CIMPS-pcs

Photo Current Spectroscopy

1. Introduction

CIMPS-pcs was designed to integrate photocurrent spectroscopy and spectro-electrochemical tasks into the service of the Thales-Zennium system environment. Established with the tunable light source TLS, one of the core applications of CIMPS-pcs is measuring the Incident Photon Conversion Efficiency IPCE of organic and dye sensitized solar cells in the wavelength range from about 370 (420) nm up to more then 1010 (720) nm (TLS02 values in brackets), representative for the most useful range of the solar light.

Like the standard light sources for CIMPS, the TLS is based on the recent LED technology. CIMPS-pcs profits from the modulation capabilities of LED in the same way like CIMPS. No mechanical choppers are necessary and instead of the more noise-sensitive Lock-In-technique the advantages of coherent frequency analysis technique can be used. CIMPS-pcs comes up as a plug & play application fully calibrated and established with the exemplary comfort of Thales: spectral data can be analyzed with the on-board package "light spectra analysis", spectral data files are covered by the preview-support of the Windows® file explorer and can be exported in manifold way as high-quality vector graphic, bitmap and ASCII data list. Online-viewing and export is possible, while measurements are still running and context-sensitive help is available using the alternate mouse button. On demand CIMPS-pcs can work together also with traditional set-ups of 3rd party light source – chopper – monochromator combinations in additional wavelength ranges, but with a little less comfort.

The two quantities photocurrent efficiency and IPCE are both automatically computed by Thales from measured data and displayed in a convenient way (Fig. 1).
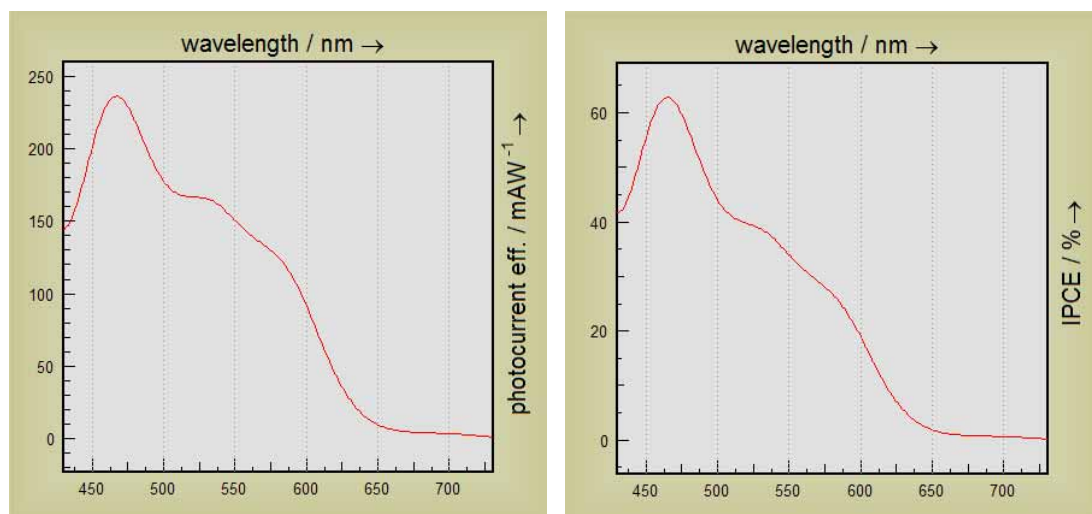

Fig. 1 Photocurrent efficiency and IPCE of an organic solar cell built up from Cr-Al-Cr-P3HT-PCBM-PEDOT-Cr-Au

Photocurrent efficiency $H_{IP}(\lambda)$ is calculated from the photocurrent $I(\lambda)$ divided by irradiance P (dimension W/m²) and illuminated area A:

$$H_{IP}(\lambda) = \frac{I(\lambda)}{P \cdot A}$$

IPCE is defined as ratio of generated photoelectrons $n_e(\lambda)$ to incident photons $n_{ph}(\lambda)$:

$$IPCE(\lambda) = \frac{n_e(\lambda)}{n_{ph}(\lambda)}$$

The number of photoelectrons $n_e(\lambda)$ can be easily calculated from the photocurrent $I(\lambda)$ and time t using the elementary charge q_e.

$$n_e(\lambda) = \frac{I(\lambda) \cdot t}{q_e}$$

The number of photons $n_{ph}(\lambda)$ is given by the irradiance P (dimension W/m²) multiplied by the illuminated area A and time t divided by the energy of a photon. The latter is determined by its wavelength λ, the speed of light c and the Planck constant h:

$$n_{ph}(\lambda) = \frac{P \cdot A \cdot t}{h \cdot \dfrac{c}{\lambda}}$$

Using these expressions IPCE calculates to:

$$IPCE(\lambda) = \frac{I(\lambda)}{P \cdot A \cdot \lambda} \cdot \frac{h \cdot c}{q_e}$$

2. Hardware and Installation

2.1. System components

The CIMPS photo current spectroscopy option is available in two different versions CIMPS-pcs and CIMPS-pcs2 differing in the hardware used. TLS01 / TLS02 use a wideband white LED light source with a separate monochromator and cover the range of 430 to 720 nm. The TLS03 uses an array of monochromatic LEDs with an internal monochromator. It covers the range of 370 to 1010 nm (minimal), 365 to 1020 nm (typical). Please refer to the chapter corresponding to your hardware.

2.1.1. CIMPS-pcs with TLS01 or TLS02

CIMPS-pcs requires a tunable light source (TLS) consisting of a high power LED light source and a monochromator unit. The light source, monochromator and photo electrochemical cell (PECC) are mounted on the optical bench according to Fig. 2. The distance d between light source unit and monochromator unit depends on the model of the TLS. The TLS01 has to be adjusted to d = 6 mm using a caliper. The TLS02 is equipped with spacers for adjusting d more easily. Push monochromator unit and light source unit together until the monochromator unit touches the spacers of the light source unit.
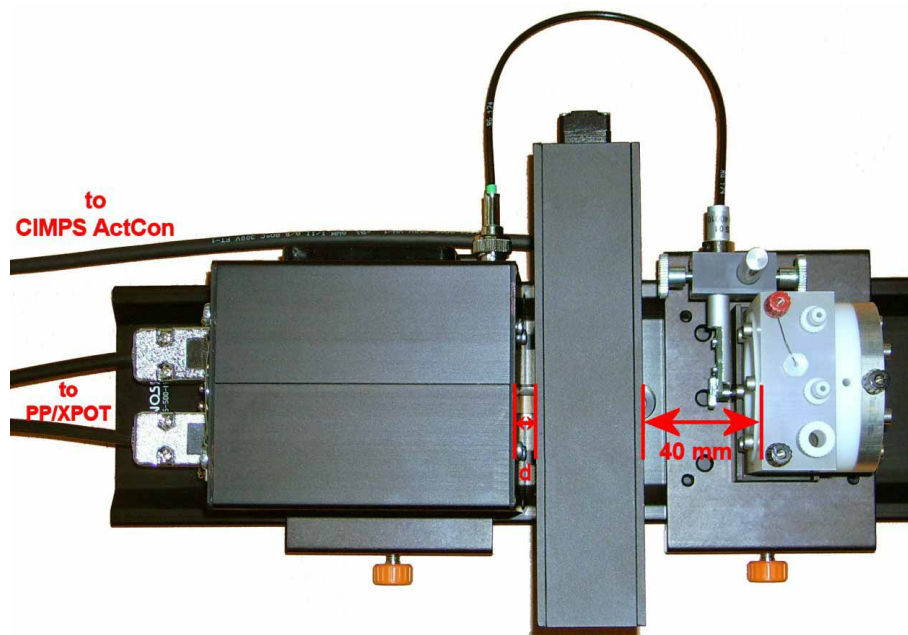

Fig. 2 Components of CIMPS-pcs mounted on the optical bench

The position of the sensor is adjusted at delivery but may be checked to comply with the dimensions given in Fig. 3.

Fig. 3 Position of the photo sensor

The probe E/I connectors of the light source are connected to the slave potentiostat (PP211 or XPOT) using the cable supplied with CIMPS. The photo sensor located in front of the cell is connected to the BNC socket of the light source.

> **!** An enclosure covering the complete optical bench is necessary to avoid detrimental effects caused by ambient light during the whole measurement time.

2.1.2. CIMPS-pcs2 with TLS03

The tunable light source TLS03 of CIMPS-pcs2 is a fully integrated unit containing a LED array, a monochromator and all electronic circuits needed for running the TLS. As the light feedback sensor is inside the light source unit, no external sensor is required.
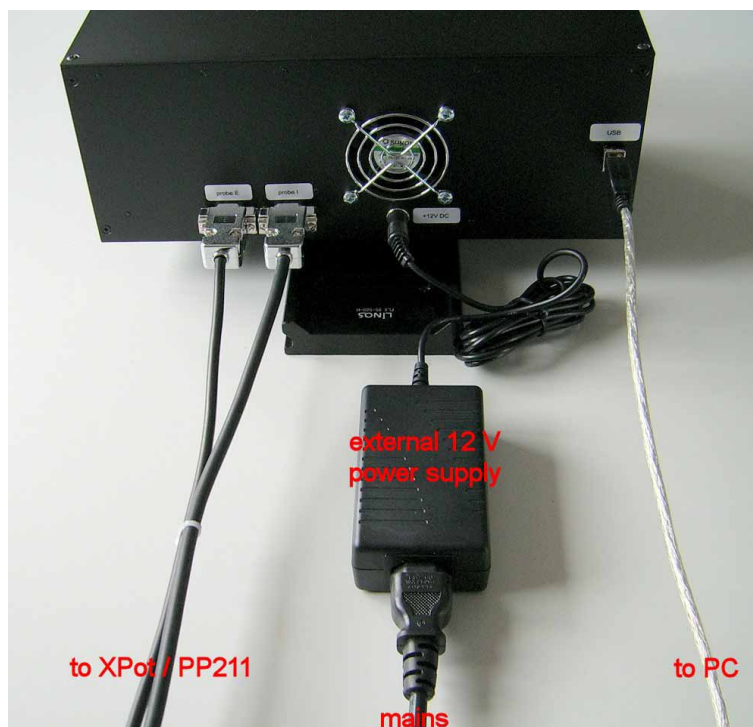

Fig. 4 Wiring of the TLS03

Connect the TLS03 to the XPot/PP211 using the probe E / probe I cable set delivered with CIMPS. Switch the XPot/PP211 off while connecting the TLS03 and secure the connectors by fastening the screws. The TLS03 is powered by an external 12 V DC power supply as shown in Fig. 4. The integrated monochromator is controlled by the PC running Thales via USB. Therefore connect the TLS03 to the Thales PC using the supplied USB cable.

Distance between the end of the glass rod of the TLS03 and the front glass of the PECC, respectively the surface of any test object should be 1 mm for optimal homogeneity and calibration accuracy (see Fig. 5). The diameter of the light beam is about 10 mm in this case. If a larger illuminated area is necessary, the optionally available TLS03 beam extender should be used. Simply increasing the distance between the end of the glass rod and the front glass results in a reduced homogeneity of the light beam and should not be done in excess.
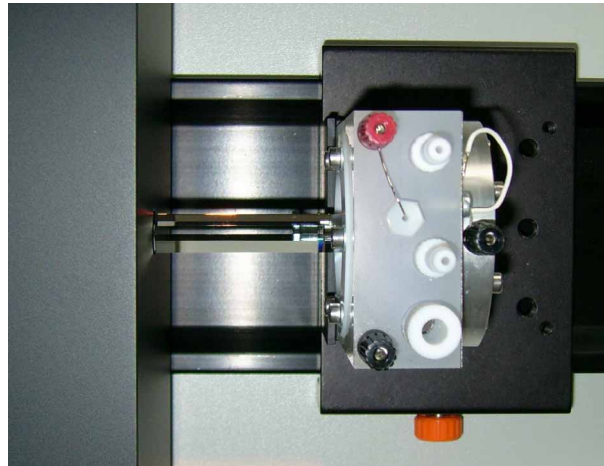

Fig. 5 Position of the PECC using the TLS03.

!	Connect the probe E and probe I cables while the XPot/PP211 is switched off. Secure the connectors with the screws to ensure they cannot get loose during operation.

!	An enclosure covering the complete optical bench is recommended to avoid detrimental effects caused by ambient light during the whole measurement time.

2.2. Monochromator controller

The monochromator of the TLS01/02 is controlled by a separate controller box (CIMPS ActCon), which is connected to the PC by an USB interface. The monochromator controller of the TLS03 is integrated into the TLS03 main unit. Driver installation and Net VI are identical for both variants.

2.2.1. Driver Installation

When the controller box / TLS03 is connected to the PC the first time the USB drivers have to be installed. In the first dialog of the hardware installation wizard (see Fig. 6 left hand side) choose the option not to connect to Windows Update. In the second dialog activate the option to manually choose the driver location.
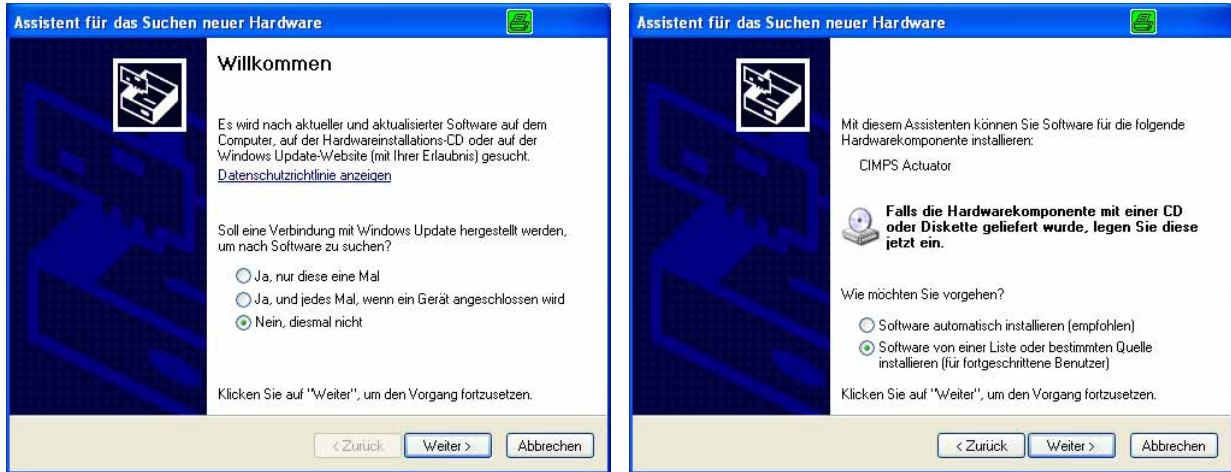
Fig. 6 Install of CIMPS Actuator USB drivers

In the next dialog (see Fig. 7, left hand side) enter the path C:\THALES\usb\FTDI and activate the option to search this path. Now the driver is installed and another dialog (see Fig. 7, right hand side) informs about the successful installation. Now Windows detects a USB serial port as second device. Proceed with the installation exactly the same way as with the first device.

Fig. 7 Install of CIMPS Actuator drivers - part 2

2.2.2. NET VI

The monochromator is integrated into Thales by a NET VI application called TLS. The concept of NET VIs is described in the separate manual Signal Acquisition and NET VI. As the NET VI is controlled completely by Thales, the application window only displays the actual status (Fig. 8). The NET VI application is started automatically during startup of CIMPS-pcs (c.f. chapter 3.1) and should not be closed during use of CIMPS-pcs.
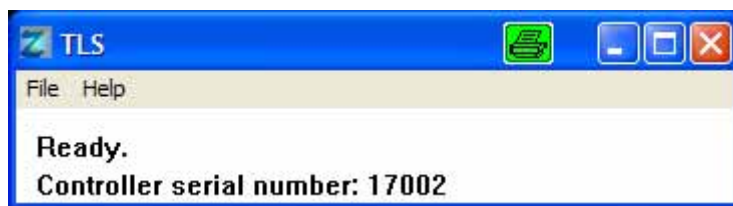

Fig. 8 CIMPS Actuator application TLS

At each start of TLS the monochromator initializes by moving the filter to both end positions. After initialization the filter returns to the home position. During shut down TLS also returns the filter to the home position. Leave the application time to perform the return action before turning off the computer.

3. Software

3.1. Startup

CIMPS-pcs is easily activated by using the pull down menu as shown in Fig. 9. In order to open the pull down menu click onto the Z-icon [icon] in the title bar of the Thales window.

Fig. 9 Start of CIMPS-abs using the pull down menu.

After initialization of the potentiostat and the monochromator, the main window of CIMPS-pcs is displayed (see Fig. 10 for TLS01/02 and Fig. 11 for TLS03).
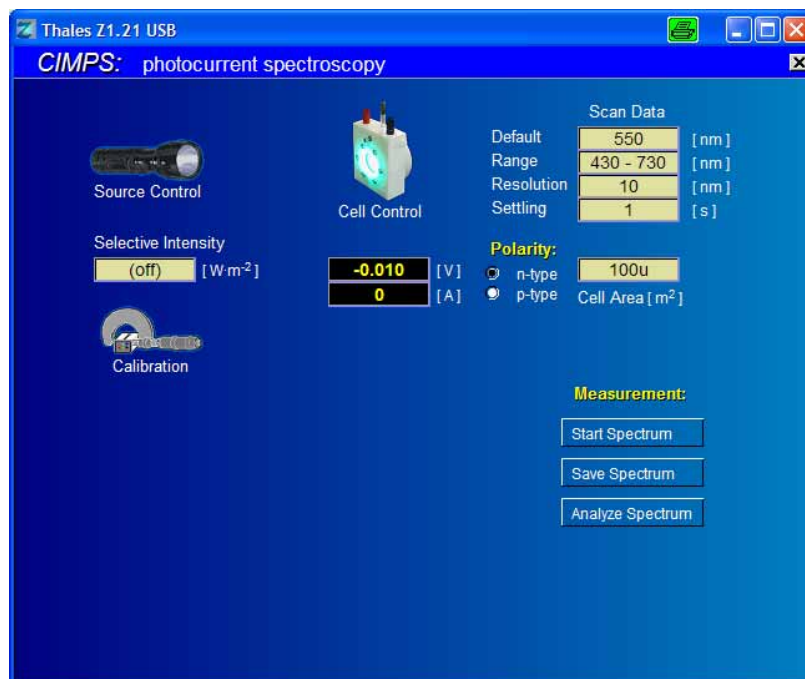

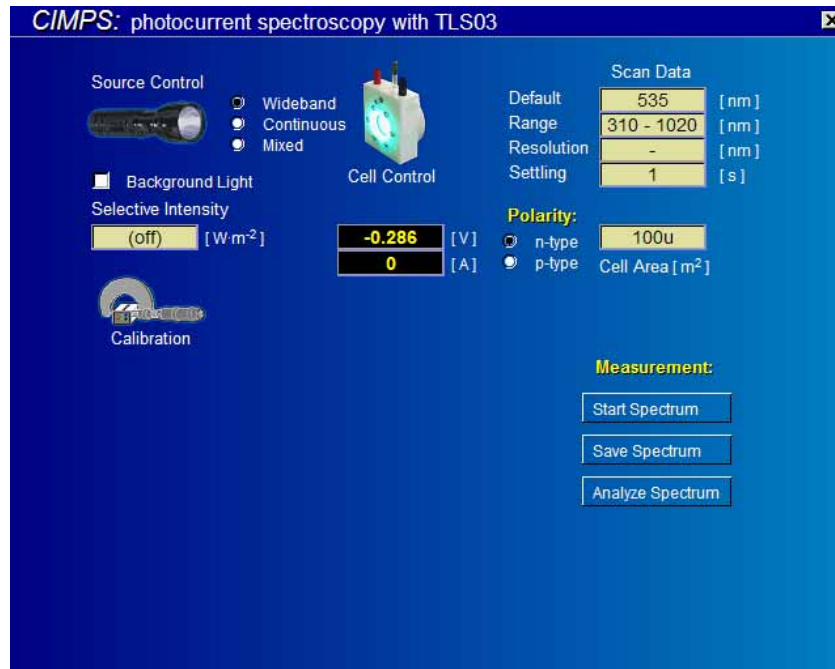Fig. 10 Main window of CIMPS-pcs with TLS01/02 after startup.

Fig. 11 Main window of CIMPS-pcs with TLS03 after startup.

It is similar to the regular CIMPS main window regarding source and cell control so chapters 3.1.2 and 4.1 of the CIMPS manual also apply here with some differences specific to CIMPS-pcs. In particular, CIMPS-pcs is restricted to photocurrent measurements. Therefore the cell control, if active, should be solely potentiostatic.

3.2. Light Source Calibration

3.2.1. Loading calibration files of TLS01 or TLS02

CIMPS-pcs requires a tunable light source (TLS) consisting of a high power LED light source and a Light sources delivered by Zahner come with a calibration file which has to be loaded before using the light source.
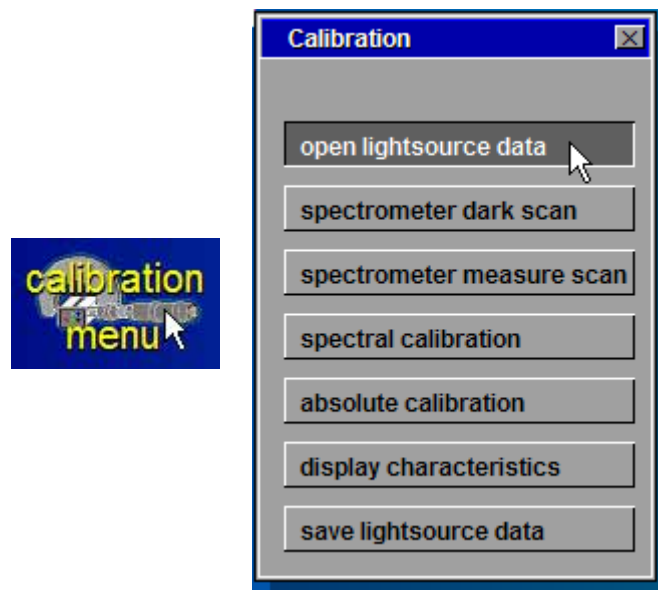

Fig. 12 Loading light source calibration data.

Click the calibration menu icon (Fig. 12, left hand side), select "open light source data" (Fig. 12, right hand side) and choose the file corresponding to the light source used in the file dialog (Fig. 13). The

name of the calibration file consists of the serial number and the ordering code of the light source, e.g. "0400tls01" for the tunable light source with serial number 400.
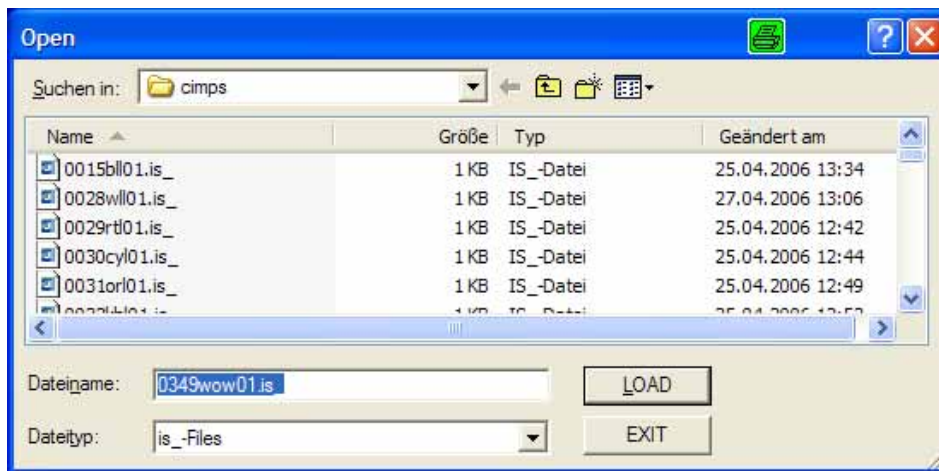

Fig. 13 File dialog for choosing the calibration file of the light source.

> **!** Factory calibration of the TLS02 is center weighted to the optical axis, i.e. the center of the light spot. Therefore maximum accuracy is reached using small samples near the optical axis. Measuring samples larger than 10 mm may result in a deviation of about 5%.
> Here increasing the distance between monochromator and sample can increase accuracy but factory calibration is not valid anymore.
> Contact Zahner for calibrating the TLS at other distances.

3.2.2. Loading calibration files of TLS03

CIMPS-pcs detects the TLS03 during startup of the software and opens the correct calibration file automatically from c:\thales\cimps. So there is no need to load the calibration file manually.

3.3. Light Source Control

3.3.1. TLS01 and TLS02

The light source control should be set to a fixed source current (usually 300 mA for the TLS01/02) in order to provide a calibrated spectrum (Fig. 14). The photocurrent determination is based on an AC measurement. Similar to CIMPS, one has to set an AC modulation amplitude in the source control window (Fig. 15) before entering a measurement by means of the "Start Spectrum" button. In contrast to CIMPS, the light source control is strictly galvanostatic, consequently one has to put in the modulation amplitude in units of Ampere (Fig. 16). A typical recommended value is 100 mA amplitude when having 300 mA DC.
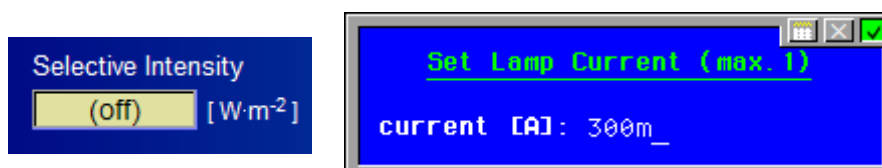

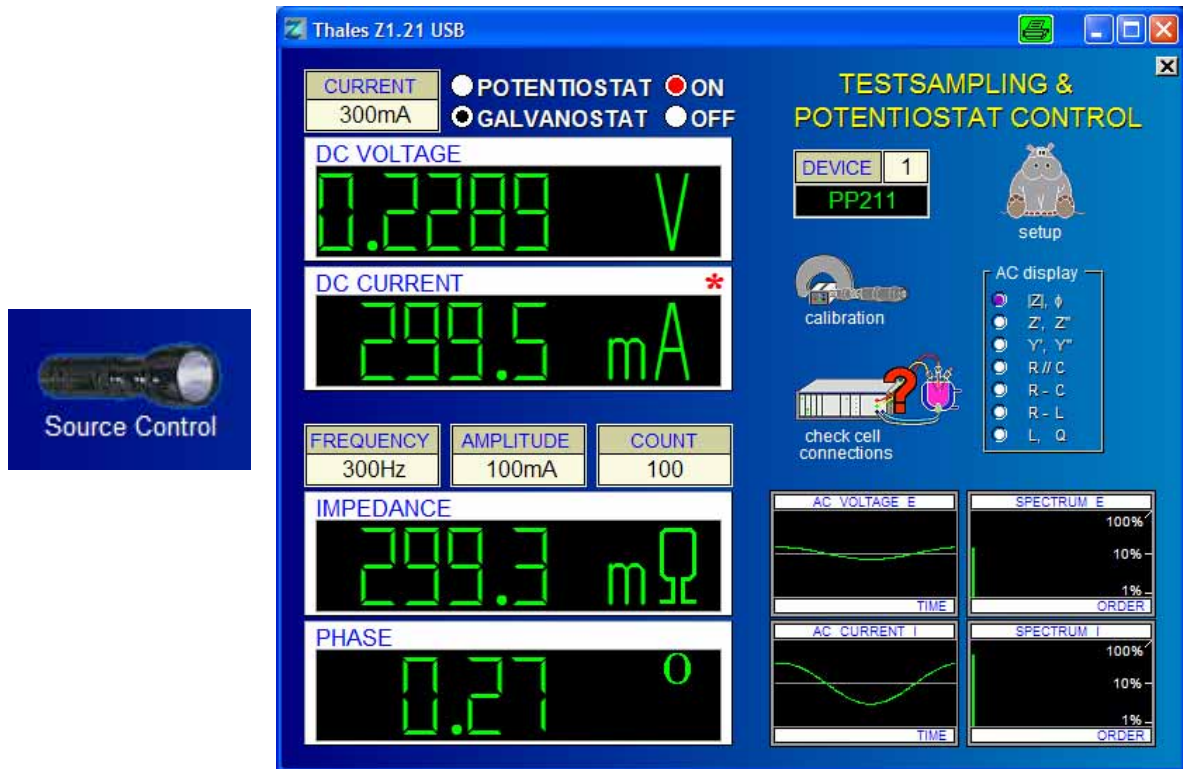Fig. 14 Setting the DC current of the light source

Fig. 15 Entering source control for setting up frequency, amplitude and number of measured periods

While CIMPS usually runs an IMPS/IMVS spectrum vs. light modulation frequency, in CIMPS-pcs the user has to decide for a characteristic modulation frequency, which is kept through the complete wavelength scan of the light. It is recommended to use not too high frequency in order to yield an AC photocurrent which appears dominated by the real part. In silicon solar cells frequencies of one KHz or higher are acceptable. For organic solar cells OSC frequencies of up to 1KHz are characteristic. A recommended value is 300 Hz, because it provides usually clearly real part dominance, but is fast enough to allow many averages. With a recommended period count of 100 cycles, the typical measurement time for one wavelength sample is about 1 s. Dye sensitized solar cells DSSC, in particular based on TiO_2, are much slower than OSC. Therefore modulation frequencies of ten Hz or even lower may be appropriate.
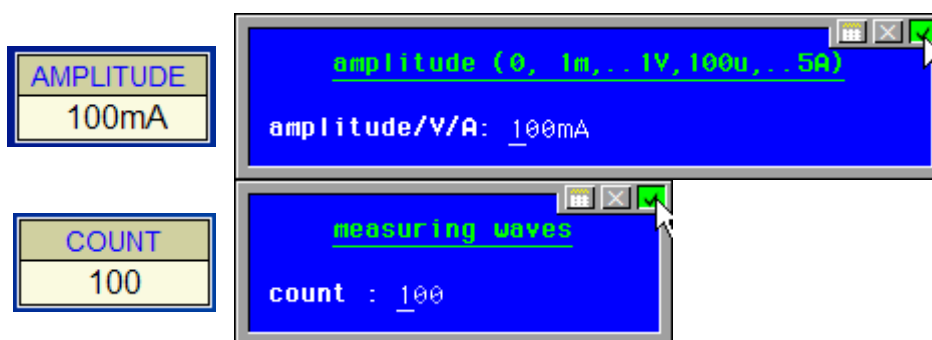

Fig. 16 Setting of amplitude and number of measured periods in source control

In case a measurement is started with the light source not properly set up, an error message is displayed (Fig. 17). By pressing the ENTER key or clicking the message box with the left mouse button the standard values of the light source (300 mA DC bias, 300 Hz, 100 mA AC amplitude, 100 counts) are set automatically and the measurement is started. When quitting the message box with the middle mouse button or the ESCAPE key the light source can be set up manually. In this case start the measurement manually, afterwards.
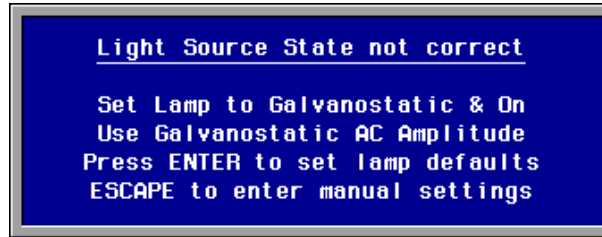
Fig. 17 Error message when starting a measurement without correct light source state.

3.3.2. TLS03

The TLS03 can be used in three different operating modes: wideband, continuous and mixed mode.

Wideband mode: Wavelength can be set in the range of 365 nm (310 nm with UV extension) to 1020 nm by automatic switching between the 23 (26) discrete sources. Resolution and spectral half width are given by the discrete wavelengths of the LEDs and vary between 10 nm and 60 nm (typical).

Continuous mode: In addition to the different wavelengths of the LED array a monochromator is used for fine tuning the wavelength. So a resolution of 1 nm with a typical half width of 15 nm is reached. This mode is limited to a range of typical 410 to 720 nm (minimum 420 to 710 nm) due to the wavelength range of the monochromator.

Mixed mode: Wideband and continuous mode are combined. Outside the monochromator range the discrete LED wavelengths are used. Within the monochromator range the wavelength is scanned in user defined steps. Due to the numerical procedure of combining the two parts of the spectrum a wavelength resolution of about 10-20 nm is recommended.

Fig. 18 Operating modes of the TLS03 light source.

Please note: In all cases light intensity varies while scanning wavelengths. Especially while switching between different LEDs, intensity may drop significantly. Using the white background illumination can be used to reduce this effect (see chapter 3.3.3).

For monochromatic illumination purposes the intensity of the TLS03 is set by clicking the selective intensity display on the main screen. It is set as percentage of the maximum available intensity for the selected wavelength in the chosen scan mode. The software automatically selects the appropriate current of the used LED so there is no need to set LED current manually. In order to perform an IPCE measurement, adjustments of the light source are controlled automatically.
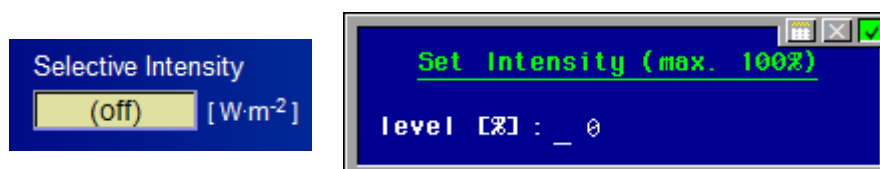

Fig. 19 Setting DC intensity of the TLS03.

While CIMPS usually runs an IMPS/IMVS spectrum vs. light modulation frequency, in CIMPS-pcs the user has to decide for a characteristic modulation frequency, which is kept through the complete wavelength scan of the light. It is recommended to use not too high frequency in order to yield an AC photocurrent which appears dominated by the real part. In silicon solar cells frequencies of one KHz or higher are acceptable. For organic solar cells OSC frequencies of up to 1KHz are characteristic. A recommended value is 300 Hz, because it provides usually clearly real part dominance, but is fast

enough to allow many averages. With a recommended period count of 100 cycles, the typical measurement time for one wavelength sample is about 1 s. Dye sensitized solar cells DSSC, in particular based on TiO_2, are much slower than OSC. Therefore modulation frequencies of ten Hz or even lower may be appropriate. Please mind, time constants of DSSC are dependent on intensity. Consider using the background light in order to shorten time constant of a DSSC (see chapter 3.3.3).

In order to set the modulation frequency, click *source control* and *access lightsource potentiostat*. Now enter *frequency* and *count*, what is the number of periods averaged for each wavelength. Differing from the TLS01/2, neither adjustments for the driver current nor for modulation amplitude and mode of the light source potentiostat are necessary. The configuration is done automatically, except for the measuring frequency and the count of integrated periods which are marked with red circles in Fig. 20.
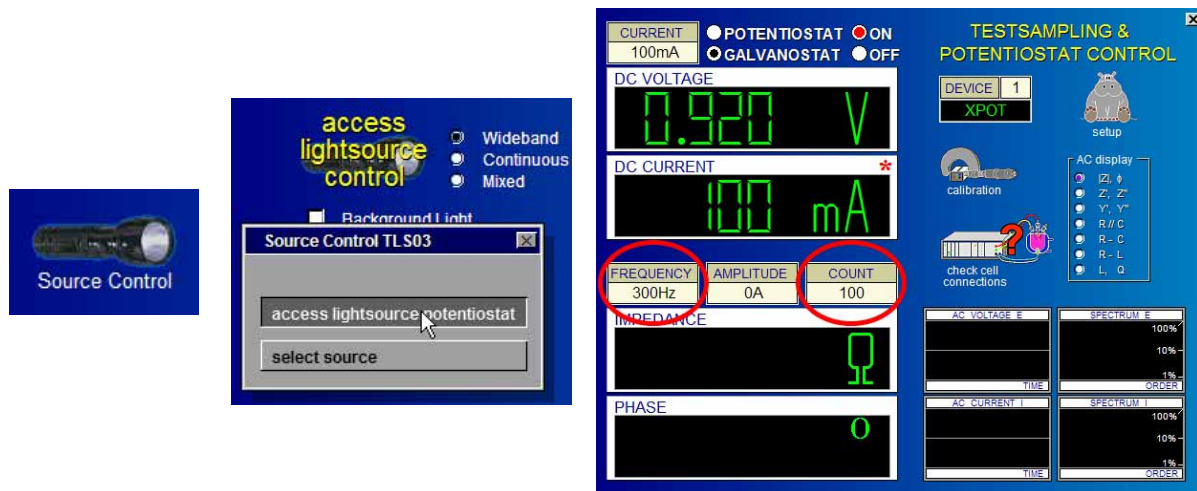

Fig. 20 Setting frequency and number of periods for photocurrent measurements.

Source control can also be used to select a wavelength for the default state of the light source. *Select source* displays a list of all available discrete wavelengths of the array as shown in Fig. 21. Here one of the available LEDs can be selected. This feature can be taken to use the TLS03 is used as standard light source for instance in CIMPS applications.
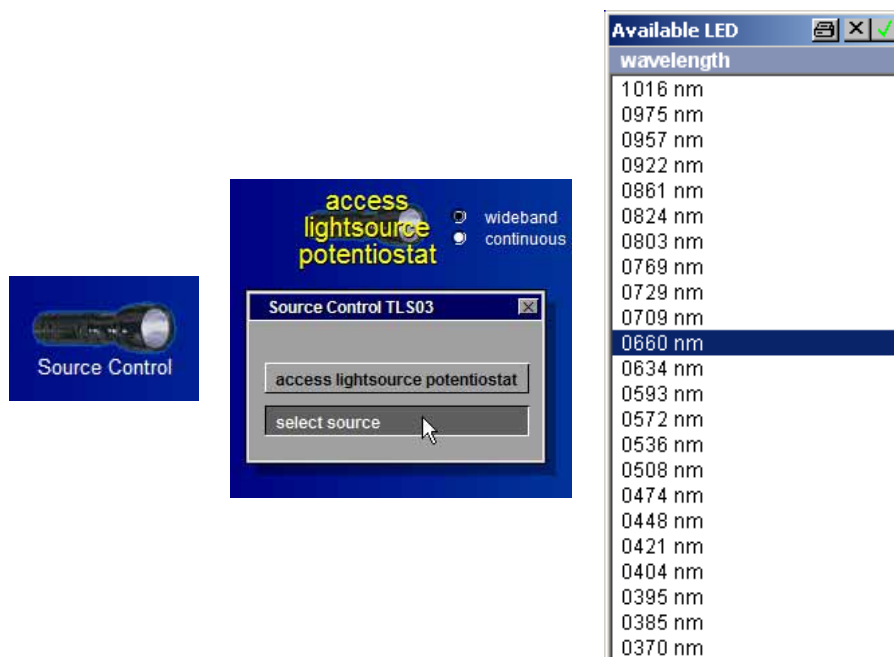

Fig. 21 Selecting a wavelength for manual setup of the TLS03.

3.3.3. Background Light TLS03

Time constants of dye sensitized solar cells (DSSC) increase at low illumination intensities. In order to shorten time constants of DSSC, measurements can be performed under an increased DC bias intensity. This is realized by switching on a constant intensity white light source integrated into the TLS03 as shown in Fig. 22.

Fig. 22 Switching background light on and off

As the photocurrent is determined in an AC measurement, the DC bias of the white background light is cancelled out and does not disturb measurement.

3.4. Cell Control

Cell control is located in the middle of the main screen. As in standard CIMPS the cell control icon is used to enter the control menu of the cell potentiostat (main potentiostat of the Zennium) as shown in Fig. 23.

In order to record the photocurrent, switch to *potentiostatic mode* and *on*. The correct setting of the voltage is crucial for obtaining correct IPCE spectra. At high intensities and / or high efficiency, the bulk resistance of the sample affects the determination of the quantum efficiency. Therefore setting the potential to 0 V only works with samples of low bulk resistance. Samples with considerable bulk resistance must be polarized to reverse voltage in order to overcome the bulk resistance.

Fig. 23 Active cell control icon and control potentiostat window

The PCS spectrum cannot be started, if the cell potentiostat is not set to "potentiostatic control" and "on" mode.

| ! | Ensure the quantum efficiency can be determined by setting a reverse voltage high enough to overcome bulk resistance of your sample. |

3.5. Measurement Parameters

The following parameters can be set after clicking into the Scan data display field:

Fig. 24 Scan Parameters for Photocurrent Spectra with TLS01/02

wideband mode	continuous mode	mixed mode
Resolution is given by the discrete LED wavelengths	Resolution can be set to user defined values	Resolution can be set to user defined values within the monochromator range

Fig. 25 Scan Parameters for Photocurrent Spectra with TLS03.

Default: Whenever no measurement is running, the light source returns to the default wavelength. It can be adjusted to arbitrary values within the according range limits in order to adjust the cell setup.
Range: The wavelength range used for photocurrent spectra. The range is limited by the capability of the tunable light source, which is typically 430 nm to 730 nm for TLS01 and TLS02. For the TLS03 the range is 420 nm to 710 nm (minimum range in **continuous** mode) respectively 365 nm to 1020 nm (typical range in **wideband** mode).
Resolution: The wavelength resolution used for photocurrent spectra. Permitted values are between 1 nm and 50 nm, recommended is 10 nm. Independently from the chosen resolution, the spectra are stored in 1 nm-steps by means of cubic spline interpolation between the samples.
In the wideband mode of the TLS03 resolution adjustment is not available due to the discrete nature of the light sources. In mixed mode of the TLS03 the setting is used within the monochromator range.
Settling: The time span the cell is given for equilibrating to the new wavelength. Permitted settling time is between 1 s and 60 s. Please consider that the settling time is calculated for the period between the correct achievement of the next wavelength position of the monochromator and the photocurrent measurement start. The total recording time may be therefore significant longer than the sum of all settling times.

Fig. 26 Cell Parameters for Photocurrent Spectra.

Polarity: Photocurrent spectra are recorded using an AC measurement in order to improve signal to noise ratio. The sign of the photo-electrical effect depends on the type of the majority charge carriers of the basic semiconductor and its connection orientation with respect to the working electrode. If the photoelectrical effect will decrease the cell current with increasing intensity, the phase relation of the photo-electrochemical transfer function comes out in an inconvenient way: The limiting case for the phase angle in the absence of reactance effects (usually approximated at low frequencies) is not zero, but ±180 degrees. The software therefore offers the possibility to change the sign meaning of the incident light intensity, what is equivalent to putting in the type of the majority charge carriers. This can

avoid the inconvenient phase relationship. Note that phase angle will only be visible in exported ASCII-data.

Cell Area: Enter the active area of the sample here to receive correctly scaled photocurrent efficiency and IPCE data. Be sure to put in m^2-units. When using samples larger than the light beam the active area is given by the light beam. Area of the TLS03 light guide is 86.6 mm^2 which is also the light beam size in vicinity of the light guide.

!	The calculation of photocurrent efficiency and IPCE relies on the illuminated cell area is set correctly. In case the entered cell area does not match the real cell area, data calculated by Thales will deviate from the real value.

3.6. Performing Measurements

After light source and cell are set up, the measurement can be started using the Start Spectrum button (Fig. 27).

Fig. 27 Button for starting a measurement.

Once the measurement is started, it will scan the photocurrent dependency vs. wavelength due to the range and resolution defined in the "Scan Data" input panel. Actual wavelength and current efficiency are displayed online during measurement as shown in like Fig. 28.
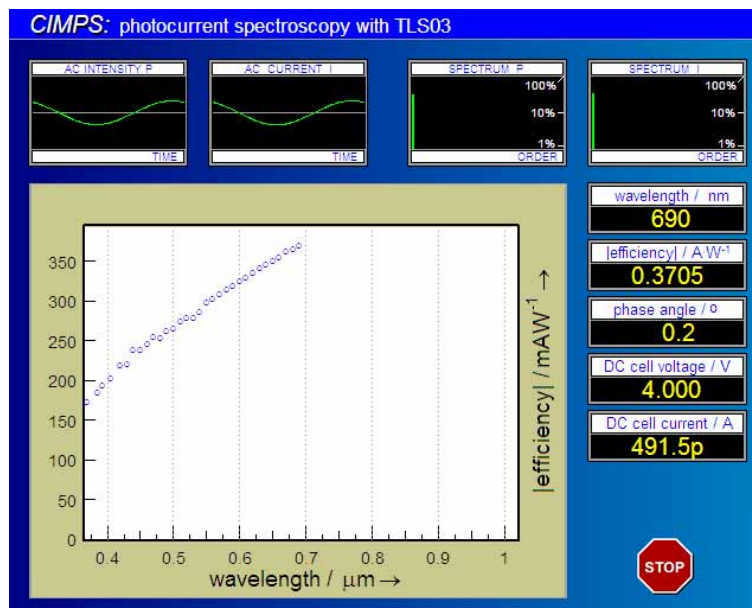

Fig. 28 Online display during measurement

A running measurement can be stopped prematurely using the *STOP* button (Fig. 29). After the measurement is finished Thales automatically returns to the PCS main screen.[1]

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[1] In case Thales should wait for user interaction before leaving the measurement screen this can be configured in the calibration file of the TLS03. Locate the entry *uflags=0* and change it to *uflags=1*. Now Thales stays in the measurement screen until the Continue button is clicked.

Fig. 29 Stopping a running measurement

If you intend to analyze the spectra quantitatively, you should specify the cell area in the "Cell Area" input panel accurately. After completion of the scan you may store the spectra as data file (Fig. 30).
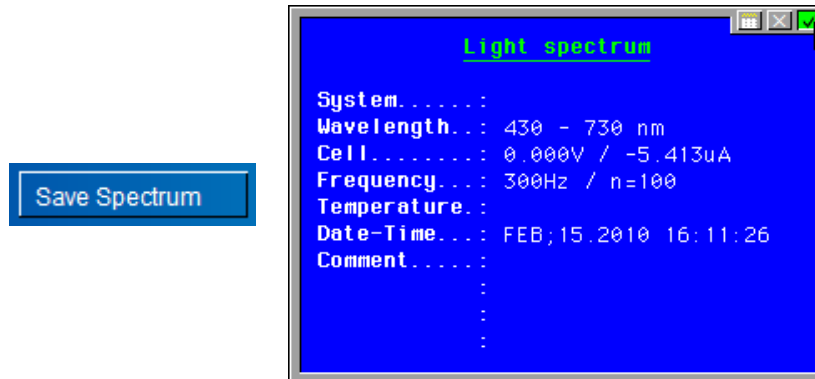

Fig. 30 Button for saving spectra and dialog box for input of additional information

Please note, spectra are always saved in 1 nm-steps by means of cubic spline interpolation between the samples. If you require the raw measurement data, start the Zahner Online Display using the pulldown menu before recording the measurement. The Online Display will save an ASCII file containing the raw data in a preset folder. Its filename consists of the date and time, the measurement was started, e.g. 2012-10-15 10-43-25.txt. For further information refer to the Online Display manual.
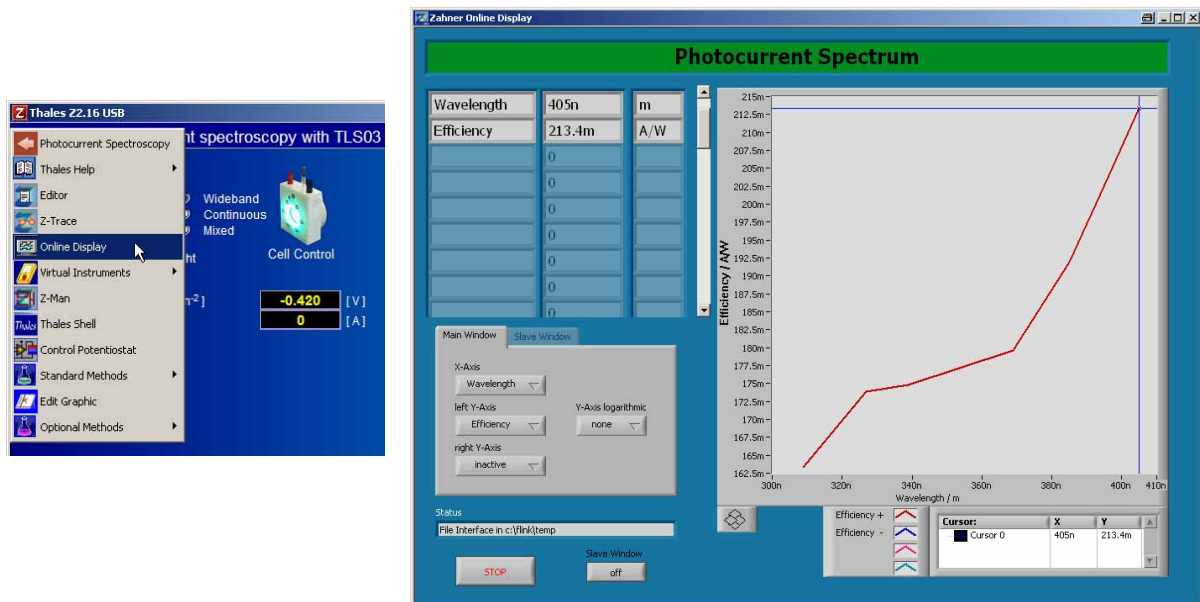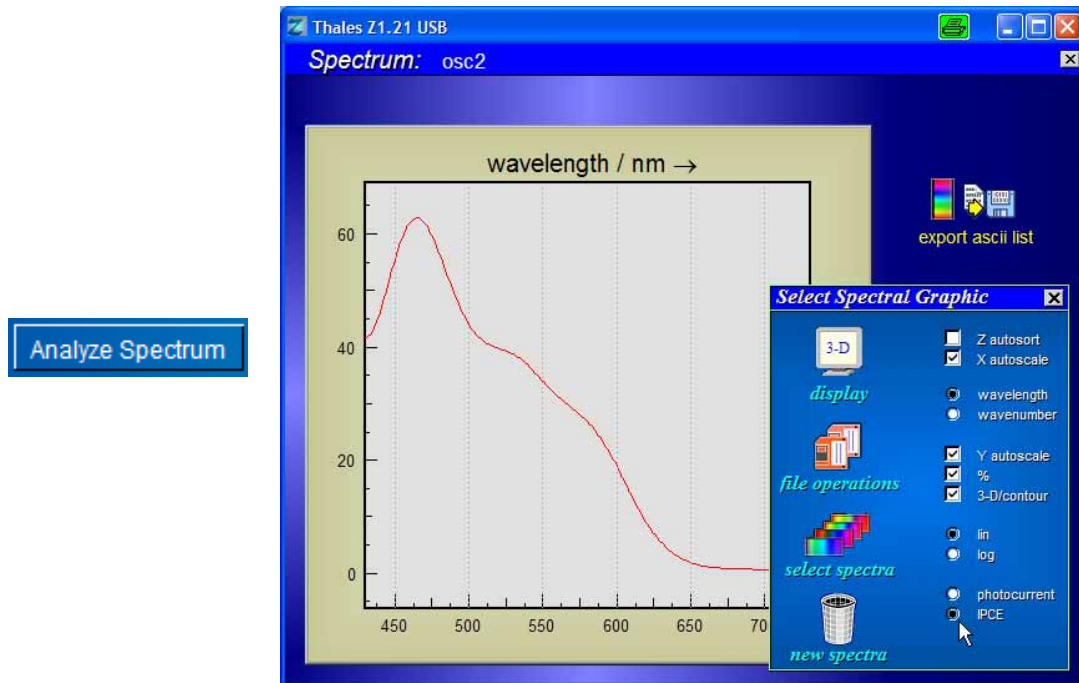

Fig. 31 Recording raw measurement data using the Online Display

3.7. Spectra Analysis

The stored spectra can be analyzed in the environment of the "light spectra analysis" program through the "Analyze Spectrum" button (Fig. 32).

Fig. 32 Analysis of saved spectra

You may enter the "light spectra analysis" program also via the pull down menu. Photocurrent spectra are detected automatically and displayed in natural units of $A/(W/m^2/nm)$ or IPCE %. Please recognize that, if you mix them with emission or absorption spectra, the program switches to the default units of $W/m^2/nm$.

4. Trouble shooting

4.1. CIMPS Actuator

Neterror: Can't connect local to remote system (127.0.0.1).
CIMPS Actuator error: Thales not running.

The TCP/IP-support used for communication between Thales and the CIMPS Actuator Net VI is disabled. Open the configuration file of Thales (default: c:\Flink\usb.ini) and locate the entry DEVICESUP=off. Change it to DEVICESUP=on and save the configuration file. Close the Thales window and reopen it in order to activate the new setting.

CIMPS Actuator error: Stepper interface not found.
CIMPS Actuator error: Stepper Interface is not responding.

Check whether the CIMPS actuator controller is connected to an USB port and switched on. Both LEDs of the actuator controller have to be on. If both LEDs are on but the controller is still not found switch it off and after ten seconds on again. This can help fixing communication problems.

CIMPS Actuator error: End switch not reached. Slider blocked/disconnected?

During initialization the slider is moved to both end switches. If they are not reached in the maximal necessary number of steps this error results. In most of the cases the actuator is simply disconnected from the controller. If not, check whether the slider is blocked, e.g. by a PECC touching the input optics of the spectrometer.

CIMPS Actuator error message box: Application could not be started because FTD2XX.dll was not found.
The CIMPS Actuator NET VI freezes showing the message "Initializing…" .

An USB-serial-converter has installed and old version of the FTDI USB driver used by the CIMPS actuator. The old version of the driver has to be removed and the new version supplied by Zahner (C:\Flink\CIMPSActuator\drivers) has to be installed. USB-serial-converters remain functional with the new version. Perform the following steps to remove the old drivers and install the new ones:
1. Unplug all USB-serial-converters and other devices using FTDI USB chips including the Zahner CIMPS Actuator.
2. Call C:\Flink\CIMPSActuator\Uninstaller\CDMUninstallerGUI.exe
3. Check, whether the Vendor ID 0403 and the Product ID 6001 are entered in the input boxes and click the button Add (see Fig. 33 left hand side). VID and PID are added to the devices pending uninstallation. Do not enter different Vendor and Product IDs here as this may remove drivers needed for running Windows properly.
4. With VID_0403 PID_6001 in the large input box click the Remove Devices (see Fig. 33 right hand side) button. Now the old drivers are uninstalled. After a short moment a dialog box "Device removed from system" informs about the completed uninstallation.
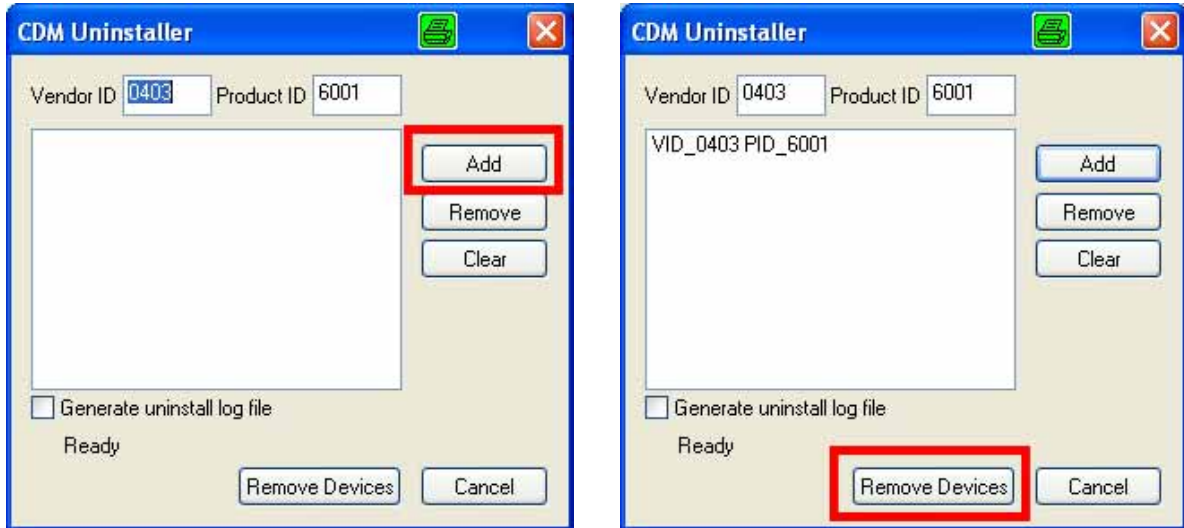5. Now the new USB-drivers supplied by Zahner can be installed according to chapter 2.2.1.

Fig. 33 Uninstallation of FTDI Drivers