Aalto University
School of Electrical Engineering
Metrology Research Institute

Farshid Manoocheri
Saulius Nevas

Instruction Manual of Diffuse Reflectance Measurements

Version 1.6
7/12/2018

1. Table of contents

2. Definition

2.1. Scope

This instruction manual describes the principle and the operation of the equipment used to realize the national scale of spectral diffuse reflectance.

2.2. Object and field of application

Reference standards: Diffuse reflectance standards directly traceable to absolute scales of spectral diffuse reflectance.

Reference spectrometer and integrating sphere-based detection unit: Used for traceability transfer from reference to working standards and for calibrating customer's samples.

2.3. Features

The measurement facility consists of the reference spectrometer of MRI [1,2] and an integrating-sphere collection unit. The system is designed to perform automated measurements of spectral diffuse reflectance by alternately irradiating a reference standard and a sample under test and comparing the reflected radiation [3]. Possible measurement geometry of irradiation/view can be either 8°/diffuse (with specular component included and excluded) or 0°/diffuse. Diffuse reflectance factor from the range of 0.05 – 1.0 can be measured over the wavelength region of 360 – 830 nm.

2.4. Spectral diffuse reflectance

Spectral reflectance of a surface is defined as the ratio of the radiant flux reflected by the surface to the flux incident upon the surface at a given wavelength λ,

$$\rho(\lambda) = \Phi_r(\lambda)/\Phi_i(\lambda)\ . \tag{1}$$

Reflectance of radiation from a surface is perfectly diffused if the incident radiant flux is reflected in all directions in accordance with Lambert's cosine law.

Generally, direct measurements of the two fluxes, i.e. reflected from a sample and incident on it, are not easily realized. Therefore, by an international agreement reflectance is characterized by reflectance factor, which is defined as the ratio of the radiant flux reflected in the direction delimited by a given cone with apex at a point of the surface

---

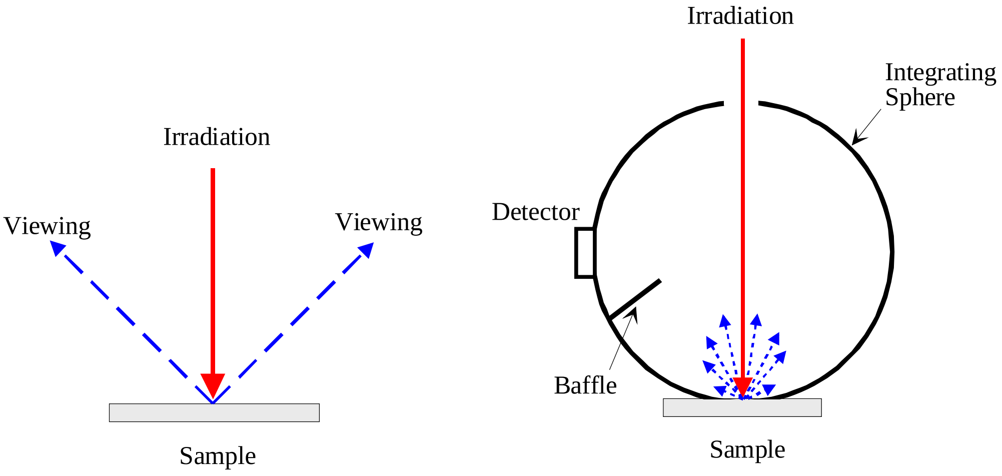
[1] Quality manual of reference spectrometer laboratory.

[2] F. Manoochehri, Licentiate Thesis, "High Precision Spectrometer for Reflectance Measurements", Helsinki University of Technology, 1993.

[3] Saulius Nevas, "Facility for measurements of spectral diffuse reflectance", Master's Thesis for the degree of Master of Science in Technology (Helsinki University of Technology, Metrology Research Institute, Espoo, Finland 2000).

under test to that reflected in the same directions by a perfect reflecting diffuser identically irradiated. The perfect diffuser is an ideal uniform Lambertian diffuser with a reflectance equal to 1. If the solid angle of the cone approaches 0, or 2π steradian, the reflectance factor approaches radiance factor β or reflectance ρ, respectively.

Both radiance factors and reflectance values are dependent not only on the material itself but also on other parameters such as the geometrical conditions for the incident and measured radiation. The geometry of irradiation and collection is usually denoted as θ_i/θ_m in subscript, where θ_i indicates geometry of the incident radiation, and θ_m indicates that of the measured radiation. The first term in the subscript may be either d for diffuse or hemispherical incident radiation or a value in degrees indicating the angle of a narrow incident beam. The second term similarly refers either to hemispherically collected reflected radiation with the specular component excluded (d) or included (t) or to the angle of observation, all angles being measured from the surface normal. Hemispherical irradiation or collection of the reflected radiation is usually accomplished by an integrating sphere. For example, $\beta_{0/45}$ and $\rho_{0/d}$ denote radiance factor for 0/45 geometry and reflectance for 0/d (normal/diffuse) geometry, respectively (Figure 1).



0 / 45 geometry
(*a*)

0 / d geometry
(*b*)

Figure 1. Determination of the (a) radiance factor for 0 / 45 geometry and (b) reflectance for 0 / d geometry.

3. Equipment

3.1. Equipment used in measurements of spectral diffuse reflectance

Equipment used in diffuse reflectance measurements consists of a reference / working standard, the reference spectrometer, a six-port integrating sphere, a computer-controlled rotation stage, a detector unit, a digital voltage meter (DVM), a beam shutter, and a control computer. A schematic of the measurement setup is shown in Figure 2.

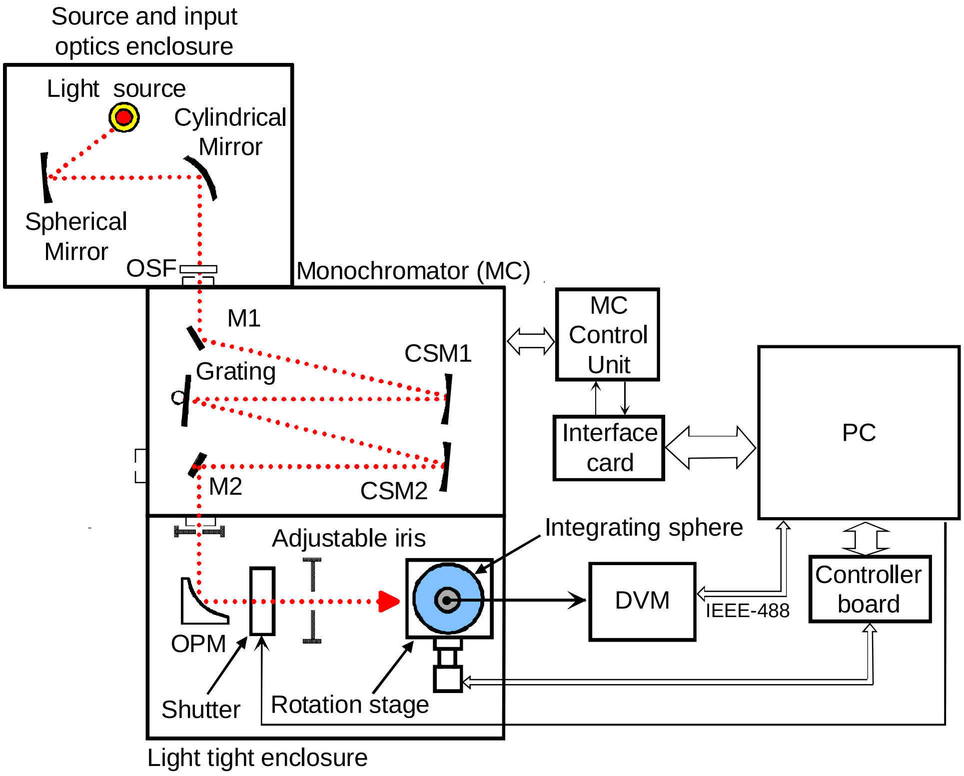


Figure 2. Schematic structure of the measurement system for the measurements of spectral diffuse reflectance. Abbreviations: OSF, order sorting filter; M1, M2, flat mirrors; CSM1, CSM2, collimating mirrors, OPM, off-axis parabolic mirror.

The reference spectrometer including light source, monochromator, input and output optics is described elsewhere [1, 2]. The other components utilized in the measurements are listed in Table 1.

Table 1. Equipment used in diffuse reflectance accessory.

	Description	Quantity	Identification
A.	Integrating sphere unit		
1.	Integrating sphere	1	Labsphere RT-060-SF
2.	0-deg. sample holder	2	Labsphere
3.	8-deg. sample holder	2	Labsphere

4.	Detector unit, built at MRI	1	Hamamatsu S5591, black anodized casing
B.	Control and data acquisition		
1.	Rotation stage	1	PI M-038.DG
2.	Controller board	1	PI C-842.20
3.	Shutter (filter wheel)	1	CVI AB301
4.	Shutter control unit	1	CVI
5.	Measurement program	1	RefSpecV3
6.	Digital voltmeter	1	HP 3458A
C.	Reference standards		
1.	White opal glass (8/d refl. factor traceable to NRC)	1	HUTDR-W1
2.	White opal glass (d/0 rad. factor traceable to PTB)	1	HUTDR-W2
3.	Grey spectralon (d/0 and d/8 rad. factors traceable to PTB)	1	HUTDR-G1
4.	Black opal glass (8/d refl. factor traceable to NRC)	1	HUTDR-B1
D.	Working standards		
1.	Diffuse reflectance standards calibrated against the reference standards and used in routine measurements	At least 1	E.g. HUTDR-W3, SRS-99, SRS-75, SRS-10

3.2. Maintenance of the equipment

- Information on the maintenance of the reference spectrometer and details on its control electronics can be found in [1] and [2].
- The integrating-sphere coating is susceptible to contamination and shock. Before starting calibration measurements the sphere is visually inspected for its state. When used, the sphere should be handled with an extreme care to prevent dust or other particles from getting into the sphere. The accessory is stored in a closet in the reference spectrometer lab, properly covered from possible sources of contamination.

- The rotation stage is checked for proper operation before being used and a repair arranged if necessary.
- The photodetector is tested for linearity every second year. This can be done by e.g. using reference ND gray filters
- The multimeter is autocalibrated every time before the start of the calibration measurements. Calibration of the multimeter is performed according to the calibration schedule of Calsched.
- The reference standards are stored with the protective caps closed whenever they are not in use. This is to keep the surfaces clean and free of physical damage. Before calibration the condition of the surface is visually checked. If there is minor visible dust, it may be carefully cleaned with a soft brush or flow of pressurized gas (air or nitrogen). If a container of pressurized air is used the operator has to follow guidelines for its safe usage in order to avoid damaging the reference standard. This includes precautions such as: to make sure that the air flow does not leave any residues on a surface before directing it onto the sample; not to shake the container when using it; keep it in upright position when the nozzle is opened. The reference standards are not to be washed. The surface can be touched neither with bare- nor with glove-protected fingers.

4. Measurement traceability and calibration

4.1. Traceability chain of spectral diffuse reflectance

The relative scale of spectral diffuse reflectance at MRI takes its traceability of diffuse reflectance in 0:d and 8:d geometries from the absolute scale maintained by the Gonioreflectometer facility at MRI. The traceability has been established by calibrating reference standards. The traceability of the reference standards is renewed every third year.

4.2. Uncertainty components

The uncertainty components in measurements of spectral diffuse reflectance are listed as follows.

Reference standard uncertainty

Reference standard uncertainty is the uncertainty associated with the reference standards at MRI that are directly traceable to absolute scales. The standards have their spectral reflectance values declared in certificates of calibration. The certificates also state corresponding uncertainties of the values provided.

Aging of reference standards

This uncertainty component originates due to the finite time interval between the renewals of traceability. Depending on the reference standard material, its exposure to the measurement beam and time elapsed since it was calibrated by an absolute scale, the reflectance properties of the standard may have been degraded. This degradation might be especially pronounced in the UV-short visible spectral region.

As an example, the aging of a white Spectralon sample has been estimated based on monitoring its reflectance throughout the period of two years. Reflectance decrease of 0.6 – 0.2 % was observed within 360 – 440-nm wavelength range. At the longer wavelengths, however, no significant changes in reflectance were detected.

Repeatability

The repeatability of the measurements has been estimated by making several measurements with the same sample and same reference, the collection unit of the facility being removed and placed back into the setup before each of the measurements.

Geometric non-equivalence

Geometric non-equivalence can be estimated by making two sample-to-reference reflectance ratio measurements. The second measurement is made with the test sample being interchanged with the reference standard. The difference between the measured reflectance ratios provides an estimate of the geometric non-equivalence between the two measurement geometries.

Dark uncertainty

Dark uncertainty is due to the uncorrected optical offset error. Its magnitude depends on the reflectance level of a sample being measured [3]. For a sample with a nominal reflectance of 0.99 measured against 0.99-reflectance reference standard it would be virtually equal to zero. However, if 0.05-reflectance sample is measured against the 0.99-reflectance reference standard the uncorrected optical offset of ±0.0005 results in ± 1.0 % uncertainty of the measured reflectance value.

Wavelength scale uncertainty

The reflectance uncertainty caused by the uncertainty in the wavelength setting is sample-dependent and is calculated as

$$u_{\rho\lambda} = u_{\lambda} \cdot d\rho/d\lambda \,, \tag{2}$$

where u_λ is uncertainty in the wavelength scale and $d\rho/d\lambda$ is the change in reflectance per unit wavelength. For white diffuse reflectance standards the largest reflectance variation normally is of 0.001 / nm or even less over the visible range. Therefore, reflectance uncertainty component caused by the 0.06-nm uncertainty in the wavelength scale is negligible for such samples.

Detector non-linearity

The photodetector of the measurement system comprises of a silicon photodiode S5591 with preamplifier manufactured by Hamamatsu. Photodiodes of this type are very similar to type-S1337 photodiodes. The linearity of Hamamatsu photodiodes has been measured [4]. The linearity of the photodiodes was found to be better than 0.01% for photocurrent values up to 100 µA. Since the difference between S5591 and 1337 is only in packaging, S5591 photodiode must have its linearity characteristics similar to those characterized for S1337. The uncertainty caused by the deviation from linearity of the detector, u_L, is estimated as, $u_{\rho L} = \rho_S/\rho_R(1-\rho_S/\rho_R)u_L$ where ρ_S/ρ_R denotes sample-to-reference standard reflectance ratio.

---

[4] Toomas Kübarsepp, Atte Haapalinna, Petri Kärhä, and Erkki Ikonen, “Nonlinearity measurements of silicon photodetectors,” Applied Optics 37, 2716-2722 (1998).

5. Measurement ranges and best measurement capabilities

Table 2 summarizes best measurement capabilities for measurements of high-quality non-fluorescent, non-glossy samples with the nominal reflectance values from the range of 0.05 – 1.0. The uncertainty estimation has been divided into two wavelength regions because of aging of the reference standards and repeatability of measurements. In addition, sample induced uncertainties such as material homogeneity are to be added as sum of squares to the measurement standard uncertainty.

Table 2. Uncertainty components in spectral diffuse reflectance measurements for non-glossy samples with nominal reflectances of 0.05 - 1.0 at UV, visible, and NIR wavelengths. The numbers are relative percent-values.

	Uncertainty Component	Standard Uncertainty (%)	
		360-440 nm	440-830 nm
	Reflectance level 0.05-0.15		
1.	Reference standard	0.27	0.27
2.	Aging of the reference standard	0.20	0.05
3.	Repeatability	0.32	0.28
4.	Geometric non-equivalence	0.10	0.10
5.	Dark uncertainty	0.12	0.12
6.	Wavelength	0.01	0.01
7.	Detector non-linearity	0.002	0.002
8.	Combined uncertainty	0.49	0.42
9.	Extended uncertainty (k = 2)	0.98	0.84
10.	Uncertainty Component	Standard Uncertainty (%)	
		360-440 nm	440-830 nm
	Reflectance level 0.15-0.75		
1.	Reference standard	0.29	0.29
2.	Aging of the reference standard	0.24	0.05
3.	Repeatability	0.15	0.11
4.	Geometric non-equivalence	0.10	0.08
5.	Dark uncertainty	0.12	0.12
6.	Wavelength	-	-
7.	Detector non-linearity	0.002	0.002

8.	Combined uncertainty	0.43	0.34
9.	Extended uncertainty (k = 2)	0.86	0.68
10.	Uncertainty Component	Standard Uncertainty (%) 360-440 nm	
	Reflectance level 0.75-1.0		
1.	Reference standard	0.10	0.10
2.	Aging of the reference standard	0.12	0.05
3.	Repeatability	0.08	0.05
4.	Geometric non-equivalence	0.10	0.10
5.	Dark uncertainty	0.02	0.02
6.	Wavelength	0.01	-
7.	Detector non-linearity	0.002	0.002
8.	Combined uncertainty	0.20	0.16
9.	Extended uncertainty (k = 2)	0.41	0.32

6. Calibration methods and procedures

6.1. Measurement method

The relative measurements of spectral diffuse reflectance are realized by comparing the flux reflected by a sample to the flux reflected by a calibrated reference standard. During the measurements the sample is fixed at the sample port of the integrating sphere and the reference standard is fixed at the reference port. The sample and the reference are successively irradiated with the spectrometer beam and the ratio of the two signals from the detector is recorded. More information of the measurement method can be found in [3].

6.2. Calibration procedures

As a first step, the reference spectrometer has to be prepared for the measurements. This includes selection of a relevant diffraction grating and the light source and calibration of the wavelength scale when necessary. The information on the spectrometer and its operation can be found in [1] and [2].

Next, the accessory for the spectral diffuse reflectance measurements has to be fixed at the output optics section of the reference spectrometer and aligned with respect to the measurement beam. At first, the integrating sphere is mounted on the rotation stage so that the rotation axis of the stage coincides with the sphere north-south axis. The detector unit is attached on the top port of the sphere. Side view of the integrating sphere fixed on the rotation stage is shown in Figure 3.

Figure 4 schematically depicts cross-section of the sphere at the equatorial plane. Ports numbered as (1), (2), (3), (4), (5) correspond to beam reference entrance, reference holder, light trap, sample holder, and beam sample entrance ports, respectively. Depending on which measurement geometry is to be used, 8-degree or 0-degree sample holders are fixed at reference standard (2) and sample (4) ports. The alignment of the sphere accessory is done by choosing its position such that the spectrometer beam would be entering the sphere through the center of the entrance port (5) and incident onto the center of the sample holder port (4). The same condition should be valid when the beam is incident onto the center of the reference entrance port (1) after the sphere is rotated to the reference position.

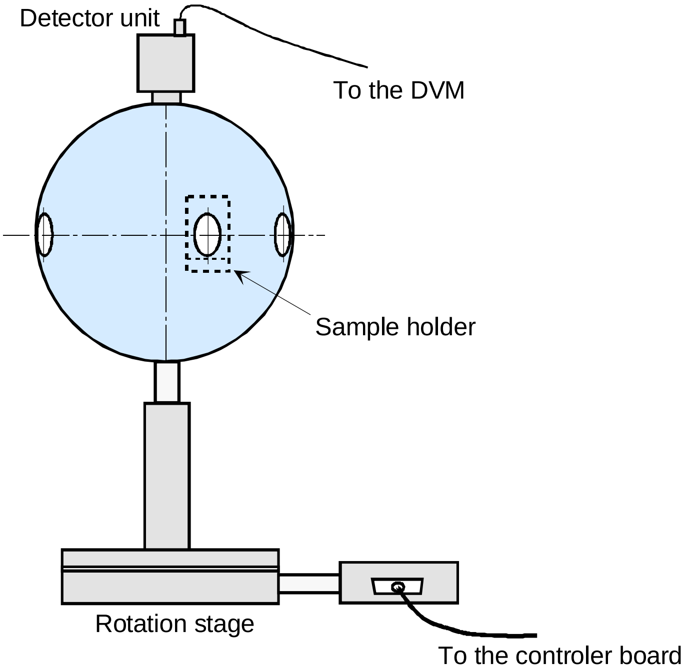


Figure 3. Side view of the integrating sphere unit mounted on the rotation stage.

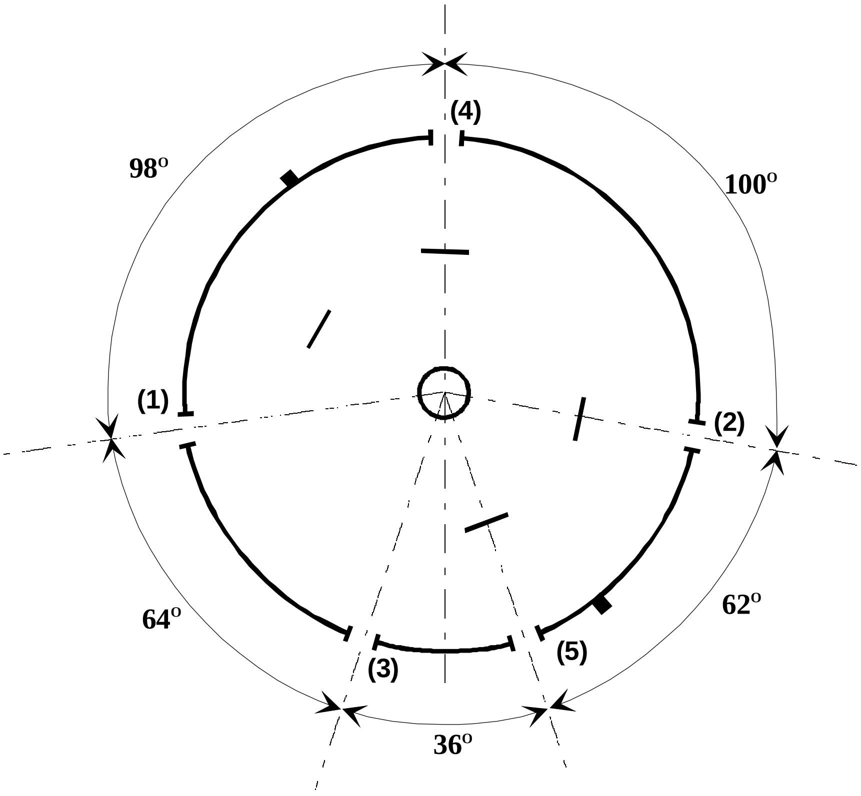


Figure 4. Schematically shown cross-section of the integrating sphere at the equatorial plane. Location of the detector port on top of the sphere is also shown.

Following the alignment steps, the optical offset has to be measured for the whole wavelength range over which the measurements of spectral diffuse reflectance are to be performed. The measurement procedure can be found in [3]. The computer control program is the same as is used in the diffuse reflectance measurements. After the scan of the optical-offset is completed the test sample and the reference standard are placed at the respective ports of the integrating sphere. Then the measurements are performed according to the settings supplied to the computer control program. To eliminate the effects of the small drifts of the instrument, the reflectance measurements are performed in a time-symmetrical sequence. The following series of readings is recorded for the measurements of a sample at a wavelength setting:

$$I_b,\ m \text{ times } (I_0, I_S, I_S, I_0),\ I_b. \tag{3}$$

Symbols I_b and I_0 denote the signal reading for the detector dark current and signal reading at the reference measurement position, respectively. Symbol I_S is signal reading at the sample position, and m is the number of repetitions chosen by the operator. Two readings are taken for each individual sample for the sake of preserving the time symmetry of the detector exposure. The average value of the two I_S readings is denoted by $\bar{I}_s$. The signal-reading data are processed by taking the average value of I_b and closest I_0 readings on both side of I_S readings, giving mean values $\bar{I}_b$ and $\bar{I}_0$. Then the ratio ρ is computed according to

$$\rho = \frac{\bar{I}_s - \bar{I}_b}{\bar{I}_0 - \bar{I}_b}, \tag{4}$$

and averaged for the m passes to obtain $\bar{\rho}$. The diffuse reflectance ρ_S then is to be calculated by using known reflectance value ρ_R of the reference standard as

$$\rho_S = \bar{\rho} \cdot \rho_R + O \cdot \rho_R \cdot (\bar{\rho} - 1), \tag{5}$$

where O denotes the determined ratio of the optical offset.

7. Laboratory accommodation and environment

Reference spectrometer laboratory is located in room 1572 in the basement of the department of electrical engineering. The laboratory is a clean room. Instructions for using the clean rooms have been given in [5].

During spectral diffuse reflectance calibrations:

- The Clean Zone **-** aggregate should be on, to prevent dust.
- Temperature should be monitored.

Temperature and relative humidity values during the calibrations are written to calibration certificates.

---

[5] P.Kärhä, “Clean room instructions / Puhdastilaohjeet”, MRI publication.

8. Records

The measurement data coming from calibrations and development of equipment is archived. The measurement notes (comments on the measurement setup etc.) are written down to a dedicated notebook (titled as “Reference Spectrometer – Calibrations & Measurements”) and/or measurement data file. The raw data files are stored in the reference-spectrometer control computer and backed-up in responsible person’s PC.

9. Certificates

Calibration certificates are handled according to [6]. In the calibration certificates included are:

- Ambient temperature and relative humidity,
- Source of traceability,
- Spectral diffuse reflectance values at the measured wavelengths and calculated uncertainties.

---

[6] Instructions on writing calibration certificates.