Small Spot Directional Absolute Reflectance IV accessory

PerkinElmer Part Number L6310208 (For L650/750/850/950/1050)

User Manual

www.omtsolutions.com

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Small Spot Directional Absolute Reflectance IV Set

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Introduction

The Small Spot directional reflectance IV set

The small spot directional absolute reflectance IV set is delivered in a polypropylene storage box containing the following items:

- The small spot directional absolute reflectance IV accessory
- A UV enhanced Glan-Thompson polariser suitable for (at least) the wavelength range 220 nm - 2500 nm
- One front surface mirror, size ∅25mm (data on CDROM).
- One miniature sample holder for circular samples up to ∅37mm (additional sample holders for circular samples up to ∅50mm and rectangular samples are available, contact OMT Solutions for info and pricing).
- A detailed manual with a step-by-step description of the alignment and measurement procedures.
- A CD-ROM with an electronic copy of the manual, UVWinLab Method files with recommended measurement procedures, and Excel workbooks for data analysis.
- A brief report containing test results obtained on the accessory prior to shipment.

The accessory is pre-aligned and fully tested at the OMT Solutions laboratory.

Features

- Absolute measurement of the square of the reflectance
- Angles of incidence in the range **7.5 - 80** degrees
- Angular calibration through averaging over "positive" and "negative" angles
- Wavelength range of 220 - 2300 nm with 150mm InGaAs detector sphere (and up to 2500 nm using the standard detector (limited by the polariser))
- Separate measurements for p- and s-polarisation
- Sample spot size < 4 mm x 5 mm (w x h) at normal incidence.

> In order to receive free updates of this manual, please forward your contact data and the serial number of your accessory by email to:
> support@omtsolutions.com
> Please write “SSIV Manual” in the subject line.
>
> Feel free to use the same email address for any questions regarding the use of the accessory.

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Principle of operation

The optical path of the spectrophotometer's sample beam through the accessory is shown in Fig. 1 below (the upper lid of the accessory is removed). After passing the polariser (P), the beam interacts with aperture A1, mirror M1, aperture A2, mirrors M2, M3 and M4, beamsplitter BS (in transmission) and mirror M5. Finally, the beam reflected by mirror M5 is directed towards the detector unit by the beamsplitter BS (in reflection). The reference beam passes the Reference Beam Compensator (RBC) and Reference Beam Attenuator (RBA). The beam size at the sample position can be changed by using different slit and Common Beam Mask values and by changing the aperture (iris diaphragm) directly after the polariser (A1). Aperture A2 limits the beam size at the sample compartment exit port and is therefore locked.

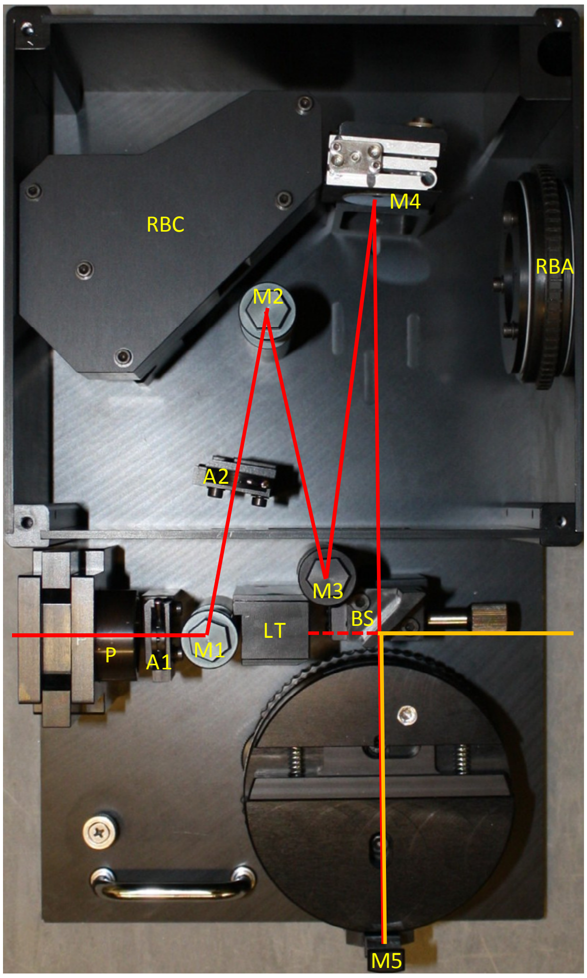

Fig. 1 Top view of the directional SSIV accessory, showing the optical path of the instrument sample beam in the I-mode (without sample)

The measurement principle of the directional absolute SSIV reflectance accessory is based on a combination of two measurements (see Fig. 2 and 3 below). In the so-called I-mode the instrument beam is interacting with five mirrors (M1 – M5) and a beam splitter (BS). In the so-called V-mode the beam additionally interacts twice with the sample. The ratio of the two scans produces the square of the sample reflectance. This method is an absolute one since a calibrated reference is not needed.

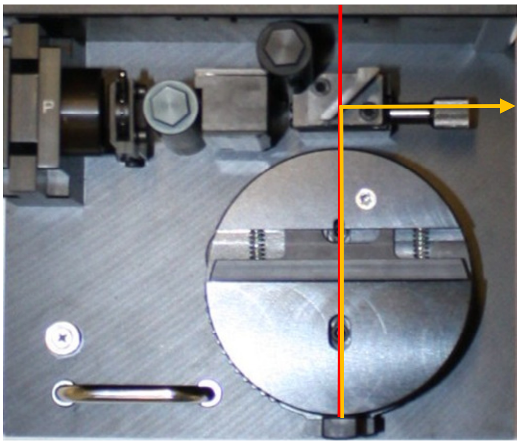

Fig. 2a. The I-mode configuration
Autozero and 100% measurements.

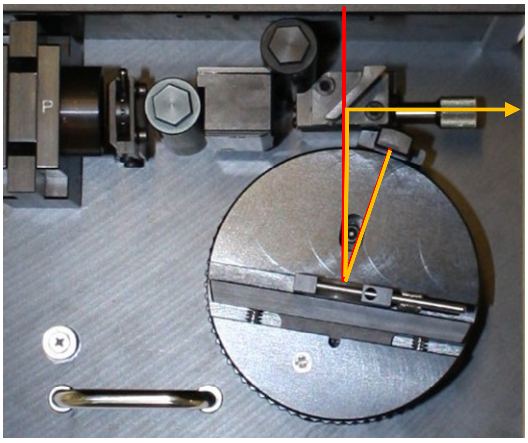

Fig. 2b. "Positive" V-configuration
Near-Normal (mirror M5 right of the sample)

In addition to (near-) normal incidence, the accessory is designed to perform measurements under oblique incidence as well. Two forms of the V -mode are possible, representing "positive" and "negative" angles of incidence:

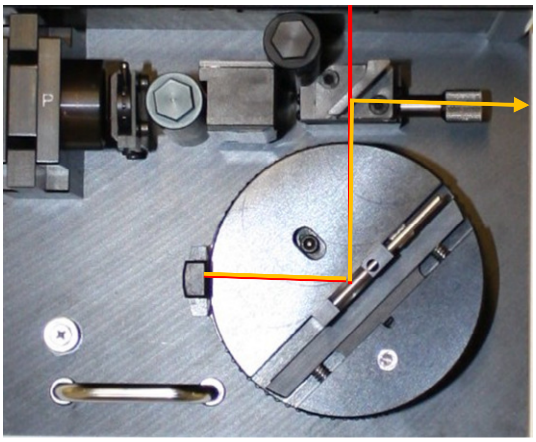

Fig. 3a, "Negative" V configuration, -45°
(mirror M5 left of the sample)

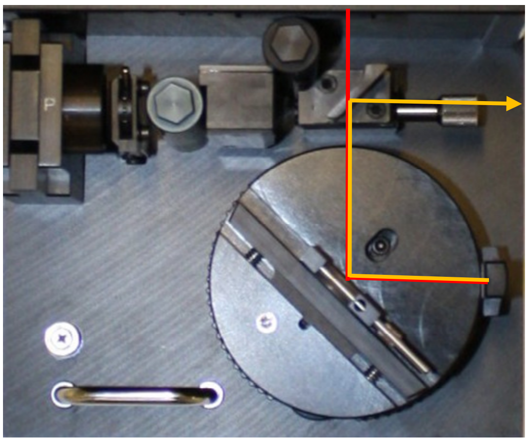

Fig. 3b. "Positive" V configuration, +45°
(mirror M5 right of the sample)

The ability to perform measurements at both “positive” and “negative” angles, enables compensating for systematic errors related to beam-shift effects and angular accuracy, by taking the average of these two types of measurements.

Applications

The Small Spot IV method is intended for small and large flat specular front surface samples having reflectance values > 25%, like reflectance standards, laser mirrors, optical solar reflectors, beam-splitters, etc.

Small samples

The SSIV is especially developed to make accurate absolute directional reflectance measurements possible in a wide range of samples sizes. Samples sizes from 100mmx100mm down to ∅10mm can be measured.

Determining the absorption of laser mirrors

Laser mirrors are optimized to have absorption close to zero at the wavelength of interest. To quantify the absorption one needs to measure the reflection, a value close to one, extremely accurately. Proper use of the SSIV set allows you to measure the reflection of laser mirrors, depending on alignment and instrument settings even at oblique incidence, with a combined standard uncertainty < 0.05% for reflectance values > 98%

Calibrating reflectance standards

The directional absolute reflectance SSIV set makes it possible to calibrate reflectance standards not only at near-normal incidence, but also at oblique incidence for P and S polarization separately. Using the SSIV accessory on front surface reference mirrors with a reflectance > 80%, values for the combined standard uncertainty are typically < 0.1% in the visible range and < 0.2% in the UV and NIR ranges for sufficient integration times.

Characterizing beam-splitters

The accessory is suitable for measuring both reflection and transmission of coated beam-splitters designed for using at oblique incidence and having a reflection and transmission in the range 25% - 60%. The accessory is less suitable for the characterization of so-called polka-dot beam splitters.

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Getting Started

Hardware requirements

The use of the reflection set requires the spectrophotometer to be equipped with:

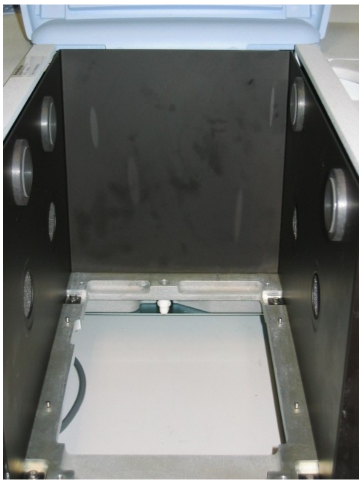
- Common Beam Depolariser (B050-1282)

As detector unit one of the following options:

- 150mm InGaAs Sphere = PREFERRED OPTION
- collection sphere L6020209
- 60mm integrating sphere unit (L6020203)
- standard detector (sensitive for misalignment) ➔ reduce aperture A2 to ∅1 mm = NOT RECOMMENDED

Installation and alignment of the SSIV accessory

1. Install the integrating sphere detector unit. (In case of the 60mm integrating sphere, remove the 8° wedge plate between integrating sphere and Spectralon target in the sample beam.)
2. Open the sample compartment
3. Remove the (standard) base plate
4. Remove the 4 magnetic windows in the sample and reference beam (at the entrance and exit port of the sample compartment) and store them in the sample compartment, high against the wall (see picture below).



5. Insert the SSIV accessory and fasten the two screws on opposite corners
6. Insert the Glan Thompson polariser in the desired orientation, P or S (read-out on top)

7. Set the monochromator of the spectrophotometer at 0 nm to produce a white light beam
8. Check the position of the sample beam on the exit port of the sample compartment and the entrance and target ports of the integrating sphere using a white piece of paper. In case of the 60mm sphere, fix a paper target to the sample entrance port of the integrating sphere and mark the position of the beam.

   If necessary, use the adjustment procedure described in the next section.
9. Insert the sample to be measured in the sample holder
10. The two rotation stages are positioned using the following procedure:
    - The rotation stages have identical scales for turning left or right, from 0° to 180°. In order to set "positive" or "negative" angles the following table can be used.

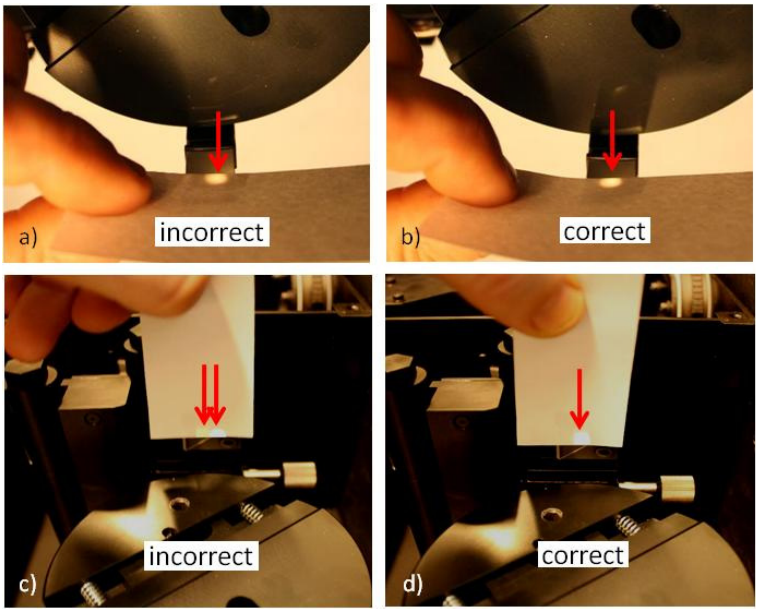
INCIDENT ANGLE SAMPLE (VALUE UPPER ROTATION STAGE)	**POSITION MIRROR M4** (VALUE LOWER ROTATION STAGE)
+7.5° (counter clockwise from 0°)	15° (clockwise from 0°)
-7.5° (clockwise from 0°)	15° (counter clockwise from 0°)
+15° (counter clockwise from 0°)	30° (clockwise from 0°)
-15° (clockwise from 0°)	30° (counter clockwise from 0°)
+30° (counter clockwise from 0°)	60° (clockwise from 0°)
-30° (clockwise from 0°)	60° (counter clockwise from 0°)
+45° (counter clockwise from 0°)	90° (clockwise from 0°)
-45° (clockwise from 0°)	90° (counter clockwise from 0°)
+60° (counter clockwise from 0°)	120° (clockwise from 0°)
-60(clockwise from 0°)	120° (counter clockwise from 0°)
+70° (counter clockwise from 0°)	140° (clockwise from 0°)
-70° (clockwise from 0°)	140° (counter clockwise from 0°)

For other angles of interest: turn the mirror M4 **exactly twice the desired angle of incidence** from the 0° position ($0° + 2\theta$).

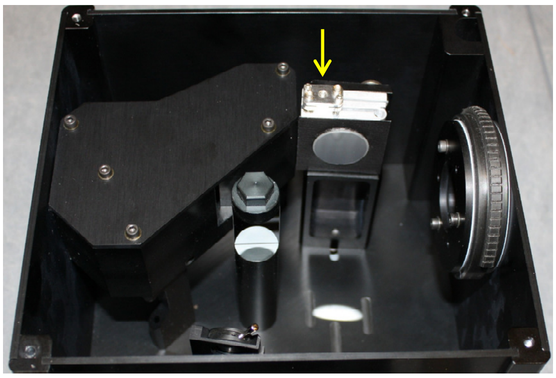
- Insert the sample and set the upper rotation stage at the desired incident angle. Then turn the lower rotation stage into the right position, corresponding to the incident angle.
- Check the position and size of the sample beam and reference beam towards the Repeat these steps for the ' – or negative' angle *)
- Remove the sample and set M5 to exactly 180° (I-mode)

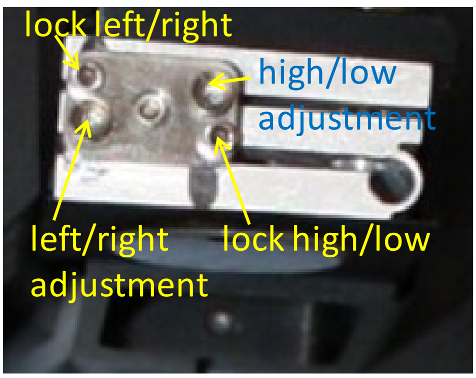
Adjusting the alignment of the incident sample beam

The alignment can be checked using a white light beam (monochromator at 0 nm) and a piece of semi-transparent paper as shown in the photographs below. Pictures a) and b) show the incorrect and correct position of the beam spot on mirror M5 (the correct position is in the middle of the mirror). Picture c) shows slightly different positions of the beam coming from the beam-splitter BS towards M5 and the beam reflected back from M5 towards the beam-splitter. Picture d) shows the correct situation where both beams coincide.



If the situation of picture a) or c) occurs, the beam can be aligned correctly by removing the cover of the compartment on the accessory (see the photograph below) and adjusting mirror M4 with the screws on the mirror holder (indicated by the pictures below, Allen key 2mm)





Adjusting the alignment of the reflected sample beam

By adjusting the translation stage that holds the beam-splitter, the reflected sample beam towards the detector compartment can be moved in horizontal direction to put the illumination spot in the middle of the detector (entrance port in case of the detector sphere)

If necessary, adjust the mirrors of the integrating sphere unit to put the position of the sample beam in the middle of the ports.

Balancing the reference beam

The signal-to-noise ratio of the measurement is optimal if the energy in the reference beam matches that of the sample beam. Therefore the reference beam passes through a Reference Beam Compensator (RBC) and a Reference Beam Attenuator. The RBC consists of an equal number of mirrors and beam splitters that are used in the sample beam's I-mode and thus compensates for the energy losses as function of wavelength. Finally, to level both beams the reference beam energy must be reduced to compensate for the apertures that are present in the samples beam. This can be accomplished by turning the wheel of the variable Reference Beam Attenuator (RBA) located on the accessory at the exit of the reference beam.

In practice, the easiest way to level both beams is to start up UVWinlab Manual control before starting the sample measurements (SSIV in I-mode with polariser inserted in sample compartment):

(1) Select Fix slits (PMT 5nm and InGaAs: 20nm)

(2) At wavelength: fill in the highest wavelength of the desired measurement range. (e.g. wavelength range 250 – 2000nm: use 2000nm)

(3) At ordinate mode: select E1 (Energy sample beam)

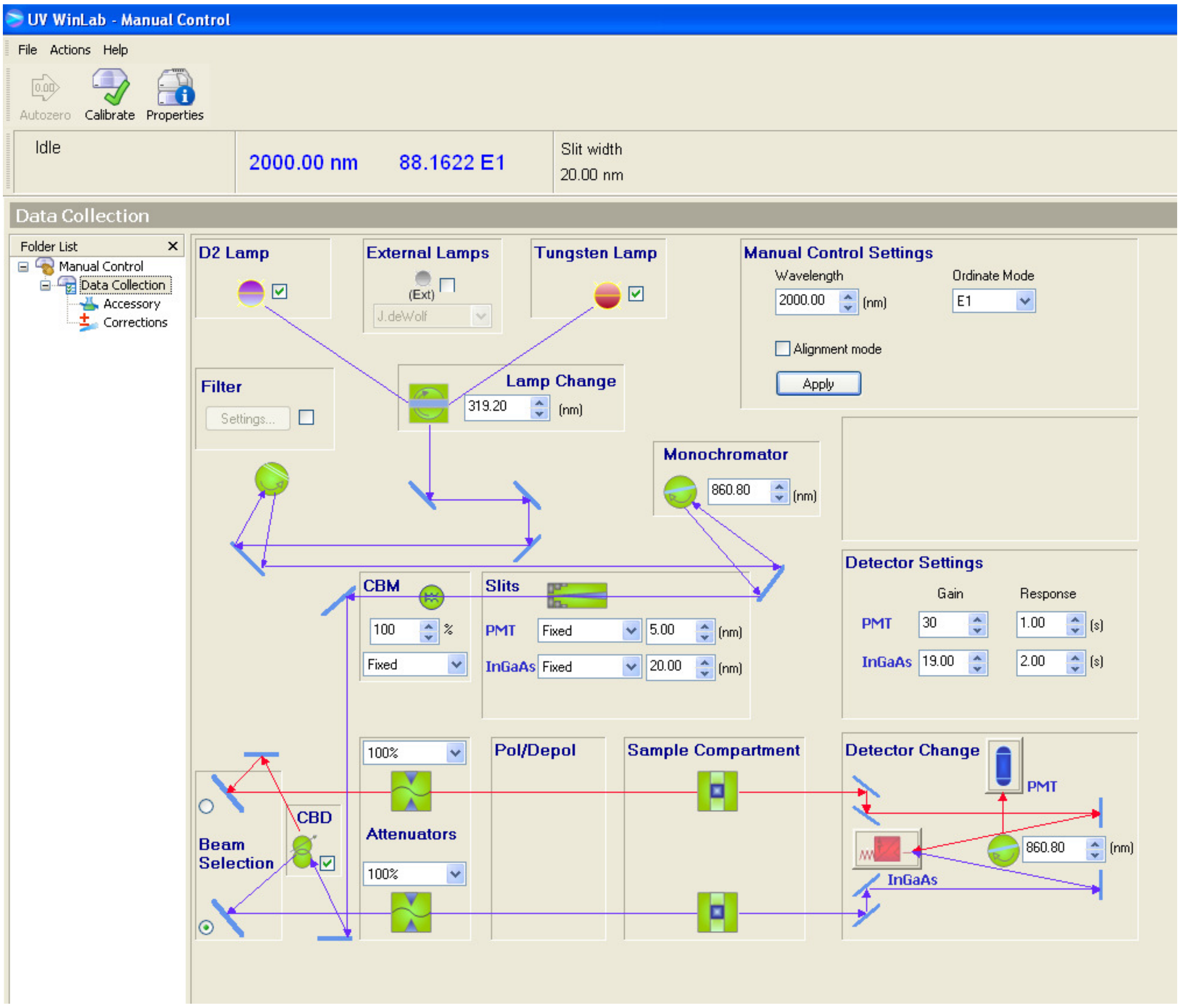
(4) Press Apply

(5) Change the Gain setting until a value between 50 E1 and 95 E1 is found (e.g. 88 E1), see picture on the next page.

(6) Switch to E2 ordinate mode (with the same Gain setting)

(7) Turn the RBA wheel until the E2 values is approximately equal (or a little bit higher than) the E1 value.

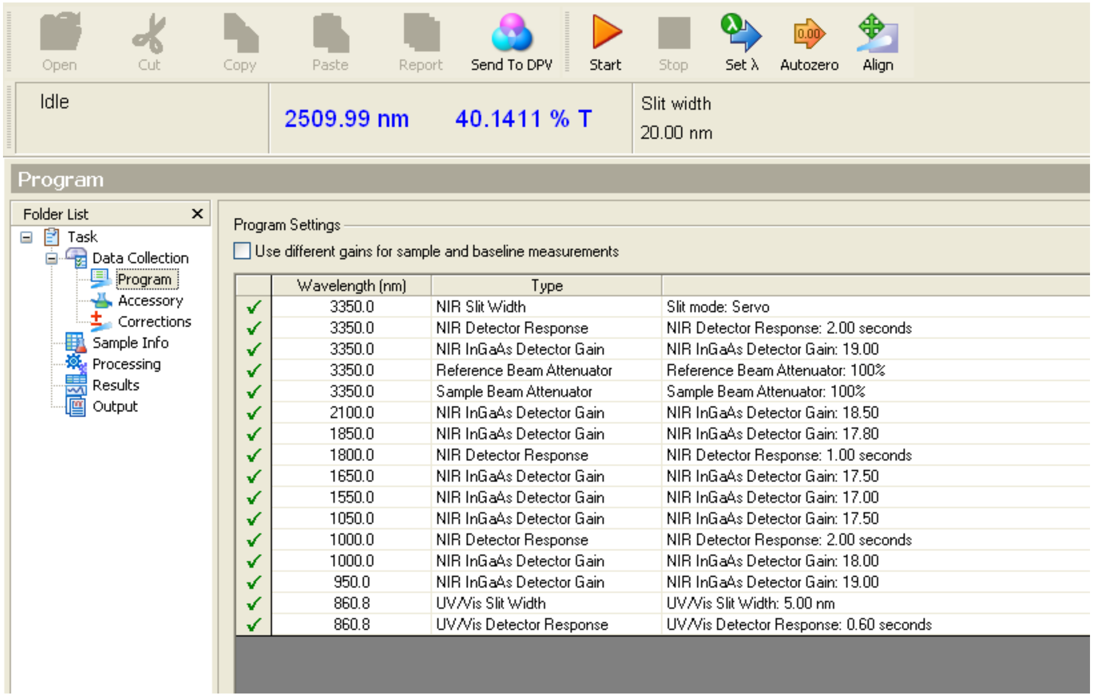
(8) Close UVWinlab Manual control and start your measurements.



UV WinLab - Manual Control
File
Actions
Help
Autozero
Calibrate
Properties
Idle
2000.00 nm
88.1622 E1
Slit width
20.00 nm
Data Collection
Folder List
Manual Control
Data Collection
Accessory
Corrections
D2 Lamp
External Lamps
(Ext)
J.deWolf
Tungsten Lamp
Manual Control Settings
Wavelength
2000.00
(nm)
Ordinate Mode
E1
Alignment mode
Apply
Filter
Settings...
Lamp Change
319.20
(nm)
Monochromator
860.80
(nm)
Detector Settings
Gain
Response
PMT
30
1.00
(s)
InGaAs
19.00
2.00
(s)
CBM
100
%
Fixed
Slits
PMT
Fixed
5.00
(nm)
InGaAs
Fixed
20.00
(nm)
100%
Attenuators
100%
Pol/Depol
Sample Compartment
Detector Change
PMT
860.80
(nm)
InGaAs
CBD
Beam
Selection

InGaAs Gain Settings

The following gain (and response time) settings were found for the SSIV on a Lambda 900 with 150mm InGaAs sphere.



	Wavelength (nm)	Type	
✓	3350.0	NIR Slit Width	Slit mode: Servo
✓	3350.0	NIR Detector Response	NIR Detector Response: 2.00 seconds
✓	3350.0	NIR InGaAs Detector Gain	NIR InGaAs Detector Gain: 19.00
✓	3350.0	Reference Beam Attenuator	Reference Beam Attenuator: 100%
✓	3350.0	Sample Beam Attenuator	Sample Beam Attenuator: 100%
✓	2100.0	NIR InGaAs Detector Gain	NIR InGaAs Detector Gain: 18.50
✓	1850.0	NIR InGaAs Detector Gain	NIR InGaAs Detector Gain: 17.80
✓	1800.0	NIR Detector Response	NIR Detector Response: 1.00 seconds
✓	1650.0	NIR InGaAs Detector Gain	NIR InGaAs Detector Gain: 17.50
✓	1550.0	NIR InGaAs Detector Gain	NIR InGaAs Detector Gain: 17.00
✓	1050.0	NIR InGaAs Detector Gain	NIR InGaAs Detector Gain: 17.50
✓	1000.0	NIR Detector Response	NIR Detector Response: 2.00 seconds
✓	1000.0	NIR InGaAs Detector Gain	NIR InGaAs Detector Gain: 18.00
✓	950.0	NIR InGaAs Detector Gain	NIR InGaAs Detector Gain: 19.00
✓	860.8	UV/Vis Slit Width	UV/Vis Slit Width: 5.00 nm
✓	860.8	UV/Vis Detector Response	UV/Vis Detector Response: 0.60 seconds

These settings were found using UVWinlab Manual Control (ordinate mode: E1). For each wavelength region the gain was changed until it reaches a value between 60 E1 and 90 E1. For more noise reduction the response time can be increased.

Each spectrophotometer and detector unit has a different energy level. Before using the SSIV accessory on your system (spectrophotometer + detector unit) it is important to test the optimal gain settings.

Inserting and removing samples

Turn the Allen key clockwise to open the sample holder and counter clockwise to close it, see photograph. It is recommended to lock the rotation stage when inserting or removing the sample to prevent the holder from closing too fast.

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Step-by-Step Procedures

UVWinLab Methods

On the CD-ROM that is supplied with the SSIV reflection set there are two standard methods available for UVWinlab 6 software. In UVWinlab Please import both methods from the CDROM. Choose edit settings if an error message occurs regarding Instrument Type.

SSIVR
Routine SSIV measurement (normal accuracy)

SSIVP
Precision SS IV measurement (high accuracy)

Routine reflectance measurement

In case of near normal measurements (<10°), the position of the polarizer is irrelevant. In case of measurements under a higher angle of incidence the polarizer is inserted in the desired orientation, P or S (read-out on top). The SSIVR method automatically calculates the square root of the measured signal and therefore yields directly the corrected values (in %).

The following scan sequence is used:

1. Autozero in I-mode (optional)
2. First sample measurement , V-mode
3. Second sample measurement , V-mode
4. etc.

Measurement procedure:

5. Select the method..
6. Set the desired wavelength range (abscissa start and abscissa end).
7. Select the "sample" page and, if necessary, change or add sample file names.
8. Set the accessory in the I-mode.
9. Set the polariser in the desired polarisation state.
10. Start the autozero scan (I-mode, without sample).

11. Insert the sample, set the angles according to the procedure described in chapter Installation and alignment of the SSIV accessory (pages 7 - 8). Click “OK” to perform a V-mode scan.

12. Repeat step 8 with the next sample (or angle) until all sample measurements are performed.

Precision reflectance measurement

The precision method contains the following 24 measurements:

Autozero in the I-mode (optional)

1. 0% (stray light) measurement P
2. 0% (stray light) measurement S
3. 100% measurement, I-mode P
4. 100% measurement, I-mode S
5. sample measurement 1 (‘ + ‘ angle), V-mode P
6. sample measurement 1 (‘ + ‘ angle), V-mode S
7. sample measurement 2 (‘ - ‘ angle), V-mode P
8. sample measurement 2 (‘ - ‘ angle), V-mode S
9. 100% measurement, I-mode P
10. 100% measurement, I-mode S
11. sample measurement 1 (‘ + ‘ angle), V-mode P
12. sample measurement 1 (‘ + ‘ angle), V-mode S
13. sample measurement 2 (‘ - ‘ angle), V-mode P
14. sample measurement 2 (‘ - ‘ angle), V-mode S
15. 100% measurement, I-mode P
16. 100% measurement, I-mode S
17. sample measurement 1 (‘ + ‘ angle), V-mode P

18. sample measurement 1 (‘ + ‘ angle), V-mode S
19. sample measurement 2 (‘ - ‘ angle), V-mode P
20. sample measurement 2 (‘ - ‘ angle), V-mode S
21. 100% measurement, I-mode P
22. 100% measurement, I-mode S
23. 0% (stray light) measurement P
24. 0% (stray light) measurement S

This method results in 6 reflectance values per polarization from which the averages are calculated. The standard deviation is used for the uncertainty analysis

Measurement procedure:

1. Select the method SSIVP.
2. Set the wavelength range (abscissa start and abscissa end).
3. Select the "sample" page and, if necessary, change or add the sample file names.
4. Set the accessory in the I-mode.
5. Set the polariser in the P polarisation mode
6. If necessary, start the autozero scan (I-mode, without sample).
7. Set the lower rotation stage to “+” or “-“ 90° (without sample). In this situation, the sample beam is interrupted. Start the first 2 (stray light) measurements , P and S.
8. Put the accessory in the I-mode and start the I-measurement (After completing each previous scan, UV Winlab responds with the message "Please insert next sample". To start the next scan, click “OK”), again for P and S
9. Insert the sample, set for 'positive' oblique incidence (‘+’ angle) according to the procedure described in chapter *Installation and alignment of the IV accessory (pages 7 - 8).* Click “OK” to perform the 2 V-mode scans, P and S.
10. Insert the sample, set for 'negative' oblique incidence (‘-’ angle) according to the procedure described in chapter *Installation and alignment of the IV accessory (pages 7 - 8).* Click “OK” to perform the 2 V-mode scans, P and S.
11. Repeat steps 8 through 10 until all scans except for two are completed.

12. Repeat step 8 for the final I-measurements.
13. Repeat step 7 for the final stray light measurements.
14. Process the measurement data using Excel workbook SSIV angle v2.0 UVWinLab v6.xls .

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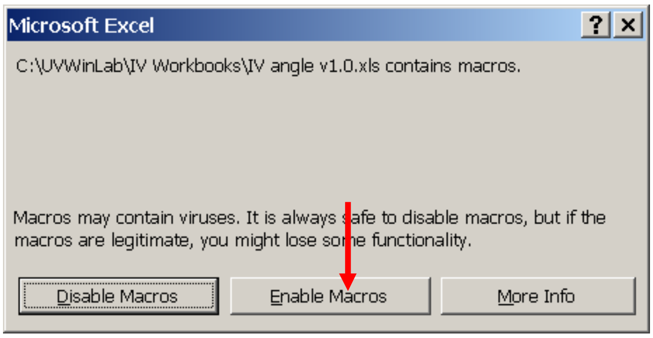
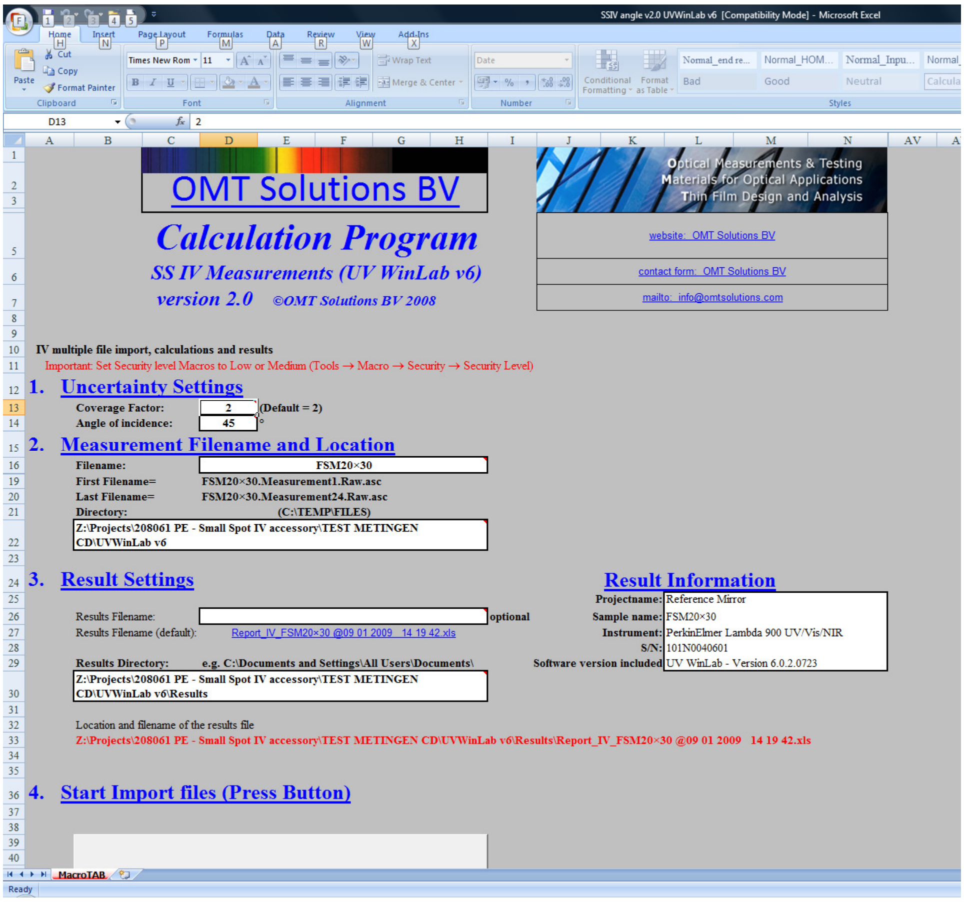
Using the Excel workbook

Open the Excel workbook SSIV angle v2.0.xls. You will get the following messagebox:



Select the button Enable Macros. The following workbook will open:



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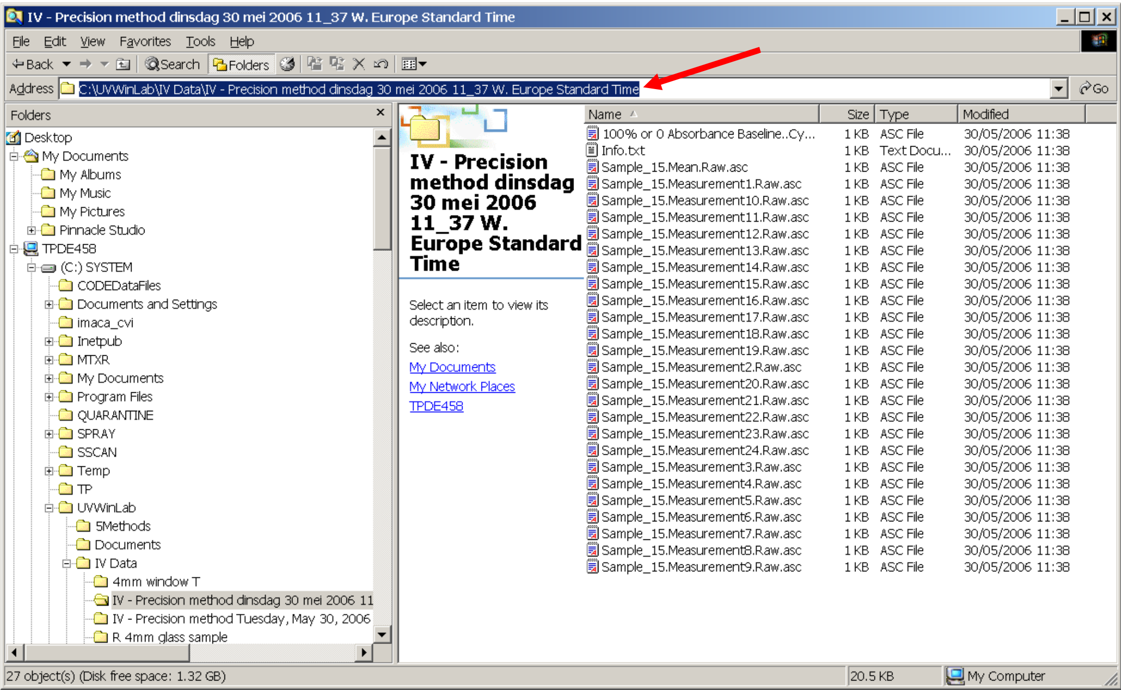
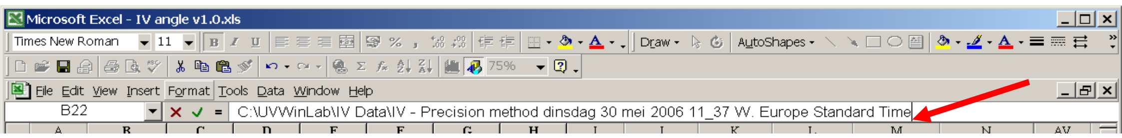
Changing data file name and location

Go to Windows Explorer and select the appropriate directory with data saved by Uvwinlab. Copy the name and path from the Address bar:



Note: Is the full name and path of the selected directory not visible in the address bar, select "Tools" ➔ "Folder Options" ➔ "View" and check "Display the full path in the address bar".

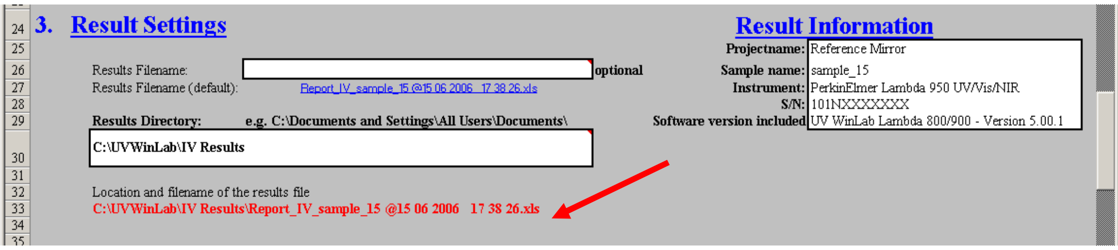
In the Excel workbook, select cel B22, delete the content, than click on the formula bar and paste the new address:



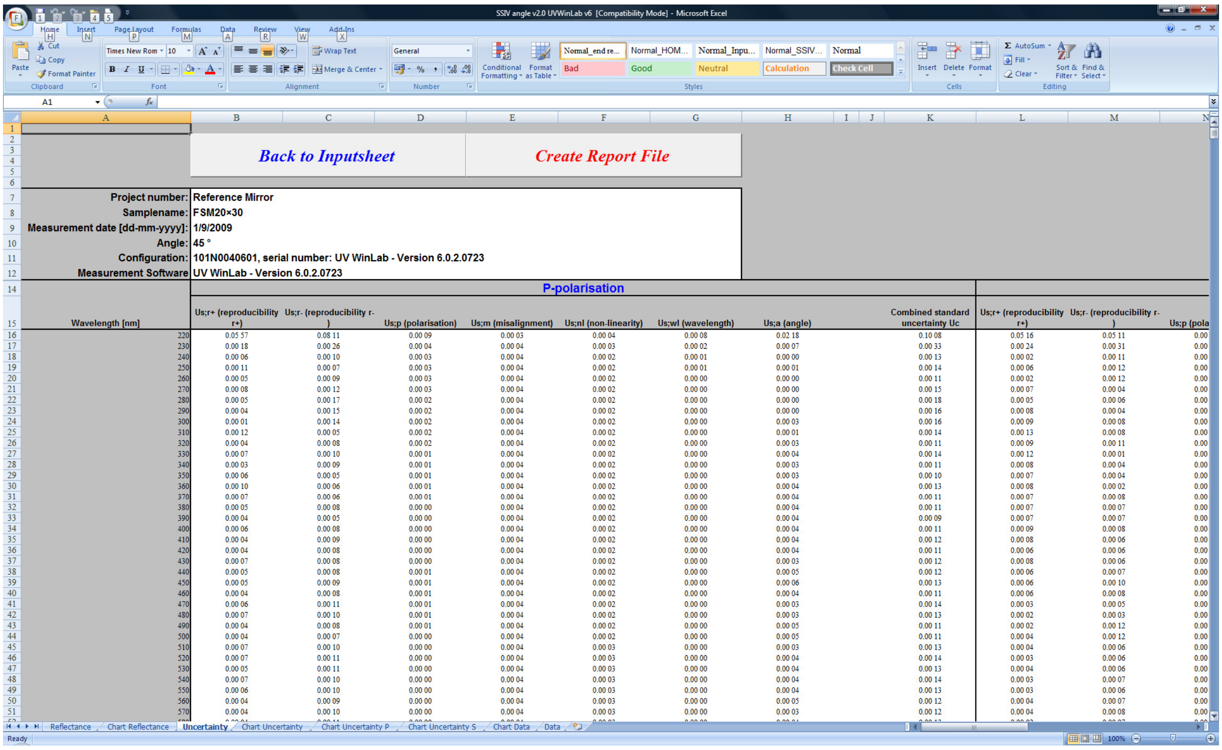
Note: Do not past directly in cel B22!

Other input cells can be adapted in a similar way or by directly typing in the required text!

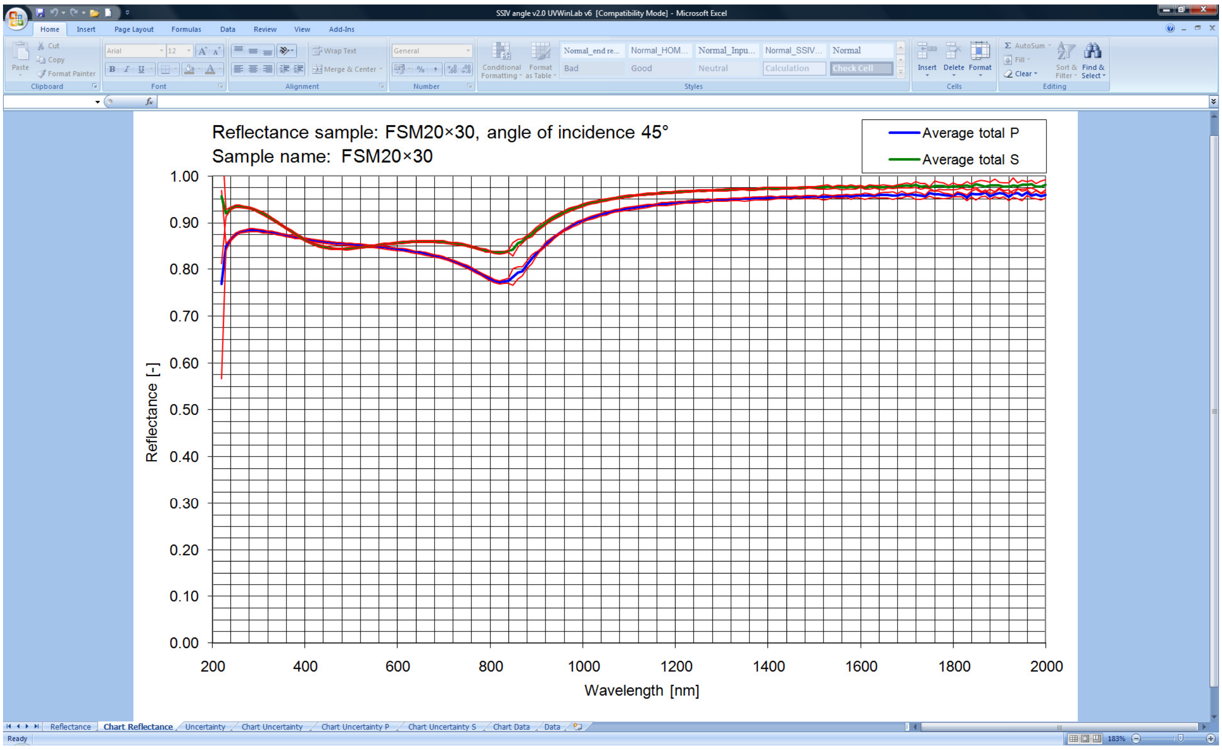
After completing the input, click on the button at the bottom of the worksheet and the data will be automatically processed and the results saved in the result file:

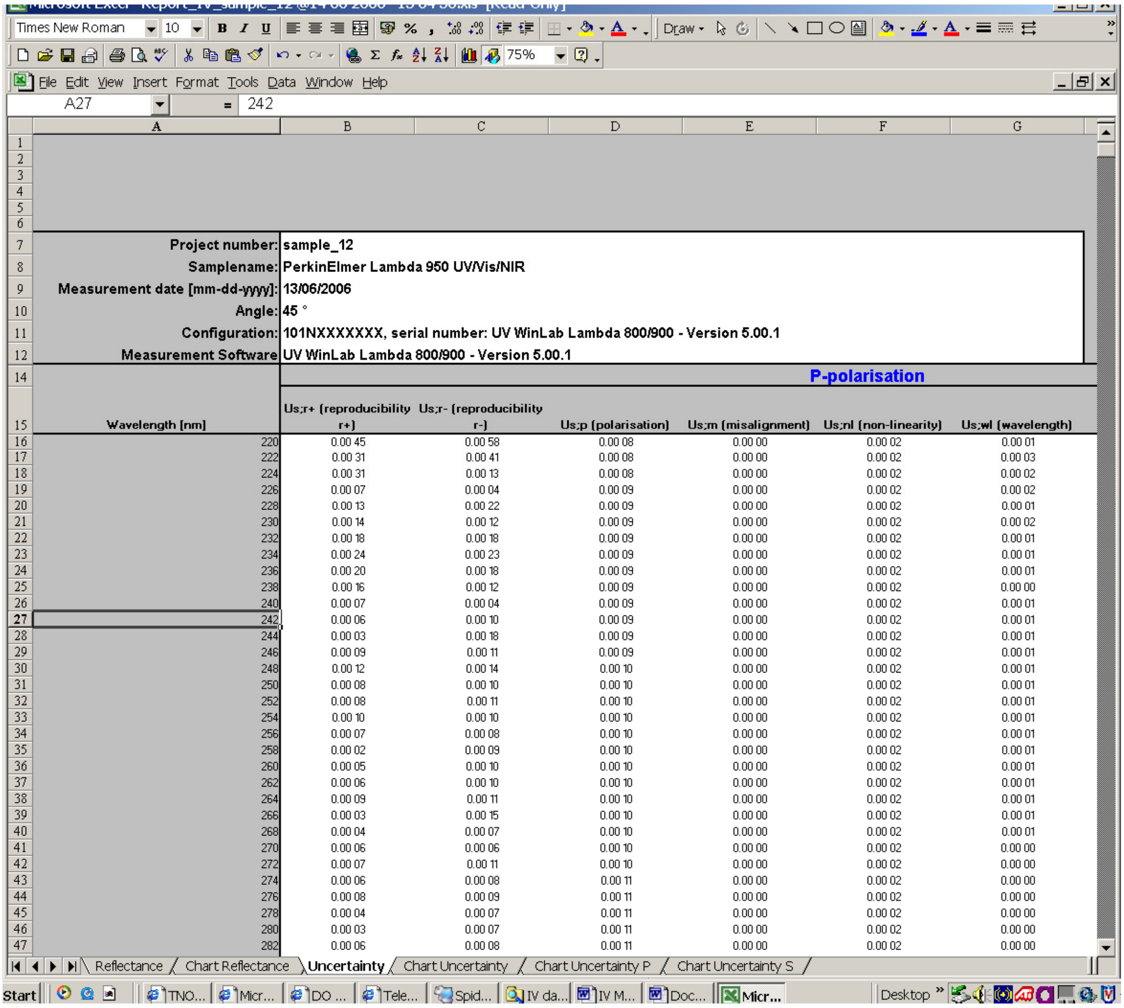


The result file is an Excel workbook containing 6 sheets that can be selected by the tabs at the bottom. The first sheet contains the Reflectance, the Combined Standard Uncertainty and the Expanded Uncertainty as specified in the Chapter "Calculations":



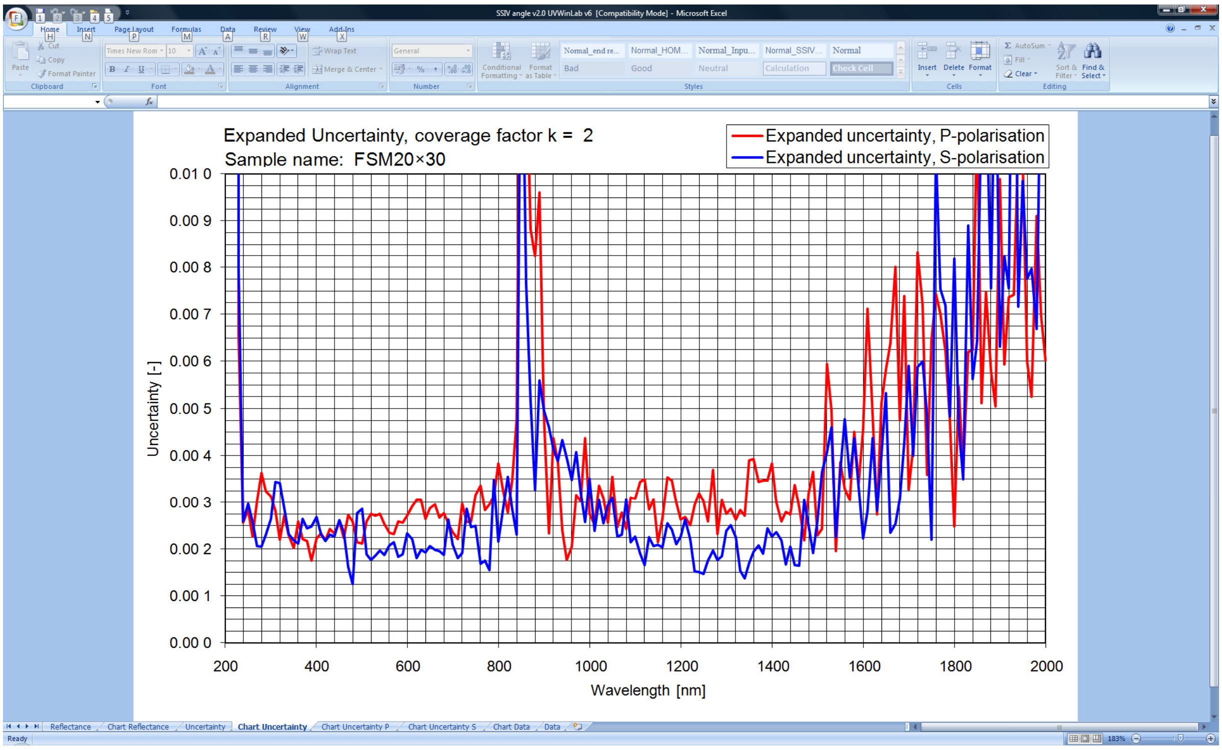
The second sheet contains a graph of the reflectance spectra. The red lines are the error bands specified by the Expanded Uncertainty:


SSIV angle v2.0 UVWinLab v6 [Compatibility Mode] - Microsoft Excel
Reflectance sample: FSM20×30, angle of incidence 45°
Sample name: FSM20×30
Average total P
Average total S
Reflectance [-]
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
200
400
600
800
1000
1200
1400
1600
1800
2000
Wavelength [nm]
Reflectance
Chart Reflectance
Uncertainty
Chart Uncertainty
Chart Uncertainty P
Chart Uncertainty S
Chart Data
Data
Ready



Project number:	sample_12
Samplename:	PerkinElmer Lambda 950 UV/Vis/NIR
Measurement date [mm-dd-yyyy]:	13/06/2006
Angle:	45 °
Configuration:	101NXXXXXXX, serial number: UV WinLab Lambda 800/900 - Version 5.00.1
Measurement Software	UV WinLab Lambda 800/900 - Version 5.00.1

	P-polarisation					
Wavelength [nm]	Us;r+ (reproducibility r+)	Us;r- (reproducibility r-)	Us;p (polarisation)	Us;m (misalignment)	Us;nl (non-linearity)	Us;wl (wavelength)
220	0.00 45	0.00 58	0.00 08	0.00 00	0.00 02	0.00 01
222	0.00 31	0.00 41	0.00 08	0.00 00	0.00 02	0.00 03
224	0.00 31	0.00 13	0.00 08	0.00 00	0.00 02	0.00 02
226	0.00 07	0.00 04	0.00 09	0.00 00	0.00 02	0.00 02
228	0.00 13	0.00 22	0.00 09	0.00 00	0.00 02	0.00 01
230	0.00 14	0.00 12	0.00 09	0.00 00	0.00 02	0.00 02
232	0.00 18	0.00 18	0.00 09	0.00 00	0.00 02	0.00 01
234	0.00 24	0.00 23	0.00 09	0.00 00	0.00 02	0.00 01
236	0.00 20	0.00 18	0.00 09	0.00 00	0.00 02	0.00 01
238	0.00 16	0.00 12	0.00 09	0.00 00	0.00 02	0.00 00
240	0.00 07	0.00 04	0.00 09	0.00 00	0.00 02	0.00 01
242	0.00 06	0.00 10	0.00 09	0.00 00	0.00 02	0.00 01
244	0.00 03	0.00 18	0.00 09	0.00 00	0.00 02	0.00 01
246	0.00 09	0.00 11	0.00 09	0.00 00	0.00 02	0.00 01
248	0.00 12	0.00 14	0.00 10	0.00 00	0.00 02	0.00 01
250	0.00 08	0.00 10	0.00 10	0.00 00	0.00 02	0.00 01
252	0.00 08	0.00 11	0.00 10	0.00 00	0.00 02	0.00 01
254	0.00 10	0.00 10	0.00 10	0.00 00	0.00 02	0.00 01
256	0.00 07	0.00 08	0.00 10	0.00 00	0.00 02	0.00 01
258	0.00 02	0.00 09	0.00 10	0.00 00	0.00 02	0.00 01
260	0.00 05	0.00 10	0.00 10	0.00 00	0.00 02	0.00 01
262	0.00 06	0.00 10	0.00 10	0.00 00	0.00 02	0.00 01
264	0.00 09	0.00 11	0.00 10	0.00 00	0.00 02	0.00 01
266	0.00 03	0.00 15	0.00 10	0.00 00	0.00 02	0.00 01
268	0.00 04	0.00 07	0.00 10	0.00 00	0.00 02	0.00 01
270	0.00 06	0.00 06	0.00 10	0.00 00	0.00 02	0.00 00
272	0.00 07	0.00 11	0.00 10	0.00 00	0.00 02	0.00 00
274	0.00 06	0.00 08	0.00 11	0.00 00	0.00 02	0.00 00
276	0.00 08	0.00 09	0.00 11	0.00 00	0.00 02	0.00 00
278	0.00 04	0.00 07	0.00 11	0.00 00	0.00 02	0.00 00
280	0.00 03	0.00 07	0.00 11	0.00 00	0.00 02	0.00 00
282	0.00 06	0.00 08	0.00 11	0.00 00	0.00 02	0.00 00



Expanded Uncertainty, coverage factor k = 2
Sample name: FSM20×30
Expanded uncertainty, P-polarisation
Expanded uncertainty, S-polarisation
Uncertainty [-]
0.01 0
0.00 9
0.00 8
0.00 7
0.00 6
0.00 5
0.00 4
0.00 3
0.00 2
0.00 1
0.00 0
200
400
600
800
1000
1200
1400
1600
1800
2000
Wavelength [nm]

Calculations

Routine measurements

In case of a routine measurement, the measurements are performed in the following sequence:

1. $M_{V,1}$ = measurement in the V-mode ("positive" angle),
2. M_I = measurement in the I-mode,
3. $M_{V,2}$ = measurement in the V-mode ("negative" angle).

The reflectance is calculated from these measurements according to:

$$R = \sqrt{\frac{M_{V,1} + M_{V,2} - 2M_0}{2M_I - 2M_0}} \quad . \tag{1}$$

Precision measurements

Precision measurements are performed in the sequence:

$$M_{0,1};\ M_{I,1};\ M_{V,1};\ M_{V,2};\ M_{I,2};\ M_{V,3};\ M_{V,4};M_{I,3};\ M_{V,5};\ M_{V,6};M_{I,4,};\ M_{0,2} \tag{2}$$

All measurements are performed for P and S-polarisation separately (by repeating each scan after switching the polariser position), resulting in 24 scans per sample.

The six reflectance values corresponding to each of the V-mode measurements are determined for P and S-polarisation separately, according to:

$$R_i = \sqrt{\frac{2M_{V,i} - M_{0,1} - M_{0,2}}{M_{I,j} + M_{I,j+1} - M_{0,1} - M_{0,2}}} \quad , \qquad (3)$$

where j = 0.5 (i + 1) for i = 1, 3, 5 (“positive” angles) j = 0.5 i for i = 2, 4, 6 (“negative” angles).

The reflectance of the sample is determined by taking the average of these six values.

Error Analysis

Evaluation and Expression of Uncertainty

The procedures below are based on the ISO Guide to the Expression of Uncertainty in Measurement [1].

The following measurement equation is valid for the reflection of an unknown sample:

$$R = \sqrt{f} \cdot \left(\tfrac{1}{2} R_+ + \tfrac{1}{2} R_-\right) + \Delta_{NL} + \Delta_{WL} + \Delta_A + \Delta_P + \Delta_M + \Delta_{NU} \quad , \qquad (4)$$

in which

f is a factor that accounts for differences in alignment between V and W mode

R_+ is the average of the reflectance values measured for “positive” angles,

R_- is the average of the reflectance values measured for “negative” angles,

Δ_{NL} is a contribution that acounts for detector non-linearity

Δ_{WL} is a contribution that acounts for a systematic deviation in the wavelength

Δ_A is a contribution that acounts for a systematic deviation in the angle of incidence

Δ_P is a contribution that acounts for a systematic deviation in the polarisation

Δ_{NU} is a contribution that acounts for a systematic deviation due to sample non-uniformity

Misalignment

The alignment factor f in (4) has a value of one (1) with a standard uncertainty $u_f < 0.001$ (va;ue based on experience). The uncertainty in the reflectance due to misalignment is proportional to u_f according to

$$u_M = \tfrac{1}{2} R^2 u_f \quad , \tag{5}$$

Standard uncertainty in the reflectance

The average reflectance values R_+ and R_- are each estimated from 3 independent observations R_i according to (3). The standard uncertainty associated with these observations is the estimated standard deviation (of the mean) according to:

$$u_{R+} = 1.32 \cdot \sqrt{\tfrac{1}{6} \sum_{i=1,3,5} \left(R_i - < R >_{1,3,5}\right)^2} \quad , \tag{5a}$$

$$u_{R-} = 1.32 \sqrt{\tfrac{1}{6} \sum_{i=2,4,6} \left(R_i - < R >_{2,4,6}\right)^2} \quad , \tag{5b}$$

In which the factor 1.32 is the Student-t factor for 2 degrees of freedom and a 68.27% confidence level (1 sigma).

Detector non-linearity

The detector non-linearity produces a systematic uncertainty component that in principle can be corrected (see Ref.'s 2 and 3). This requires a thorough investigation of the instrument in use.

Our research (see Ref. 3) has shown that, when a measurement is made with a background correction (values between 0% and 100%), the non-linearity error of the Lambda 900 approximates the function

$$\Delta_{NL} = C(1 - M)M \quad . \tag{6}$$

where M is the measurement value (between 0 and 1) and C a constant which is wavelength dependent. According to this equation, the non-linearity error is zero at 0% and 100% and has its maximum at M = 0.5 (50%). The constant C in (6) can be determined using the Double Aperture Method as described in Ref. 3.

If we don't make a non-linearity correction, we chose $\Delta_{NL} = 0$ in equation (4). The standard uncertainty associated with Δ_{NL} is

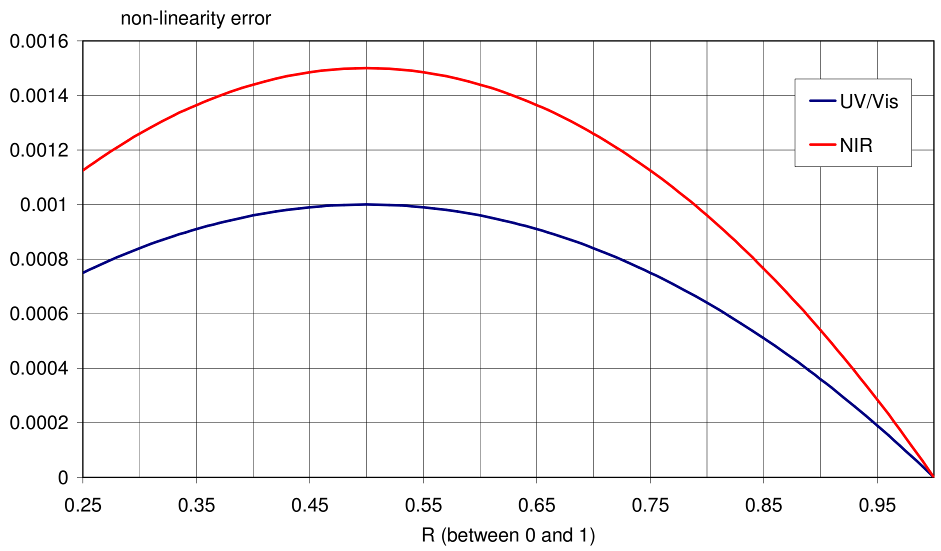
$$u_{NL} = \tfrac{1}{4} C(1 - R)R \qquad . \qquad (7)$$

We can obtain a safe estimate for C by using the limits of the photometric accuracy of the Lambda 900 as specified by Perkin Elmer. Using these specifications, we find:

- In the UV/Vis range (specified photometric accuracy = 0.2%) ➔ C = 0.008
- In the NIR range (specified photometric accuracy = 0.3%) ➔ C = 0.012

The factor ¼ is a correction for the fact that we measure R^2 and for the coverage factor of 2 that is assumed to be associated with the specified photometric accuracy:

Given the reflectance range in which the IV accessory operates, the non-linearity errors according to these specifications and Eq. (7), follow the curves shown in the graph below:



Wavelength uncertainty

The correction for a systematic deviation in the wavelength Δ_{WL} is assumed to be zero with a standard uncertainty that can be estimated using wavelength standards.

Unless the measured spectrum is flat, the uncertainty in the wavelength will yield an uncertainty in the ordinate. Taking into account that we measure the square of the reflectance, the standard uncertainty due to this effect is given by:

$$u_{WL} = \tfrac{1}{2}\left|\frac{\partial R}{\partial \lambda}\right| u_{\lambda} \approx \tfrac{1}{2}\left|\frac{\Delta R}{\Delta \lambda}\right| u_{\lambda} \quad . \tag{8}$$

Typical values for the standard uncertainty in the wavelength scale of the Lambda 900 are

- In the UV/Vis range ➔ $u_\lambda = 0.1$ nm
- In the NIR range ➔ $u_\lambda = 0.15$ nm

Uncertainty in the angle of incidence

The uncertainty in the angle of incidence is determined by the uncertainty in the angular setting of the rotation stage.

The effect of the random uncertainty in the angular setting is "hidden" in the reproducibility of the measurement (given by equation (5)). The systematic error in the angular setting is associated with the accuracy of the sample rotation stage, for which the standard uncertainty is $u_\theta = 0.042°$.

The correction for a systematic deviation in the wavelength Δ_A is assumed to be zero with a standard uncertainty that can be estimated with

$$u_A = \tfrac{1}{2}\left|\frac{\partial R}{\partial \theta}\right| u_{\theta} \approx \tfrac{1}{2}\left|\frac{\Delta R}{\Delta \theta}\right| u_{\theta} \quad . \tag{8a}$$

or alternatively from the differences in R_+ and R_- according to

$$u_A = \frac{1}{2\sqrt{3}}\left|R_+ - R_-\right| = \frac{1}{6\sqrt{3}}\left|R_1 - R_2 + R_3 - R_4 + R_5 - R_6\right| \quad , \tag{8b}$$

for which we asume a rectangular statistical distribution of Δ_A.

Uncertainty in the polarisation

The uncertainty in the angle of the polariser ($\vartheta \approx 1°$) results in an uncertainty in the reflectance at oblique incidence that can be estimated with

$$u_P = \frac{1}{2\sqrt{3}}\left|R_P - \frac{R_P \cos\vartheta + R_S \sin\vartheta}{\cos\vartheta + \sin\vartheta}\right| = \frac{1}{2\sqrt{3}}\left|R_P - R_S\right| \frac{\sin\vartheta}{\cos\vartheta + \sin\vartheta} \quad . \tag{9}$$

The uncertainty is the same for P and S polarisation.

Combined standard uncertainty

The combined standard uncertainty in the measured reflectance is obtained according to

$$u_C = \sqrt{(u_{R+})^2 + (u_{R-})^2 + (u_{NL})^2 + (u_{WL})^2 + (u_A)^2 + (u_P)^2 + (u_M)^2 + (u_{NU})^2} \quad (10)$$

Expanded uncertainty

The expanded uncertainty U provides an interval R-U to R+U about the result R within which the value of R can be asserted with a high level of confidence.

The expanded uncertainty is determined by multiplying the combined standard uncertainty u_C of (9) with a coverage factor k (for which commonly a value k=2 is chosen).

References

1. Guide to the Expression of Uncertainty in Measurement, ISBN 92-67-10188-9, 1st Ed. ISO, Geneva, Switzerland (1993).

2. Mielenz, K.D. and Eckerle, K.L., Spectrophotometer at the National Physical Laboratory, J. Res. Of the National Bureau of Standards – A. Physics and Chemistry, Vol. 76A, 1972.

3. Nijnatten, P.A. van, Calibration of neutral density glass filters to produce transmittance standards, 5th ESG Conference “Glass Science and Technology for the 21st Century”, Prague, 1999.