

# CIMPS

## Controlled Intensity Modulated Photo Spectroscopy

The screenshot displays the CIMPS software interface with the following sections:

- Source Control:** Includes an icon of a light source and a control for "Actual Average Intensity" set to "(off)" [W m<sup>-2</sup>].
- Cell Control:** Includes an icon of a cell and displays a voltage of "-1.712" [V] and a current of "0" [A]. It also features a "Polarity:" section with radio buttons for "n-type" and "p-type".
- Calibration:** Includes an icon of a calibration tool and a "Normalized Intensity / Volt" section with a value of "1" [W V<sup>-1</sup>m<sup>-2</sup>] and a wavelength range of "472, 25" [nm, Δnm].
- Charge Extraction:** Contains three buttons: "Setup Q-extraction", "Start Q-extraction", and "Last Q-extraction".
- Time Domain Measurement:** Contains three buttons: "Setup Time Domain", "Start Time Domain", and "Show Time Domain", along with three checked checkboxes: "Cell On Phase", "Cell Off Phase", and "Light Transients".
- Transfer Function:** Includes a "Sweep & EIS setup" window icon and radio buttons for "photocurrent" and "photovoltage".
- Measurement:** Contains three buttons: "Start Static TF", "Start Dynam. TF", and "Start Max. P & FF".
- Display:** Contains three buttons: "Last Static TF", "Last Dynam. TF", and "Last Max. P & FF".



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# 1. General

The ZAHNER CIMPS measurement system has been designed with focus on the special demands of dynamic photo-electric investigations like IMPS and IMVS, popular today for instance in alternative solar cell research. Besides all traditional electrochemical investigations supported by THALES - like impedance measurements, cyclic voltammetry, current-potential curves, etc. – now mixed photo electric transfer functions, known as Intensity Modulated Photo Spectra (IMPS / IMVS), can be measured. Also the steady-state type transfer functions DC-current and DC-voltage vs. intensity are implemented. Recently the CIMPS software features were expanded to support the standard solar cell investigations like maximum power, efficiency and fill factor as well and with the new time-domain measurement feature TDT, the pulse-, step- and transient behaviour of photos-sensitive objects can be studied also.

An Electrochemical Workstation ECW (IM6/IM6ex or Zennium) main module is used for the standard investigations. The photo-sensitive object (PSO) must be connected to the ECW's main potentiostat. The impedance transfer function  $Z^*$  (Eq. 1) will be obtained in the usual way by means of potentiostatic or galvanostatic controlled dynamic investigations:

$$Z^* = \frac{U^*}{I^*} \quad \begin{array}{l} Z^* = \text{impedance of the photosensitive cell } [\Omega] \\ U^* = \text{electric respective electrochemical potential of the cell } [V] \\ I^* = \text{electric current through the cell } [A] \end{array} \quad \text{Impedance Eq. 1}$$

For IMPS / IMVS applications an additional slave potentiostat (XPOT, PP2XX family) drives the light source and controls the illumination of the PSO. The slave potentiostat is controlled by the ECW through a special interface card (EPC4x) and connected to the card input #1. Main and slave device are addressed individually from the 'Control Potentiostat' panel in the usual way, described in detail in chapter 4 'Control Potentiostat' of the [EIS manual](#). However, it is recommended to use the special entries 'Access lightsource potentiostat' and 'Access cell potentiostat' of the CIMPS control panel described later.

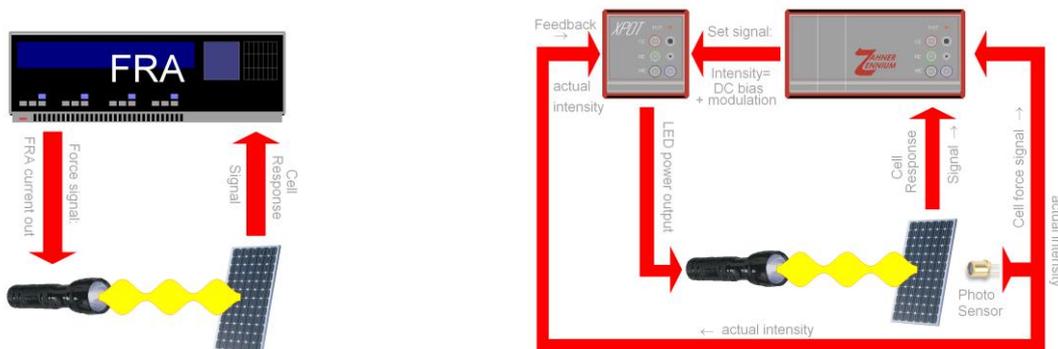


Fig. 1. Traditional arrangement for IMPS (left hand side) and the schematic of the CIMPS principle, applied on a solar cell as PSO (right hand side). In the case of CIMPS, a photo-diode detector feedback loop forces the light intensity at the site of the cell to follow exactly the sum of the DC- and AC-intensity set values.

The application of the photo-electrical transfer functions IMPS and IMVS are well known in literature since several years as 'Intensity Modulated Photo Spectroscopy IMPS' (refer for instance to the end of this chapter). With its first complete measurement system for photo-electrical transfer functions on the market CIMPS 'Controlled Intensity Modulated Photo Spectroscopy', ZAHNER introduced several decisive improvements. Traditionally IMPS (Fig. 1 left) determines the transfer function of a PSO by correlating the system response with the stimulation force set signal (usually derived from the LED supply current). In contrast to that, CIMPS (Fig. 1 right) correlates the system response with the actually stimulation intensity signal  $P_{act}$  (in the following called P) measured by means of a photo-

sensor at the site of the PSO. Besides this,  $P_{act}$  is stabilised by means of a potentiostatic feedback loop. Therefore CIMPS evaluates the transfer function with much higher precision. The shortcomings of the intensity control and modulation, like time drift, non-linearity and frequency dispersion, are automatically cancelled (see also the more detailed working scheme regarding the feedback principle in Fig. 2).

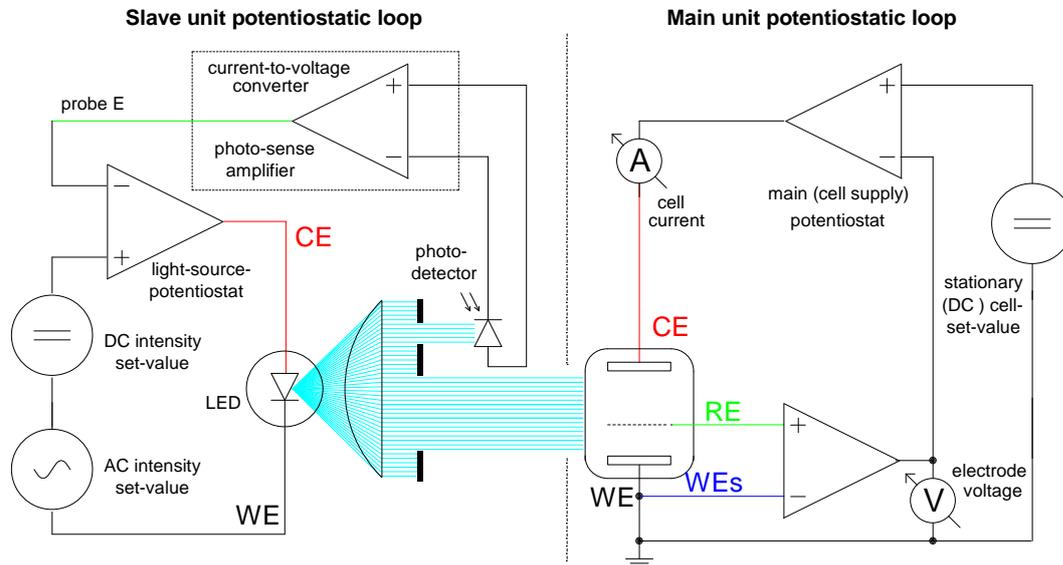


Fig. 2. Schematic of the CIMPS principle, applied on an PSO in an electrochemical cell. The photo-diode detector / sense amplifier feedback loop forces the light intensity to follow exactly the sum of the DC- and AC-intensity set values.

When investigating photo-electrochemical systems by CIMPS, the instantaneous value of the light intensity  $P$  is used to determine the transfer function. The carrier support for the illuminator units (LDA) has an integrated Photo-Sense-Amplifier which delivers an intensity-proportional voltage output. It is usually connected to the external photo-diode sensor via a BNC connector.

The light source can then be enclosed within the potentiostatic loop of the slave potentiostat. Its feedback loop will compensate fluctuations and drifts of the light source itself and enables a linear, sinusoidal modulation and the long term intensity stability necessary for longer measurement time. The voltage measuring channel of the slave will then provide the signal, proportional to the stimulating light intensity  $P$ , within the dynamic signal routing system of the ECW Frequency Response Analyser (FRA). The information on the actual  $P$  as well as the set-value  $P_{set}$  of  $P$  is then accessible through the actually measured voltage respectively the set-voltage of the slave potentiostat. Measured voltage and set-voltage are exactly proportional to a certain intensity. The proportionality factor  $FP$  (Eq. 2) is supplied for every light source delivered by Zahner as part of an individual calibration data set, which is valid for a well defined geometric arrangement described later. It is recommended to open the corresponding calibration file. From then on, the exact intensity value can be set and read out from the 'set / actual intensity' input field of the CIMPS control panel. Please consider, that within the 'Control Potentiostat' panel of the slave, the control of  $P$  is still expressed in units of Volt [V], but from the CIMPS control panel, and within in the measurement graphs and in the automatic protocols it is indicated as power/area [ $Wm^{-2}$ ].

If the stationary photo intensity  $P$  must be modulated by superposition of an AC signal of some mV for IMPS / IMVS measurements, the selected AC amplitude should be typically in the range of 5% to 50% of the stationary DC value.

The proportionality factor  $FP$  (Eq. 2) between set / measured voltage from the LDA PHOTO AMP and the light intensity at the site of the cell depends on the individual arrangement. If the arrangement differs from the calibration state, it can be determined by comparison of the actual intensity with the corresponding set voltage of the slave. If an absolute scale calibration is still desired for the evaluated data, the value of  $FP$  in [ $W \cdot m^{-2} \cdot V^{-1}$ ] should be changed accordingly (Fig. 15). The  $FP$  can also be determined automatically by the calibration-function of the CIMPS control panel described later.

$$P = UP \cdot FP \quad [FP] = 1 \cdot \frac{W}{V \cdot m^2} \quad \begin{array}{l} UP = \text{light proportional electric potential [V]} \\ P = \text{specific light intensity [W/m}^2\text{]} \end{array} \quad \text{Eq. 2}$$

Using the standard settings, the internal transfer function  $ZLD^*$  (Eq. 3), 'photo source efficiency frequency response' of the light emitting system can be measured optionally. This function is unnecessary when using the ZAHNER LDA, but it is recommended to check  $ZLD^*$ , if an alternate light source or detection system is used.

$$ZLD^* = \frac{UP^*}{ILD^*} \quad [ZLD^*] = 1 \cdot \frac{W}{A \cdot m^2} \quad \begin{array}{l} UP^* = \text{light proportional electric potential [V]} \\ ILD^* = \text{current of the light source [A]} \end{array} \quad \begin{array}{l} \text{Photo source} \\ \text{efficiency frequency} \\ \text{response} \end{array} \quad \text{Eq. 3}$$

The main aim of CIMPS, the measurement of the cross transfer functions for IMPS and IMVS,

$$H_{IP}^* = \frac{I^*}{P^*} \quad [H_{IP}^*] = 1 \cdot \frac{A \cdot m^2}{W} \quad \text{Photo-current efficiency frequency response } \mathbf{IMPS} \quad \text{Eq. 4}$$

and

$$H_{UP}^* = \frac{U^*}{P^*} \quad [H_{UP}^*] = 1 \cdot \frac{V \cdot m^2}{W} \quad \text{Photo-voltage efficiency frequency response } \mathbf{IMVS} \quad \text{Eq. 5}$$

have both been realized by CIMPS as a software extension of the THALES EIS program. Within the standard EIS configuration, the internal routing of the ECW's FRA acquires both channels, necessary for a transfer function determination, together from just one selected source – for instance both current as well as voltage from the main potentiostat for the cell under test. The script software adds the possibility to mix the transfer function components from different sources: In the case of CIMPS, where the slave potentiostat is responsible for the light source supply, one channel of the frequency response analyser is connected to the intensity-proportional voltage from the slave (the output of the LDA PHOTO AMP), while the other signal can be chosen from the main potentiostat (cell current  $I$  in the case of IMPS, Eq. 4, and cell voltage  $U$  in the case of IMVS, Eq. 5 respectively).

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 photo-electrical effect will decrease the open-circuit potential 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  $\pm 180$  degrees. This leads to an inconvenient phase angle scaling in the Bode diagram and an uncommon shape of the complex-plane plot, which contradicts the intuition, thinking in 'impedance' categories. The software therefore offers the possibility to change the sign meaning of  $P$ , what is equivalent to putting in the type of the majority charge carriers. This can avoid the inconvenient phase relationship (Fig. 11).

## 1.1 General IMPS / IMVS Application Hints

Light induced processes like photosynthesis are of fundamental significance in the world. In technique, the "photo-electric effect" occurring at illuminated interfaces like semiconductor junction barriers is of great importance. Here, the electric voltage and the current flowing at the interface site are depending on the illumination. Light intensity with photo-voltage on the one hand and with photo-current on the other hand is building two typical force-response couples for a dynamic transfer function analysis similar to EIS. Like the analysis of the impedance transfer function in the EIS, the **I**ntensity **M**odulated **P**hoto **S**pectroscopy can help understanding the complex systems, in particular when photo-electric effects are playing a significant role.

Alternative solar cell concepts are favorite research objects for IMPS / IMVS. A general aspect in solar cells is, besides the considerations of charge carrier generation efficiency from light, how to get the

charge from the site of origin to the collecting electrodes. In monolithic SC fields one can treat this mainly in terms of the inner series and shunt resistance where the first one should be low and the second one should be high to achieve optimum efficiency. In alternative SC the role of the time turns up: here charge carrier diffusion speed is slow enough to be in the order of magnitude of the charge carrier lifetime. Therefore the expression  $1 - \tau_{diff} / \tau_{life}$  is a good measure for the “dynamic efficiency”, what means the balance between charge carrier diffusion time constant  $\tau_{diff}$  and charge carrier recombination time constant  $\tau_{life}$ : the shorter the diffusion time the more charge can reach the collecting electrodes within the lifetime limited by recombination.

The determination of these time constants is a typical task for the AC techniques IMPS & IMVS.

Following the literature [1-4], electron diffusion time constant  $\tau_{diff}$  is the limiting magnitude for the photocurrent flow, if the charge migration is not hindered by an electrical field. Therefore it is claimed, that  $\tau_{diff}$  dominates the IMPS spectrum as characteristic time constant in the case, that the SC is polarized to short circuit condition.

Complementary, under open circuit conditions no charge can vanish through the electrodes. Instead, every photo charge has to recombine. Therefore it is claimed, that  $\tau_{life}$  dominates the IMVS spectrum as characteristic time constant in the case, that the SC is in open circuit condition.

IMPS & IMVS can be parameterized individually and triggered manually by the user. Besides, for a fast standard test procedure one can use the automatic  $\tau_{diff} / \tau_{life}$  evaluation feature described in [chapter 4.1.1](#).

However, the model concept behind such a procedure does not take into account the real physical reasons for the limited charge carrier migration speed and also ignores the influence of other contributions to the overall network transfer function like the impedance of the counter electrode. Bay and West [5] proposed therefore an alternative DSSC model, which directly takes into account the porous structure of the photo anode material. It can be used as a network component in the simulation & fitting program SIM, which is able to model and fit photoelectric transfer functions in the same manner as impedance spectra.

1. P.E. Jongh, D. Vanmaekelbergh, *J. Phys. Chem.* **B 101** (1997) 2716-2722
2. L. Dloczik, O. Ileperuma, I. Lauermann, L.M. Peter, E.A. Ponomarev, G. Redmond, N.J. Shaw, I. Uhlendorf, *J. Phys. Chem.* **B 101** (1997) 10281-10289
3. G. Schlichthoerl, N.G. Park, A.J. Frank, *J. Phys. Chem.* **B 104** (2000) 2044-2052
4. R. Kern, R. Sastrawan, J. Ferber, R. Stangl, J. Luther, *Electrochim. Acta* **47** (2002) 4213-4255
5. L. Bay, K. West, *Solar Energy Materials & Solar Cells*, **87** 613-628 (2005).

## 2. Hardware set-up

### 2.1 Connecting the slave potentiostat to the ECW

#### 2.1.1 XPOT

Use the thick black cable with an 8-pole Lemosa plug at one end and a 9-pole D-Sub male plug at the other end. Connect the D-Sub9 plug to the upper female D-Sub9 socket 'EPC' at the back plane of the XPOT. Finally connect the LEMOSA plug to input #1 of the ECW EPC4X plug in card. The device address of the XPOT will then be 1 (Fig. 3).



Fig. 3. The XPOT to mainframe connection.

#### 2.1.2 PP2XX

Use the thick black cable with an 8-pole Lemosa plugs at one end and a 9-pole D-Sub male plug at the other end. Connect the D-Sub9 plug to the upper female D-Sub9 socket 'EPC' at the back plane of the PP2XX. Finally connect the LEMOSA plug to input #1 of the ECW EPC4X plug in card. The device address of the PP will then be 1 (Fig. 4).

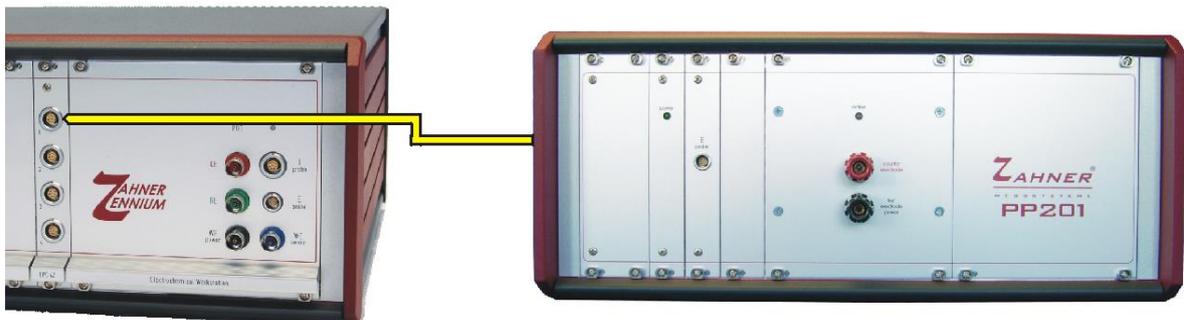


Fig. 4. The PP2XX to mainframe connection.

## 2.2 Connecting the light source carrier LDA to the slave

The light source will be connected to the current outputs 'counter electrode' and 'working electrode' of the slave potentiostat. The ZAHNER LDA has a ready made cable set provided for that purpose, together with the connection cable from the photo-sense amplifier output of the LDA to the voltage input 'probe E' of the slave. Be sure not to mix the plug assignments (Fig. 5 to Fig. 7). No damage, but a malfunction of the set-up will occur in this case.

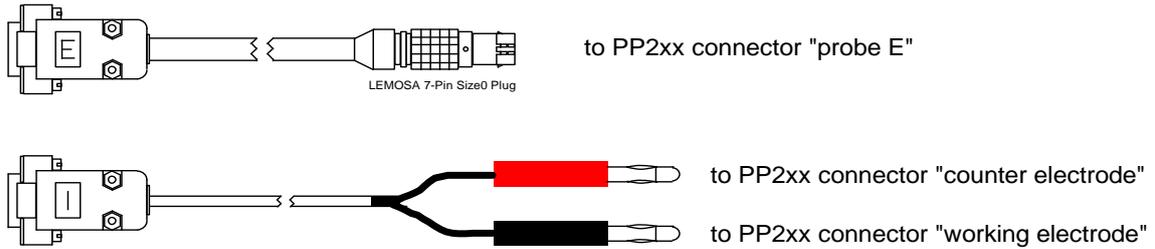


Fig. 5. Connection cables between ZAHNER-LDA and PP2xx.

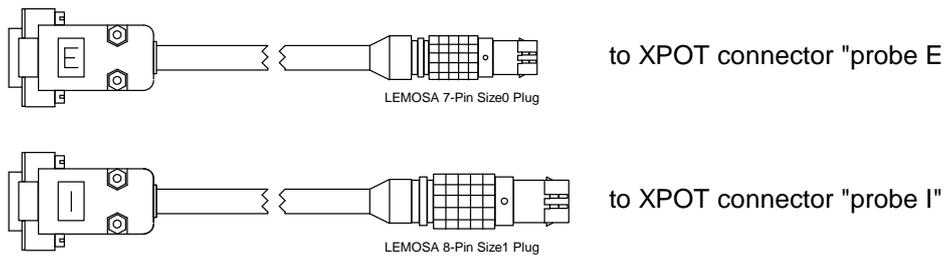


Fig. 6. Connection cables between ZAHNER-LDA and XPOT.

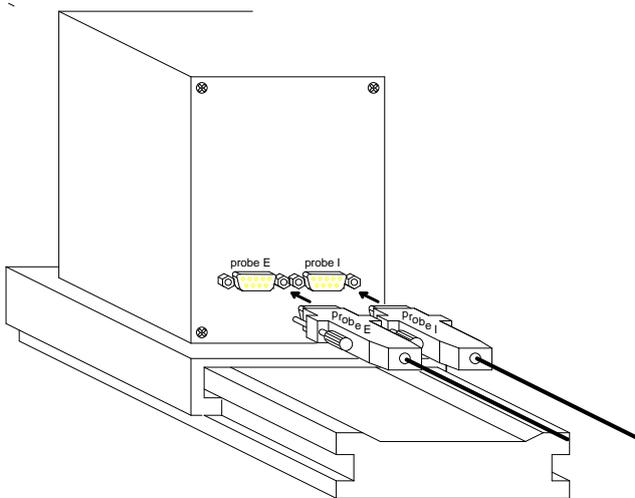


Fig. 7. Application of the probe E and probe I cables to the Light Source Carrier connectors.

## 2.3 Change of light sources

LED light sources can be exchanged very easily by plugging them into the LDA. Align the light source so the label with the type and serial number is on top. In this position the alignment pin of the light source matches the notch in the front plate of the LDA as shown in Fig. 8. Push the light source firmly into the LDA so there is no gap between the front plate of the LDA and the ring of the light source (see Fig. 8). In order to remove a LED light source pull it out using the knurled-head screws.

When changing the light source ensure to load the corresponding calibration file in the Thales software. Light sources of the 02-series are detected by software and Thales opens the calibration file automatically. Using light sources of the 01-series and BUVZ02, the calibration file has to be opened manually.

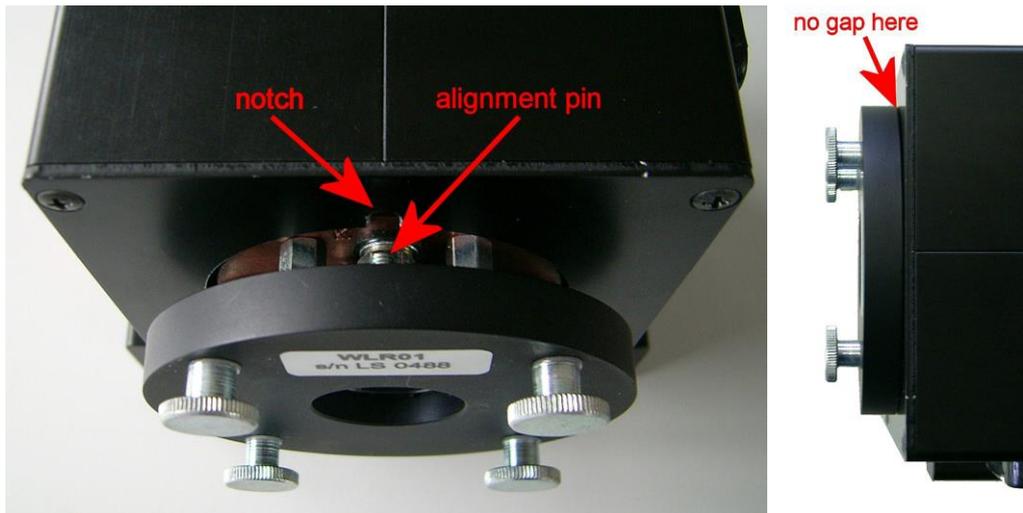


Fig. 8. Changing light sources.

## 2.4 Mechanical and geometrical adjustment of the light source / cell set-up

The exact intensity calibration can only be maintained by reproducing the same mechanical and geometrical properties during the measurement which were valid during calibration. In the following (Fig. 9) these adjustments are described. The sensor assembly comes preadjusted, normally only the distance between light source and sample holder has to be adjusted.

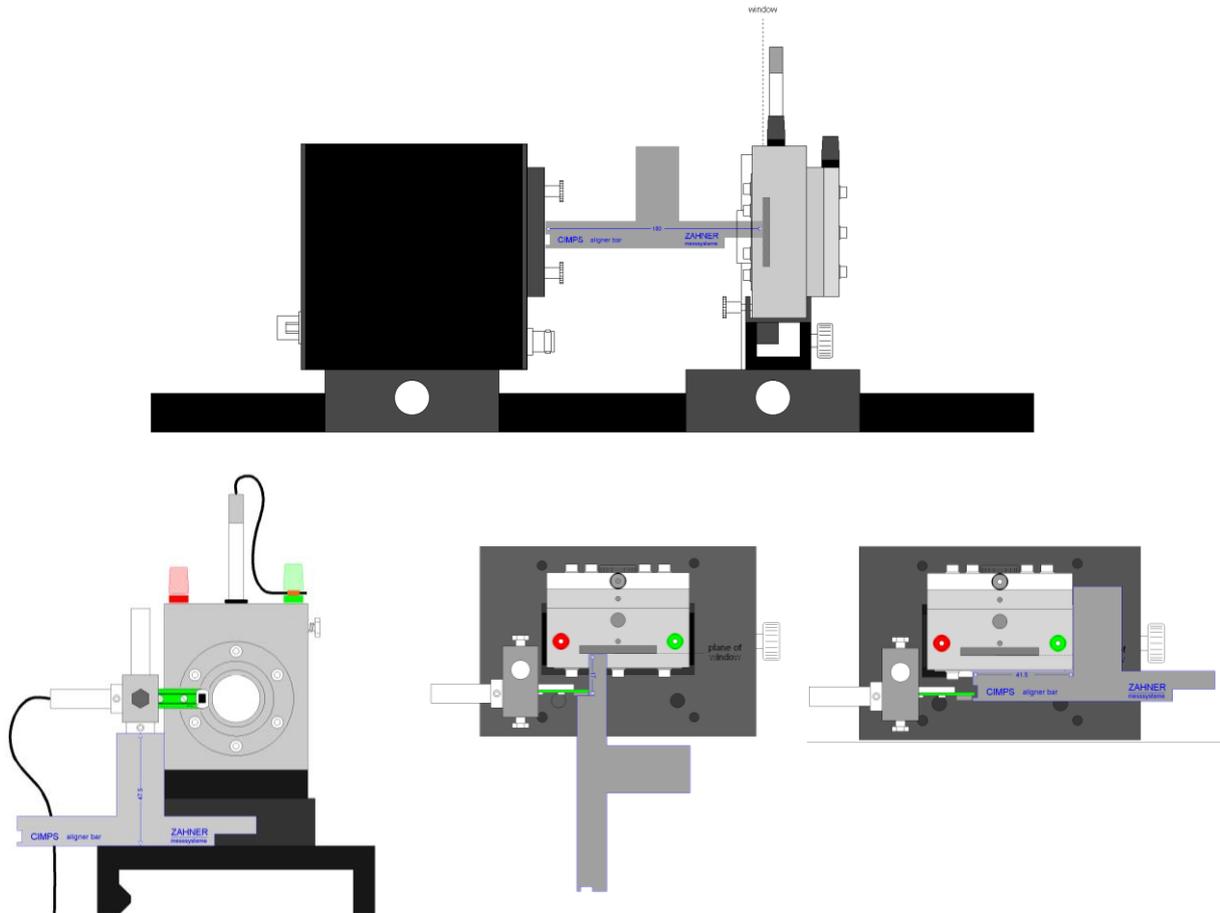


Fig. 9. Correct adjustment of the LDA illuminator box, the PECC and the photo sensor using the Zahner aligner bar.

The nominal distance between front ring of the light source and the reference plane, i.e. the sample position is 100 mm (see upper part of Fig. 9). Using the PECC this is the position of the front glass. The distance between the front side of the feedback sensor and the front ring of the light source is 83 mm i.e. 17 mm in front of the sample (see lower middle of Fig. 9).. The height of the feedback sensor above the base plate is given by the lower side of the retainer ring of 47.5 mm (see lower left of Fig. 9). Perpendicular to the light beam the edge of the sensor is 41.5 mm from the edge of the PECC (see lower right of Fig. 9). If no PECC is available, the corresponding distance from the plate holder is 44 mm.

In case CIMPS was delivered together with CIMPS-pcs the photo sensor and PECC holder of CIMPS-pcs are used for both set-ups. Refer to the [CIMPS-pcs](#) manual for the correct adjustment of the photo sensor in this case.

In case CIMPS was delivered together with CIMPS-abs an additional sensor is included in the CIMPS-abs set-up. The sensor position for standard CIMPS is according to Fig. 9, for the correct sensor position of CIMPS-abs refer to the [CIMPS-abs](#) manual.

## 3 CIMPS Software

### 3.1 Starting the CIMPS Application

#### 3.1.1 Software call

It is recommended to start the CIMPS software by means of the pull-down menu. Touch the  Z-icon on the task bar of the Thales window with the mouse to open the pull-down menu (Fig. 10) and navigate → Optional Methods → Photo-Electrochemical Tests → Controlled IMPS / IMVS.



Fig. 10. Access to Thales application software, which is not present as individual icon on the Thales desktop.

The CIMPS is based on a SCRIPT program and therefore in principle open for user-modifications. Instead of using the pull-down menu for opening the pre-compiled runtime-version, the experienced users may alternatively open the SCRIPT source located on the PC hard drive in the folder

**'c:\thales\script\cimps'**

load the CIMPS source file from the HD, link it and run it. To do that, proceed as follows:

1. Start Thales and navigate to the **SCRIPT** panel
2. Navigate to **Edit Script -> File Operations -> Open**
3. Navigate to the folder **c:\thales\script\cimps**
4. Load the file **cimps.is\_**
5. Return to the SCRIPT panel (CLOSE, middle mouse button or ESC)
6. Click on **Link Script**

Loading and linking may take a few seconds. After linking the CIMPS functions are available on the SCRIPT panel. If you have left CIMPS intermediately, you may navigate to the **SCRIPT** panel for re-entry in this start-up configuration.

The start-up-procedures will end up in the display of the CIMPS main control panel Fig. 11.

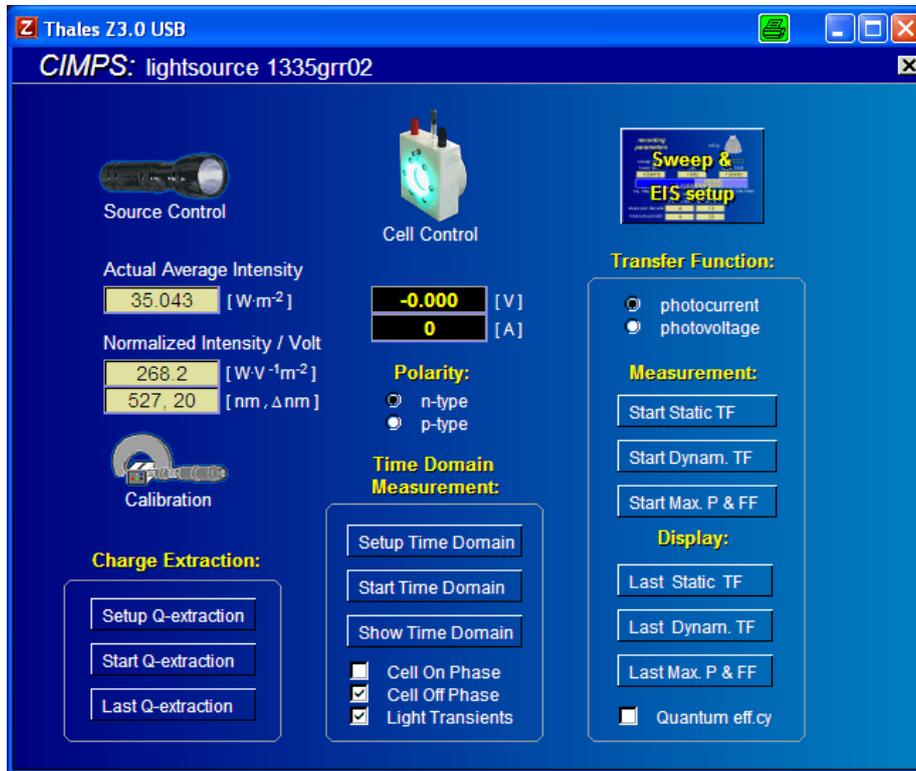


Fig. 11. CIMPS main control panel.

### 3.1.2 Light source calibration files

In order to support quantitative measurements, it is necessary to inform the software about the specific properties of the light source actually in use.

Zahner light sources are shipped together with a detailed description of their properties in form of a calibration file. These files are stored in the folder '**c:\thales\cimps**' after finishing the installation of the calibration data CD. Thales detects light sources of the 02-series and loads the corresponding calibration file automatically. Using light sources of the 01-series or the BUVZ02 the calibration file has to be loaded manually as shown in Fig. 12 after cold start and after every change of the light source. The calibration file names are built systematically from the series number, which provides the leading characters, and the ordering code of the items, for instance, 0028wll01.is\_ means the calibration file of the item series# 28, which is a white light emitter.

Each calibration file is valid for a distinct combination of a light source and a sensor. In case several sensors are delivered they are labelled with consecutive numbers, e.g. S01, S02, S03. Here the number of the sensor is appended to the file name of the corresponding calibration file. For example the calibration file for the WLL01 with serial number 28 in combination with sensor S02 is named 0028wll01-s02.is\_. Ensure to open the correct calibration file for your set-up. When in doubt which sensor is used for a specific set-up refer to the file **c:\thales\cimps\sensors.txt**. In case only one sensor (S01) is delivered, one single calibration file for each light source exists and the number of the sensor is omitted in the file name.

The automatic detection of 02-series light sources cannot distinguish between different sensors but automatically opens the calibration file with the shortest file name. In case this does not coincide with the actual optical setup the correct calibration file has to be opened manually.

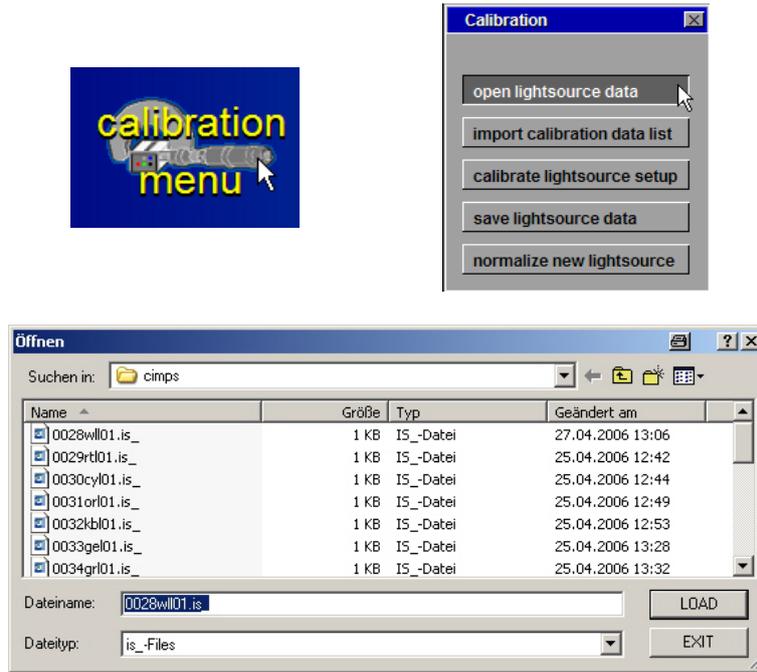


Fig. 12. Opening an individual light source characteristic data file through the calibration menu.

Together with the calibration variables, the calibration file contains a table of the spectral data (Fig. 13). You may copy the list into any spread sheet software to visualize the individual spectrum. Besides this, a graph of the spectrum is present in the same folder in form of a Windows® Enhanced Meta File, (for instance '0028wll01.emf' for the source of the example above) which may be imported directly into programs like Word® or CorelDraw® (Fig. 14).

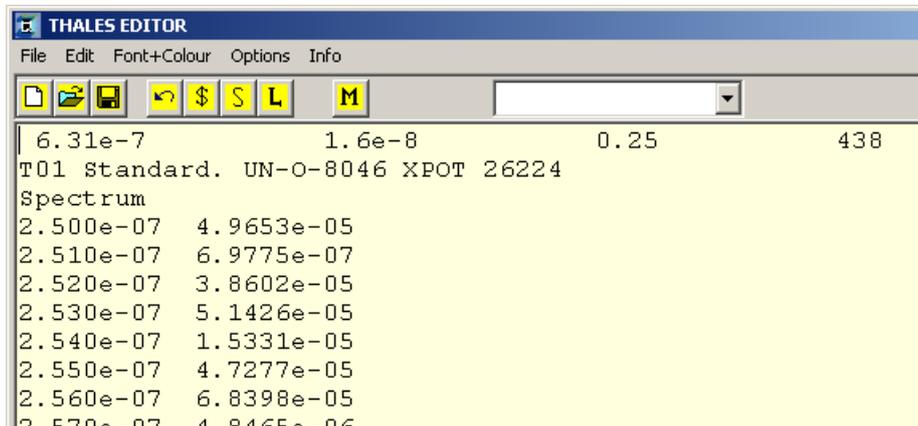


Fig. 13. The table starting after the keyword 'Spectrum' in the calibration data file contains the spectral data of the individual light source.

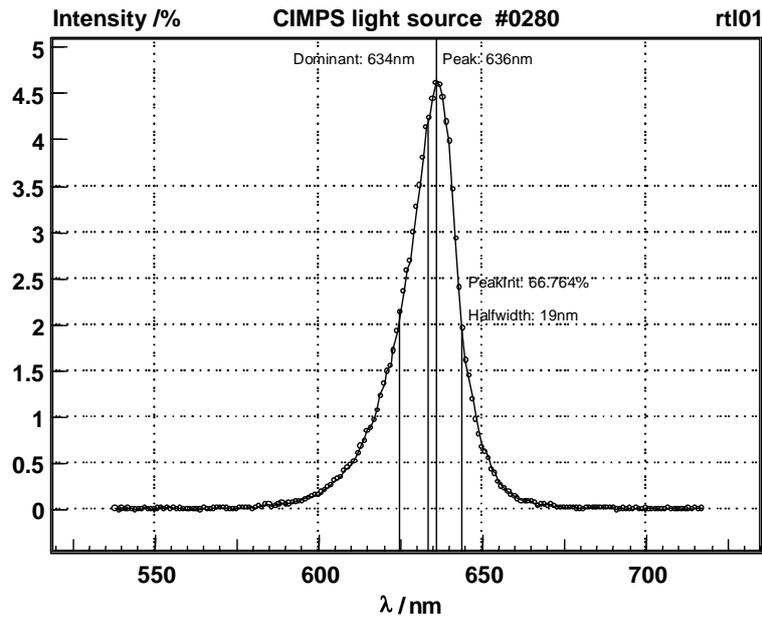


Fig. 14. The relevant part of the spectrum of an individual light source is present in form of a file.emf as graphics in the folder 'c:\thales\cimps' for the calibration data.

In the case of an unknown light source or a modified geometry light source calibration can be modified manually by opening the 'Normalized Intensity / Volt' input field (Fig. 15).



Fig. 15. Opening and editing the 'Normalized Intensity / Volt' input field.

The user may put in here the proportionality factor FP as 'Normalized intensity' (Eq. 2), which defines, 'how much Watts/m<sup>2</sup>' belong to 1 Volt of sensed output voltage of the LDA's photo-sense amplifier. Besides this, the user should protocol the dominant wave length and bandwidth of the illuminator for automatic documentation, and the additional characteristics, which enable the software to protect the light source against overload.

## 4 CIMPS Measurement Set-Up

### 4.1 Dynamic Measurements EIS, IMPS and IMVS

In the CIMPS control panel the left hand side is reserved for the control of the light source. Use the button 'Source control' (Fig. 16 left) to enter immediately the potentiostat control menu of the light source potentiostat only to adjust AC modulation.

The middle part of the CIMPS main menu is reserved for the control of the cell under test. Use the button 'Cell control' (Fig. 16 middle) to enter immediately the control menu for potentiostat of the photo-electrochemical cell. Here you are free to adjust the cell state. This state must correspond with the selected transfer function TF method: use potentiostatic on mode for IMPS and photo-current measurement, use galvanostatic or off mode for IMVS and photo-voltage measurement.

The right hand part of the CIMPS main menu is provided for the setup, control, start and view of TF measurements. Use the button 'EIS & Sweep setup' to adjust the frequency sweep conditions for the dynamic measurements or to enter the standard EIS. Use this entry, if you want to measure the cell impedance (Eq. 1) or the photo-source efficiency (Eq. 4 & 5). It is also possible to enter the cell - as well as the lightsource control potentiostats here, but it is recommended to use the direct access to avoid mixing-up.

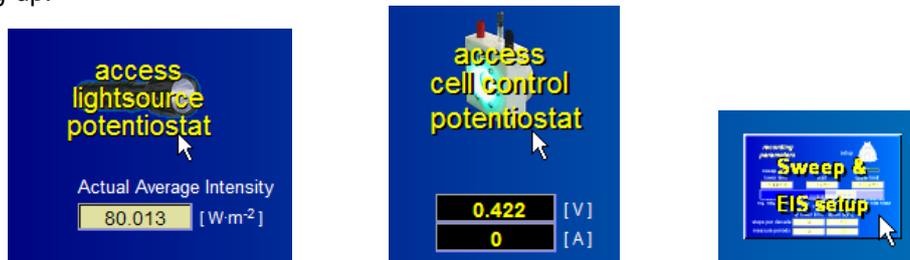


Fig. 16. Entry buttons for all CIMPS setup and potentiostat adjustments, impedance and photo-source efficiency measurements.

After pressing 'EIS & Sweep setup' the main menu of the EIS program appears (Fig. 17). Set up frequency ranges and resolution according to your measurement aims. Please consider, that forcing the instrument into frequency ranges, which cannot be covered successfully by the object's properties, may increase the risk of parasitic oscillations. Typical upper frequency limits are 100KHz for small monolithic silicon devices, 1 to 10KHz for IMPS and 100Hz to 1KHz for IMVS on organic or oxide-based solar cells. Generally, higher efficiency allows a higher upper frequency limit.

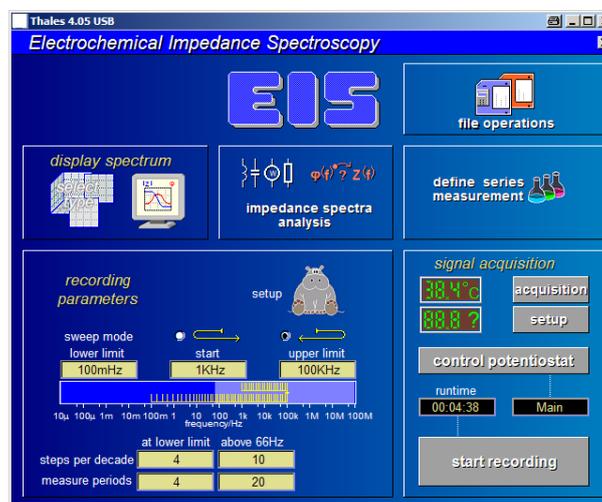


Fig. 17. EIS program main menu called by the CIMPS script button 'EIS & Sweep setup'.



Fig. 18. Potentiostat control panel of the cell when called by the CIMPS script button 'Control cell'.

In the 'Control potentiostat' panel (Fig. 18) for the cell you may use all adjustments usual for cell control.

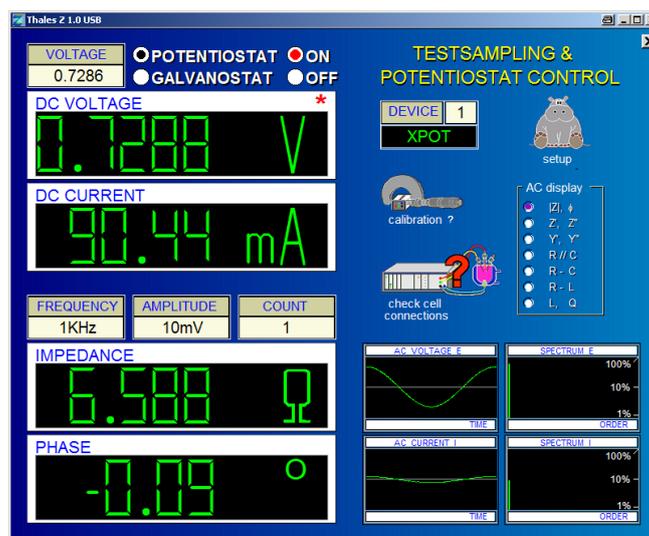


Fig. 19. Potentiostat control panel of the slave when called by the CIMPS script button 'Control source'. In the state displayed, AC measurement conditions are established.

If the slave potentiostat menu (Fig. 19) is entered by the 'Control source' button, it will come up identically to the appearance in the standard EIS program. Please recognise, that in spite of this, the meaning of the virtual instruments is different from the standard case. The displayed set / measured potentials refer to the voltage from the photo-sense amplifier proportional to light intensity.

It is strongly recommended to use the 'Control Potentiostat' panel only to adjust the light source to a defined AC modulation if desired, and use exclusively the entry 'Set intensity' of the CIMPS control panel to control the light intensity and the on/off-state of the light.

For the general handling details of the 'Control Potentiostat' panel please refer to chapter 4 of the [EIS manual](#).

Differing from the "control source" entry, the CIMPS panel provides a possibility to put in the DC set value for the intensity as natural units in  $[W m^{-2}]$  (Fig. 20).



Fig. 20. From the CIMPS panel, the set value for the intensity can be put in as natural units.

The standard measurements like the impedance of the PSO and the efficiency of the light source are accessible through the entry 'Sweep & EIS setup'. The main application of CIMPS is providing the dynamic photosensitive efficiency measurement of the studied object (Fig. 21 and Fig. 24).

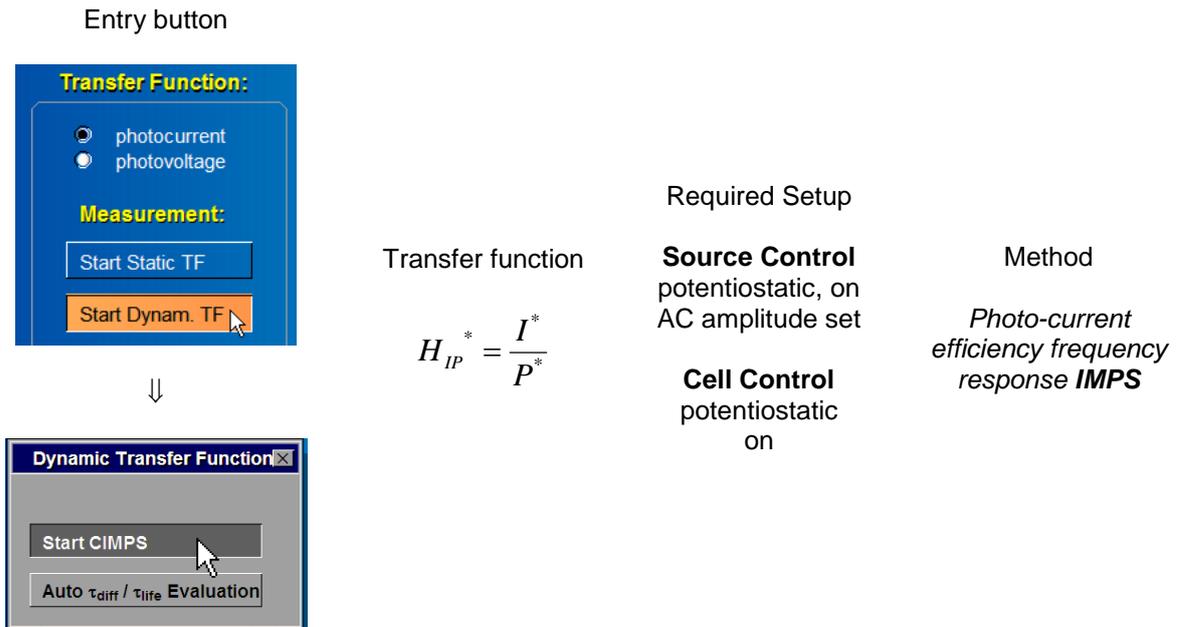


Fig. 21. Overview IMPS dynamic photo-current efficiency measurement.

The photo-current efficiency frequency response measurement IMPS can be initiated using the entry button while the appropriate state of the transfer function type switch is set (Fig. 21). A submenu appears where you can start the measurement manually using the button <Start CIMPS>. The function entered by means of the second button "Auto  $\tau_{diff}/\tau_{life}$  Evaluation" is described in the next chapter. The frequency response recording menu (Fig. 22) of the EIS program is entered and the measurement will be started immediately, if the adjustments of the main and slave potentiostat match the requirements for the IMPS-determination: be sure, that the electrochemical cell is set up to potentiostatic control, both main as well as illumination potentiostats are switched on, and the light source potentiostat is set to dynamic measurement (an AC amplitude is set). If the requirements are not fulfilled, message boxes will be displayed accordingly (Fig. 23).

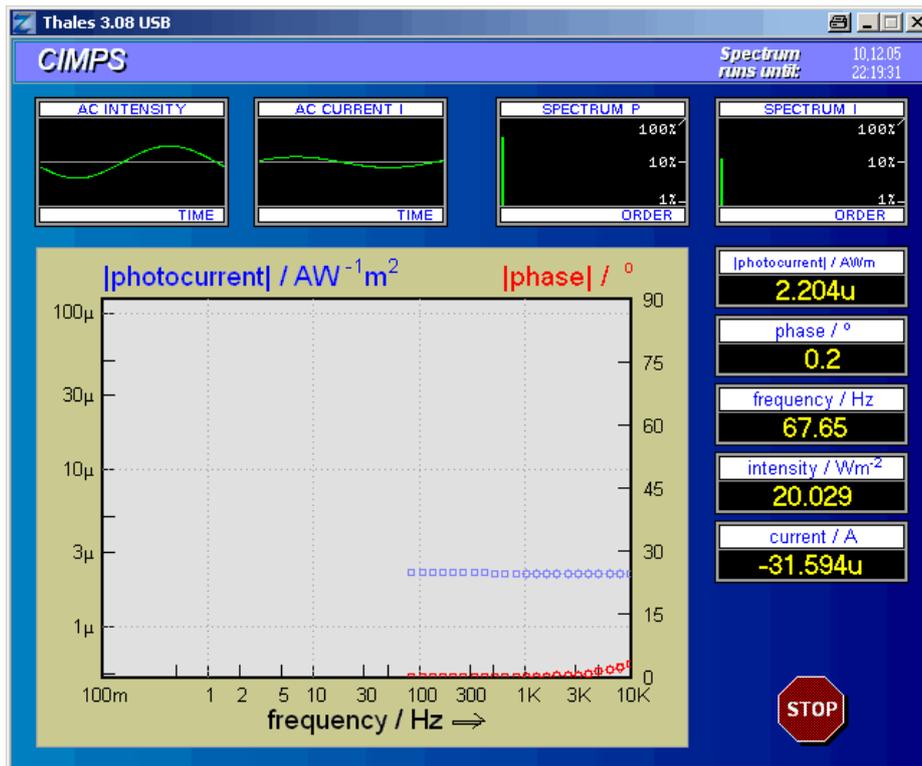


Fig. 22. The frequency response recording menu when entered through the 'Start dynam. TF' button and the TF-switch is set to 'photo-current' (IMPS).

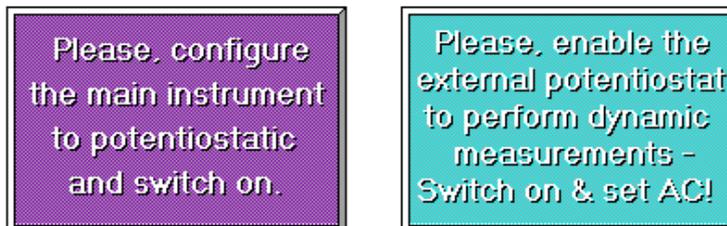
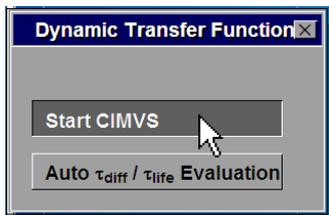
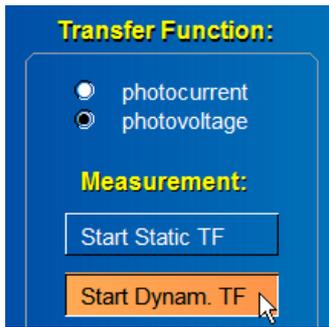


Fig. 23. This message boxes will be displayed, if the CIMPS script photo-current efficiency measurement is called, but the conditions do not match the IMPS-determination requirements.

The photo-voltage efficiency frequency response measurement IMVS can be initiated using the entry button when "photovoltage transfer function" is selected, A submenu appears where you can start the measurement manually using the button <Start CIMVS>. (Fig. 24). The function entered by means of the second button "Auto  $\tau_{diff}/\tau_{life}$  Evaluation" is described at the end of this chapter. The frequency response recording menu (Fig. 25) of the EIS program is entered and the measurement will be started immediately, if the adjustments of the main- and the slave potentiostat will match the requirements for the IMVS-determination: be sure, that the electrochemical cell is set up to galvanostatic control or switched off, the illumination potentiostat is switched on and set to dynamic measurement (an AC amplitude is set). If the requirements are not met, message boxes will be displayed accordingly (Fig. 26).

Entry button



Transfer function

$$H_{UP}^* = \frac{U^*}{P^*}$$

Required Setup

**Source Control**  
potentiostatic, on  
AC amplitude set

**Cell Control**  
galvanostatic on  
or off

Method

*Photo-voltage  
efficiency frequency  
response IMVS*

Fig. 24. Overview IMVS dynamic photo-voltage efficiency measurement.

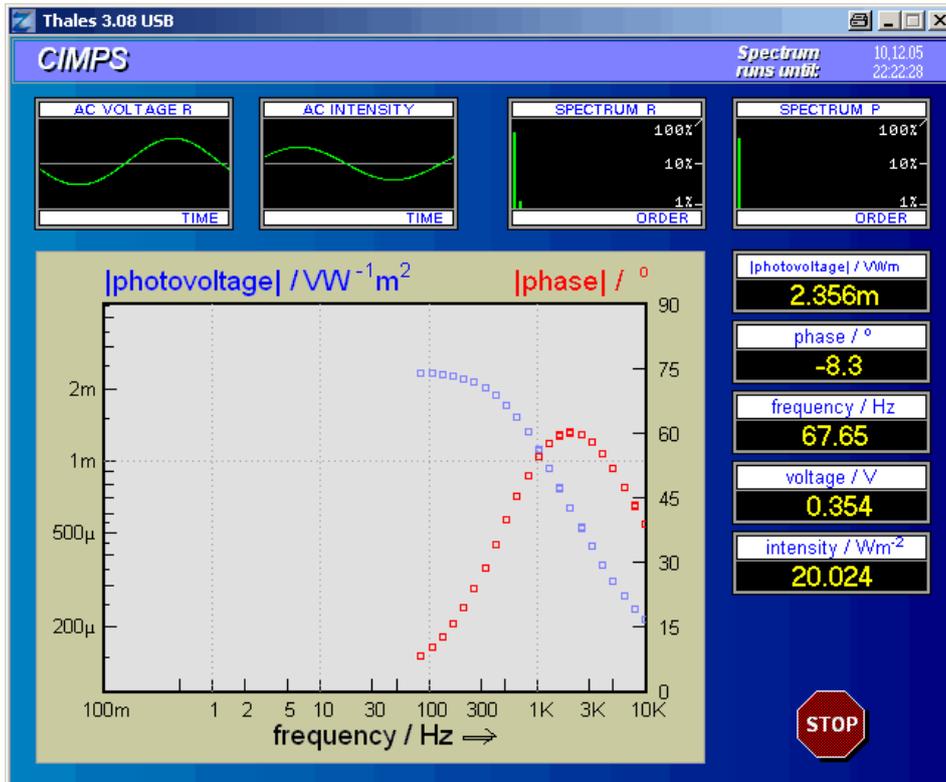


Fig. 25. The frequency response recording menu when entered through the 'Start dynam. TF' button, and the TF switch is set to 'photo-voltage' (IMVS).

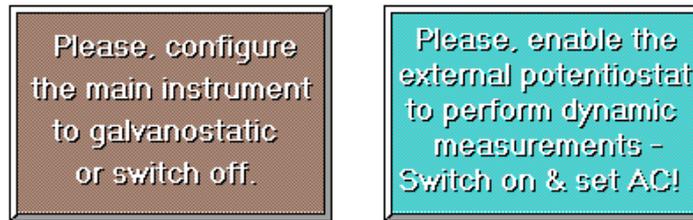


Fig. 26. This message boxes will be displayed, if the CIMPS photo-voltage efficiency measurement is called, but the conditions do not match the IMVS-determination requirements.

After the measurement of IMPS or IMVS the data can be visualised, exported or stored on the mass storage devices as known from the standard EIS measurements. Please recognise, that the impedance-based representations of complex resistance, capacitance, dielectric constant and modulo will make no sense when applied to photo-electrochemical spectra and are therefore not correctly supported in contrast to Bode- and complex-plane representations. Stored IMPS or IMVS measurement data can be opened by the SIM program and visualised, treated and analysed in the usual ways, apart from the modelling of the photo-electrochemical properties. A correct model applied must take into account the photoelectric effect by a current source modelling in an appropriate USR-model.

IMPS or IMVS-spectra are two-pole minimum phase system transfer functions only in the case of correct polarity adjustment (n- or p-type working electrode). In the case of wrong polarity the results of the ZHIT-rule check may lead to misinterpretations. It is recommended to adjust the WE polarity for that case (Fig. 27).

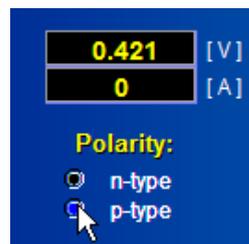


Fig. 27. The icon field for toggling the conductivity type of the working electrode material (bottom).

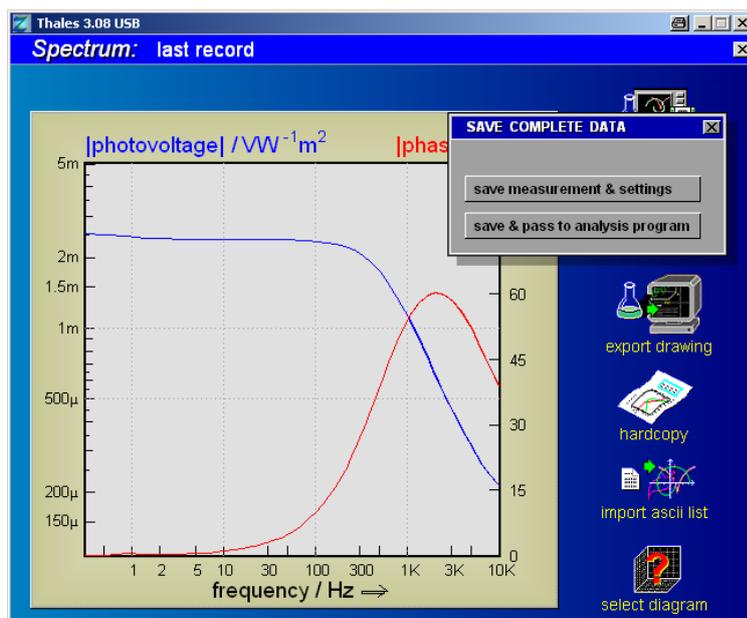


Fig. 28. After completion of dynamic IMPS or IMVS-measurements the measurement display menu will come up. Use this menu to save or visualise the data. Escaping from the measurement display menu will lead back to the CIMPS control panel.

### 4.1.1 Auto $\tau_{diff}/\tau_{life}$ Determination

As discussed in [chapter 1.1](#), an important issue of IMPS / IMVS is the time constant determination of DSSC and hybrid SC. Due to individual experimental conditions it is done usually by manual parameterize and triggering the measurement like described above. For routine measurements the whole procedure can be performed also automatically (Fig. 29).

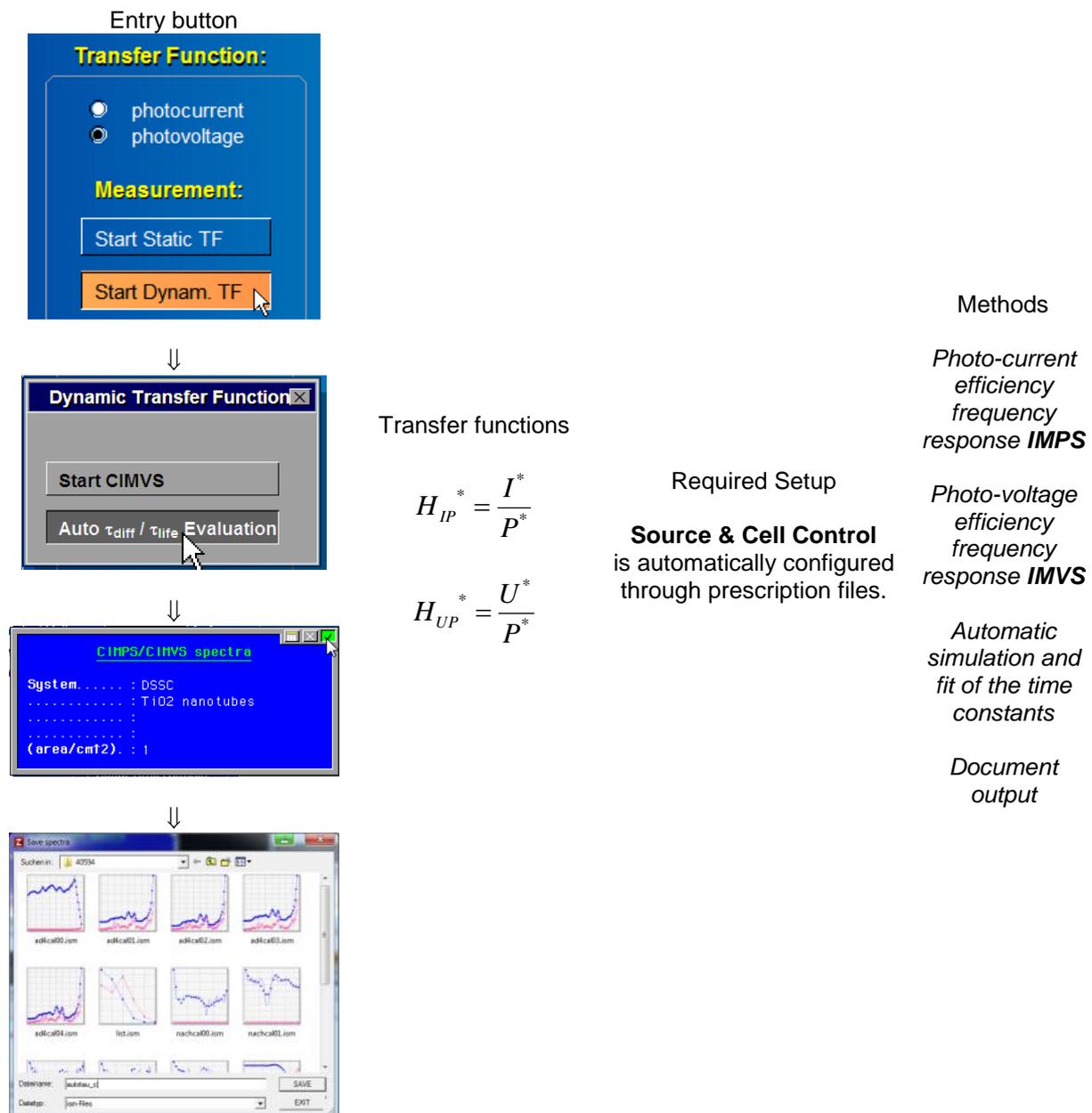


Fig. 29. Performing Auto  $\tau_{diff}/\tau_{life}$  Determination.

Prior to the measurement, THALES will pop up an input box and ask the user for a comment to the experiment. The file manager opens then and requests a file path / name for the result data. THALES performs first a CIMPS measurement at short circuit conditions using the manually selected intensity in order to evaluate  $\tau_{diff}$ . If no intensity was set, the software will request intensity information from the user. THALES also uses the actually set intensity modulation amplitude: If it is set to zero (recommended) THALES will set it to an appropriate value automatically.

Any other adjustments, like for the frequency range are performed automatically by means of the impedance measurement file “c:\thales\cimps\dummy\_c.ism” as a prescription file. If the user wants to change or edit the parameter settings for the Auto  $\tau_{diff}$  CIMPS measurement, he has to proceed in a similar way like modifying parameters from a prescription file in script environment: open the file in the appropriate THALES program – here the EIS measurement main menu – change parameter settings, perform the measurement and store the file by replacing the original file. **It is strongly recommended to backup the original file previously.**

The prescription file “dummy\_c” is preset to frequency range values appropriate for the  $\tau_{diff}$  determination of most DSSC types. For Organic-, Perovskite- or hybrid SC the upper frequency limit may be set about ten to hundred times higher, for TiO<sub>2</sub>-Nanotube-DSSC the lower frequency limit may be set lower.

After the CIMPS measurement the cell potentiostat state will change to open circuit mode and THALES will perform a CIMVS measurement. Here the adjustments, like for the frequency range are set automatically by using the impedance measurement file “c:\thales\cimps\dummy\_p.ism” as a prescription file. The prescription file “dummy\_p” is preset to frequency range values appropriate for the  $\tau_{life}$  determination of most DSSC types. The hints for other SC types regarding the frequency limits sketched above are also applicable for the modification of “dummy\_p.ism”.

After completion of the CIMPS / CIMVS measurement, the data are stored automatically and the simulation- and fitting program SIM is started. Both the CIMPS as well as the CIMVS data are opened and fitted using the prescription files “c:\thales\examples\models\dssc\_c.isf” respectively “c:\thales\examples\models\dssc\_p.isf”. The results of the fittings are passed back to the Auto  $\tau$  evaluation program and processed into a document. A menu will pop up allowing the document to be pasted into the Windows® clipboard or sent directly to the standard printer (Fig. 30). Besides, the document is accessible for further editing in the CAD panel.

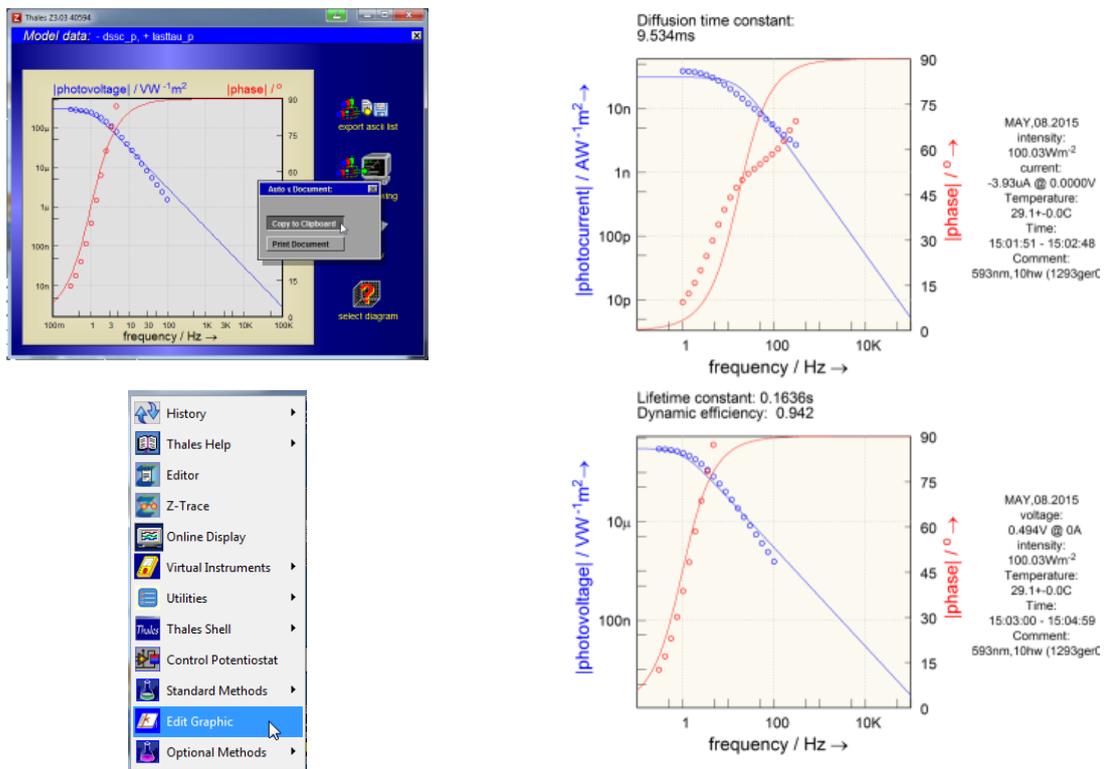


Fig. 30. After the Auto  $\tau$  evaluation the user can choose (left hand side) the output operation of the document (right hand side) to the clipboard or to the printer.

## 4.2 Static Photo-Electrochemical Transfer Function Measurements

Besides the dynamic CIMPS methods, the CIMPS script offers the possibility to measure the static characteristics of the photo-current and the photo-voltage vs. the illumination intensity. These methods may help to identify the photo-sensitive potential ranges, and, for instance, the sign (correlated with the basic semiconductor type with respect to the working electrode) and the magnitude of the photo-effect.



Fig. 31. Entry buttons for the measurement of the DC photo-current- (left) and DC photo-voltage characteristic (right).

To perform these methods, set up the cell and the light source in the appropriate way: the DC photo-current characteristic is measured with the cell under potentiostatic control, while the DC photo-voltage characteristic is acquired under open-circuit- or galvanostatic conditions – analogous to the set-up of the corresponding dynamic methods. No AC amplitude must be chosen for the cell- as well as the light source potentiostat. If the settings do not match the need for the selected method, analogous to the AC case the corresponding messages will be displayed.

After activating the entry buttons (Fig. 31), an input box for the selection of the scan conditions will come up (Fig. 32).

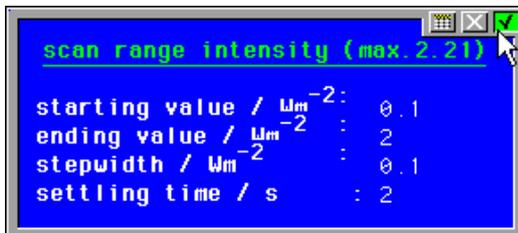


Fig. 32. Input box for the user input of the scan conditions in the case of the DC photo-current or photo-voltage characteristic measurement.

The starting- respectively ending values will define the intensity range and direction, covered in the measurement. The step-width characterises the resolution (and the sample count). Analogous to the acquisition of current-to-voltage curves, a certain stabilisation time can be defined. This allows the system under test to settle to a final response value after each individual intensity step.

The measurement starts as soon as the input box is quit. Instead of an on-line graphic, two virtual instruments will display the progress of the actual intensity and the photo-current- respectively voltage (Fig. 33).



Fig. 33. Two virtual instruments inform the user, while a DC photo-voltage characteristic is running. The second display shows the photo-current instead of the photo-voltage, if the current characteristic is selected.

After the measurement is complete, the current graphic of the measured DC characteristic is displayed and a small menu offers saving or export of the data as a text-list (filename.txt) or the direct export of the graph into the Windows clipboard (Fig. 34). Besides the copy into the clipboard, an editable graphic file may be created in the Thales CAD environment. If 'Save Data' is selected, an input box will be opened. The user is enabled to put in the filename and measurement comments (Fig. 35). When the box is quit, the text data file is written to the standard export path of Thales.

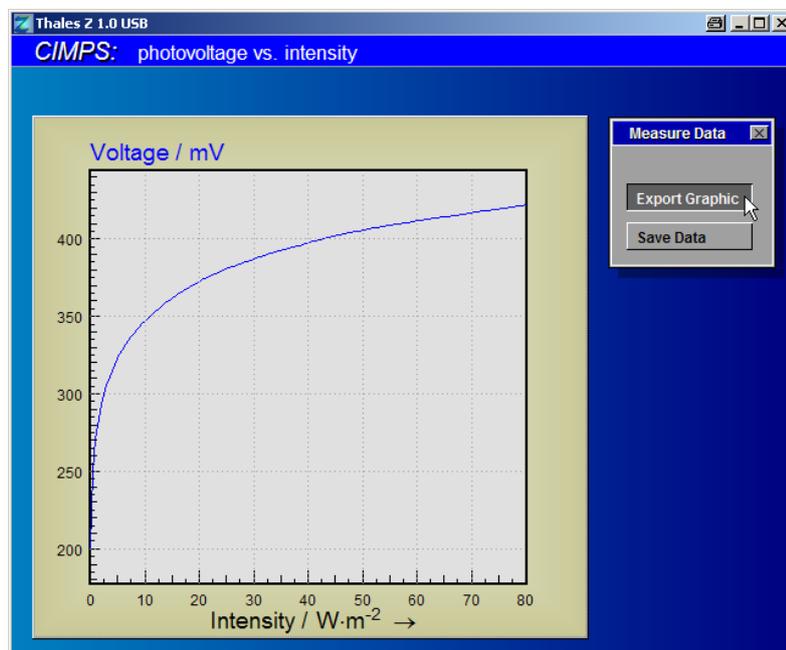


Fig. 34. After the measurement of a DC photo-current(-voltage) characteristic is completed, the result is displayed graphically. The 'Measure Data' menu offers the possibility to copy the graphics directly to the Windows clipboard ('Export Graphic') and in parallel into the CAD graphic editor or to save (export) the data as a text file list.

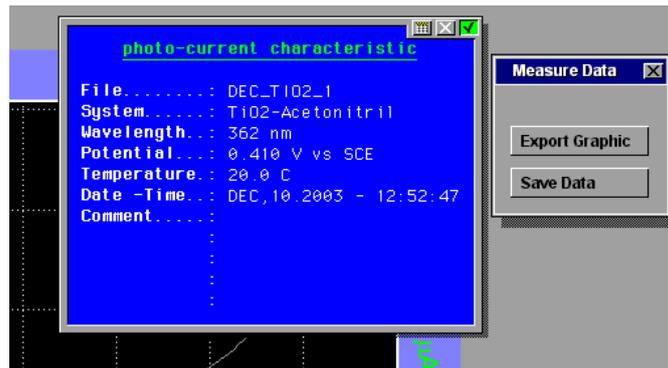


Fig. 35. The filename- and comment input box coming up after the selection of 'Save Data'.

The measurement parameters can be saved as default for future sessions. After the desired parameters are set, click the calibration icon (Fig. 36, left hand side). In the calibration menu select *save actual settings* (Fig. 36, right hand side). The actual settings for maximum power / fill factor, static transfer functions and time domain measurements are saved now and will be retrieved automatically when starting CIMPS. In order to return to the factory default settings select *load default settings*.

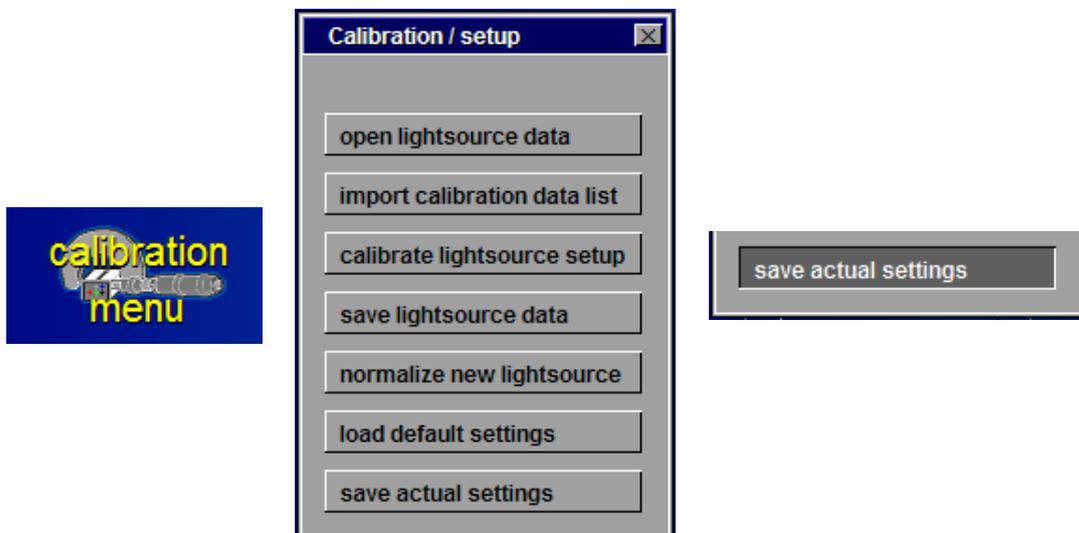


Fig. 36 Saving measurement parameters as default

### 4.3 Maximum Power and Fill Factor Measurements

Besides the dynamic and static TF methods, the CIMPS supports the standard solar cell investigations like maximum power, efficiency, quantum efficiency and fill factor. The Maximum Power  $P_{max}$  is defined as the power at the point where the current-voltage product is maximal in the current-voltage characteristic between the open circuit- and the short circuit conditions. The determination is performed at a certain fixed intensity.

The Fill Factor FF is defined as the quotient between  $P_{max}$  and the virtual power calculated from the product between the open circuit voltage OCP and the short circuit current  $I_{sc}$  (Eq. 6).

$$FF = \frac{P_{max}}{OCP \cdot I_{sc}}$$

FF = Fill Factor  
 $P_{max}$  = Power at the maximum power point of the current-voltage characteristic  
 $I_{sc}$  = Short circuit current of the solar cell [A]  
 OCP = Open circuit voltage of the solar cell [V]

Fill Factor  
Eq. 6

FF measurements can be performed with calibrated ZAHNER light sources as well as with additional sources, for instance a third-party AM-0.5 unit. In the latter case it is recommended to sense the intensity by means of the ZAHNER LDA sensor somewhere in the beam. Then the FP factor should be determined experimentally (it is the quotient between known intensity and the observed sense voltage at the slave potentiostat, Equ. 2) for this arrangement and put in to the FP-input field of the CIMPS control panel. This will insure that the automatic protocol and the graphics are supplied with correct intensity values.

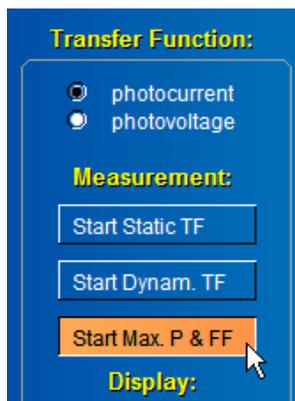


Fig. 37. Starting a Maximum Power and Fill Factor Measurement

The cell potentiostat should be set to open circuit conditions prior to the measurement start (Fig. 37), in order to enable the software to determine the actual OCP exactly. Otherwise a message will occur (Fig. 38):

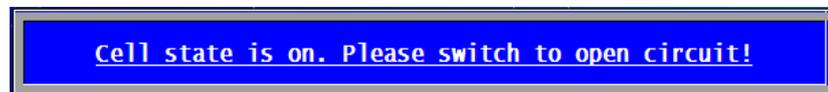


Fig. 38. Cell on state message, if FF is forced while the cell potentiostat is on.

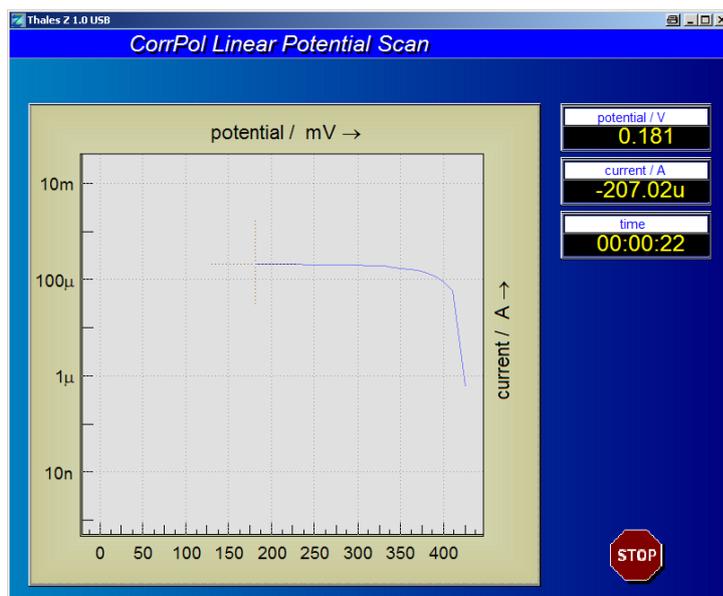


Fig. 39. On line display of the current-voltage characteristic performed after calling the 'Maximum power / Fill Factor' function.

After a successful start of the FF measurement a current-voltage characteristic scan (performed in the 'POL' environment) is initiated between the actual OCP and zero voltage (Fig. 39).

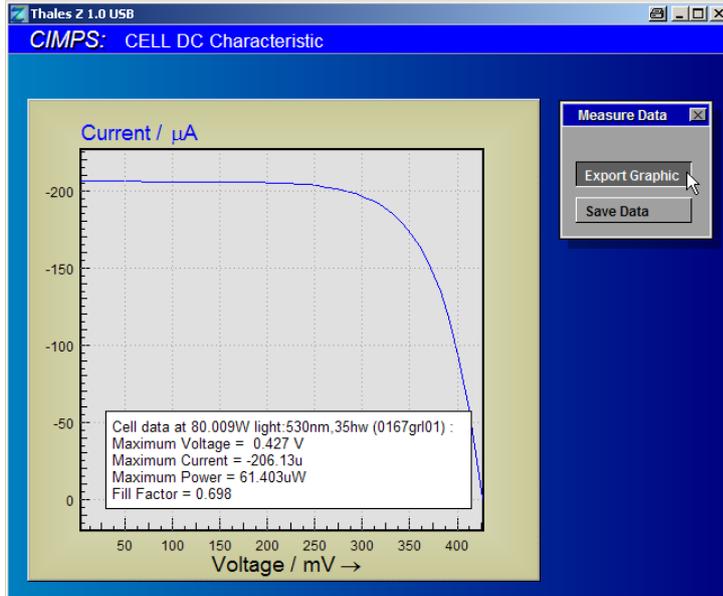


Fig. 40. Final display of the current-voltage characteristic performed by the 'Maximum power / Fill Factor' function. The box inside the graph provides the desired results.

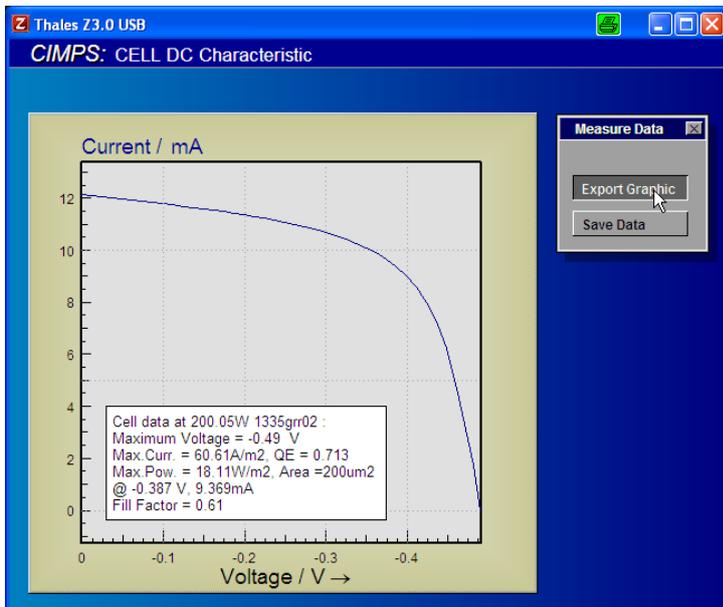
After the measurement is completed, the current-voltage characteristic is displayed again in linear scale and the determined data for OCP,  $I_{sc}$ , FF and  $P_{max}$  are displayed (Fig. 40 upper). Now the results may be exported as graphics and / or stored as data file.

Quantum eff. cy

When quantum efficiency option at the CIMPS main page is checked you can define an electrode active area value. In this case the quantum efficiency  $QE$  is calculated automatically and the graphic output is enhanced (Fig. 40 lower) by the area value and the  $QE$  value, calculated from the maximum current  $I_{max}$  [A] at zero voltage, the specific light intensity  $P$  [ $W \cdot m^{-2}$ ], the active cell area  $A$  [ $m^2$ ], the wavelength  $\lambda$  [m] and the natural constants Planck constant  $h$ , vacuum light speed  $c$  and the electron's elementary charge  $q_e$  after:

$$QE = \frac{I_{max}}{P \cdot A \cdot \lambda} \cdot \frac{h \cdot c}{q_e}$$

Please consider that  $QE$  can be only an estimate value, if a non-monochromatic light source, like white light is used.



The measurement parameters can be saved as default for future sessions. After the desired parameters are set, click the calibration icon (Fig. 41, left hand side). In the calibration menu select *save actual settings* (Fig. 41, right hand side). The actual settings for maximum power / fill factor, static transfer functions and time domain measurements are saved now and will be retrieved automatically when starting CIMPS. In order to return to the factory default settings select *load default settings*.

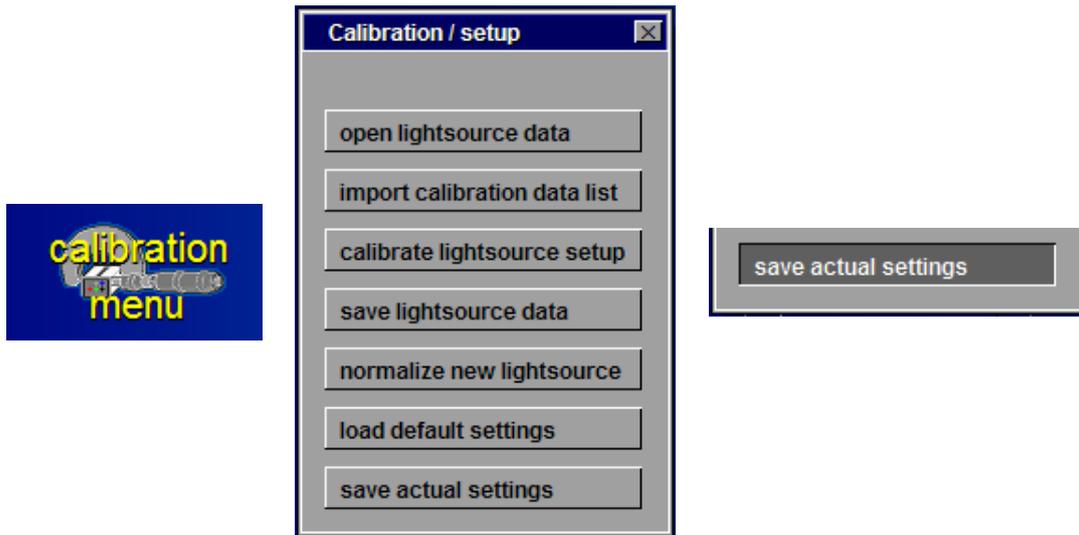


Fig. 41 Saving measurement parameters as default

## 4.4 Time Domain and Intensity-Transient Measurements

It is often advantageous, that linear dynamic measurements under frequency variation, like IMPS and IMVS can be put in relation to measurements of transient behaviour in the time domain. CIMPS supports time domain measurements under potentiostatic control of the cell (POL phase) as well as under open circuit conditions (OCP phase). A sequence of both phases may be performed also. Optionally the light intensity may be switched automatically in parallel between different power states in order to enable the recording of light on / off or intensity value transients. Time-domain and transient measurements (TDT) can be set up and controlled by means of the appropriate field in the CIMPS main panel (Fig. 11). You may specify the time- and sampling conditions with the 'Set up time domain measurements' panel (Fig. 43), which is opened from the corresponding menu button (Fig. 42).

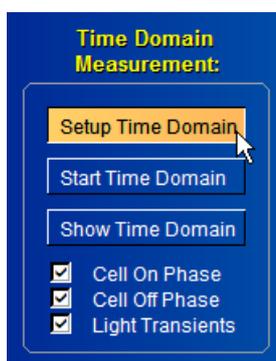


Fig. 42. Enter the 'Set up time domain measurements' panel by means of the menu button 'Setup Time Domain' from the 'Time Domain Measurement' field in the CIMPS main panel.

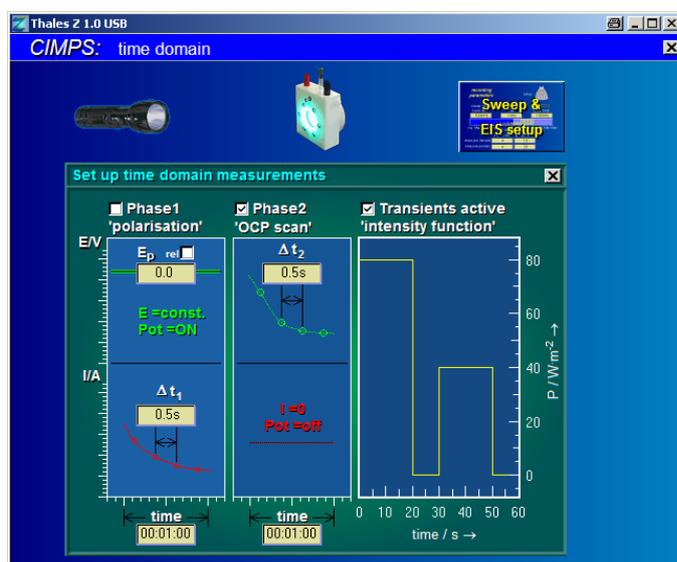


Fig. 43. By means of the 'Set up time domain measurements' panel the conditions of TDT measurements can be defined.

The TDT panel has a structure, which is very similar to the POL panel, with one important difference: no 'linear scan' is supported. The corresponding field in the TDT panel is reserved for the display and set-up of the intensity transient function, which supports the change of the intensity automatically at certain points in time, while the POL phase 1 and / or phase 2 is running. Please Enable / disable phase 1 'polarisation' and phase 2 'OCP scan' with the corresponding checkboxes. Define the set potential for phase 1 as absolute value (checkbox 'U<sub>P</sub> rel.' un-checked) or as voltage referred to the actual OCP (checkbox 'U<sub>P</sub> rel.' checked).

Put in the sample times  $\Delta t_1$  and  $\Delta t_2$  in units of seconds, and the measurement time for phase 1 and phase 2 in hours, minutes and seconds in the format 'hh:mm:ss'.

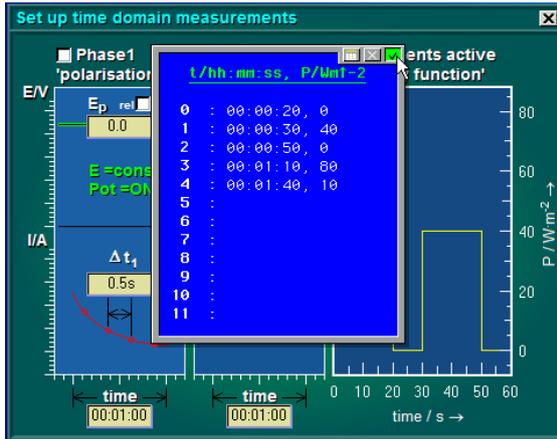


Fig. 44. By means of the 'Set up time domain measurements' panel the conditions of TDT measurements can be defined.

Touch and confirm the 'intensity function' display field in order to define the time-dependent intensity transient function. An input box will appear (Fig. 44). Put in the transition points in time in the format 'hh:mm:ss' and add the intensity value after typing a separating comma. The time input is eased by the function of the alternative mouse button in this box: it is preset to suggest the string '00:00:00'.

In the example displayed in Fig. 44, the intensity would change as follows: phase 1 is suppressed (the corresponding checkbox for phase 1 'polarisation' is unchecked), the measurement starts with the OCP phase 2 under the initial intensity, defined from the CIMPS panel and displayed as 'Actual Average Intensity'. After 20s the intensity will be shut down to zero.

After another 10s (30s after start) the intensity will be set to 40 W/m<sup>2</sup> and 50s after start the intensity is shut down again. The last two input lines 3: '00:01:10, 0' and 4: '00:01:40, 10' will have no effect, due to a total measurement time of '00:01:00' equivalent to 60s, defined for phase 2. If one would change the conditions of the example by enabling phase 1 'polarisation', the intensity changes would again begin referenced to the overall start. In this case, all five transient points would get in effect, due to a total time of now 120s. In general, the initial intensity at start will be established again after the completion of the scan.

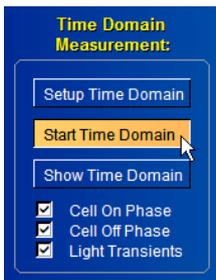


Fig. 45. A time domain measurement is started by means of confirming 'Start Time Domain' in the Time Domain Measurement section of the CIMPS panel.

After pressing 'Start Time Domain' (Fig. 45), a POL online window for potentiostatic polarisation will be displayed, if 'phase 1' was enabled (Fig. 46).

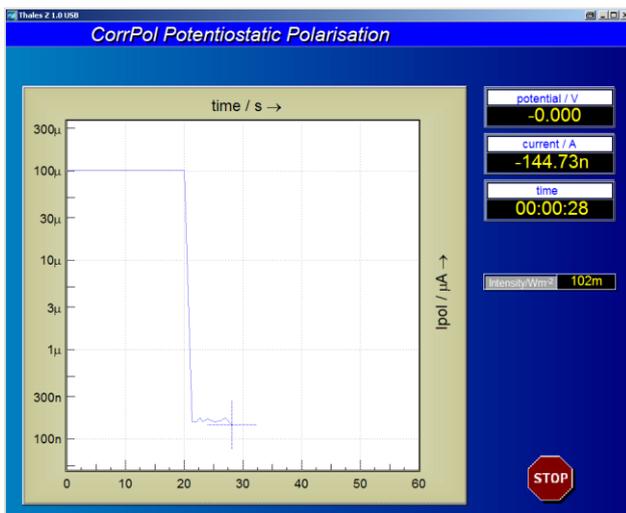
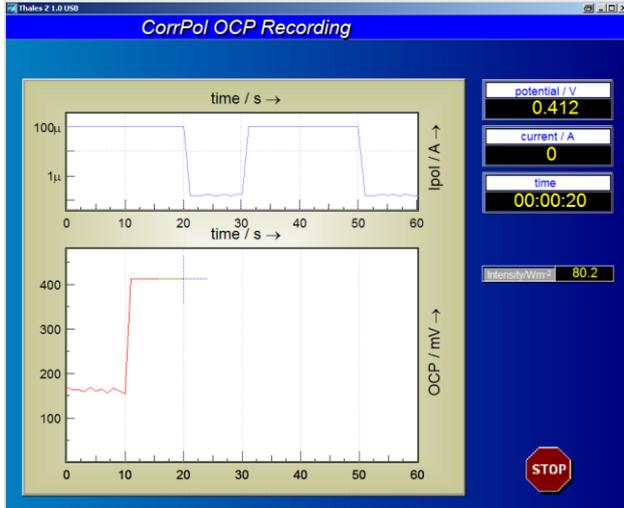
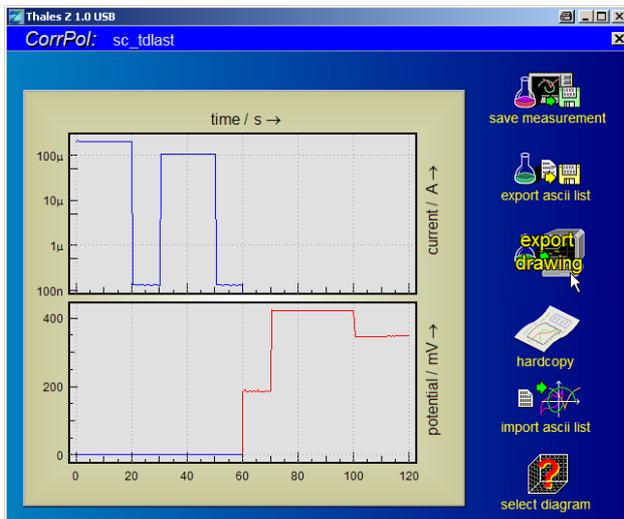


Fig. 46. POL online window for potentiostatic polarisation appearing after start of a TDT measurement. The 'Intensity transient' function is enabled.



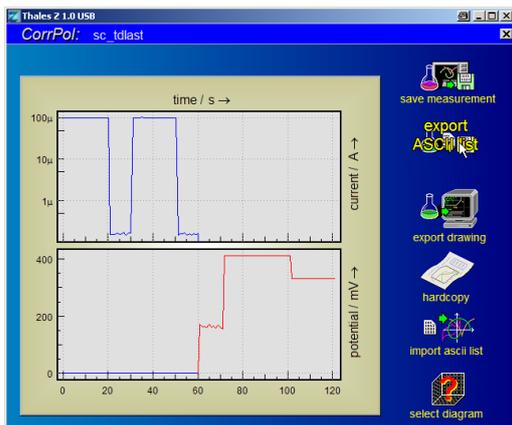
If 'phase 2' OCP recording is enabled, too, then a second POL online window will appear after completion of 'phase 1' (Fig. 47).

Fig. 47. POL online window for potentiostatic polarisation appearing after start of a TDT measurement. The 'Intensity transient' function is enabled.



After completion of the TDT scan, the tool-bar of the 'last measurement' window may be used in the usual way to save, treat and export the data (Fig. 48).

Fig. 48. POL 'last measurement' window for both potentiostatic polarisation as well as OCP recording after completion of a TDT measurement.



```

TIMES EDITOR
File Edit Paste Clear Colors Info
File.....: sc_tdlast - JAN,19,2009
System.....: O8C
Control.....: 22.2+|-|,02C
Temperature....: 22.2+|-|,02C
Time.....: JAN,19,2009
Comment.....: 15:55:55 - 15:57:59
              DC-Characteristic
              For Time Domain
              and Transient
              measurements

Electr.area/eqcm:
polarization data
Lines: 122
Columns: 4

Number  Time/s  Potential/V  Current/A  Intensity/Wa-2
1       0.0    -4.6366e-05 -1.0046e-04 4.009e+01
2       1.0    -4.6366e-05 -1.0045e-04 4.009e+01
3       2.0    -4.6366e-05 -1.0045e-04 4.009e+01
4       3.0    -4.6366e-05 -1.0044e-04 4.009e+01
5       4.0    -4.6366e-05 -1.0045e-04 4.009e+01
6       5.0    -4.6366e-05 -1.0045e-04 4.009e+01
7       6.0    -4.6366e-05 -1.0044e-04 4.009e+01
8       7.0    -4.6366e-05 -1.0044e-04 4.009e+01
9       8.0    -4.6366e-05 -1.0046e-04 4.010e+01
10      9.0     -4.6366e-05 -1.0046e-04 4.009e+01
11     10.0    -4.6366e-05 -1.0044e-04 4.009e+01
12     11.0    -4.6366e-05 -1.0044e-04 4.009e+01
    
```

Fig. 49. The data list (right), exported from the POL 'last measurement' window (left) contains an additional column with the protocol of the intensity course.

While a TDT measurement is running, the actual intensity, read out as a data acquisition channel, is shown beyond the virtual instruments for time, current and voltage in an additional small display. Details about the handling of additional data acquisition channels can be read in the [Signal Acquisition manual](#). Like with any additional data acquisition channel, the export ASCII list provides additional columns for the data.

Generally, the result of any actual measurement can be shown offline again, as long, as no additional measurement of the same type will overwrite the last result (Fig. 50).

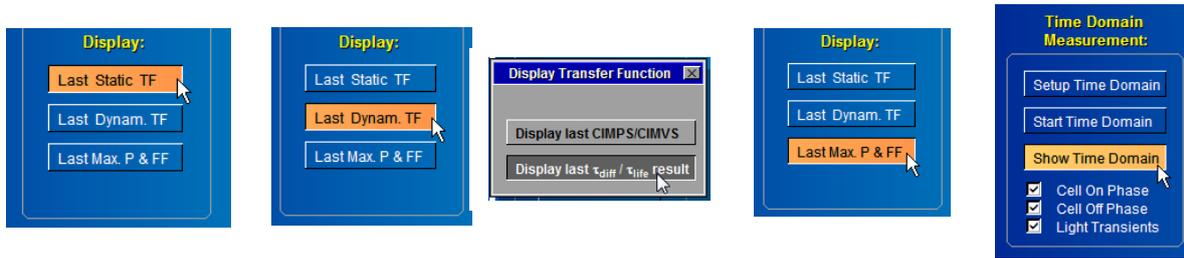


Fig. 50. The CIMPS control panel provides the possibility to display the results of the last measurements of all supported methods.

The measurement parameters can be saved as default for future sessions. After the desired parameters are set, click the calibration icon (Fig. 51, left hand side). In the calibration menu select *save actual settings* (Fig. 51, right hand side). The actual settings for maximum power / fill factor, static transfer functions and time domain measurements are saved now and will be retrieved automatically when starting CIMPS. In order to return to the factory default settings select *load default settings*.

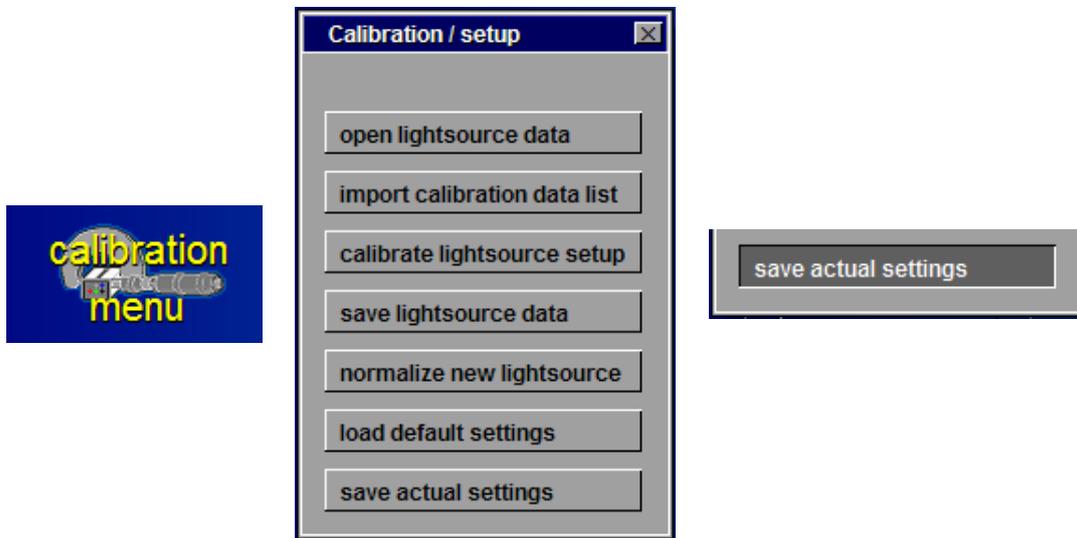


Fig. 51 Saving measurement parameters as default

## 5 Charge Extraction after N.W. Duffy, L.M. Peter et al.

### 5.1 General

In the article

“A novel charge extraction method for the study of electron transport and interfacial transfer in dye sensitised nanocrystalline solar cells”

Electrochemistry Communications 2 (2000) 658-662,

N.W. Duffy, L.M. Peter et al describe a procedure, how the kinetics of a DSSC can be investigated in a non-linear regime, as a supplement to the linearizing methods IMPS and IMVS. The working principle is based on the following steps (see also the time sequence Fig. 52 left):

1. The DSSC is kept in steady state un-illuminated under short circuit conditions.
2. Light is switched on and synchronously the DSSC is set to open circuit conditions.
3. After reaching a steady state of the OC voltage due to the illumination, light is switched off.
4. For a selectable delay time the OCV of the DSSC is allowed to relax (delay time may be set to zero as well)
5. Now the present charge in the DSSC is determined by forcing short circuit conditions, while the current flow is integrated.
6. After a sufficient time necessary to extract all DSSC charge the measurement is finished.

Fig. 52 right shows the typical time characteristics of the DSSC cell voltage and the extracted charge.

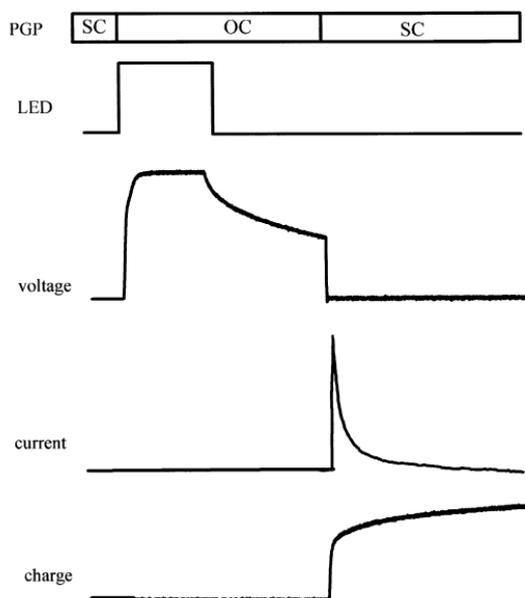


Fig. 2. Open circuit (OC) short circuit (SC) sequence showing the relationship between the illumination and the measurement of potential and charge in the charge extraction experiments.

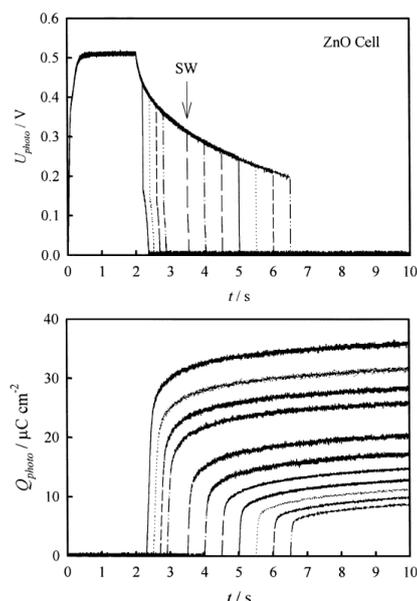


Fig. 3. Experimental transients for the ZnO cell. The upper plot shows a series of decay transients that have been interrupted at different times by short circuiting the cell. The points at which the cell is short circuited through R can be seen (e.g. at SW). The lower part of the figure illustrates the series of charge transients obtained by integrating the short circuit current after different decay periods.

Fig. 52. Control sequence of the charge extraction program after L.M. Peters (left) and typical results (right). Copy from the original paper.

An analogue method was integrated into the THALES CIMPS program. Use the menu field in the lower left corner of the CIMPS panel (Fig. 53) to set up, perform and visualize charge extraction measurements.

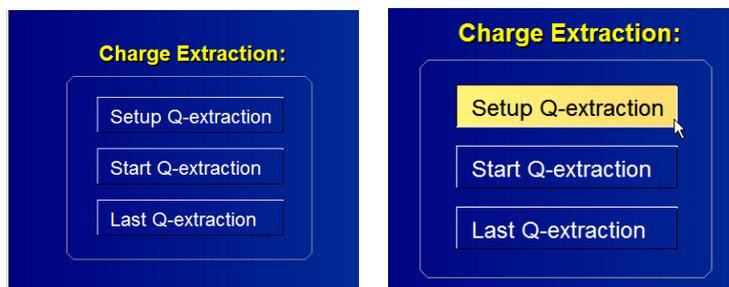


Fig. 53. Charge extraction menu field and set-up entry of THALES CIMPS.

## 5.2 Setting up CIMPS Charge Extraction “CCE”

Entering the set-up will display the input field to set / edit the characteristic parameters (Fig. 54).

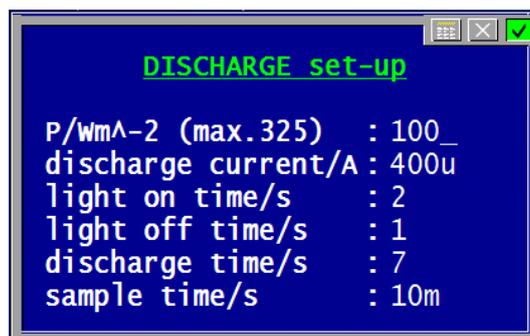


Fig. 54. Input field for the charge extraction control parameters.

1. **discharge current/A**: the THALES CIMPS Charge Extraction “CCE” method differs slightly from the original technique after L.M. Peter. In the latter an electronic switch conducts the charge into an analogue integrator circuit. This would need a different hardware set-up and connection technique compared to CIMPS. In CCE an equivalent method was developed, which allows to keep the same set-up like in all CIMPS methods without changing the wiring and renouncing on additional hardware. Instead of an analogue switch with a final inner resistance, a high initially galvanostatic controlled discharge current supplied by the standard cell potentiostat is used. A fast software control stops the discharging as soon as the target voltage value is reached. An iterative loop using successively smaller and, if necessary, inverse currents pulls out the rest of the charge correctly which may arrive the electrode later, always keeping the discharge voltage very close to the target voltage. Use an initial current in the range of some 100  $\mu$ A up to some 100 mA depending on the size and power of your DSSC. The value is not critical and can be fixed easily after an initial test which is recommended when changing the general type of cell. Putting in a value of zero forces the program to automatically estimate an initial discharge current by a test EIS measurement prior to the CCE.
2. **light on time/s**: set this time long enough to be sure, that the OCV under light is settled.
3. **light off time/s**: set this time according to your intention. In order to reconstruct and plot the inverse charge vs. time course start with zero and continue with CCE experiments with increasing light off times, see for example in the Fig. 52 right hand side to get an idea.
4. **discharge time/s**: set this time long enough to be sure, that the discharging is complete.
5. **sampling time/s**: set this time in order to get a good compromise between the necessary time resolution and the crop up of unnecessary data trash.

### 5.3 Starting a CCE measurement

After correctly setting up the CCE parameters, the CCE measurement may be started by activation of the corresponding button “Start Q-extraction” of the CCE menu field (Fig. 55 left). An online-graphic will appear (Fig. 55 right). The horizontal axis is the total measurement time, while the vertical axes are reserved for the online-display of the actual cell voltage (left, blue, absolute value/V) and for the actually extracted charge (right, red, absolute value/C).

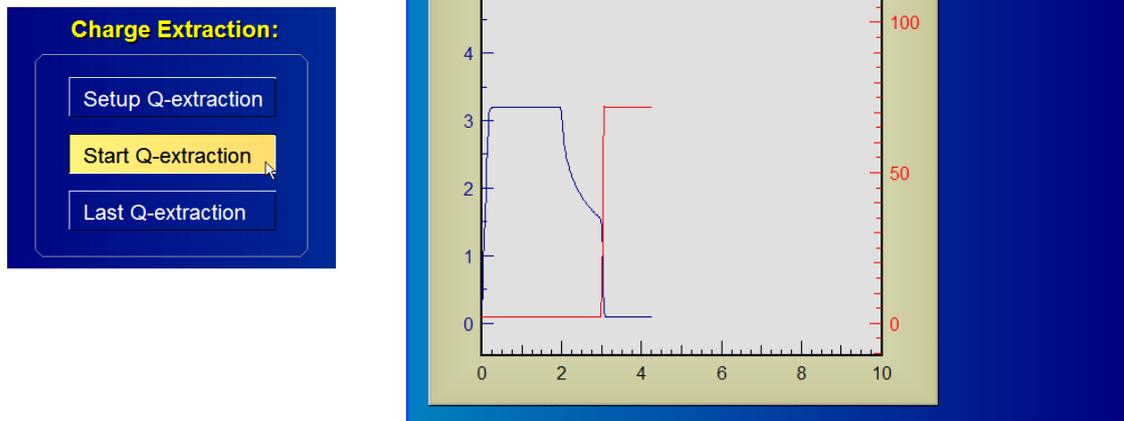


Fig. 55. Starting a CCE (left) will cause the online display window appear. The time course of the actual voltage and charge will be displayed.

After completion of the CCE the program will enter the “Last Q-extraction” function automatically.

## 5.4 Display the last CCE

An existing CCE measurement may be visualized by activation of the corresponding button “Last Q-extraction” of the CCE menu field (Fig. 56 left). The graphic representation of the last CCE measurement will appear (Fig. 56 right). The horizontal axis is the total measurement time, while the vertical axes are reserved for the data display of the cell voltage (left, blue, signed value/V) and for the extracted charge (right, red, signed value/C).

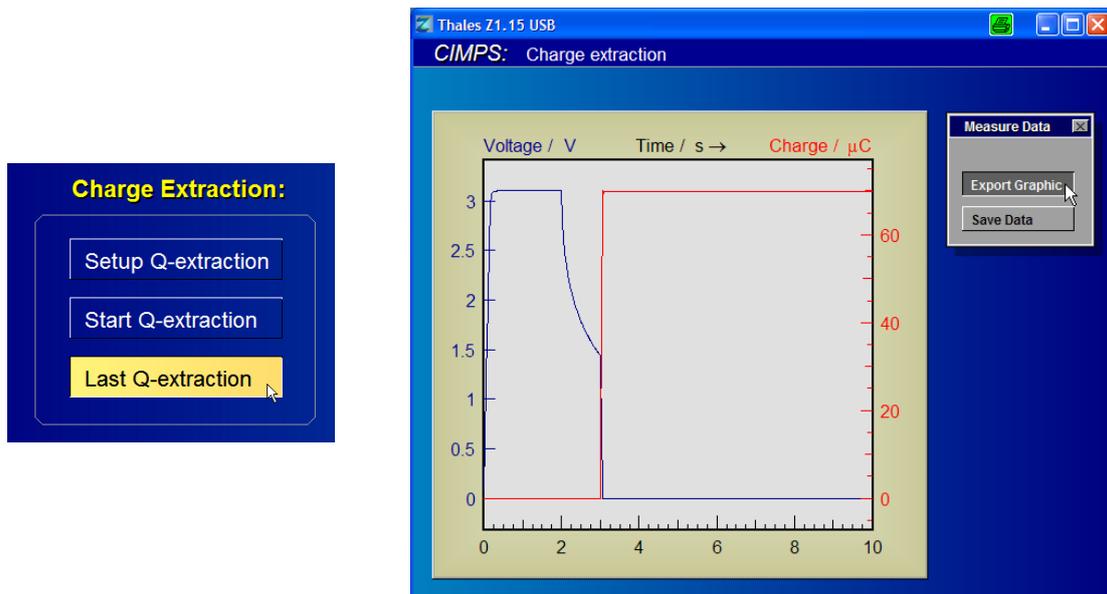


Fig. 56. The CCE menu field button “Last Q-extraction” (left) is used to open the display of an existing CCE measurement (right). The last voltage and charge time course (signed values) will be displayed. The sub-menu “Measure Data” coming up, offers export possibilities.

The sub-menu “Measure Data” (Fig. 56 right) will appear at the right hand side of the display field. It can be used to export the graphics and to save the data in the Thales usual way (Fig. 57). Saving the data will create a data list.txt, where the total charge is introduced as comment line (Fig. 58, Fig. 59).

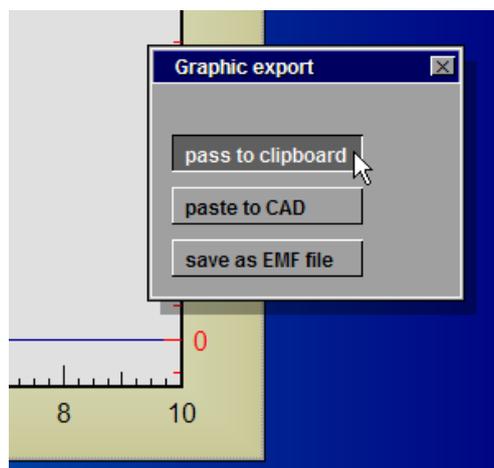


Fig. 57. Pressing the “Export Graphic” button of the “Last Q-extraction” menu offers the graphic export possibilities to be used like in the other THALES program parts.

Activating “Export Graphic” opens the corresponding Thales standard menu in order to copy, edit or save the graphic of the actual CCE measurement (Fig. 57).

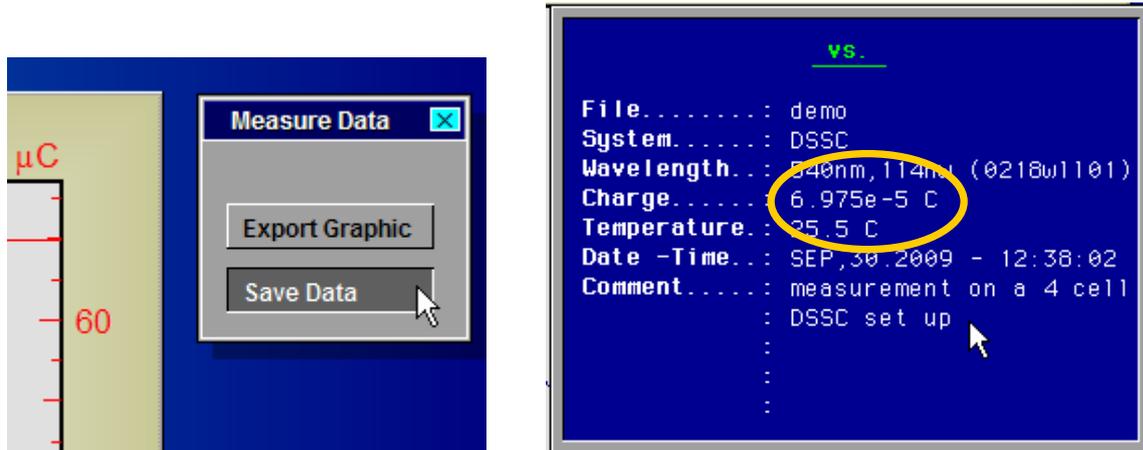


Fig. 58. Pressing the “Save Data” button of the “Last Q-extraction” menu opens the Thales standard comment input box. The charge determined in the last measurement is displayed in the 4<sup>th</sup> line.

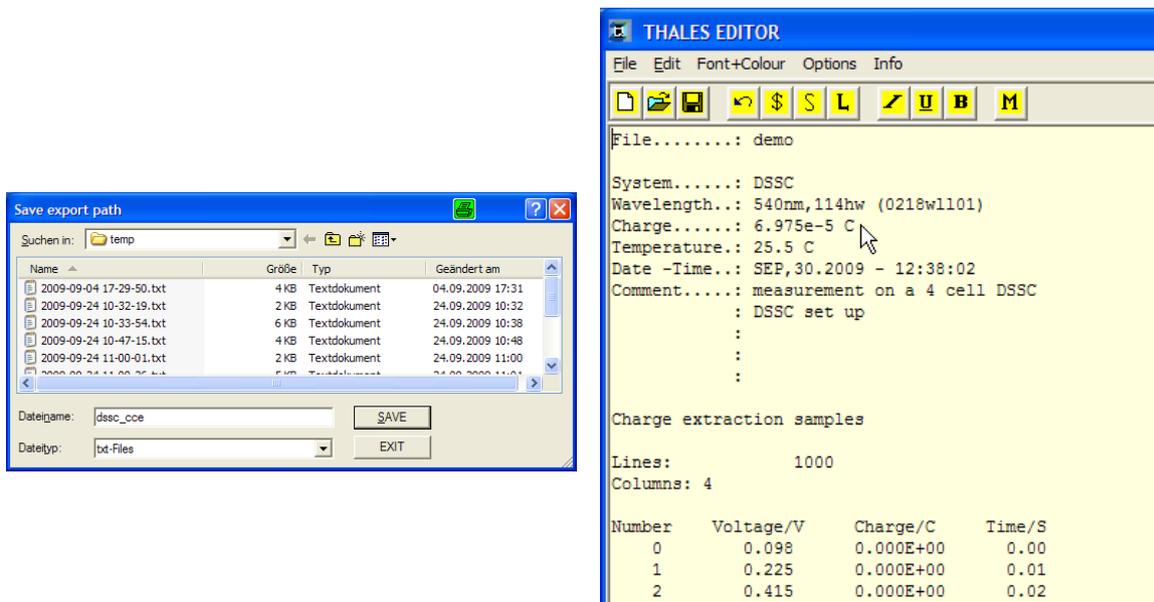


Fig. 59. Saving CCE data will create a data file.txt containing the comment box text and the CCE data list.

## 6 Intensity Calibration Procedures

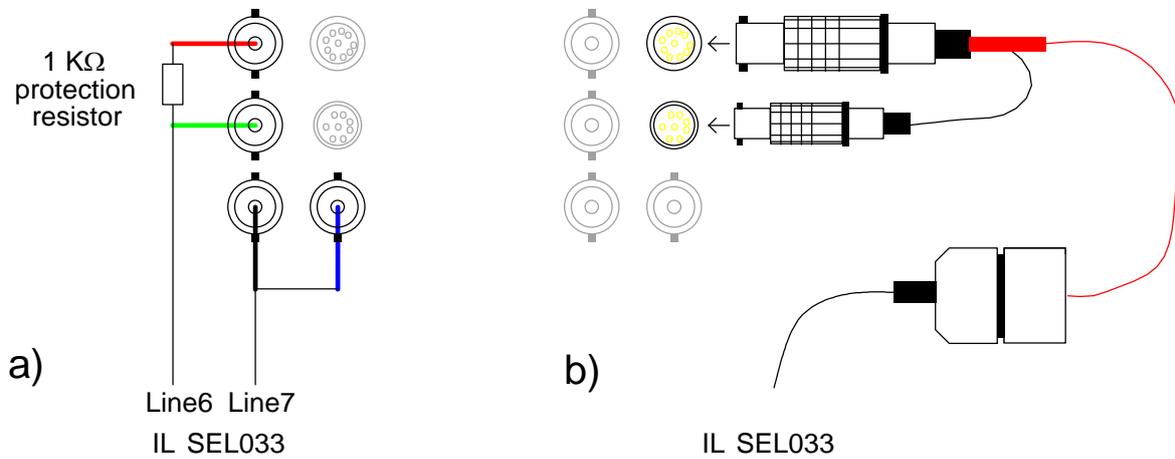


Fig. 60. Connection scheme for the calibrated photo-detector IL SEL033: a) delivered by International Light (Polytec), b) delivered by Zahner (including adaptor/connector set).

The Zahner LDAs are delivered with calibration values for the light intensity available in a distance of 100 mm in the centre of the beam. The intensity value can be set precisely only, if the light sources and the sensor of the delivery are used in the optical set-up shown in Fig. 9. Also the corresponding characteristic data of the actual light source have to be present in the program (Fig. 12).

In the case, that the set-up must differ from the set-up described, but a precise information on the absolute intensity is necessary, one must determine the intensity at the site of interest (usual at the PSO's site) by means of an individual calibration procedure.

For that purpose, a Polytec/InternationalLight detector type SEL033 with type-W-optics can be adapted. If the SEL033 is connected to the ECW main potentiostat as a PSO (Fig. 60), the CIMPS panel supports an automatic routine for the calibration. As a prerequisite, the SEL033 must be ordered with calibration certificate, together with a file, containing the calibration table. The calibration table is usually given as a rich-text-file.rtf. The CIMPS calibration software expects a plain ASCII table instead for import. It can be converted by the following procedure:

1. Open the Polytec/InternationalLight detector SEL033 calibration-file.rtf in a text-processing environment (like Microsoft Word). It should look like shown in Fig. 61.
2. Mark the complete text and move it into the Thales text editor by copy&paste. It should then look like shown in Fig. 62.
3. Save the file somewhere as "amos-text"-file.is\_ like shown in Fig. 63.

WaveLength	9L 1200 W/cm2	y	Relative Response	Normalize	(A)(cm2)(W- 1)
250	1,06E-05	32,8843784	3,09E+06	9,26E-02	5,765E-03
260	1,55E-05	44,6780392	2,89E+06	0,08647872	5,385E-03
270	1,64E-05	46,6118126	2,84E+06	0,08506476	5,297E-03
280	1,21E-05	39,246702	2,07E+06	0,08744108	5,445E-03

Fig. 61. Typical Polytec/InternationalLight detector SEL033 calibration file.rtf under MS-Word.

λ	WaveLength	W/cm <sup>2</sup>	y	Relative	Response	Normal
250	1,06E-05	32,8843784	3,09E+06	9,26E-02	5,765E-03	
260	1,55E-05	44,6780392	2,89E+06	0,08647872	5,385E-03	
270	1,64E-05	46,6118126	2,84E+06	0,08506476	5,297E-03	
280	1,31E-05	38,2426295	2,92E+06	0,08744198	5,445E-03	

Fig. 62. SEL033 calibration table in the Thales text editor after copy & paste.

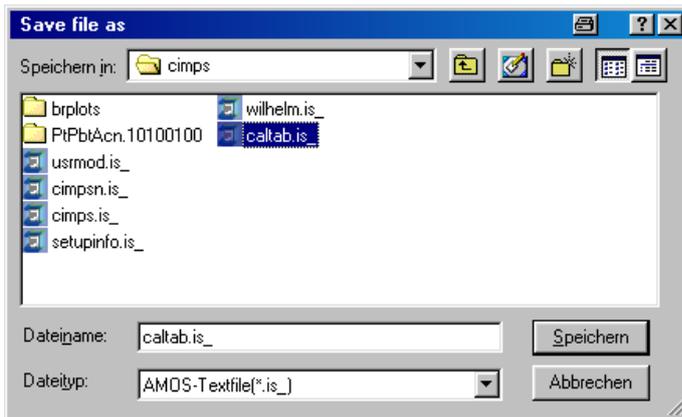


Fig. 63. Choose AMOS-Textfile(\*.is\_) to save the SEL033 calibration file.

It is recommended to order the Polytec/InternationalLight detector SEL033 directly from Zahner. The cable fittings and the tailored calibration table file are then in the delivery, and the import procedure described above can be omitted.

The actual calibration procedure is entered by pressing the Calibration menu icon (Fig. 64).



Fig. 64. Calibration menu icon to open the menu for intensity calibration functions.

The calibration menu (Fig. 65) offers five functions. The three functions “import calibration list”, “calibrate lightsource setup” and “save lightsource data” should be performed in sequence. In this first step, a calibration file.is\_ has to be selected from the file menu for import (Fig. 66).

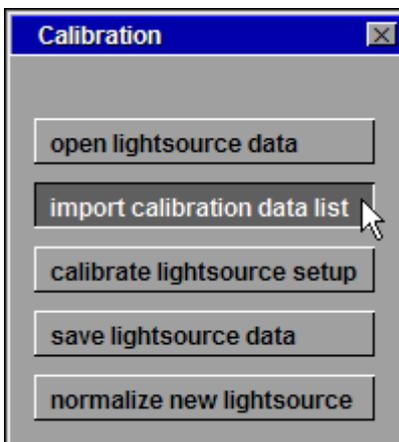


Fig. 65. Calibration menu. ‘Import calibration data list’ is activated.

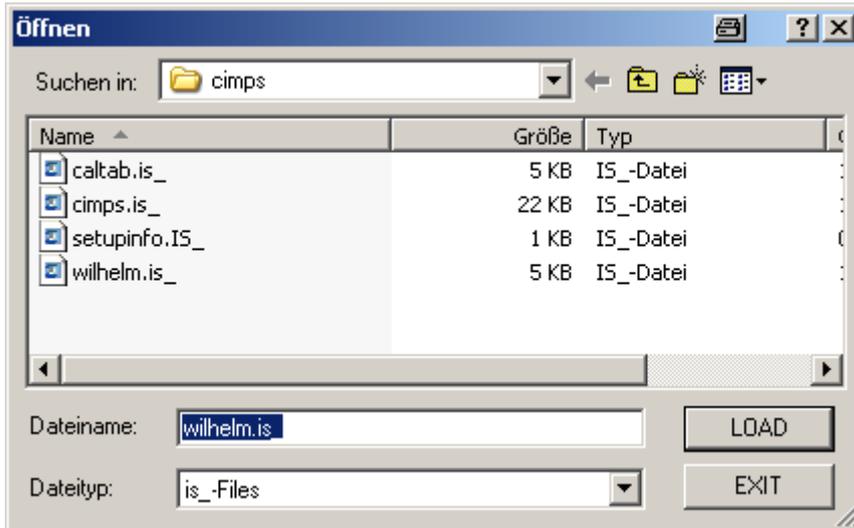


Fig. 66. Opening the AMOS-compatible plain text file.is\_ containing the calibration table.

The calibration curve is then displayed and should look similar to Fig. 67.

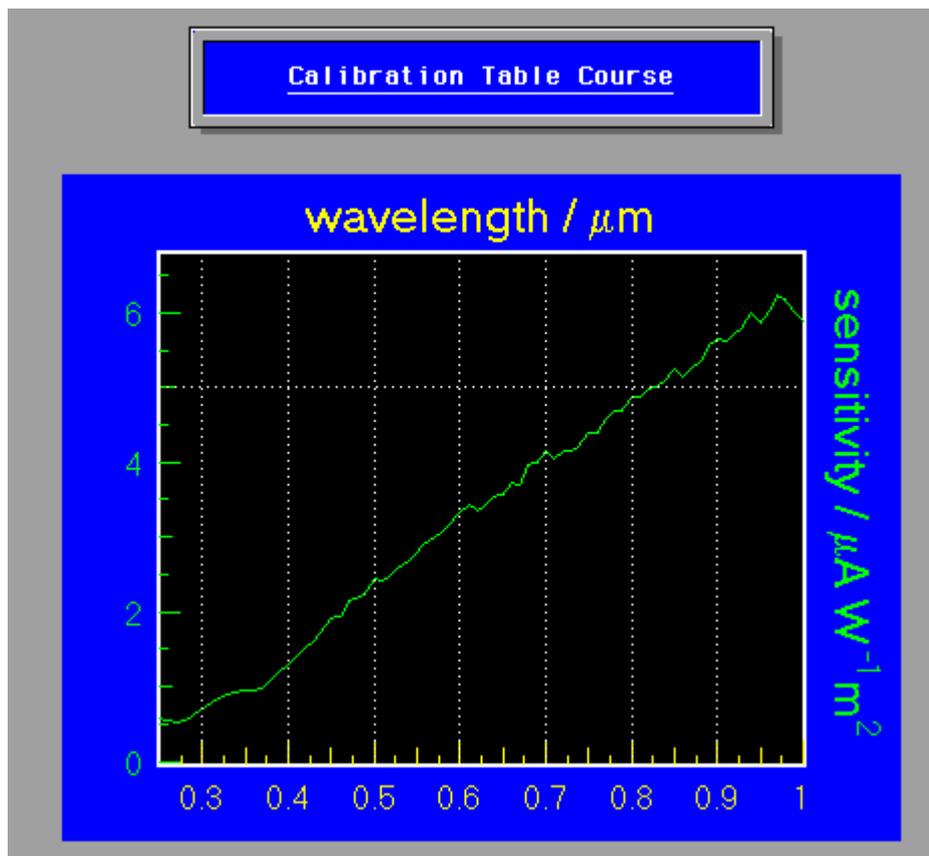


Fig. 67. Calibration curve after import of the calibration table file.is\_.

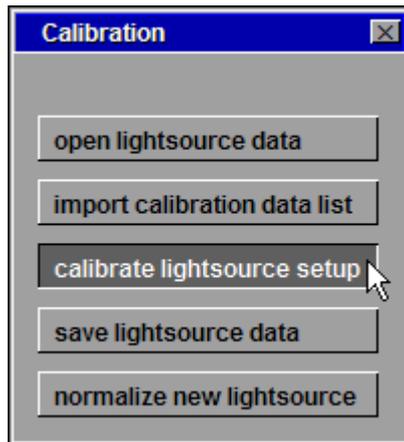


Fig. 68. The second step of the calibration procedure.

For the next step of the calibration procedure, the “calibrate light source setup” (Fig. 68), the SEL033 detector has to be mounted at the place of the photo-electrochemical cell, like sketched in Fig. 69 and connected to the ECW main potentiostat (Fig. 60). The photo-sensor diode in the delivery has to be mounted like sketched and connected to the PHOTO-AMP external BNC input.

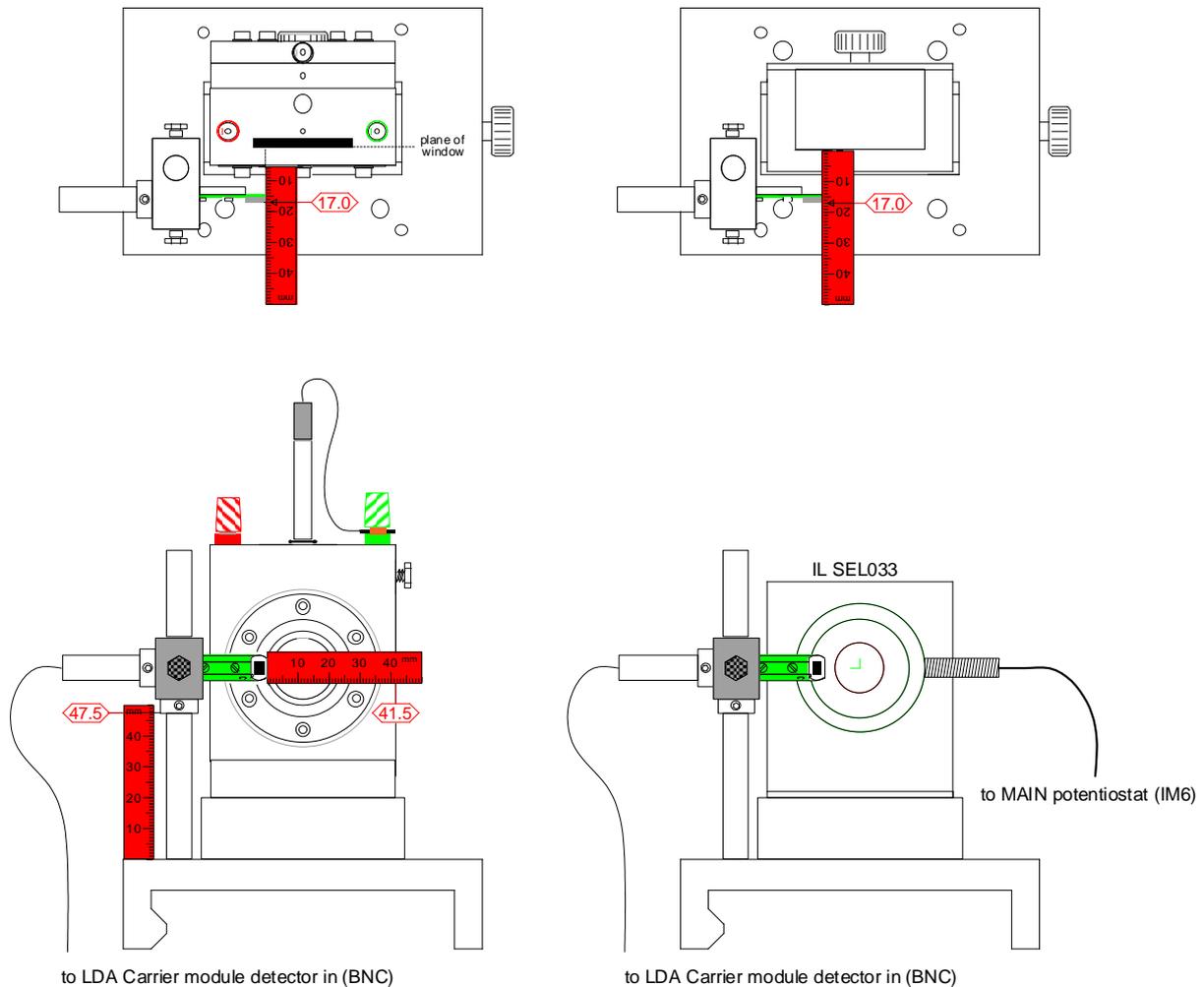


Fig. 69. Arrangement of the Zahner CIMPS photodetector together with the Polytec/InternationalLight detector SEL033 for the calibration procedure (right hand side) compared to the standard arrangement (left hand side). The measures given correspond to the Zahner calibration set-up.

All environmental light should be excluded to ensure the accuracy of the calibration. After pressing the “calibrate light source setup” menu button this calibration step takes place and ends with the input box message Fig. 70. The user should now input the nominal wavelength and the specified bandwidth of the illuminator under test. Please consider, that the input dimension is in *Meters* !

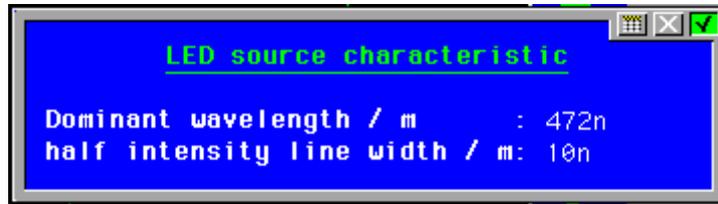


Fig. 70. After the second step of the calibration procedure, an input box expects wavelength information about the LDA under test.

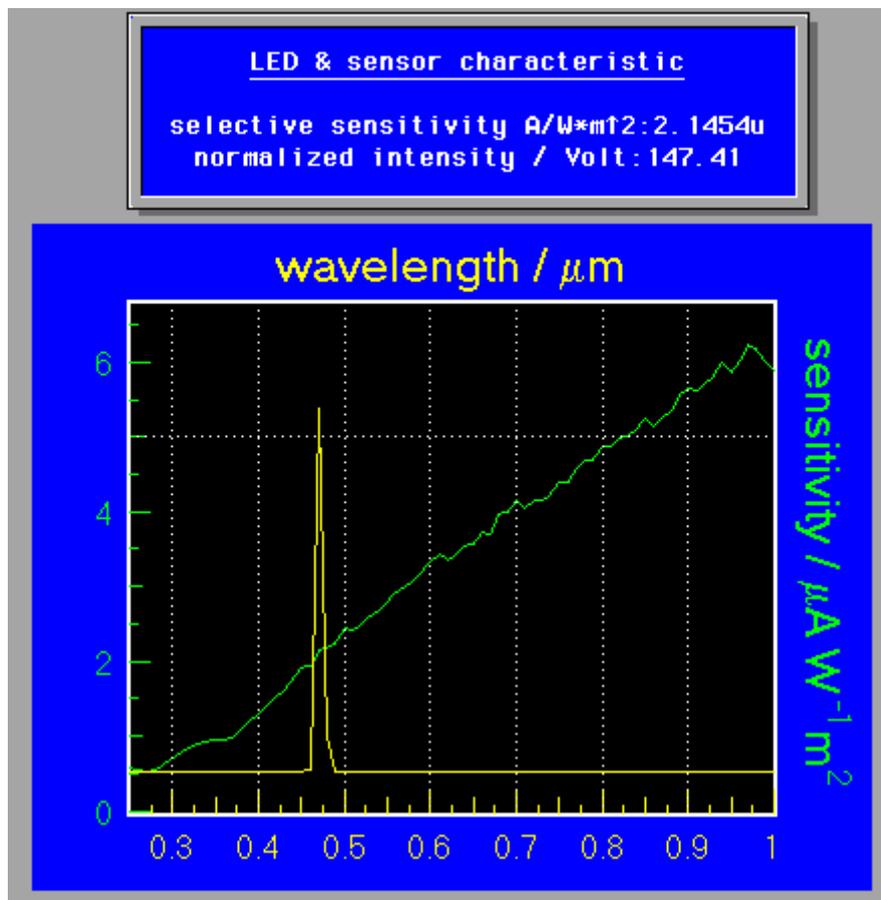


Fig. 71. After the input of the wavelength information, the calibration program calculates the characteristics for the LDA under test.

The calibration program now calculates the characteristics for the LDA under test. The values found are automatically introduced into the current CIMPS panel (Fig. 15) and can be stored (Fig. 72).

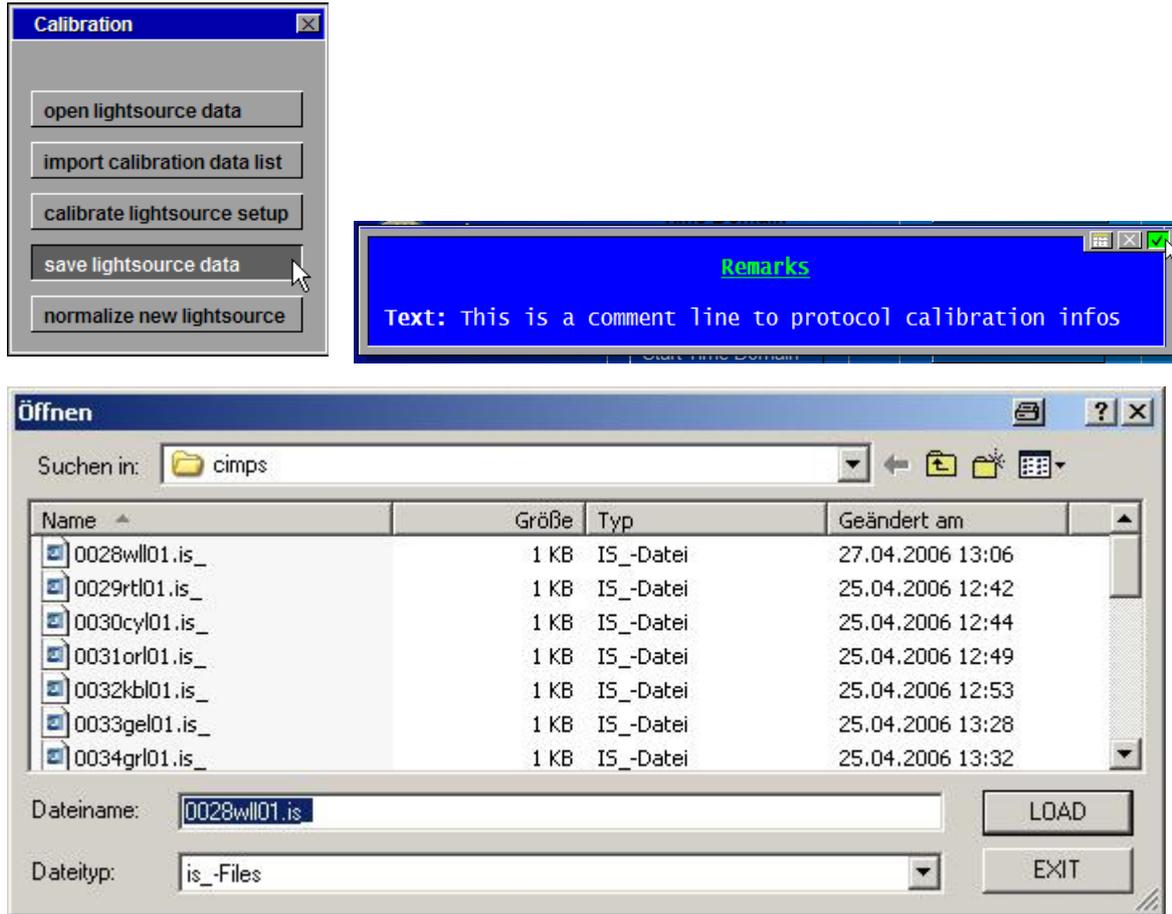


Fig. 72. Saving an individual light source characteristic data file found by calibration.

It is recommended to use a file name beginning with the series number digits. You may put in also a comment line (max. 255 characters) to document the calibration circumstances. Please consider, that the comment line is also used by the optional program packages like CIMPS-abs to mediate control information to the spectrometer.

For high-precision calibration purposes a spectrometer, which is directly supported by the CIMPS calibration software may be ordered from ZAHNER and used additionally.

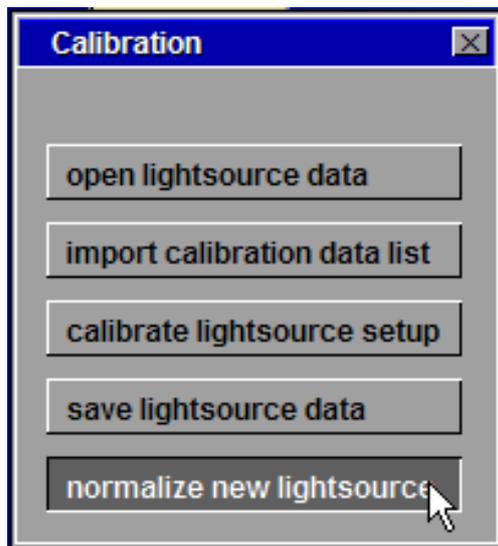


Fig. 73. Re-calibration of light sources, which were delivered after the delivery of the main CIMPS set-up.

Generally, a precise calibration can be performed only in the presence of all components, which have effect on the sensitivity of the set-up. This includes the sensor photo diode. At delivery time of the CIMPS set-up, all sources are calibrated exactly. Sources, ordered after this date, can only be calibrated exactly at customers site (calibration set-up necessary) or, if the CIMPS set-up is sent back intermediately to Zahner. Nevertheless, a relative accurate approximate calibration can be performed automatically, if a late delivered source is processed immediately with the 'normalize new lightsource' function (Fig. 73). It is based on the assumption, that the output power at the nominal calibration current does not change significantly between calibration at Zahner and normalization at customers site. After normalization one should replace the original calibration data file with the new one by means of the 'save lightsource data' function described above.

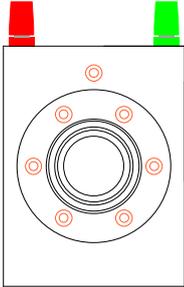
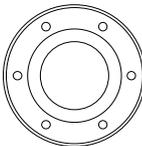
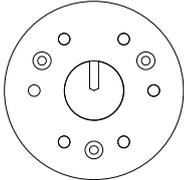
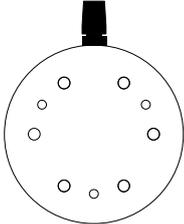
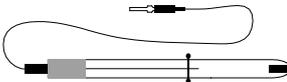
## 7 Tables, Optical and Mechanical Specifications

### 7.1 Specification of the Light Source Characteristics

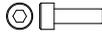
CIMPS can be used together with different sets of LED light sources. In order to enable the software to calculate in correct natural units, the light sources are delivered together with an individual specification data set in form of a calibration data file. Besides a spectral density data list of the relevant spectrum, it contains information on the dominant wavelength and line width and the calibration values determined in the measurement set-up discussed in the chapter below. You may use the input field shown in Fig. 15 right hand side to edit the characteristic parameters, if appropriate.

Parameter	Meaning	Unit
Normalized intensity / Volt, Factor FP (Eq. 2).	A certain voltage measured by the photo-sense amplifier and/or controlled by the source potentiostat belongs to a characteristic intensity measured in the calibration set-up.	Radiation energy density [ $W/m^2$ ] referred to one Volt measured at the photo-sense amplifier output.
Dominant wavelength	The wave length of the half intensity integral of the light source spectral energy distribution.	Wavelength in meter [m].
Half intensity line width	The width of the spectral energy distribution of the light source, assuming a bell shape.	$\Delta$ Wavelength in meter [m].
Intensity at 100mA	An estimate value for the light source intensity measured in the calibration set-up at the moment of delivery. It serves for the maximum intensity calculation (together with the LED maximum current) and for an estimate calibration of LEDs, delivered <i>after</i> the CIMPS set-up delivery. It can also be useful for a test of the LED aging.	Radiation energy density [ $W/m^2$ ] at an LED current of 0.1A.
LED maximum current	Specified maximum continuous LED drive current. Please recognise, that running a light source close to the maximum current will reduce the lifetime significantly. The shorter the wavelength, the more dramatic is this degradation effect.	Ampere [A].

## 7.2 PECC – Photo-Electrochemical Cell Components

Position	Count	Description	Drawing / Picture
1	1	cell body PTFE 80mmx60mmx25mm	
2	1	flange PTFE diameter 60mm	
3	1	window diameter 31.6mm	
4	1	o-ring sealing 26x2	
5	1	o-ring sealing 22x2	
6	1	specimen holder with basin PTFE diameter 60mm thickness 10mm	
7	1	working electrode holder with binding post Aluminium diameter 60mm thickness 8mm	
8	1	Platinum ring electrode	
9	1	Ag/AgCl reference electrode	

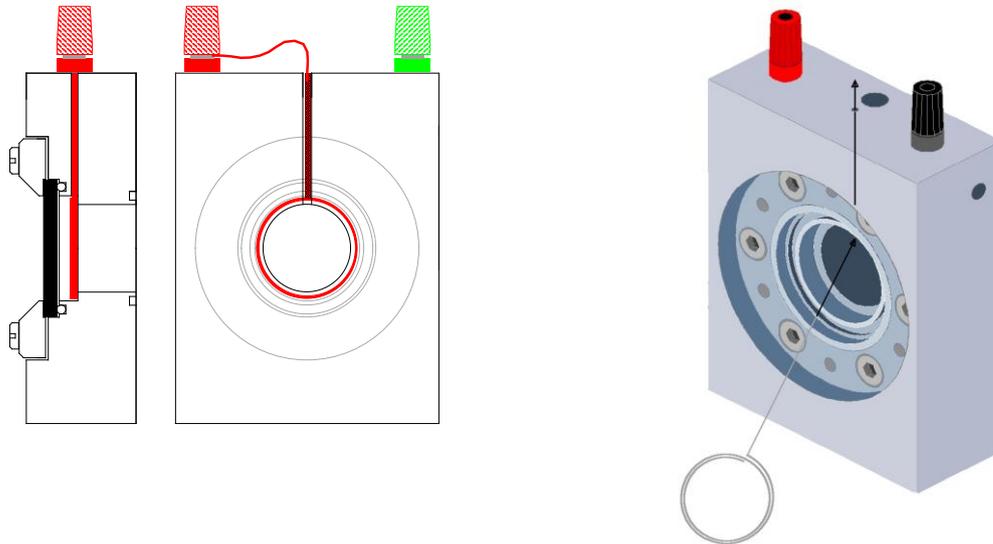
PECC - Cell components (continued)

<i>Position</i>	<i>Count</i>	<i>Description</i>	<i>Drawing / Picture</i>
10	6	bushing	
11	6	allen screw M3x10	
12	6	allen screw M3x25	
13	12	shim	

**PECC – tools & spare parts**

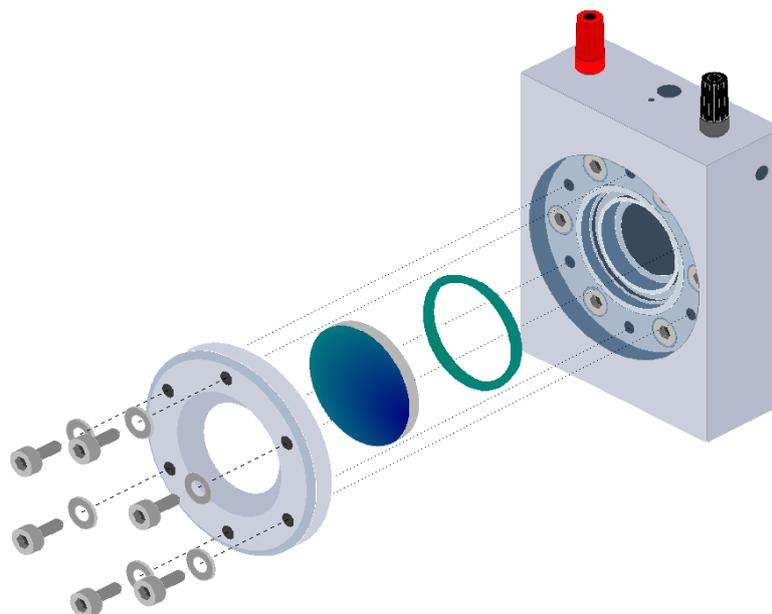
Position	Count	Description	Drawing / Picture
14	1	hex socket driver 1.5mm	
15	1	hex socket driver 2.0mm	
16	1	hex socket driver 2.5mm	
17	4	o-ring sealing 26x2	
18	4	o-ring sealing 22x2	

### The counter electrode (CE)



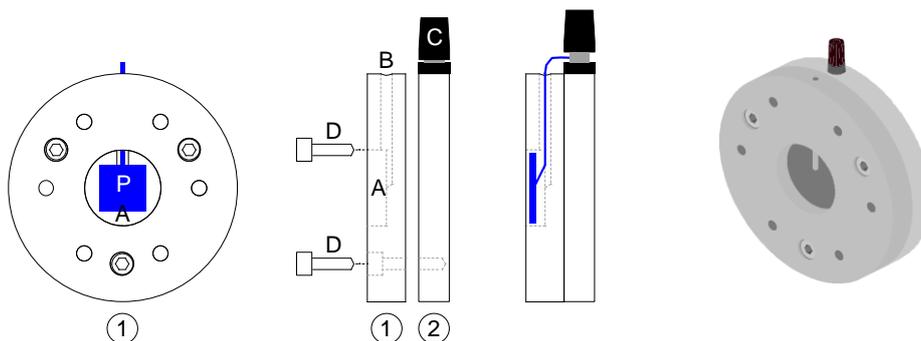
The Platinum counter electrode (CE) is located in the chamber behind the optical window. A 2 mm drilling hole leads the wire to the top of the cell body. The electrode will be fastened to the red connector.

### The optical window



In order to mount the optical window place the green 26x2mm o-ring into the groove at the front of the cell. Place the window above the ring and fix the flange with 6 screws M3x12.

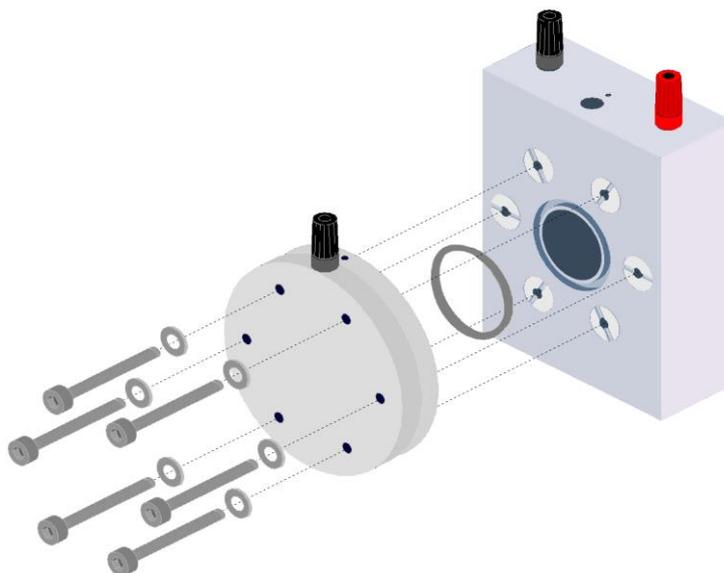
### The working electrode assembly (WE)



The working electrode assembly consists of an insulating specimen holder (1, PTFE) and a conducting plate (2, Aluminium). Specimen holder and plate are fixed by 3 screws M3x10 (D). They can easily be screwed off for cleaning purposes. In this configuration the required electrolyte volume is  $7.9 \text{ cm}^3$  and the light path length in the electrolyte is 23 mm.

Place the specimen (P) in the small basin (A) in the middle of the specimen holder and lead the electric contact (wire) through the hole (B). Finally contact the wire to the black binding post (C) of the plate.

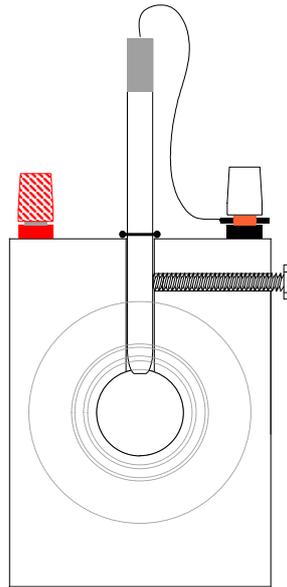
The working electrode assembly will be mounted at the backside of the cell body using the black 22x2mm o-ring and 6 screws M3x25.



The WE assembly can be used also “inverted”, turned  $180^\circ$ , if a metallic conducting sample under test with square or disk shape and dimensions between 25 mm and 34 mm length / 40 mm  $\varnothing$  is used. In this configuration the required electrolyte volume is  $6.3 \text{ cm}^3$  and the light path length in electrolyte is 18 mm. The assembly screws are then ending at part 1, PTFE and the conducting plate part 2, Aluminium is then pressing the sample on the O-ring. When fastening the screws in this case, consider the softness of the PTFE material!

The wetted (active) specimen area is then  $\approx 3.14 \text{ cm}^2$ . The estimate ratio between incoming light and light intensity on the sample is (in non-absorbing aqueous medium)  $\approx 3.16$ , so that an effective surface of  $1 \text{ cm}^2$  can be assumed for photocurrent efficiency calculations. In non-aqueous media specific absorption has to be considered (for instance Acetonitrile at 325 nm  $\approx 18$ ).

### The reference electrode (RE)

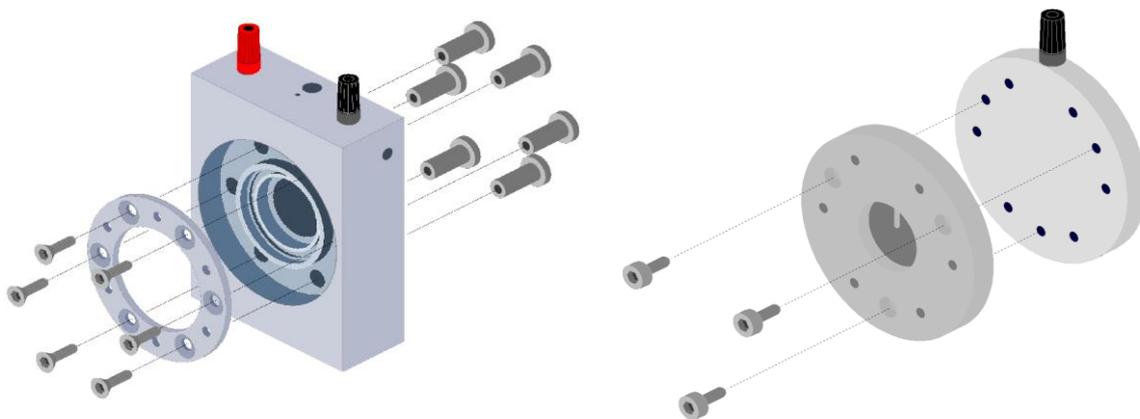


Place the Ag/AgCl reference electrode in the channel of 6 mm in diameter located in the middle of the top of the cell body. Then either fix the depth by using the small o-ring or the plastic screw at the right of the cell. To connect the RE to the potentiostat the black binding post should be used.

Attention: When using the plastic screw to fix the reference electrode you should tighten it with very little force only. Tightening the screw too hard may damage the glass body of the RE.

### Dismounting the PECC

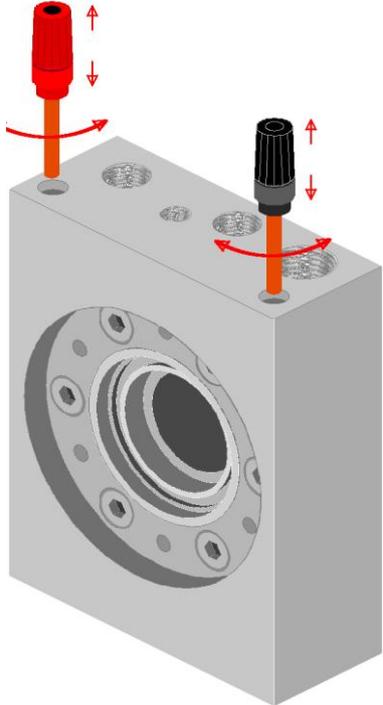
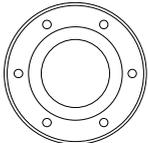
For cleaning purposes the PECC can totally be dismounted.



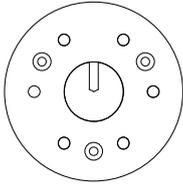
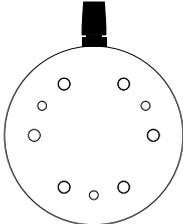
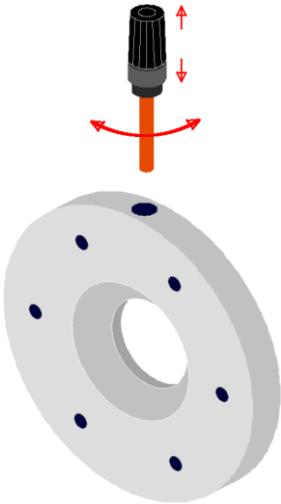
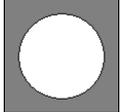
## 7.3 PECC2 – Photo-Electrochemical Cell Components

The optionally available PECC2 differs from the PECC mainly in the following properties:

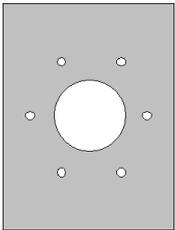
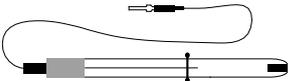
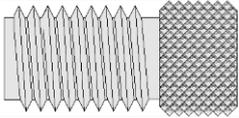
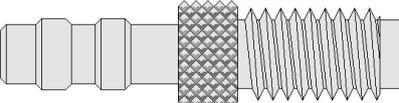
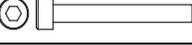
1. The cell body material is not PTFE, but PCTFE, which is harder and therefore enables more complex working structures.
2. The free diameter of the cylindrical electrolyte chamber is 18 mm in the case of the PECC2 instead of 20 mm in the case of the PECC.
3. Gas inlet and gas outlet tubes and olives are foreseen for gas purging in order to enable for instance oxygen free working.
4. The rear side of the PECC2 is covered with a stainless steel sheet which acts as
  - a.) contact material for the working electrode
  - b.) EMI shielding
  - c.) Transparent light blocker for absorbance measurement
5. The cell rear side aluminium mounting disk has a hole from the same diameter as the electrolyte chamber to act as light entrance and transparent light outlet for absorbance measurements.
6. Counter electrode, reference electrode and gas inlet / outlet contain additional O-rings or rubber disks for gas tightening.
7. A syringe with a long, blunt truncated needle is recommended to ease the filling / empty procedure without air bubbles. It is recommended to use the syringe, because the electrolyte filling can be done more precise and clean.

<i>Position</i>	<i>Count</i>	<i>Description</i>	<i>Drawing / Picture</i>
1	1	cell body PCTFE 80 mm x 60 mm x 25 mm	
2	1	flange PTFE Ø 60 mm	
3	1	BK7 / quartz window Ø 31.6mm	

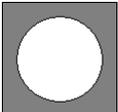
PECC2 - Cell components (continued)

Position	Count	Description	Drawing / Picture
4	1	o-ring sealing glass window 26x2 mm	
5	1	o-ring sealing rear side 20x2 mm or 20x2.5 mm	
6	2	o-ring sealing for gas inlet / outlet 3,5x1 mm	
7	1	rubber disk for counter electrode Ø4 mm	
8	1	o-ring sealing reference electrode 5,6x1mm	
9	1	specimen holder with basin for small samples  PTFE Ø 60 mm thickness 10 mm	
10	1	working electrode holder with binding post  Aluminium Ø 60 mm thickness 8 mm	
11	1	working electrode holder with binding post and hole for rear side illumination or transmission measurement  Aluminium Ø 60 mm thickness 8 mm  Please note, the working electrode itself is not included in delivery. TCO- coated glass can be ordered separately from Zahner.	
12	1	Conductive foam 30 x 30 mm	

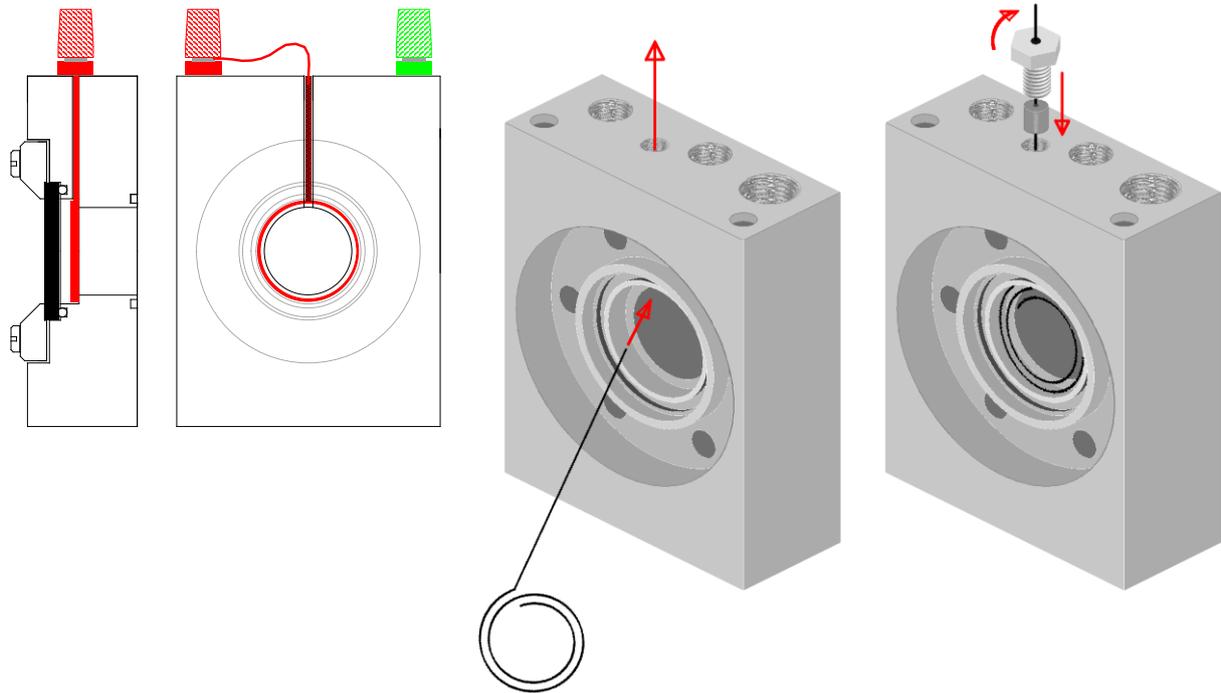
PECC2 - Cell components (continued)

<b>Position</b>	<b>Count</b>	<b>Description</b>	<b>Drawing / Picture</b>
13	1	Conducting metal sheet Stainless steel 80 x 60 mm	
14	1	Platinum ring electrode	
15	1	Ag/AgCl reference electrode	
16	1	Reference electrode fixture	
17	1	Counter electrode fixture	
18	2	Gas inlet / outlet fixture / olive, tube side Ø 5/6mm	
19	6	bushing	
20	6	allen screw M3x10	
21	6	allen screw M3x25	
22	12	shim	

**PECC2 – tools & spare parts**

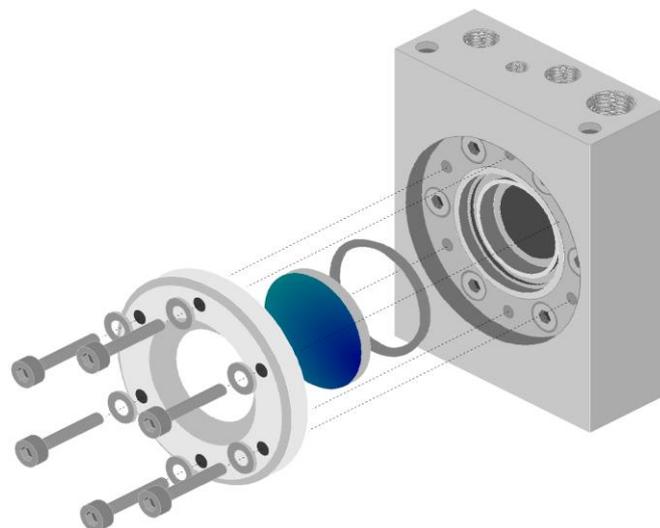
<b>Position</b>	<b>Count</b>	<b>Description</b>	<b>Drawing / Picture</b>
23	1	hex socket driver 1.5mm	
24	1	hex socket driver 2.0mm	
25	1	hex socket driver 2.5mm	
26	4	o-ring sealing 26 x 2 mm	
27	1	o-ring sealing 19 x 2.5 mm	
28	4	Conductive foam 30 x 30 mm	

**The counter electrode (CE) mounting**



The Platinum counter electrode (CE) is located in the chamber behind the optical window. A 2 mm drilling hole leads the wire to the top of the cell body. The electrode is tightened with a rubber disk by means of the fixing screw and the wire end must be fastened to the red connector.

**The optical window**



In order to mount the optical window place the green 26x2mm o-ring into the groove at the front of the cell. Place the window above the ring and fix the flange with 6 screws M3x12.

## The working electrode assembly (WE)

### Standard WE Configuration

The PECC2 can be used in the same way like the PECC for small sample diameters, or favourably with specimen samples, which are able to cover the electrolyte chambers diameter to some excess.

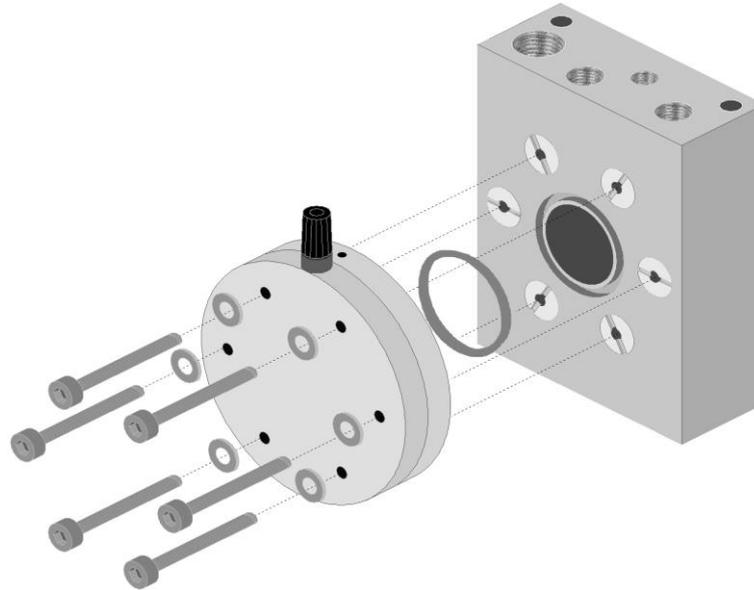
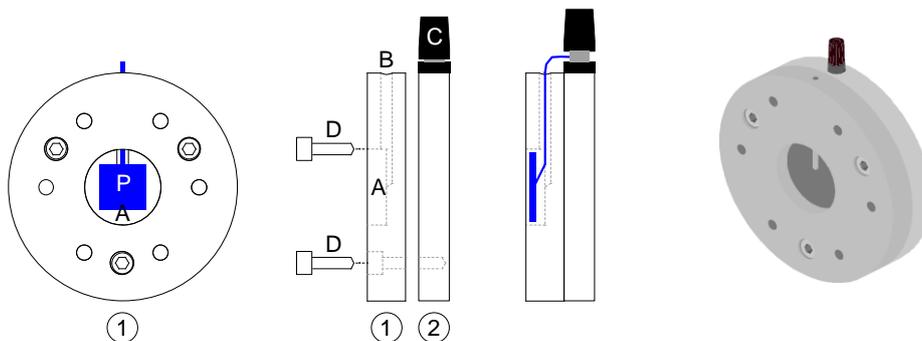


Fig. 74. Standard configuration for working electrode

The standard WE holder is used for samples smaller than 18 mm diameter, which are fixed inside the chamber of the PTFE flange. Using the standard WE holder the required electrolyte volume is 7.2 cm<sup>3</sup> and the light path length in the electrolyte is 23 mm.



The working electrode holder consists of an insulating specimen holder (1, PTFE) and a conducting plate (2, Alu). Specimen holder and plate are fixed by 3 screws M3x10 (D). They can easily be screwed off for cleaning purposes.

Place the specimen (P) in the small basin (A) in the middle of the specimen holder and lead the electric contact (wire) through the hole (B). Finally contact the wire to the black binding post (C) of the plate.

## Transparent WE Configuration

Samples, which have a minimum diameter of 25 mm (at least covering the electrolyte chamber tightening O-ring) and a maximum diameter of 40 mm (fitting still between the hexagonal arranged mounting holes), can be mounted tight and contacted automatically. The wetted (active) specimen area is then  $\approx 2.54 \text{ cm}^2$ . The required electrolyte volume in transparent WE configuration is  $5.9 \text{ cm}^3$  and the light path length in the electrolyte 18 mm.

If the sample material is conducting, the working electrode connection is established simply by means of the aluminium working electrode retainer ring.

If the sample material is conducting only on the electrolyte faced side (TCO glass, the light blue disk in the sketch), use the square conductive foam sheet with the disk shaped spare hole in the centre between the sample and the cell. It will establish an electric contact between the conducting TCO surface and the stainless steel sheet, which in turn has a contact wire to the aluminium working electrode retainer ring.

Please note the sample material (the light blue disk in the sketch) is not included in delivery as it is specific for each customer. Standard TCO-coated glass is available separately from Zahner on request.

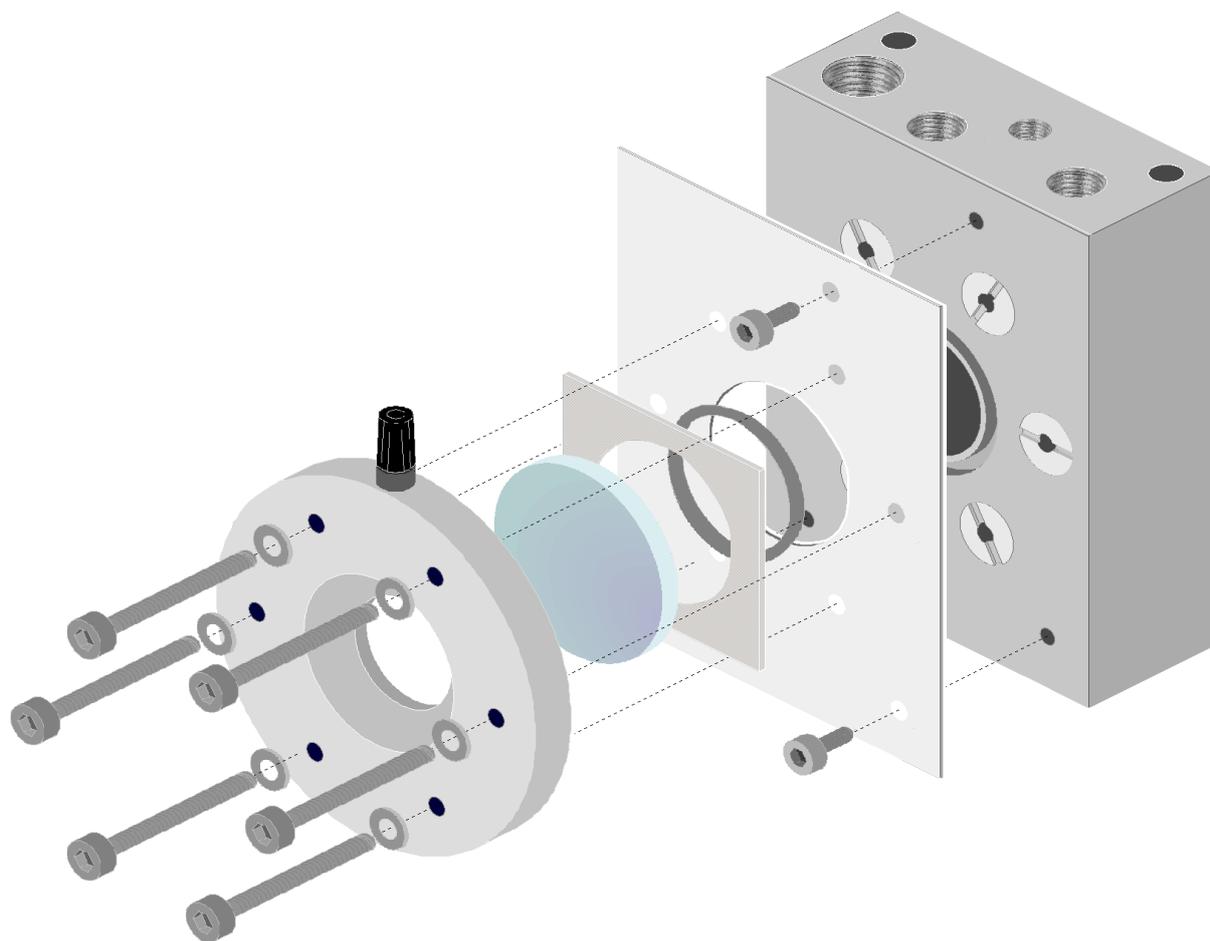
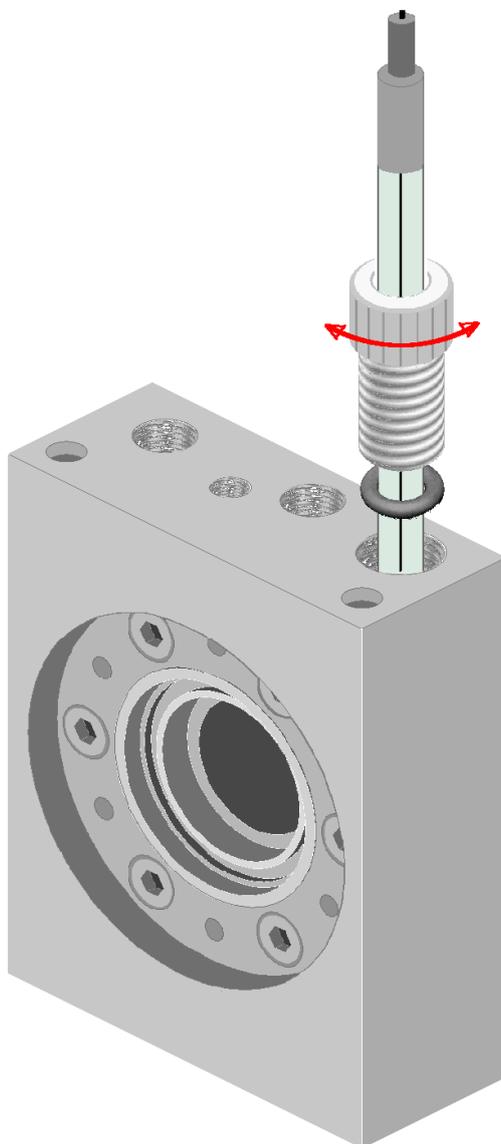


Fig. 75. Transparent configuration for working electrode

The estimate ratio between incoming light and light intensity on the sample is (in non-absorbing aqueous medium)  $\approx 3.16$ , so that an effective surface of  $0.81 \text{ cm}^2$  can be assumed for photocurrent efficiency calculations. In non-aqueous media specific absorption has to be considered (for instance in Acetonitrile at 325 nm the damping factor is  $\approx 18$ ).

**The reference electrode (RE)**

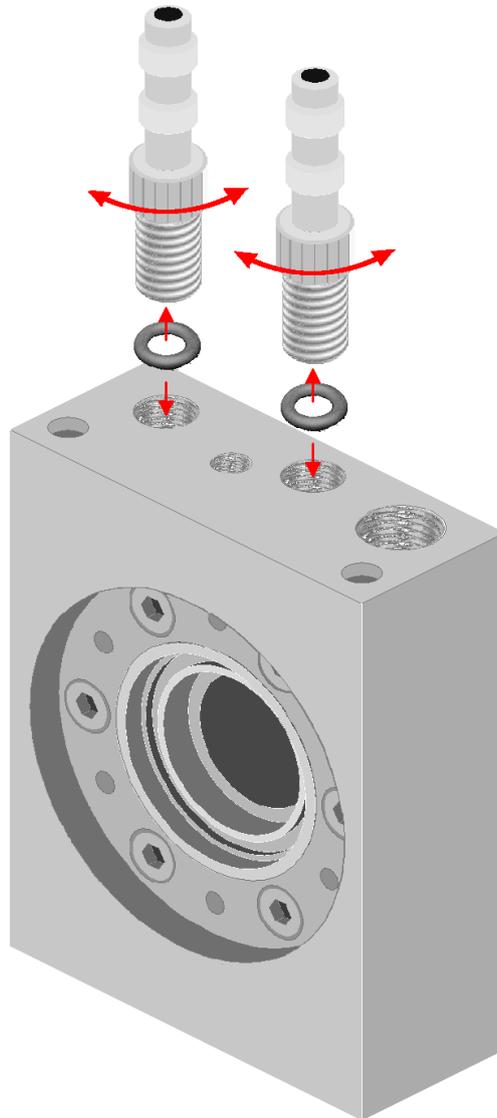


Place the Ag/AgCl reference electrode in the channel of 8 mm in diameter located on the right hand side (view from the optical window side) of the top of the cell body. Fix the depth by moving it cautiously to the hole ground, then move it back about 1-2 mm and fix it with the screw. This procedure is recommended after filling the cell with electrolyte in order to enable on the one hand a reliable electrolytic contact between electrolyte and reference cell mouth and excluding isolating gas bubbles in front of the electrode on the other hand. To connect the RE wiring to the potentiostat the black binding post should be used.

**Attention:** When using the PTFE screw to fix the reference electrode you should tighten it with very moderate force only, just to get it gas tight. Tightening the screw too hard may damage the glass body of the RE or the thread of the fixture screw. Tighten the screw with the fingers may be difficult due to lack of space. You may use a small pair of pliers with more success, but keep the stability of PTFE in mind !

It is recommended to check the electrolyte conduction path between RE and CE and between WE and CE respectively by means of a two-pole impedance measurement after installation. Use the potentiostatic three electrode configuration only after having performed the upper tests successfully.

**Installing the gas inlet / outlet**



Put the O-rings into the bottom of the gas inlet hole located on the left hand side (view from the optical window side) of the top of the cell body and into the gas outlet located slightly right out of the centre on top of the cell body. Screw the fixtures, until the connections are gas tight.

**Attention:** When using the plastic screw olives for gas inlet / outlet you should tighten them with moderate force only. Tightening the screw too hard may damage the thread of the fixture screw. Tighten the screws with the fingers may be difficult due to lack of space. You may use a small pair of pliers with more success, but keep the stability of PTFE in mind !

Use not too stiff gas tubes (best case based on silicon rubber, inner  $\varnothing$  5mm) in order not to break the PTFE worked olive fixtures.

**Dismounting the PECC2**

For cleaning purposes the PECC2 can totally be dismounted, like the PECC.

