry 34
4.2. Spectrophotometric characterization of filter-radiometer components 35
4.3. Importance of correlation analysis 37
4.4. Propagation of uncertainties and correlations in the spectral irradiance scale 38
4.5. The procedure for propagating uncertainties and correlations applied to the thin-film analysis 39
5. Conclusions **41**
References **43**
Abstracts of Publications **49**

1. Introduction

1.1. Background

Spectrophotometric measurements are used for quantifying optical properties of materials and artifacts: reflection, transmission, or absorption of light waves at different wavelengths of the spectrum. The optical properties of a material may depend on factors such as its chemical composition and concentration, thermodynamic conditions, or structural characteristics of the surface and bulk. Thus knowledge of the optical properties can be utilized in studying physical / chemical properties of materials and artifacts as well as in monitoring of technological, (bio) chemical, or environmental processes. Moreover, accurate spectrophotometric measurements help ensuring the right color and appearance of a product, which may have a major contribution to its commercial success. Furthermore, defining the properties of an optical component may be of primary importance for its applicability for a certain purpose. Therefore, the spectrophotometric measurements are widely used in areas such as chemical [1], biochemical [2], pharmaceutical [3], paint, and paper industries, optical / optoelectronic technology, and environmental monitoring [4], just to mention a few. Needless to say, in today's hi-tech world of ever-accelerating technologies, when dimensions of manufactured features shrink down to the nano-scale and volumes in the optical communications sky rise toward the tera-scale, the characterization measurements have to meet increasingly stringent requirements for the accuracy and reliability.

One of the most interesting and important application of the spectrophotometric measurements is the characterization of optical thin-film coatings. Thin films are the building blocks in the optical / optoelectronic technology. Thus the technology is highly dependent on knowledge of the optical parameters of deposited thin-film layers. The complex index of refraction and the layer thickness need to be known accurately in order to achieve the design characteristics of manufactured optical components such as: a narrow band-pass interference filter, a highly-reflective mirror, an antireflection-coated lens, a polarizer, a wavelength-division multiplexer (WDM) or a gain-flattening filter for an optical-fiber amplifier.

The optical parameters of a coating are widely derived from the results of the spectrophotometric measurements [5, 6, 7, 8, 9, 10, 11]. For this purpose, a physical model of the spectrophotometric properties of a layer is often fitted to the measurement data over the entire spectral region of interest. Although the characterization methods benefit from the computational resources of modern computers that were not available a few decades ago, accuracy of the spectrophotometric measurements remains an important precondition for the analysis to yield reliable results. This is illustrated also by the fact that the organizers of the conference on Optical Interference Coatings (OIC), which takes place every third year, for the ninth topical meeting in 2004 have decided to include a Measurement Problem as a contest for the participants [12]. A part of the Measurement Problem was measuring the spectral transmittance and reflectance of a single dielectric layer on a fused silica substrate, from which the complex index of refraction and the thickness of the layer had to be determined.

The accuracy of the spectrophotometric measurements is mostly limited by systematic errors. It has been demonstrated that presence of the systematic errors in the measurements, such as normalization drift in dual-beam instruments, may have a dramatic effect on the determined optical parameters of thin films [13]. Thus for the reliable characterization of interference coatings, a number of possible systematic errors in the spectrophotometric measurements need to be identified and their effect on the derived optical parameters must be understood.

Characterization of visually-perceived properties of a product, such as the whiteness of paper or the color of a cloth, often involves measurements of spectral diffuse reflectance. Hence, accurate and harmonized measurements of the diffuse reflectance are of vital importance for the industries. The measurements are usually performed relative to a reference standard traceable to an absolute scale. At present, only a few absolute scales of spectral diffuse reflectance exist in the world. The absolute scales are predominantly based on integrating-sphere techniques, where the sphere is used either for collection of the diffusely reflected flux or for the diffuse irradiation of an artifact. The history of such measurements started with the works by A. H. Taylor [14] and H. Sharp and W. F. Little [15] published in 1920. At that time, the integrating sphere was a brilliant solution to the technical problem of reliably probing the diffusely reflected radiant flux. Although there were certain limitations in the theory of their methods, these contributions were a basis for further research on the application of the integrating spheres. As a result of intense research on the subject during the rest of the 20th century, a range of theoretical and practical problems have been solved, eventually yielding reliable and accurate measurement systems adopted by major national metrology institutes (NMIs) such as National Institute of Standards and Technology (NIST), USA [16], National Research Council (NRC), Canada [17], and Physikalisch-Technische Bundesanstalt (PTB), Germany [18, 19]. Many NMIs have also established integrating-sphere based relative scales of spectral diffuse reflectance.

The technological breakthrough in the electronics technology during the last decades of the 20th century made possible direct probing of the diffusely reflected flux. In this approach, a gonioreflectometer with a detector of a narrow field-of-view is utilized. The reflected flux is determined from measurements at numerous positions on a spherical surface at a certain distance from the measured artifact. To make such measurements feasible, highly linear photodetectors with a dynamic range of at least 10^4 were needed as well as automation of the measurement instrumentation had to be implemented. PTB was the first amongst NMIs to develop an automated gonioreflectometer for measuring spectral reflection characteristics [20]. Later, gonioreflectometric measurement systems were built at NIST [21] and National Physical Laboratory (NPL), UK [22]. However, so far only the gonioreflectometer at NPL is used to establish absolute scales of total hemispherical reflectance factors in the visible (VIS) part of the spectrum [23]. The other NMIs prefer to keep their integrating sphere-based scales while using their gonioreflectometers for determining bidirectional reflectance characteristics: bidirectional reflectance distribution function (BRDF) and bidirectional radiance factors [24]. Hence up to the present moment NPL has been the only NMI in the world having their absolute hemispherical reflectance factor scales based on the gonioreflectometric measurements. However, some discrepancies between the gonioreflectometer results and those from the integrating-sphere techniques have been reported; the gonioreflectometer results were found to be higher [23]. This raised questions about the reality and origin of the discrepancy, whether it was due to the different manner in which the samples were probed.

Another important field of applications where the spectrophotometric measurements with high accuracies are needed is characterization of devices, such as filter radiometers (FRs), utilized for the optical radiation measurements. These devices are employed in determination of the spectral irradiance and luminous intensity of light sources, where a functional relationship is fitted to the FR data. The measurement methods are based on thoroughly characterized properties of the FRs. Thus the accuracy of the measured spectral irradiance and the luminous intensity of a source is related to the uncertainties in the characterization of the devices. According to the rule of propagation of uncertainties, the uncertainties in the FR data propagate through the entire process of deriving the spectral quantities. Moreover, it has been shown that due to certain effects correlations can be introduced in the FR data [25]. Traditionally such correlations have been neglected even at the NMIs level. However, at least at the level of the primary spectral scales, the correlations have to be included in the propagation of uncertainties as they have an effect on the output uncertainties and correlations.

1.2. Progress in this work

The main goals of the research summarized in this thesis have been studying reliability of the metrology of optical thin-film coatings based on the spectrophotometric measurements and improvements of the realizations of spectral diffuse reflectance and spectral irradiance scales maintained at the Metrology Research Institute of Helsinki University of Technology – the Finnish National Standards Laboratory for optical quantities.

The first research topic of the thesis is covered in Chapter 2 where methods for the characterization of optical thin-film coatings are briefly reviewed and the spectrophotometric characterization is analyzed for the sources of systematic measurement errors and their effect on the determined optical parameters. A motivation for the research on the reliability issues in the spectrophotometric characterization of optical coatings was the expertise in the area of optical measurements that has been gathered at our institute during the last fifteen years. The capability of performing accurate measurements of spectral regular transmittance and reflectance [26, 27, Publ. III] was a good starting point for studying the characterization of thin films both at normal and oblique angles of incidence [Publs. I, II]. By employing a model of the spectral transmittance / reflectance of thin-film samples, systematic errors in the measurements were simulated and their effect on the determined thin-film parameters analyzed. The study explained the effect that various systematic errors in normal and oblique-incidence spectrophotometric measurements have on the determined optical parameters of thin-film coatings. The obtained results of the analysis are summarized in Chapter 2. The systematic effects have to be especially considered when commercial spectrophotometers are used. For example, utilizing converging beams in the spectral transmittance and reflectance measurements at oblique angles of incidence, which is the property of most commercially available instruments, may cause substantial errors in the characterization results. The consistency of the modeling results and the importance of accurate spectrophotometric measurements have been confirmed by measuring and characterizing several thin-film samples.

Chapter 3 provides an overview of diffuse reflectance scales maintained by prominent NMIs around the world and describes the realization of the scales at HUT. The scale of spectral diffuse reflectance at HUT has been upgraded from the relative scale, traceable to the primary scales at NRC and PTB, to own absolute scale of total hemispherical reflectance factors [Publ. IV]. A gonioreflectometer has been designed and built that is capable of measuring bidirectional reflectance distribution characteristics. Absolute values of the total reflectance factors are derived by angular integration of such measurements. At present in the world, this is the second traceable absolute scale where the total hemispherical reflectance factors are derived without the use of the integrating spheres [24]. The developed system has been thoroughly characterized and the budget of uncertainties established. The new gonioreflectometer-based scale has been compared to the earlier relative scale. Agreement between the gonioreflectometer results and the integrating sphere-derived values was found to be within the measurement uncertainties. Although a certain discrepancy of apparently systematic origin can be noticed, the agreement is better than in the case of earlier published results comparing the reflectance factor values derived by the gonioreflectometric and the integrating sphere-based approaches [23]. Thus the earlier findings were only partly confirmed.

In Chapter 4, the characterization of the FR components and the importance of such characterization for the realization of the primary spectral irradiance scale at HUT are briefly discussed. The thorough characterization of the components of the

FRs results in accurate determination of absolute spectral irradiance over the spectral region of 290 to 900 nm [Publ. V]. Furthermore, the detector-based spectral irradiance scale at HUT has been extended into the near ultraviolet (UV) wavelengths region. FRs have been developed for measuring the radiation from UV sources, down to 250 nm, and an intercomparison between HUT, NPL and Bureau National de Metrologie – Institut National de Metrologie (BNM-INM), France of their characterization techniques has been done [Publ. VI]. The results emphasize the importance of wavelength scale for reliable characterization of narrow-bandwidth FRs.

The importance of including correlations through the FR characterization into the uncertainty analysis is also discussed in Chapter 4. Up to the present moment, the uncertainty calculations even in the primary spectral irradiance scales have been carried out without taking into account possible correlations between pairs of spectral values. At HUT, for the first time correlations in the FR data have been included in the uncertainty analysis of the fitted spectral irradiance values [Publ. VII]. Effects of the correlations originating through systematic errors in the FR spectral responsivity data as well as correlations through fitting Planck's radiation law have been studied. The results have led to a new method of optimizing the selection of FR central wavelengths and, furthermore, a practical range of uncertainties can be given in the case of correlations in the FR data.

Chapter 4 also demonstrates how the procedures for propagating correlations and uncertainties in the FR data can be applied to the uncertainty analysis in the case of thin-film characterization. The procedures are alike since in both cases they involve the process of propagation through the spectral fitting. Thus here the available uncertainty and correlation propagation procedures could provide an estimate of the standard and mutual uncertainties of the determined optical parameters of a thin-film layer.

2. Characterization of optical thin-film coatings

Design of bulk optical components, such as lenses or absorption-type filters, is based on the knowledge of the optical parameters of the materials utilized in the design. Knowing the optical parameters with high accuracy is even more important in the case of multilayer interference coatings, where the optical thickness of each layer is designed to match a certain number of half-wavelengths. Although it is relatively straightforward to characterize and to reproduce optical parameters of bulk materials, these tasks are much more demanding in the case of thin-film coatings. The optical properties of deposited layers are highly dependent on the technological processes involved in the deposition. As a result, the optical parameters of a coated material may vary and differ significantly as compared with their values for bulk-form material. Furthermore, not all materials that are deposited as optical coatings can be found in the bulk form. Hence, the optical parameters of a coating can hardly be known in advance. Thus accurate characterization of thin-film coatings is a must for the successful design and production of multilayer optical components.

2.1. Optical parameters of thin films

The goal of optical characterization procedures is to determine the optical parameters of a thin-film coating. Normally they include the complex index of refraction $N(\lambda) = n(\lambda) - ik(\lambda)$ and the thickness of the layer d. The real part n is often referred to as refractive index and the imaginary part k as extinction coefficient. The complex index of refraction N is related to material properties: the electric permittivity ε and electric conductivity σ of the material,

$$N^2 = \varepsilon - i\frac{4\pi\sigma}{\omega}, \qquad (1)$$

where $\omega = 2\pi c/\lambda$ is the angular frequency of the electromagnetic oscillations, c is the speed of light in vacuum, and $n = \sqrt{\varepsilon}$.

The optical parameters define how the incident light waves interact with the optical coating. The relationship between the optical parameters and the propagating wave is derived from the Maxwell's equations [28]. The electric field vector of the incident light wave hence can be written in the complex notation as

$$\overline{E} = \overline{E}_0 \exp\{\overline{\kappa}[i(ct - \overline{r}n(\lambda)) - \overline{r}k(\lambda)]\}, \quad (2)$$

where E_0 is the field amplitude, t denotes time and r position variables, and $\kappa = 2\pi/\lambda = \omega/c$ represents the wave number with vacuum-wavelength λ. From Eq. (2), the physical meaning of the complex index of refraction is obvious. The real part $n(\lambda)$ governs the phase velocity $v(\lambda) = c/n(\lambda)$ of the electromagnetic waves in the medium and hence the dispersion of the waves. It is also evident from the equation that while traversing the film layer with thickness d, the wavefront acquires a phase change of $\beta = (2\pi/\lambda)n(\lambda)d$. The imaginary part $k(\lambda)$ is responsible for the attenuation of E_0. As one can notice from (2), a single-pass absorption loss in the layer is defined by $\gamma = (2\pi/\lambda)k(\lambda)d$.

At an interface between two media, the light gets partly reflected and partly transmitted (Figure 1). The reflection and transmission at the interface can be quantified by applying boundary conditions to the Maxwell's equations. They require that at the boundary between two media the tangential components of both the electric and magnetic field vectors ought to be continuous. The analysis leads to coefficients known as Fresnel coefficients [29]. They are defined in terms of the complex index of refraction of the two media, the incidence angle and the polarization state of the incident light.

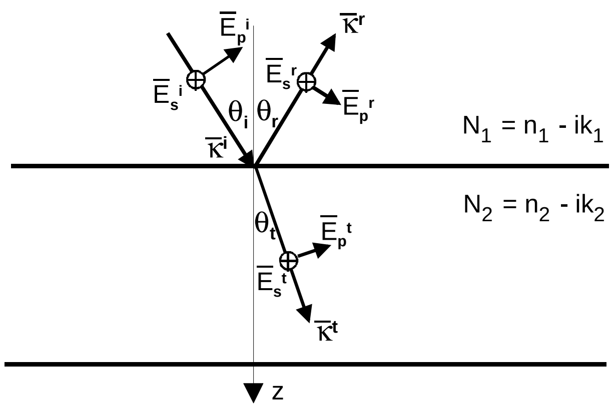


Figure 1. Transmission and reflection of light waves at a boundary between two media. For a given wave vector $\overline{\kappa}$, the electric field vector $\overline{E}$ is decomposed into two orthogonal components: lying in the plane of incidence $\overline{E}_p$, and perpendicular to the plane of incidence $\overline{E}_s$. Subscripts *i*, *r*, and *t* denote incidence, reflection, and transmission through the interface, respectively. θ denotes the angle between $\overline{\kappa}$ and the interface normal *z*. $N_{1,2}$ are the complex indices of refraction of the two materials.

Because of the partial reflections at the sample interfaces (Figure 1), multiple interreflections occur both in the layer and in the substrate. The complex amplitudes of all such interreflections can be summed directly in the case of purely monochromatic light. In the case of semi-monochromatic irradiation, as obtained from the output of a monochromator, the coherence length L_C with respect to the layer thickness d and the substrate thickness L has to be taken into account. It is inversely proportional to the spectral width $\Delta\omega$ of the light, $L_C = c/\Delta\omega$ [30]. Hence for a spectrophotometer beam with a finite bandwidth $\Delta\omega$, a typical situation is $d << L_C << L$. Thus the interreflections in the thin-film layer are coherent while in the substrate they are not. The non-coherent interreflections do not interfere among each other, thus the intensities rather then the amplitudes are to be summed. These considerations lead to explicit expressions for both the intensity transmittance and reflectance of coated samples [Publ. I]. A convenient way of describing the spectrophotometric characteristics of a multilayer coating is provided by the transfer matrix approach [29, 31, 32].

For some optical coatings, additional layer parameters are required for adequate description of their optical properties. Such parameters include the surface roughness and bulk inhomogeneity [33]. Large-scale roughness harmonics cause light scattering while small-scale roughness changes the reflection and transmission coefficients of the interface [34]. Thus the interface roughness may affect the measured regular transmittance and reflectance. The bulk inhomogeneity is variation in the refractive index of the layer across its thickness. It reveals itself in the shifts of transmittance / reflectance extrema from the transmittance / reflectance of the uncoated substrate [35, 36, 37].

2.2. Characterization methods

Optical characterization of thin films has been a subject of intense research during the last decades as the technology and the fields of application of optical coatings have been expanding all the time. Hundreds, if not more, of papers devoted to determination of the optical parameters have been published. Hence the variety of characterization methods is really huge. Nevertheless, the characterization methods can be classified based on several criteria. As noted by Dobrowolski *et al.* [5], one of the general criteria for the classification is the number of measurement wavelengths simultaneously used in the determination of the thin-film parameters: single-wavelength methods and multiwavelength methods.

In the single-wavelength methods, typical quantities that are measured include transmittance, reflectance, the phase change of transmission or reflection, and the amplitude and phase difference between *s*- and *p*-polarized reflected or transmitted beams. The number of independent measurements normally equals the number of unknown optical parameters. The experimental data are gathered by using spectrophotometric, ellipsometric (Figure 2), or interferometric techniques. The ellipsometry is one of the most popular among the methods due to its relative simplicity and capability of characterizing very thin layers.

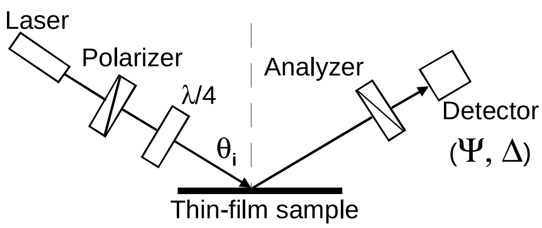


Figure 2. Principle of null ellipsometry. The sample is illuminated with a polarized beam. The polarization state of the incident beam is adjusted to compensate for the change in the relative amplitude ψ and the phase Δ between *s*- and *p*-polarization components that is introduced by the sample.

The single-wavelength methods potentially are capable of accurate results. However, because of their single-wavelength nature the methods are susceptible to both random and systematic errors in the measurements. Furthermore, expressions relating the optical parameters to the measured quantities are very complex. Therefore, the optical parameters are generally derived by successive iterations, which often leads to multiple solutions. Moreover, even slight measurement errors may cause convergence to a wrong solution or no solution at all. In some methods, the ambiguity problem is solved by normal-incidence measurements with different film geometry [38, 39], by additional oblique-incidence measurements [40, 41], or by employing error analysis techniques, which enables to select a combination of oblique-incidence measurements that would yield best results for the derived parameters [42, 43, 44].

In the multiwavelength approach, the transmittance / reflectance is measured over a certain spectral range and the whole data set is used in the derivation of the optical parameters of thin-film coatings. Thus the sensitivity to the measurement errors is reduced. The optical parameters of a coating can be determined based on the Kramers-Kronig relations, on curve fitting to the measured spectra, or on analysis of the transmittance / reflectance minima and maxima (envelope methods). Moreover, in recent years spectroscopic ellipsometry has become an important approach to the characterization of thin films. It combines the best features of both the single-wavelength and the multiwavelength methods,

In principle, the Kramers-Kronig methods require the transmittance / reflectance to be measured for all possible wavelengths [45, 46, 47, 48]. In practice, the measurements are made over a limited range of wavelengths, which requires corrections to be applied at the limits of the measured wavelength range. The expressions for the spectral characteristics are complicated, which require approximations to be used in the derivation of the complex index of refraction. This may lead to uncertainties in the obtained values.

In contrast to the Kramers-Kronig methods, the multiwavelength curve fitting methods do not require the measured spectral range to be wider that the wavelengths of interest of the optical parameters. In this approach, the complex index of refraction is described by dispersion equations and a model of the transmittance / reflectance of a thin-film sample is fitted to the measured spectra. Depending on the type of the coating material, various dispersion equations can be used, such as: interband transition model (Lorentzian) [5, 49], useful for dielectric materials; free electron gas model (Drude) [5], suitable for some metals; a combination of the Lorentz and Drude models [5]; analytical formulas (Sellmeier [50],Cauchy [51, 52]), used in spectral regions away from the absorption band; Forouhi dispersion equations [53], applicable to a wide class of amorphous dielectrics and semiconductors; or arbitrary modified equations.

In the envelope methods, the optical parameters are inferred from the extrema in the measured spectra. The analysis is based on mathematical expressions relating the maxima and minima in the measured transmittance / reflectance spectra to the optical parameters of thin film [54, 55, 56, 57, 58]. Compared to the other multiwavelength methods, these methods are relatively simple. On the other hand, the envelope methods do not benefit from all the available experimental data.

During recent years the spectroscopic ellipsometry has become a powerful tool capable of characterizing both single layers and multilayer stacks [59, 60, 61, 62, 63]. As implied by the name, the approach is based on fitting the modeled ψ and Δ to the measured spectra over a range of wavelengths. The experimental data are fitted by adjusting the coefficients of the dispersion equations describing $n(\lambda)$ and $k(\lambda)$ and the thickness of the layer. The critical step involved in the fitting is a proper selection of the dispersion equations (parameterization of the unknown dielectric functions).

The above-mentioned methods are all based on the classical approach. However, recently novel non-classical techniques have been reported, such as the entangled-photon ellipsometry with coincidence-detection [64, 65]. The advantage of the new approaches is that they are practically free of problems associated with the calibration of source or detector. The new quantum-mechanical schemes to the characterization of optical coatings may possibly lead to new limits of capabilities barely imaginable by any classical approach.

2.3. Inverse synthesis

The term of inverse synthesis was introduced by Dobrowolski *et al.* [5] to describe the multiwavelength characterization method where a powerful thin-film synthesis program was employed to adjust the constants of dispersion equations until a good fit is obtained between measured and calculated spectral transmittance and/or reflectance curves. In the paper it was also pointed out that the constants in the dispersion equations do not necessarily have to have a physical meaning since the equations are used only as a convenient vehicle to describe the variation in $n(\lambda)$ and $k(\lambda)$ required to fit the measurement data. The main criteria when selecting the type of the dispersion equations is their capability of adequately describing $n(\lambda)$ and $k(\lambda)$ with the least possible number of constants in the dispersion formulas.

For the spectrophotometric quantities measured at $i = 1\ldots p$ wavelengths, the adjustment is carried out by minimization of a single-valued merit (discrepancy) function M that is defined in terms of the differences between the measured values S_i and the calculated values $S_{i,calc}$,

$$M = \sqrt{\frac{1}{N}\sum_{i=1}^{p}\left(\frac{S_i - S_{i,calc}}{\Delta S_i}\right)^2}\,, \tag{3}$$

where ΔS_i denotes the uncertainty with which the ith spectral value has been measured. Thus employing an optimization procedure yields the constants in the dispersion equations as well as the film thickness. Moreover, the method allows to increase the sensitivity or to avoid convergence to a spurious solution in the case of demanding coatings, such as metal or semiconductor films. For this purpose the merit function can include a combination of the spectrophotometric quantities measured at sensitive angles of incidence.

Since the paper by Arndt *et al.* [6], the minimization of the discrepancy functions for the derivation of the optical parameters of thin films has become a major approach in many research laboratories and companies involved in production of optical coatings. The powerful feature of the inverse synthesis is that the optical parameters are retrieved by utilizing all the available spectral data, not just a part of it as in the case of envelope methods. The approach of the inverse synthesis has been adopted also in this work [Publ. I].

2.4. Effect of systematic errors in spectrophotometric measurements

It is obvious that while fitting spectrophotometric measurement data, the choice of an adequate model is very important. However, a proper model is not enough in order to avoid errors in the determined optical parameters. It has been demonstrated that presence of systematic errors in the measurement data, such as the normalization drift in dual-beam instruments, may have a significant effect on the spectrophotometric characterization results [13]. The random errors in the measured spectra do not have so much influence due to fitting to a multitude of spectral points, which has an averaging effect on the errors of random nature. Hence identifying the sources of possible errors in the spectrophotometric measurements and understanding their effect on the determined optical parameters is of interest to every laboratory or company seeking reliable characterization of optical coating.

A number of systematic errors of different origin may be affecting the spectrophotometric measurements. Although having a purpose-built and thoroughly characterized instrument allows the errors to be minimized [66, Publ. III], this is not always possible when an ordinary commercial spectrophotometer is used for the measurements. In addition to the normalization drift, the measurement results may be biased by effects such as:

- nonlinearity of the detection system,
- interreflections between optical components,
- deviations in the spectrophotometer wavelengths,
- stray light,
- poor spatial uniformity of the measurement beam and responsivity across active area of the detector,
- temperature changes, etc.

The effect of the most important systematic errors has been studied in publication I. Theoretical analysis was based on a computer-simulated transmittance spectrum. The modeled spectrum was intentionally modified to simulate the presence of each of the systematic error components. The effect of the errors was determined by comparing the optical parameter values derived from the error-biased spectrum with the original values used in the simulations. The results of the analysis are summarized in a qualitative form in Table 1. It can be seen from the table that the nonlinearity of the detection system of a spectrophotometer has similar impact on the determined optical parameters as the drift of the system. A deviation in the wavelength scale of an instrument has the largest effect on the determined physical thickness of the layer. The wavelength shift also somewhat affects the determined $n(\lambda)$, especially in the shorter wavelengths region where the dispersion starts getting stronger [Publ. I].

Table 1. Effect of the systematic errors in the spectrophotometric measurements.

Error	Effect on the determined optical parameters		
	n	***d***	***k***
Detection system drift (decrease in the transmittance)	Overestimate	Underestimate	Overestimate
Detector nonlinearity	Overestimate	Underestimate	Overestimate
Wavelength shift toward longer wavelengths	Overestimate	Overestimate	–

The experimental results presented in publication I confirm the importance of high-accuracy spectrophotometric measurements for the reliable determination of the optical parameters of thin-film coatings. Figure 3 shows an excellent fit to the measured transmittance of an Al_2O_3 coating deposited on a Corning 7059-glass substrate. The determined values of the refractive index can be read from the right axis of the figure. The analysis revealed no noticeable absorption in the coated layer throughout the measured spectral range, which is also evident when comparing the transmittance peaks to the substrate curve. The layer thickness was found to be 723.1 nm.

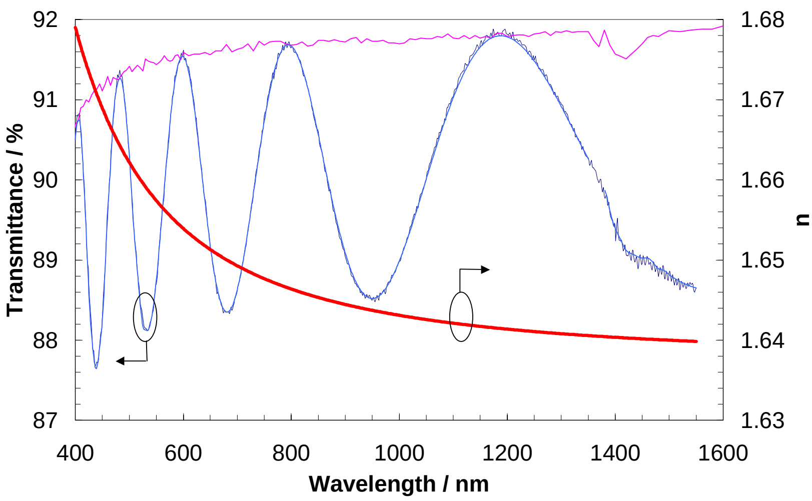


Figure 3. Experimental data for an Al_2O_3 thin-film sample [Publ. I]. The measured (oscillating curve with the apparent noise component), fitted (smooth curve) and substrate (top curve) transmittances are depicted. The derived refractive index of the layer *n* is also plotted.

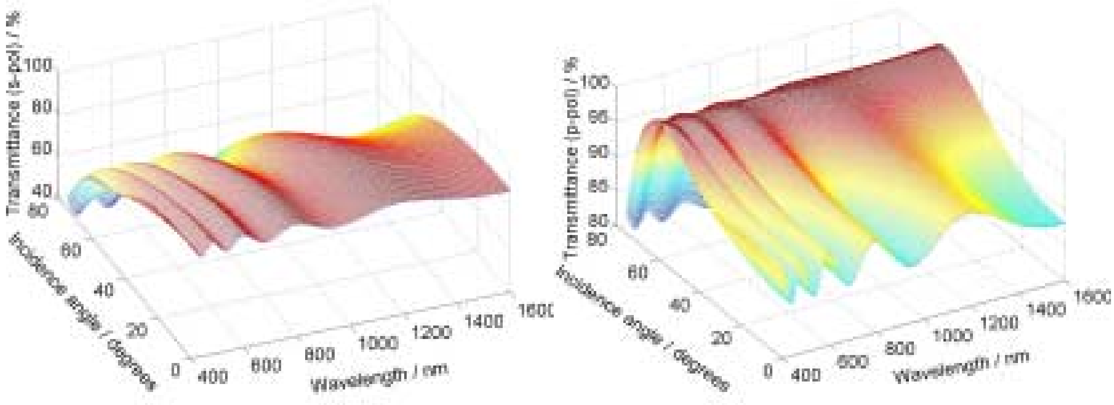
2.5. Systematic effects in oblique-incidence measurements

As it was mentioned in the description of the inverse synthesis approach to the determination of thin-film optical parameters, the experimental data utilized in the analysis may comprise also measurement results collected at oblique angles of incidence [5]. The oblique-incidence data can increase the sensitivity of the characterization method with respect to the determined optical parameters, although the normal incidence transmittance measurements may be the easiest to carry out. For example, the transmittance at the Brewster's angle with *p*-polarized light shall provide extra sensitivity to the determined *k* values. Thus in addition to the normal-incidence data, the transmittance or reflectance measured at as high incidence angles as the Brewster's angle are sometimes needed to be included in the discrepancy function of (3). Furthermore, the reflectance measurements are always made at oblique incidence [Publ III]. Therefore, in order to compare the reflectance and transmittance measurement results, also the transmittance data at the oblique angles of incidence should be available.

While utilizing oblique-incidence spectrophotometric data, in addition to the systematic effects studied in publication I there are other factors to be aware of [Publ. II]. Because the transmittance / reflectance measurements are made with polarized beams at oblique angles of incidence, one has to deal with systematic effects of:

- error in the angle of incidence,
- misalignment between the incidence and polarization planes,
- converging, diverging, or poorly collimated beam.

The importance of these factors is evident from Figure 4 that demonstrates a simulated transmittance spectra of a coated fused-quartz substrate for *s*- and *p*-polarized light as a function of both wavelength and incidence angle. The simulations were done based on the determined optical parameters of the Al_2O_3 thin-film coating.



a) **b)**

Figure 4. Simulated transmittance of a thin-film sample as a function of wavelength and incidence angle: a) for *s*-polarized beam; b) for *p*-polarized beam. In the simulations, the determined optical parameters of the Al_2O_3 layer were used.

It is clear that any uncertainty in setting the incidence angle reduces reliability of the characterization results despite the fact that the measurements could be accurate otherwise. In commercial spectrophotometers with limited space in the sample compartment and converging beams, it may be difficult to determine the angle accurately. The angle errors originate mostly from the error in defining the 0° incidence. The effect of the incidence angle error can be verified both experimentally and by simulations.

Oblique-incidence spectrophotometric measurements are normally made with linearly polarized beams. The linear polarization state is defined with the help of an adequate polarizer. Thus the angle between the plane of the polarization and the plane of incidence must be set precisely to 0° and 90° in order to be able to distinguish the two eigen polarizations. Otherwise the measurements cannot be regarded as made with purely *s*- or *p*-polarized light.

Collimation of the spectrophotometer beam is an important factor to be considered since a distribution in the angle of incidence arises in the case of a non-collimated beam. Thus the transmittance measured at the nominal incidence angle is in fact an average value of all the partial transmittances within the angle distribution. It has to be noted that the two values are not the same, especially at a larger incidence, since the transmittance dependence on the angle of incidence is not linear (Figure 4).

The effect of the systematic factors on the determined optical parameters of thin films was studied by modeling in publication II. The conclusions of the analysis were as summarized in Table 2. The study revealed that significant refractive index errors, of the order of 1%, may be obtained when the spectrophotometric measurements are performed with converging beams as found in many commercially available instruments. Incidence angle errors and undefined polarization state of the beam was shown to have an effect on the determined optical parameters as well. Hence spectral transmittance and reflectance of thin-film samples at larger incidence angles should be preferably measured with well collimated beams, at precisely determined angles, and with properly aligned polarization plane of the beam.

Table 2. Effect of the systematic errors in oblique-incidence measurements.

Systematic cause	**Results in:**
Underestimation of the incidence angle	*Overestimation* of the refractive index
Misalignment between the polarization and incidence planes	*Underestimation* of the refractive index
Beam *convergence*	*Overestimation* of the refractive index

The importance of the systematic issues was also verified experimentally [Publ. II]. The transmittance spectra of a SiO_2 layer deposited on a fused-quartz substrate were measured throughout the wavelength range of 400 nm to 950 nm. The measurements were made at our laboratory by using the high-accuracy reference spectrophotometer [66] with a collimated beam incident onto the sample at 0°, 10°, 30°, and 56.4° angles. The 56.4° incidence angle was determined to be the Brewster angle for the sample. The measured transmittance with *p*-polarized beam at this incidence was practically 100%, within 0.04%.

The optical parameters of the SiO_2 layer were determined by fitting both *s*- and *p*-polarization transmittances simultaneously. However, the results were practically the same when the *s*- and *p*-polarization transmittances were analyzed together or separately. In the characterization, the refractive index of the coating was described by the Cauchy equation,

$$n(\lambda) = A + B/\lambda^2 + C/\lambda^4, \quad (4)$$

where *A*, *B* and *C* are the equation coefficients adjusted during the fitting. The extinction coefficient *k* was not included in the fitted model since absorption was found to be absent for the thin-film layer throughout the whole spectral range of interest. Thus the film thickness *d* was the fourth fitting parameter.

The refractive index derived from the transmittance at the Brewster's angle was within 0.2% as compared to the normal incidence results. The agreement for the smaller angle-of-incidence results was better than 0.1%. The thicknesses of the layer determined from the measurements at 0°, 10°, 30°, and 56.4° incidence angles are presented in Table 3. The table also shows the deviations between the derived physical and optical thicknesses with respect to the results from the normal incidence data. Thus the derived optical parameters were found to be consistent over the normal to Brewster's angles of incidence demonstrating a very high accuracy of optical parameter determination with our instrument. The small deviations among the results of the characterization at different incidence angles were explained by the simulations for the systematic effects.

Table 3. The physical and optical thicknesses of the layer determined from the transmittance data at various incidence angles. The values are compared to the normal-incidence data.

Incidence angle	*d*, nm	Δ*d*, %	*nd*, nm (λ = 555 nm)	Δ*nd*, %
0°	716.2	–	1068.7	–
10°	716.1	-0.02	1069.0	+0.03
30°	716.1	-0.02	1069.1	+0.03
56.4°	714.7	-0.20	1068.0	-0.07

3. Characterization of diffuse reflectance standards

Diffuse reflectance standards are needed by many companies and laboratories that are utilizing diffuse reflectance measurements in applications such as the determination of the whiteness of paper. In their measurements, commercial instruments are commonly used where the reflectance of a test sample is compared with that of a calibrated reference standard. The characterization of the reference standards is achieved via an absolute measurement method. Because of the rigorous requirements for the design, characterization, maintenance and measurement procedures, only few NMIs around the world are equipped with a reflectometer capable of providing characterized standards and calibration services directly traceable to an absolute method.

3.1. Definitions

In essence, the term of diffuse reflection refers to the specific angular distribution of the reflected radiant flux. The perfect diffuse reflection as shown in Figure 5 is only possible from the surface of a perfect reflecting diffuser that reflects isotropically in all directions without absorption and transmission losses. Although no material exists that would satisfy such definition, the perfect reflecting diffuser is by international agreement the primary standard for diffuse reflectance measurements. Secondary standards are calibrated in terms of the perfect reflecting diffuser with help of an absolute method.

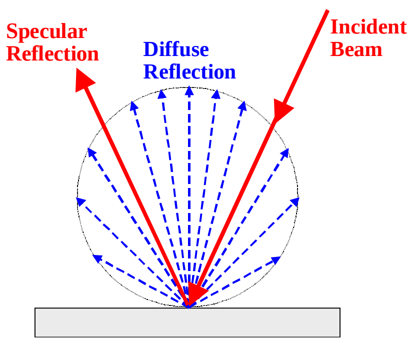


Figure 5. Reflection of a light beam in the two ideal cases: specular (continuous line) or perfectly diffuse (dashed lines).

Two terms are used to define the measured quantities in terms of the perfect reflecting diffuser: reflectance factor and radiance factor [67]. By the definition, the reflectance factor R is the ratio of the radiant flux reflected in the direction delimited by a given cone with apex at a point of the surface under test to that reflected in the same direction by a perfect reflecting diffuser identically irradiated. If the solid angle of the cone approaches 0, or 2π steradian, the reflectance factor R approaches radiance factor β or reflectance ρ, respectively. The reflectance ρ represents the ratio of the total radiant flux Φ_r, reflected by the surface, to the flux Φ_i, incident upon the surface,

$$\rho = \Phi_r / \Phi_i \,. \tag{5}$$

Hemispherical reflectance factors are normally used for diffusely reflecting samples. The samples are measured under standardized geometrical conditions such as incidence at 0° and collection of the diffuse component (0/*d*), or incidence at 8° and collection over the whole hemisphere (8/*t*). The difference between the total and the diffuse hemispherical collection of the reflected radiant flux is that the specular component is or is not included.

3.2. Diffuse reflectance scales

The role of a diffuse reflectance scale is to relate the reflectance of a standard under specified geometrical conditions to that of a perfect reflecting diffuser. Primarily, such a task requires involvement of an absolute method. A survey of the methods is available from CIE [68]. As it was mentioned in the introductory chapter, at present only a few primary absolute scales of spectral diffuse reflectance exist in the world. Moreover, the absolute scales of hemispherical reflectance factors are predominantly based on the integrating-sphere techniques. These techniques are able to provide reliable results through relatively simple measurement procedures. However, issues related to the port openings and the symmetry of the sphere as well as nonuniformity, aging, and contamination of the coating need to be addressed.

HUT, as the Finnish National Standards Laboratory of optical quantities, has been maintaining a relative scale of spectral diffuse reflectance. Up to now, HUT has been providing calibration service based on direct comparison with transfer standards obtained from the absolute scales of NRC and PTB.

The absolute diffuse reflectance scale at NRC is based on the method by Sharp and Little [15] that was modified by Budde [17]. In the measurements, an integrating sphere coated with barium sulphate paint is utilized. The sphere provides diffuse irradiation of a sample mounted at its port. The reflected radiance is measured normal to the sample surface. By comparing this radiance to the measured radiance of the sphere wall, the spectral radiance factor in $d/0$ geometry is obtained. The calculation also involves corrections for the sphere imperfectness owing to the existence of the sample surface at the sphere port and the port openings through which the light is projected and the reflected radiance is measured. The NRC absolute reflectometer can also be converted to the inverse geometry reflectance measurements, $0/d$.

In the absolute scale of PTB, a Korte method [69] modified by Erb [18] is employed. Like in the NRC scale, a barium sulphate-coated integrating sphere is used for diffuse irradiation of the sample. The difference in this method is that the measured sample is mounted near the centre of the sphere, with its surface in the equatorial plane. The lamp is also mounted internally and irradiates one hemisphere, which produces diffuse irradiation of the sample by the other hemisphere. The radiance factor of the sample in $d/0$ geometry is obtained from the alternately measured radiance of the sample and that of the sphere wall.

The realization of the absolute diffuse reflectance scale at NIST [16] is based on the method by Van den Akker [70]. The characteristic feature of this method is the use of an auxiliary integrating sphere in addition to the main integrating sphere. The auxiliary sphere is involved in measuring the reflectance of the wall of the main integrating sphere under the irradiation it receives. Comparing the reflectance of the wall to that of the sample yields directional hemispherical reflectance factor.

3.3. Gonioreflectometric determination of hemispherical reflectance factors

The gonioreflectometric approach to the determination of the hemispherical reflectance factors provides an alternative to the use of the integrating spheres. The approach is based on the integration of measured angular distribution of the reflected flux [20, 22, 23]. To this moment, NPL has been the only NMI to adopt such technique for the realization of the hemispherical reflectance factor scales [24].

Recently, a gonioreflectometer-based absolute scale of spectral diffuse reflectance has also been established at HUT. A detailed description of the realization of the new absolute scale of HUT is given in publication IV.

The developed gonioreflectometer consists of a light source and goniometric detection systems (Figure 6) controlled by a PC. The source system is built around a double monochromator operating in subtractive dispersion mode. The bandpass of the monochromator is selected with the help of rectangular-shaped variable-size slits. Routinely, a nominal bandpass of 5.4 nm is used in the measurements. The narrow-bandpass radiation emerging from the output slit of the monochromator is shaped into a nearly-collimated beam with clear edges, linearly polarized, and directed toward the detection system. The core of the detection system is a heavy-duty turntable driven by a stepper motor. The turntable enables an imaging detector to be set to any angular position in the horizontal plane with respect to the sample surface at its rotational axis. The distance between a 25-mm circular aperture at the detector and the sample surface is L = 485 mm. This defines a solid angle of 0.002 sr for the collection of the reflected radian flux. The flux of the incident beam is measured with the sample translated out of the beam, the detector at its reference position and the aperture underfilled (Figure 6). For the alternate measurements of the full-intensity beam and the reflected flux, the detector includes a low-noise variable-gain transimpedance amplifier.

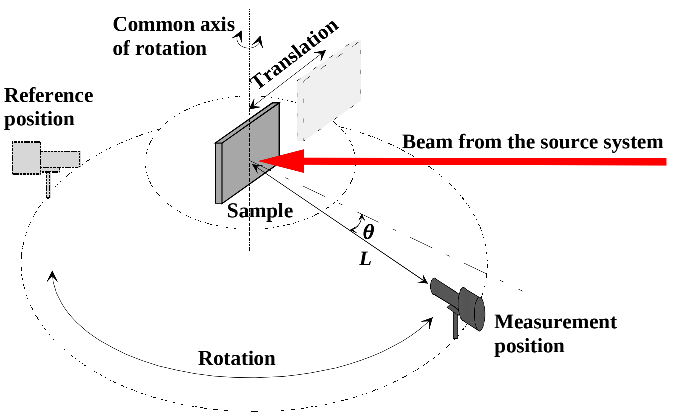


Figure 6. Schematic of the gonioreflectometer arrangement for alternate measurements of the incident beam (the sample out of the beam, the detector at its reference position) and the reflected flux (the detector at an angular position θ from the normal of the sample).

The 0/d reflectance of a diffuse reflectance standard is determined through a series of angle-resolved measurements that are normally made over the angle range of 10° to

85° with a 5° increment. The reflectance factor value is obtained by integrating the measured angular distribution of the reflected flux $\Phi(\theta)$,

$$R = \int_0^{\pi/2} \frac{\Phi(\theta)}{\Phi_i(\theta)} \frac{4L^2}{D^2 \cos(\theta)} \sin(2\theta) d\theta \,, \tag{6}$$

where θ, Φ_i, D, and L denote the polar angle, the incident flux, the diameter of the aperture, and the distance between the aperture and the test sample, respectively. In the calculations, an average of the measurement results obtained with *s*- and *p*-polarized beams is used.

3.4. Results of intercomparison

Several diffuse reflectance standards were characterized by using the developed gonioreflectometer facility [Publ. IV]. The reflectance factors of the samples in 0/*d* geometry were determined over the wavelength range of 360 nm to 820 nm with a 20-nm increment. The obtained values were compared with those derived from the earlier relative scale at HUT, which is traceable to the absolute scale of NRC and PTB. Figure 7 depicts an example of such comparison for a white spectralon sample. The deviation between the gonioreflectometric measurement results and values from the relative scale in general was found to be within the uncertainties. For white samples, a discrepancy of apparently systematic origin exceeded the combined standard uncertainties at only one measurement wavelength. Thus the comparison only partly confirmed the earlier results obtained by the absolute scale of NPL [23], where approximately by a factor of two higher discrepancy between their gonioreflectometer-obtained 0/*d* reflectance and PTB-traceable values was reported.

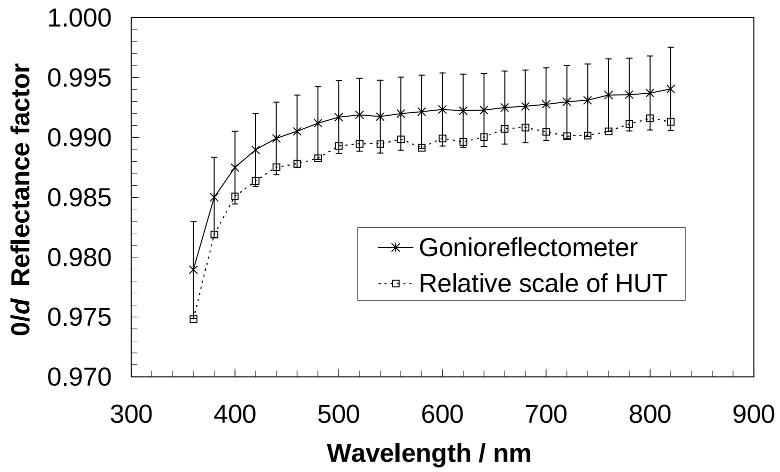


Figure 7. 0/*d* reflectance of a spectralon sample. The gonioreflectometer results and the values from the relative scale of HUT are shown. The error bars represent the combined standard uncertainties of the two sets of values.

4. Characterization of filter radiometers

4.1. Principle of filter radiometry

Filter radiometers (FRs) are used in establishing absolute scales of spectral irradiance [71, 72, 73, 74, 75, Publ. V]. In such applications, accurately characterized FRs can be utilized in either direct measurements of the radiation output of light sources or in the determination of the radiation temperature of black-body radiators. However, the full advantage of filter radiometry is gained in the direct measurements of lamps under calibration [Publ. V], where an accurately established spectral responsivity scale can be directly transferred to a spectral irradiance scale. Thus the shortest traceability chain can be obtained to a cryogenic radiometer, which is presently the most accurate instrument in the radiometry [76].

Normally, a FR consists of a precision aperture followed by a bandpass filter and a photodetector element. The purpose of the aperture is to define the solid angle and area for the measurements while the filters are needed to define the wavelength range of the measurements. The components of the FRs can be characterized separately or as a package [Publs. V, VI].

The derivation of the spectral irradiance of a lamp using FRs is based on a modified Planck's radiation law,

$$E_c(\lambda) = \frac{Bc_1\varepsilon'(\lambda)}{\lambda^5\{\exp[c_2/(\lambda T)] - 1\}}, \tag{7}$$

where c_1 and c_2 are determined in terms of fundamental constants, B is an auxiliary factor, $\varepsilon'(\lambda)$ represents the effective emissivity of the light source, and T is the effective radiation temperature of the filament. The effective emissivity $\varepsilon'(\lambda)$ includes the emissivity of the filament material and the transmittance of the glass envelope of the lamp. In the visible (VIS) to near infrared (NIR) wavelengths region, it can be well described by a P-th degree polynomial, with P ranging from 3 to 7 [77, 78]. In the UV region, the emissivity of tungsten has a complex structure thus a separate interpolation polynomial might be useful to have [79, Publ. V].

The spectral irradiance is obtained by fitting expected FR current signals to the measured values. With each filter installed in the FR, the expected signal from the detector can be expressed as

$$i_c = A\int E_c(\lambda)R(\lambda)\tau(\lambda)d\lambda, \tag{8}$$

where A, $R(\lambda)$, and $\tau(\lambda)$ denote the area of the aperture, the interreflection-corrected responsivity of the trap detector, and the transmittance of the filter, respectively. The difference between the measured photocurrent and the calculated signal i_c is minimized by adjusting the parameters B and T in the first stage and then fitting the emissivity polynomial $\varepsilon'(\lambda)$ in the next stage.

4.2. Spectrophotometric characterization of filter-radiometer components

Primarily, the transmittance $\tau(\lambda)$ of the bandpass filters of the FRs is a spectrophotometric quantity and hence the object of the spectrophotometric characterization. The transmittance of the filters, which normally are narrow-band interference filters with full-width at half-maximum (FWHM) of 10-20 nm, need not only to be measured within the pass-band, but also throughout the whole wavelength interval within which the detector can collect the signal. The out-of-band measurements are necessary in order to avoid measurement errors due to possible leakage of the filters. The thorough characterization of the filters used in the FRs of the HUT spectral irradiance scale is accomplished by using the high-accuracy reference spectrophotometer [66]. The contribution of the characterization uncertainties to the overall irradiance measurement uncertainty is presented in publication V.

The reflectance of the filters also needs to be known. Knowledge of the backside-reflectance of the FR filters allows compensating an error in the FR signal that arises due to the interreflections between the filter and the trap detector. Modifications in the reference spectrophotometer that are necessary for the reflectance measurements, the measurement procedures, the uncertainty estimates and an example of the results for a few interference filters are given in publication III.

The reference spectrophotometer has also been used in characterizing the spectral responsivity of the FR detectors. The absolute responsivity of silicon trap detectors utilized in the FRs are measured by the cryogenic radiometer at a few laser wavelengths and interpolated to other wavelengths by means of a model for the internal quantum efficiency and the reflectance of the diode. In the near UV, where the modeling is difficult, the responsivity is transferred from the VIS by using a pyroelectric radiometer. This is accomplished by an arrangement where the spectrophotometer beam is incident alternately on a calibrated pyroelectric radiometer and the trap detector [80]. The characterization of the detectors in relation to the irradiance scale realization is discussed in publication V.

The spectrophotometer beam can be also used in characterizing the FR as a package. The most important requirement for such application is the uniformity of the spectrophotometer beam since the measurements are normally performed by overfilling the aperture. In such a manner, wide band-gap FRs designed for the UV were characterized [Publ. VI]. A much more expensive alternative for the spectral irradiance-responsivity measurements would be the use of a tunable-wavelength laser [81]. A comparison of the characterization techniques has been carried out by HUT, NPL, and BNM-INM. The results are presented in publication VI. The intercomparison of the monochromator- and the laser-based characterization methods emphasized the importance of the wavelength scales for reliable characterization of narrow-bandwidth FRs. The wavelength scales of the participating institutes were found to deviate more than the stated uncertainties. This could not have been detected in the earlier international intercomparisons of spectral responsivity or spectral transmittance because typically artifacts of rather flat spectral characteristics have been used.

4.3. Importance of correlation analysis

Knowledge of the correlations between correlated input quantities is required by the internationally agreed rules for propagating uncertainties in measurements [82],

$$u_c^{\,2}(y) = \sum_{i=1}^{N} u_i^{\,2}(y) + 2\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} u_i(y)u_j(y)r(x_i, x_j), \qquad (9)$$

where $u_c(y)$, $u_i(y)$, and $r(x_i,x_j)$ are the combined standard uncertainty of the output quantity, the standard uncertainty of the output quantity generated by the uncertainty in the ith input quantity, and the correlation coefficient between the ith and jth input quantities, respectively.

Correlations in the spectral irradiance values are important when the values are combined in subsequent measurements or parameter estimation, such as determination of the color coordinates. Gardner [83, 84, 85] has shown that in a number of radiometric and photometric quantities formed as ratios of sums of spectral quantities, correlation effects generally lower the uncertainty compared to that obtained by ignoring correlations.

Moreover, correlations may also exist in the FR responsivity data and have an effect on the uncertainty of the derived spectral irradiance values. Thus complete characterization of the FRs would require identifying the correlations, which then could be included in the uncertainty calculation for the derived spectral quantities. In spite of this, the uncertainty analyses so far have assumed no correlations to be present between different spectral values. However, during the past years concerns about the effects of possible correlations on the primary spectral scales of NMIs have arisen [25, 84].

4.4. Propagation of uncertainties and correlations in the spectral irradiance scale

There are two major sources of possible correlations in the FR-based spectral irradiance scales: correlations in the FR responsivity data and correlations through fitting the modified Planckian distribution to the measurement data. The correlations in the FR data may arise through common systematic errors in the FR responsivity characterization, through fitting to the cryogenic radiometer data, and through multiplying factors, such as the aperture area or a calibration multiplier to the spectrally-flat responsivity of a pyroelectric radiometer. The task of evaluating the correlations and including them into the propagation of uncertainties through the spectral irradiance scale is not simple when conventional methods are used. Furthermore, the rule of propagation of uncertainty [82] applies to the case of one output quantity only. Recently, Wöger [86] proposed a powerful matrix formalism that in essence represents a generalized rule of the uncertainty propagation and can be used to transform both the uncertainties and the correlations of the measured values into the uncertainty matrix (or the variance-covariance matrix) of several output quantities.

The method by Wöger [86] was applied to studying the propagation of uncertainties and correlations in the FR data [Publ. VII]. Reasonable estimates of the input correlations were obtained based on the uncertainties of the FR characterization. The correlation coefficients and the uncertainties in the FR measurement data were used to produce an input uncertainty matrix, which then was propagated through the least-squares fitting procedure in a two stage process. In the first stage, a variance-covariance matrix of the coefficients of the effective emissivity polynomial from (7) was yielded. In the second stage, the obtained matrix resulted in a variance-covariance matrix of the calculated spectral irradiance values.

As a result of the uncertainty propagation, the effect of the correlations in the input data and of those through fitting the measurement data was identified. The output uncertainties in the case of correlations in the input data were found to be within two practical limits: the input uncertainties and the output uncertainties obtained assuming non-correlated FR measurement data. Another useful finding was that the uncertainty propagation procedure can be utilized in optimizing the selection of FR central wavelengths.

4.5. The procedure for propagating uncertainties and correlations applied to the thin-film analysis

As an example, the procedure of propagating uncertainties and correlations through the process of least-squares fitting [Publ VII] has been also applied to studying uncertainties in the determined optical parameters of the SiO_2 sample that is considered in chapter 2. In the uncertainty / correlation analysis, the normal-incidence transmittance data were used [Publ. II]. For the purpose of illustration, all spectral transmittance values were assigned a standard uncertainty of 0.1%, which then was used to form the diagonal of the input uncertainty matrix. In the first stage of the uncertainty propagation, the input matrix yielded the variance-covariance matrix of the coefficients A, B, and C from the Cauchy equation (4) and of the film thickness d. For the 0.1% transmittance uncertainty, the uncertainty propagation estimated a 0.14% relative standard uncertainty in the derived layer thickness d. In the second stage of the uncertainty and correlation propagation, the variance-covariance matrix associated with A, B and C yielded the uncertainty matrix for the calculated index of refraction. The obtained relative standard uncertainties are plotted in Figure 8 (solid curve). The figure also shows the derived refractive index of the SiO_2 coating. As a comparison, the uncertainty propagation was also done by assuming a fixed correlation coefficient $r = 0.5$ between all pairs of the measured spectral transmittance values. Such high correlations could be possible under certain systematic effects, e.g. normalization in a dual beam instrument. The resulting uncertainties are depicted in Figure 8 as well (dashed curve). It has to be noted, however, that the presented uncertainties do not include the uncertainty component due to the lack-of-fit error.

When comparing the two curves one can notice that the uncertainties calculated in the case of uncorrelated measurements have stronger wavelength-dependence. The uncertainties show same oscillations as a function of wavelength, which is caused by the 4^{th}-order wavelength-dependence of $n(\lambda)$ in (4). For most of the spectrum, the uncertainty values for this sample are by a factor of two lower as compared to the measurement uncertainties. The short-wavelength region of the spectrum is particularly interesting as there the relative uncertainties in the refractive index values are close to those of the measured transmittance. Hence the input uncertainties of random-origin are not effectively reduced at these wavelengths. However, including the correlations between all pairs of the spectral transmittance values attenuates the oscillations and makes the variation in the output uncertainties smoother.

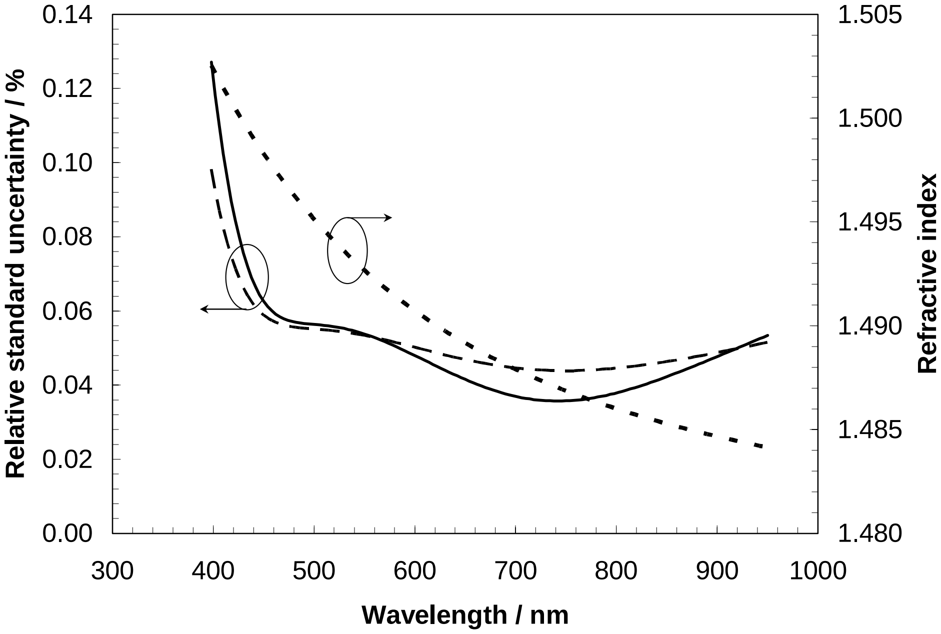


Figure 8. Determined refractive index of a SiO_2 layer and the relative standard uncertainties of its spectral values propagated from 0.1% uncertainties in the normal-incidence transmittance data. Two cases of the uncertainties are considered: uncorrelated (solid curve) and correlated (dashed curve) transmittance data with the correlation coefficient $r = 0.5$ between all pairs of the measured spectral values.

5. Conclusions

In this thesis, application of high-accuracy spectrophotometric measurements in the characterization of optical thin-film coatings, standards for diffuse reflectance measurements, and components of filter radiometers is described. The characterization of thin-films is analyzed for the effects of systematic errors in the measurements on the determination of thin-film optical parameters. A newly developed gonioreflectometer and its utilization for realizing the Finnish national standard of diffuse reflectance factors are described. Thorough characterization of filter radiometer components, which is an important contributor to the realization of the national primary scale of spectral irradiance, is discussed, including correlations in the filter radiometer responsivity data and their effect on the uncertainties of the derived spectral irradiance values.

Effects of several systematic errors in the spectrophotometric measurements on the determined optical parameters of thin-film coatings were analyzed. The study yielded an important conclusion for the characterization of thin films with oblique-incidence measurements. The use of commercial spectrophotometers may have a substantial impact on the accuracy of the characterization results. The presented experimental results obtained with the high-accuracy spectrophotometer of HUT demonstrated that consistency among the derived thin-film parameters at various incidence angles is possible. In addition, a research is planned to compare experimental results of the characterization from transmittance and reflectance data obtained at various incidence angles using the high-accuracy spectrophotometer and the gonioreflectometer setup at HUT.

The newly established absolute scale of spectral diffuse reflectance is at the present moment the second in the world, where the hemispherical reflectance factors are derived through gonioreflectometric measurements. The test measurements revealed that the agreement with the integrating sphere-based methods is within the measurement uncertainties. In the other gonioreflectometer-based diffuse reflectance scale, larger discrepancies exceeding the measurement uncertainties had been earlier reported. The developed measurement system was used in the key comparison measurement of spectral diffuse reflectance, CCPR-K5, organized by the Consultative

Committee for Photometry and Radiometry (CCPR). The analysis of the key comparison results is currently in progress.

The thorough characterization of the components of the filter radiometers contributed to a successful realization of the spectral irradiance scale at HUT. The intercomparison of the characterization techniques emphasized the importance of the wavelength scale for reliable characterization of narrow-bandwidth filter radiometers. For the first time, effects of correlations due to the characterization of the filter radiometers were studied. The results of correlation analysis led to a method of optimizing the selection of filter-radiometer wavelengths and to a practical range of irradiance uncertainties in the case of correlations in the input data. Currently a research project is under way to extend the measurement capabilities at HUT further into the UV (200 nm – 290 nm) and the NIR (900 – 2500 nm) spectral regions.

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Abstracts of publications

I. **“Determination of thin-film parameters from high accuracy measurements of spectral regular transmittance,”** *Metrologia* **40**, S200-S203 (2003).

The importance of reliable spectral transmittance measurements for reliable thin-film characterization is demonstrated. By using a model of the spectral transmittance of thin-film samples, the effect of various uncertainty components in transmittance measurements on the determined thin-film parameters is analysed. The experimental results for aluminium dioxide and tantalum pentoxide thin-film samples show good agreement with the model.

II. **“Optical metrology of thin films using high-accuracy spectrophotometric measurements with oblique angles of incidence,”** in *Advances in Optical Thin Films*, C. Amra, N. Kaiser, H. A. Macleod, eds., *Proc. SPIE* **5250**, 234-242 (2004).

Oblique-incidence spectrophotometric measurements are considered for reliable determination of the refractive index and thickness of thin-film coatings. By using a model of the spectral transmittance of thin film samples, the effect of systematic factors on the determined thin-film parameters is analyzed. The optical parameters of a silicon-dioxide sample determined from the experimental results obtained with the HUT spectrophotometer are consistent for the incidence angles between 0 and 56.4 degrees, demonstrating high accuracy of film-parameter determination.

III. **“Precision spectrometer for measurement of specular reflectance,”** *Rev. Sci. Instrum.* **73**, 2237-2241 (2002).

The HUT reference spectrometer was modified for measuring specular reflectance in the wavelength range of 300 to 850 nm. The instrument is based on a diffraction-grating monochromator, reflecting optics, sample control mechanics and detection systems with linear responsivities. Relative standard uncertainties between 0.14% and 0.32% were estimated for the reflectance measurements. For spectral reflectance between 1.5% and 15%, the results of test measurements using samples with known reflectances confirm that for all geometries the relative deviations are less than 0.36%. A set of ultraviolet (UV)-interference filters was measured in the UVB wavelength range, and the results are used as a part of filter radiometer characterization.

IV. “**Gonioreflectometer for measuring spectral diffuse reflectance,”** Accepted for publication in *Applied Optics*.

The report addresses gonioreflectometric determination of the reflectance factors involving hemispherical collection of the reflected flux, which is an alternative to the integrating sphere-based methods. Detailed description of a gonioreflectometer built at the Helsinki University of Technology is presented. The instrument is used to establish an absolute scale of total diffuse reflectance factors throughout the spectral range of 360 nm to 830 nm. The hemispherical reflectance factors are obtained through integration of the gonioreflectometric measurement results. The reflectance factors of white high-quality artifacts can be determined with a combined standard uncertainty of 0.21%. Results of test measurements were found to be in agreement with the values traceable to other absolute scales based on integrating-sphere methods.

V. **"Spectral irradiance measurements of tungsten lamps with filter radiometers in the spectral range 290 nm to 900 nm,"** *Metrologia* **37**, 305-312 (2000).

A method of measuring the absolute spectral irradiance of quartz-halogen-tungsten lamps is described, based on the known responsivity of a filter radiometer, the components of which are separately characterized. The characterization is described for the wide wavelength range essential for deriving the spectrum of a lamp, from 260 nm to 950 nm. Novel methods of interpolation and measurement are implemented for the spectral responsivity of the filter radiometer. The combined standard uncertainty of spectral irradiance measurements is less than 1.4 parts in 10^2 from 290 nm to 320 nm (ultraviolet B) and 4 parts in 10^3 from 440 nm to 900 nm (visible to near-infrared). As an example, the derived spectral irradiances of two lamps measured at the Helsinki University of Technology (HUT, Finland) are presented and compared with the measurement results of the National Institute of Standards and Technology (NIST, USA) and the Physikalisch-Technische Bundesanstalt (PTB, Germany). The comparisons indicate that the HUT spectral irradiance scale is between those of the NIST and the PTB in the wavelength range 290 nm to 900 nm. The long-term reproducibility of the spectral irradiance measurements is also presented. Over a period of two years, the reproducibility appears to be better than 1 part in 10^2.

VI. **"Intercomparison of characterisation techniques of filter radiometers in the ultraviolet region,"** *Metrologia* **40**, S50-S54 (2003).

Narrow-band filter radiometers at 248 nm, 313 nm, 330 nm and 368 nm wavelengths were used to compare calibration facilities of spectral (irradiance) responsivity at HUT, NPL and BNM–INM. The results are partly in agreement within the stated uncertainties. Use of demanding artefacts in the intercomparison revealed that the wavelength scales of the participating institutes deviate more than expected. Such effects cannot be seen in typical intercomparisons of spectral responsivity or spectral transmittance, where spectrally neutral samples are used.

VII. **"Effect of correlations in fitting spectral irradiance data,"** *Metrologia* **41**, 246-250 (2004).

The uncertainty of a primary spectral irradiance scale based on filter radiometers (FRs) is studied by analysing the propagation of uncertainties and covariances through a spectral interpolation process, when a modified Planck's radiation law is fitted to the measurement data. The advantage of performing the uncertainty analysis in optimizing the selection of the FR wavelengths is demonstrated. We also estimate the effect that correlations in the FR signals have on the uncertainty of the fitted spectral irradiance values. In the case of correlated input data, the results of the uncertainty propagation are found to be within two practical limits: uncertainty values in the FR data and the values obtained by uncertainty propagation with uncorrelated FR signals.