

CIMPS-PCS

Photocurrent spectroscopy

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1 Introduction

CIMPS-PCS is designed for measuring Incident Photon to Current Efficiency (IPCE) of photoelectrodes, or organic or dye-sensitized solar cells. For the IPCE measurements, Zahner provides dedicated tunable light sources (TLS) with LEDs covering the following wavelength ranges:

TLS-03: 365 nm to 1020 nm

TLS-03 UV: 290 nm to 1020 nm

In analogy to controlled IMPS, CIMPS-PCS is capable of modulating the LED light intensity, allowing for IPCE measurements without having to use a mechanical chopper. Avoiding the noise-prone Lock-In-technique, the advantages of the coherent frequency analysis technique can be utilized (further explanation can be found in the application note [CIMPS-IPCE](#)).

The CIMPS-PCS is delivered as a fully calibrated plug & play setup. The measured spectral data can be analyzed either with the onboard software package "light spectra analysis" or by the Zahner Analysis software. The measured files can be opened by the preview support of the Windows® file explorer and exported in numerous output formats such as high-quality vector graphics, bitmap and/or ASCII data list.

During the IPCE measurements, the photocurrent efficiency (dimension: A/W) and IPCE (%) are automatically calculated by Thales from the measured data and stored together with the measurement. Both spectra can be easily viewed in the Zahner Analysis software or "light spectra analysis" software.

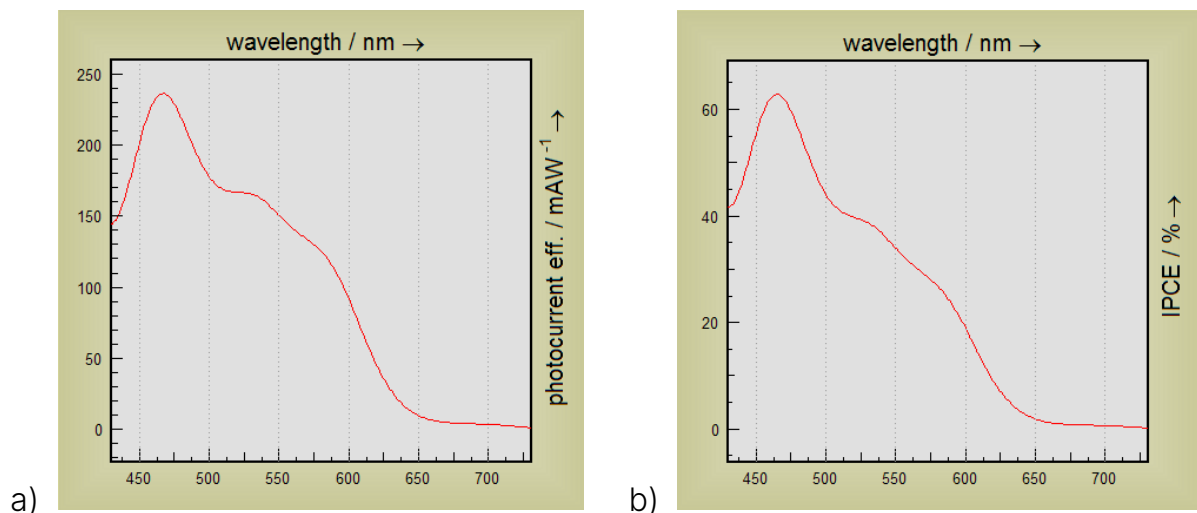


Fig. 1: (a) Photocurrent efficiency and (b) IPCE of an organic solar cell built up from Cr-Al-Cr-P3HT-PCBM-PEDOT-Cr-Au.

1.1 IPCE calculation

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

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

IPCE at a wavelength (λ) is defined as the ratio of the number of photo-generated charge carriers $n(\lambda)$ (electrons or holes), to the number of incident photons $n_{ph}(\lambda)$.

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

The number of photo-generated charge carriers $n(\lambda)$ can be easily calculated from the photocurrent $I(\lambda)$ and time t using the elementary charge q_e .

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

The number of photons $n_{ph}(\lambda)$ is given by the irradiance P , 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 :

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

Using these expressions, the IPCE at a wavelength (λ) can be calculated by the following formula.

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

$IPCE(\lambda)$ is a unit-less quantity.

2 Hardware

The tunable light source (TLS03) of CIMPS-PCS is a fully integrated unit containing an LED array, a monochromator and all electronic circuits required for running the TLS03. As a light feedback sensor is installed inside the TLS03 light source unit, no external sensor is required (in contrast to other CIMPS setups). The feedback sensor ensures the illumination with the correct light intensity. The feedback from the sensor is also used to reduce the drifting and aging effect of LEDs. Further information can be found in application note [C in CIMPS](#).

Connect the TLS03 to the PP211/PP212 using the **probe E - probe I** cable set delivered together with CIMPS-PCS. Keep the PP211/PP212 switched off while connecting the TLS03 and secure the connectors by fastening the screws. Loosely connecting probe E and probe I ports at the back of the TLS03 light source may damage the TLS03. The TLS03 is powered by an external 12 V DC power supply as shown in Fig. 2. The integrated monochromator is powered and controlled by the PC/laptop, running Thales via USB.

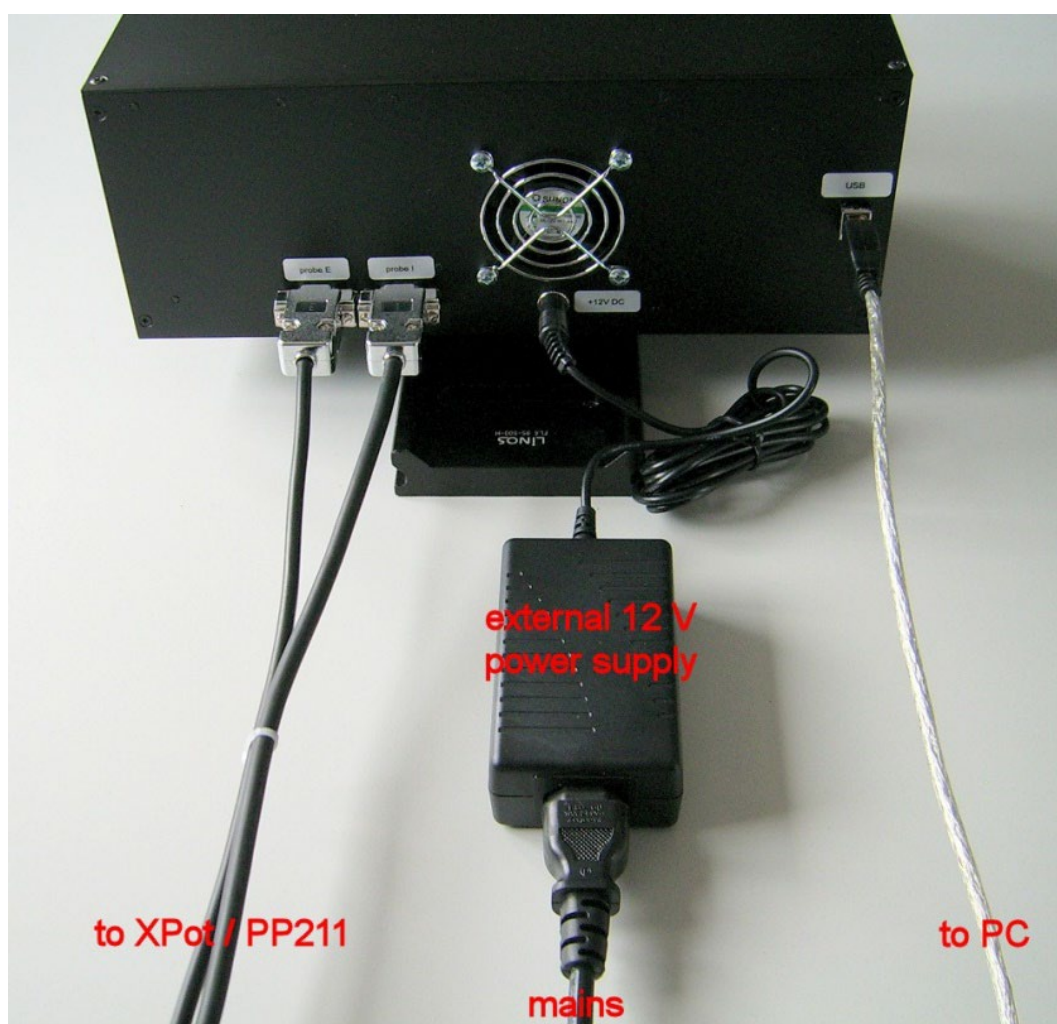


Fig. 2: Cable connections to the TLS03 light source. Properly fasten the screws of the probe I and probe E connectors to avoid unintentional unplugging.

The distance between the end of the light guide (glass rod) of the TLS03 and the solar cell (or front/back side of the photoelectrochemical cell or the surface of any

test object) should be ~1 mm for optimal light cross-sectional homogeneity and calibration accuracy (see Fig. 3). With 1 mm distance between the light guide and the solar cell, the area of the hexagon light beam is 1 cm². Increasing the distance between the end of the glass rod and the front glass may increase the illumination area, however, it will result in a reduced cross-sectional homogeneity of the light beam and should not be overdone.



Fig. 3: Correct positioning of the solar cell relative to the TLS03. The optimal distance between the light guide of TLS and the solar cell is ~1 mm.

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

Using a Faraday cage is recommended when working in the current ranges of milli-ampere (mA) or below, to avoid electromagnetic disturbance from the surrounding. A Faraday cage must be grounded to the back panel of the ZENNIUM series potentiostat. Further information can be found in the manual [Getting started and installation](#).

The solar cell (or test object) will be connected to the BNC connectors of the ZENNIUM series potentiostat for measuring the photocurrent.

3 Software

The CIMPS-PCS software is started by using the pull-down menu as shown in Fig. 4. In order to open the pull-down menu, click on the Z-icon in the title bar of the Thales window.

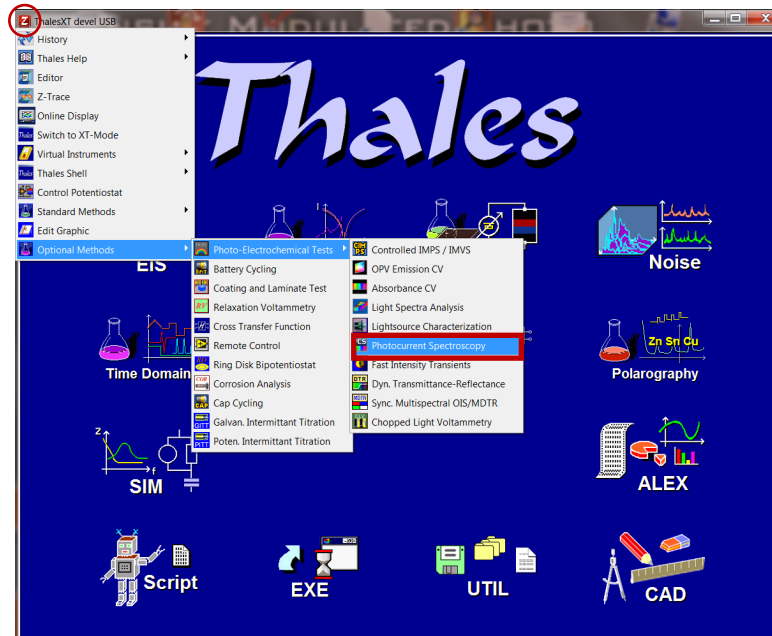


Fig. 4: Starting the routine for the CIMPS-photocurrent spectroscopy software for IPCE measurements.

Clicking on **Photocurrent Spectroscopy** starts the “CIMPS-pcs” software (Fig. 5) and TLS interface window (Fig. 6).



Fig. 5: CIMPS: photocurrent spectroscopy software window.

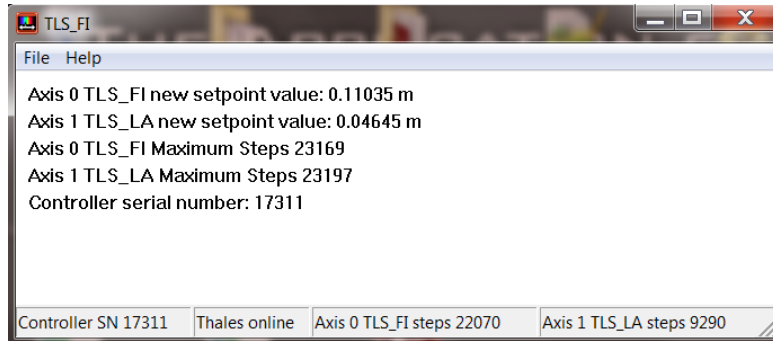


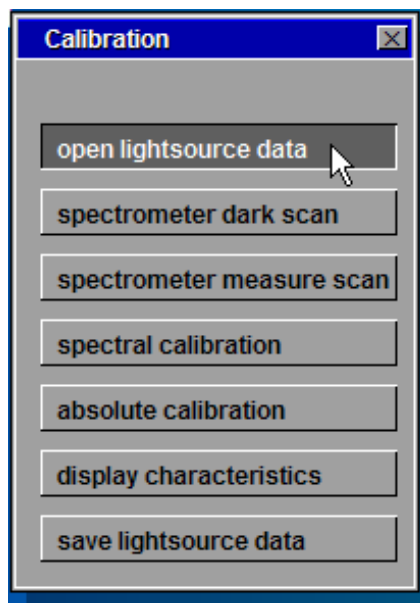
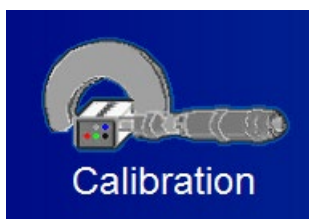
Fig. 6: TLS interface (do not close this window while using the TLS).

3.1 Calibration file

Fig. 5 shows the main software interface for the IPCE measurement. By starting the PCS software, Thales will automatically detect the attached TLS03 and will indicate the serial number of the attached TLS03 at the top of the screen (see example below).

CIMPS-pcs: lightsource 1029tls03

Here the attached TLS03 (serial number 1029) is shown. If the TLS03 is not detected automatically, the user can open the correct calibration file manually by clicking on the **calibration** icon and then clicking on **open lightsource data** in the submenu.



The user can find the correct calibration file in the C:\THALES\cimps folder. The file name follows the format XXXXtls03.is_, with XXXX indicating the serial number of the connected TLS03.

The TLS03 may also be used with Zahner’s photoelectrochemical (PECC) cell. Generally, the TLS03 is only calibrated for the front side (electrode side) illumination of the PECC, however upon request, an additional PECC back side (electrolyte side) calibration can be done for the TLS03. With this calibration, the user can illuminate the PECC from the back side of the cell.

For the PECC backside illumination, the correct calibration file must be selected from the C:\THALES\cimps folder prior to starting the IPCE measurement.

3.2 Setting up the light source

For selecting an LED from the TLS03, click on the flashlight icon (**access lightsource control**) and then click on **select source**. This will open a table where the wavelength, full width at half maximum (FWHM), as well as the maximum power of each LED are listed.

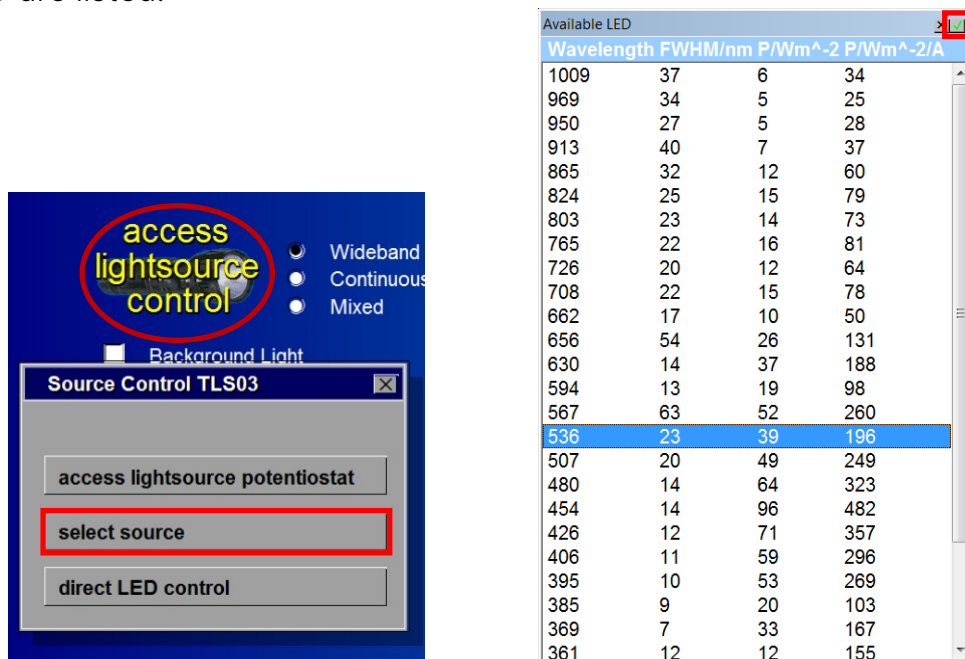
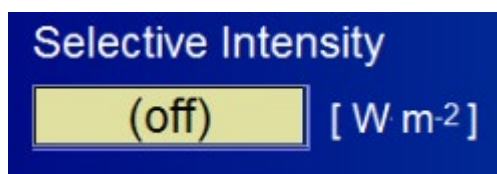


Fig. 7: Table showing the individual LEDs in the TLS03 with their respective wavelengths, FWHM, and maximum power output.

To select an LED, click on the respective LED and click on the green tick (Fig. 7). To turn on the selected LED, click on **Selective Intensity** and type in an intensity between 0% and 100%.



Here, 0% means LED off and when a value above 0% (say 50%) is provided then the selected LED will turn on at a power of 50% in relation to the power listed in Fig. 7 for the selected LED.

Once an LED is selected, the user can also exit the PCS software and carry out routines such as the IMPS/IMVS or chopped light voltammetry (CLV), using the TLS03.

The TLS03 in CIMPS-PCS is strictly operated in **galvanostatic mode** (see Fig. 8) while, in contrast, the TLS03 is operated in **potentiostatic mode** for IMPS, IMVS, and CLV measurements. When using the TLS for IMPS/IMVS or CLV measurements,

1. Select the LED in the CIMPS-PCS software (according Fig. 7).
2. Exit the CIMPS-PCS software without turning on the LED of the TLS03.
3. Start the desired IMPS/IMVS or CLV software.
4. Set the intensity in the software to turn on the TLS03 LED.
5. Perform the measurement.
6. Set intensity back to zero to turn off the LED before closing the software.

By this procedure, the TLS will be operated in the **potentiostatic mode**.

Clicking on **access lightsource potentiostat** in Fig. 7 opens the control potentiostat window (Fig. 8) of the TLS. When an LED is turned on, this window displays how much bias current is required for running the LED at the specified intensity. Here, the user can furthermore define the **FREQUENCY**, at which the LED's light will be modulated for the IPCE measurement, and the **COUNT**. The COUNT defines the number of repetitions for a single IPCE measurement. The default configuration comprises a FREQUENCY of 77 Hz and a COUNT value of 100.

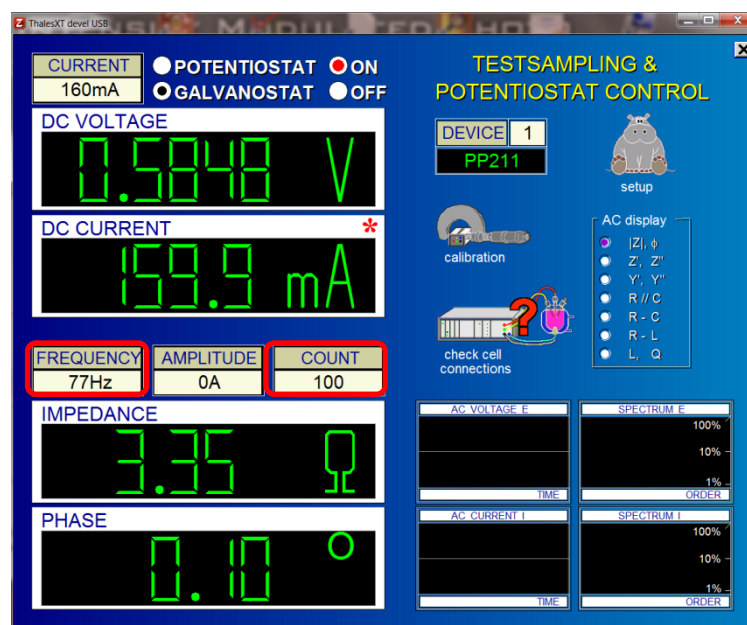


Fig. 8: The control potentiostat window for the TLS, displaying the current/voltage supplied by the PP211/PP212 (DEVICE = 1) for the TLS during operation.

It is not recommended to use very high frequencies for the IPCE measurement, to always ensure a sufficiently high AC response dominated by the real impedance part (impedance with a phase shift of zero). Finding a suitable frequency range is crucial for the IPCE measurements and depends on the material under investigation. Further information can be found in the application note [CIMPS-IPCE](#). For silicon or III-V solar cells, frequencies up to 1 kHz or higher are acceptable for IPCE measurements. For oxides or organic solar cells (OSC), typical frequencies range up to 1 kHz. A recommended standard value is 300 Hz, because it usually ensures the dominance of real part impedance, while it is fast enough to allow for a high number of counts for averaging. Considering a recommended period count of 100 cycles, the typical measurement time for a single wavelength IPCE data point is about 1 s. Dye-sensitized solar cells (DSSC), in particular, based on TiO_2 , are significantly slower than OSC, therefore, modulation frequencies of ten Hz or even less may be appropriate. Please bear in mind that time constants of electron transport in DSSC are dependent on the light intensity. Consider using the background light in order to shorten the time constants of a DSSC (see section 3.5).

In Fig. 8, setting up an AC amplitude for the light modulation is not required as it is chosen automatically by the Thales software for the IPCE measurement. After setting the desired modulation FREQUENCY and COUNT, press **Esc** or close the control potentiostat window to get back to the main CIMPS-PCS window.

3.3 Cell control

After setting up a suitable modulation frequency for the TLS03 light source, a suitable voltage must be applied to the test object (i.e., solar cell) for the IPCE measurements. This voltage range is usually set close to the point of maximum photocurrent. Normally, the IPCE is measured in reverse bias conditions. To apply a voltage to the test object, click on Cell Control.

This will open a similar window as that of Fig. 8. Click on VOLTAGE to enter the desired voltage and then turn on the potentiostat in potentiostatic mode (see Fig. 9).



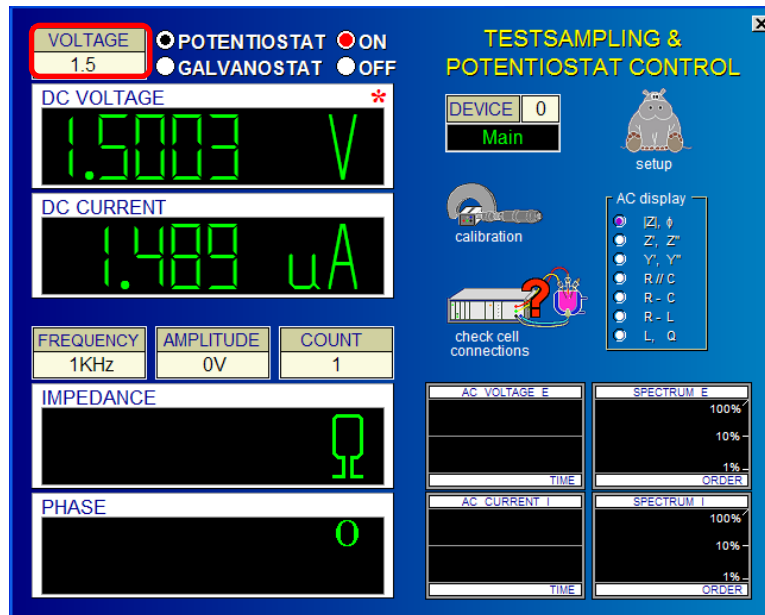
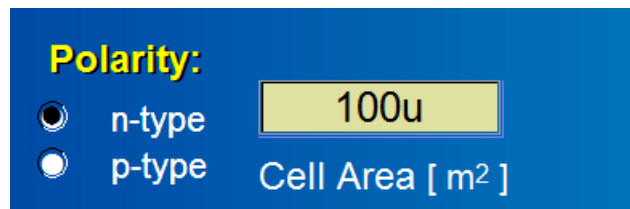


Fig. 9: Control potentiostat window for the test object (solar cell or photoelectrode). DEVICE 0 indicates that the main ZENNIUM series potentiostat is selected.

After turning on the main potentiostat, press **Esc** or close the control potentiostat window to get back to the main CIMPS-PCS window.

3.4 Solar cell or photoelectrode

For the IPCE measurements, the cell area must be known. In CIMPS-PCS, the cell area is provided in square meter (m²) unit. The provided area value must be accurate, otherwise the calculated IPCE value and photocurrent efficiency will be wrong.



Here, n-type/p-type refers to the doping type of the test object i.e., photoelectrode and the correct doping type must be chosen.

For solar cells, use the polarity (n-type/p-type) where the phase shift in IPCE measurement is closer to 0°. If the phase shift is in the range of ±90 degrees to ±180 degrees, change the polarity and restart the IPCE measurement.

3.5 Background light

Besides the LED array, the TLS03 contains a background white light. This background light is useful for the test objects when the light intensity threshold for the onset of photocurrent is high or have longer time constants of electron transport (e.g., for DSSC). As different LEDs in the TLS03 have different maximum light output intensities (see Fig. 7), using the background light helps decreasing the

time constant of electron transport during the IPCE measurements with the LEDs having low output intensities. This allows for fast IPCE measurements with low settling time. As the background light source provides a constant light illumination, the effect of induced photocurrent (DC current) by background light can be removed easily after the IPCE measurement.

Frequency modulation of the background light is not possible.

The intensity of background light can be adjusted between 0 – 100 %.

During IPCE measurements over a wavelength range, when the TLS03 switches from one LED to another, the illumination light intensity on the test object may decrease during the switching process. This drastic decrease in light intensity can induce the state of non-equilibrium in the test object. With the background light turned on, the drastic change in illumination light intensity can be avoided during the LED switching process, preventing non-equilibrium conditions in the test object.

3.6 IPCE measurement mode

In CIMPS-PCS, 3 IPCE measurement modes are available.

- 1) Wideband mode
- 2) Continuous mode
- 3) Mixed mode



In wideband mode, the LEDs listed in Fig. 7 are used for the IPCE measurement. The maximum wavelength range in the wideband mode depends on the TLS03 type (with or without UV extension). Resolution and spectral half width of the LEDs are given by the discrete wavelengths of the LEDs and vary between 10 nm and 60 nm (typical).

In continuous mode, a monochromator is used in the visible light range (410 nm – 720 nm) besides the LEDs. The monochromator allows for a fine tuning of the wavelength leading to a minimum resolution of 1 nm with a typical half width of 15 nm.

Mixed mode is a combination of both wideband mode and continuous mode. Here, in the UV range ($\lambda < 410$ nm) and the IR range ($\lambda > 720$ nm), the wideband mode is used whereas in the visible light range (410 nm – 720 nm) the continuous mode is applied. The resolution in the continuous mode is defined by the user, however, due to the numerical procedure of combining the two parts of the spectrum, a wavelength resolution of about 10-20 nm is recommended.

After choosing the desired IPCE measurement mode, the wavelength range and the resolution (for continuous and mixed mode) can be defined in the IPCE **Scan Data** section.

Scan Data		
Default	566	[nm]
Range	280 - 1020	[nm]
Resolution	-	[nm]
Settling	1	[s]

Here, the **Settling** time defines the time difference between the light illumination and the start of the IPCE measurement.

The allowed values range between 1 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. Therefore, the total recording time may be significantly longer than the sum of all settling times.

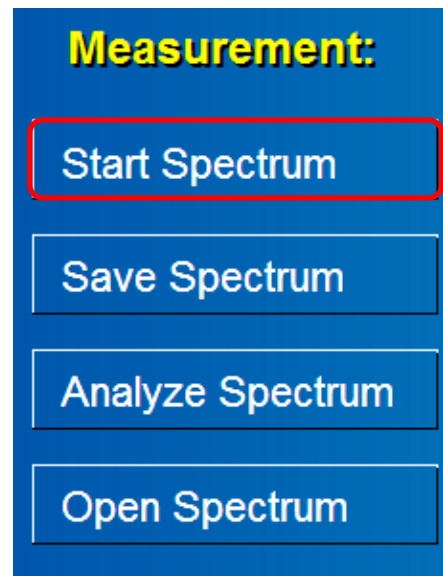
4 IPCE measurement

Once the hardware and software (IPCE parameters) are set up, the IPCE measurement can be started by clicking on **Start Spectrum**.

After the IPCE measurement is completed, the measured spectrum can be saved using **Save Spectrum**.

Analyze Spectrum opens the Spectral Analysis software. Further discussion on Spectral Analysis software is provided in section 5.

Open Spectrum loads the already saved IPCE spectrum in the CIMPS-PCS window. It also modifies the current IPCE measurement parameters of the CIMPS-PCS software.



The IPCE measurement is always carried out at 100% LED light intensity

The TLS03 uses a modulation frequency similar to IMPS to carry out the IPCE measurement. To understand the IPCE measurement process and the effects of different variables (background light intensity, light modulation frequency and applied bias voltage to the solar cell etc.) on the IPCE values, please refer to our application note [CIMPS-IPCE](#).

An image of the IPCE measurement is shown in Fig. 10.:

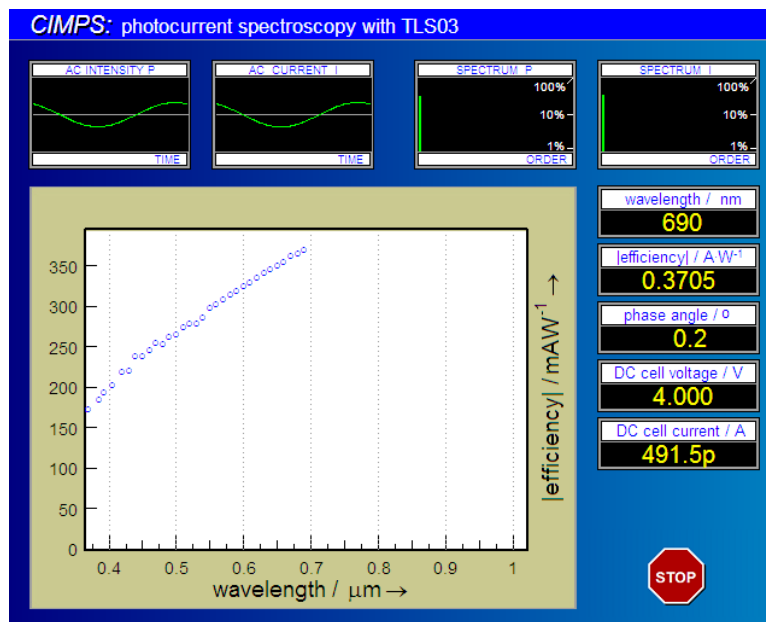
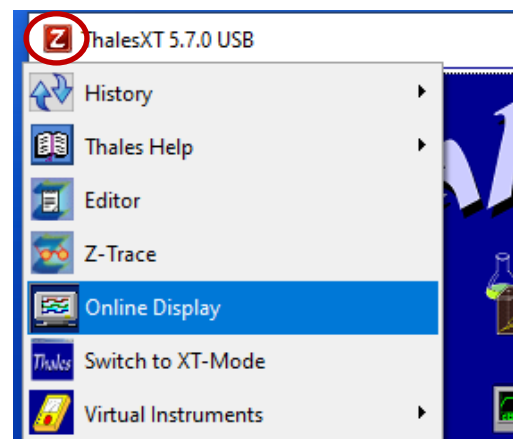


Fig. 10: IPCE measurement (mixed mode): The photocurrent efficiency is shown online during the measurement.

A running measurement can be stopped prematurely using the *STOP* button. After the measurement is finished, Thales automatically returns to the PCS main screen.¹

IPCE spectra are always saved in 1 nm-steps by means of cubic spline interpolation between the IPCE measurement points. If the raw measurement data (text file) is required, it can be retrieved from the C:\THALES\temp folder. The filename of the saved raw IPCE data file consists of the date and time when the measurement was started, e.g. 2012-10-15 10-43-25.txt.

The text file will only be saved if the online display is started before starting the IPCE measurement. In the standard settings, the online display is always active while using the Thales software. If the online display window is closed, the user can open the online display window again by click on the Z-icon on top of the Thales software and then on “Online Display”.



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 will stay in the measurement screen until the Continue button is clicked.

5 Spectral Analysis

The stored spectra can be analyzed in the environment of the “light spectra analysis” program through the “Analyze Spectrum” button.

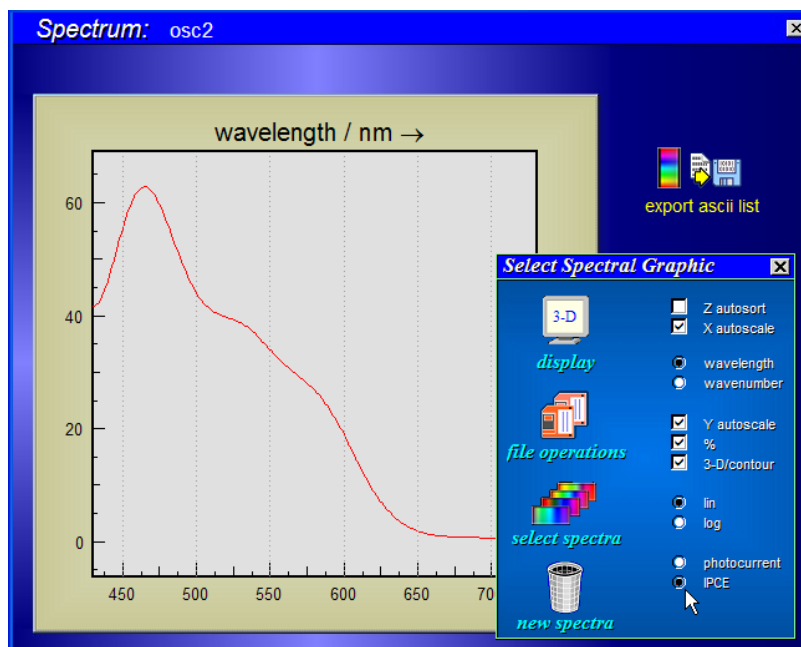


Fig. 11: Spectral Analysis window.

The measured photocurrent spectrum is detected automatically and is 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 $W/m^2/nm$.

The user may enter the “light spectra analysis” program also via the pull-down menu.

