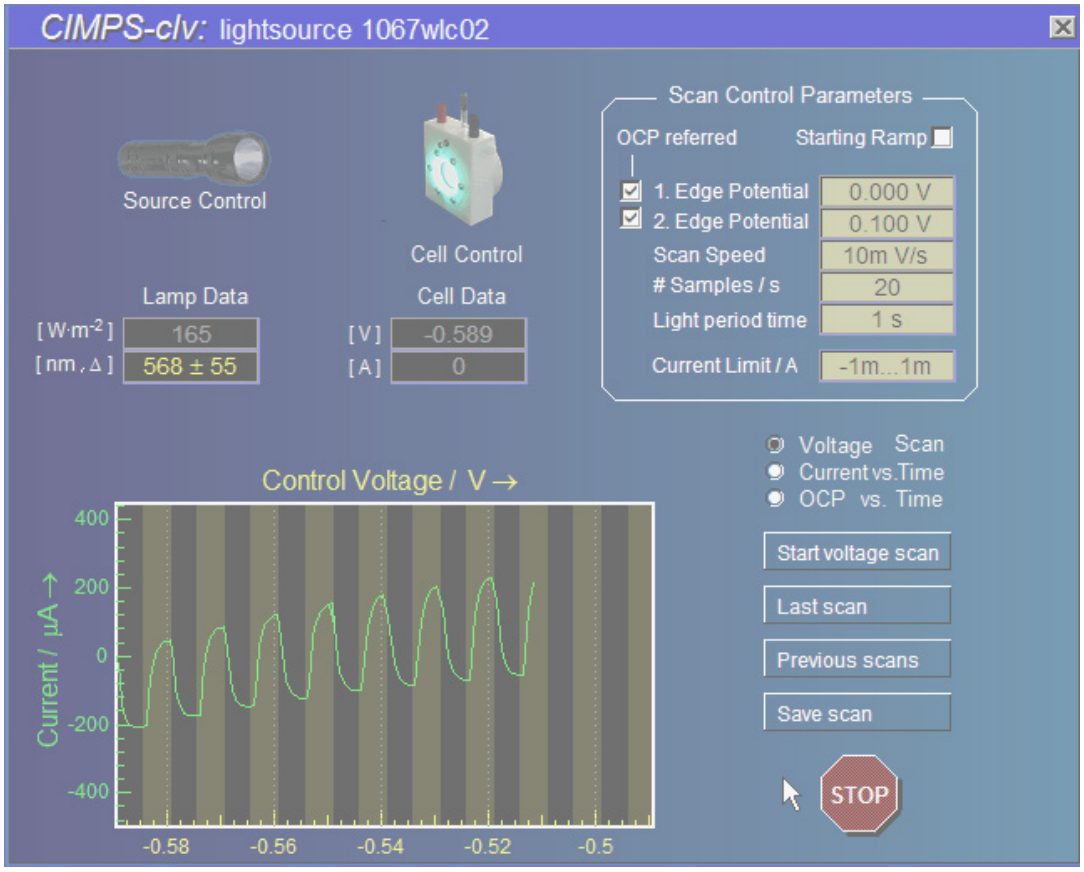
CLV

Chopped Light Voltammetry



1. Introduction

CLV is an often used technique to get a first impression of the photo-electrical response of an unknown system under test. Many photoactive systems may change sign and magnitude of the photocurrent when changing the potential.
CLV scans the current-to-voltage characteristic of a sample, while an illuminating light source is periodically switched on and off. The DC characteristic of a non-sensitive ("blind") object does not change under illumination. In the case of a photo-sensitivity, the DC characteristic is superimposed with the periodically changing contribution of the photocurrent.
CLV helps to find out the sensitive potential ranges and to estimate the relative photoelectric response compared to the DC current. From the behaviour of the current sign in relation to the illumination one can conclude to the nature of the photoelectrical process: n-semi-conducting related contributions cause anodic-, p-semi-conducting contributions cause cathodic photocurrent to flow. Photo-conduction can be identified, if the photocurrents sign changes according to the DC current sign.
The investigation of the time dependency of the photo-electrical response of a system may be of interest even without scanning the potential for instance due to drift or aging or due to the change of the external conditions. For this application the CLV can be set to photocurrent recording vs. time at constant polarization voltage and to photo voltage recording vs. time in open circuit mode.
CLV is included in the CIMPS standard methods catalogue and the hardware set-up is nearly identical to the CIMPS set-up.

2. Startup

Chopped light voltammetry (CLV) is easily activated by using the pull down menu as shown in Fig. 1. In order to open the pull down menu, click onto the Z-icon in the title bar of the Thales window.

Fig. 1 Start of CLV using the pull down menu

After the initial hardware self test, the main window of CLV is displayed (Fig. 2).

Fig. 2 Main screen of CLV

3. Light Source Control

Clicking the torch light icon opens the light source control menu (Fig. 3). If your light source is not detected automatically, use the *open calibration data* entry to load the calibration file of the light source used. Now intensity of the illumination phases can be directly set in W/m² by means of the *set intensity* function (Fig. 4). If the light source is actually switched off, you are asked for setting it in the on state (Fig. 5).

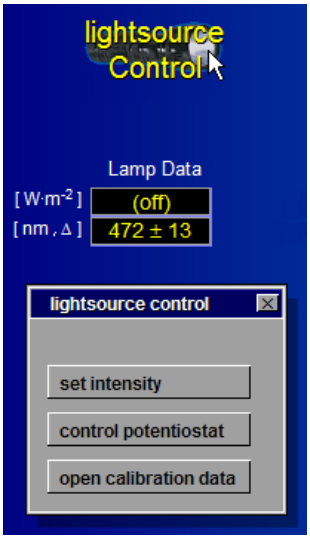


Fig. 3 Light source control

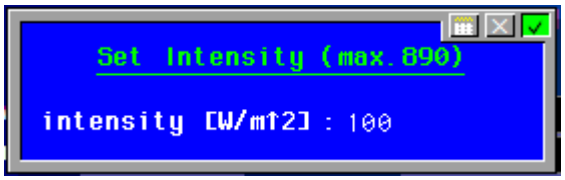


Fig. 4 Setting the light source intensity

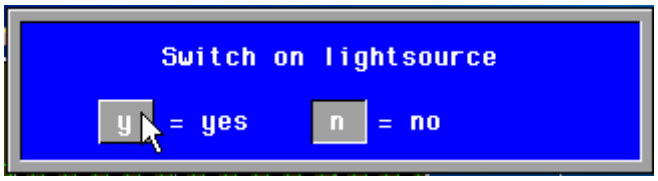


Fig. 5 Light source switch

The *control potentiostat* function is reserved here for testing the light source under manual control and for checking the DC current consumption of the illuminator.

4. Cell Control

Cell control (Fig. 6) can be used to access the control page "*testsampling*" of the cell potentiostat (internal potentiostat of Zennium / IM6). The state of the cell potentiostat is handled analogous to similar scan techniques (I/E, CV, POL) in the software with the actual state assumed as default state. If the potentiostat is in the "on" state, it will remain switched on after the scan / record. If the potentiostat is in the "off" state on start, it is automatically switched on in potentiostatic mode, except *OCP recording* mode is selected. The on-switching potential depends on the *Starting Ramp* mark in the *Scan Control Parameter* section. If the mark is not set it will be performed at the *1. Edge Potential* of the voltage scan, respectively the set polarization potential in *Current recording* mode. If the *Starting Ramp* function is activated, the switching is done at the actual OCP, followed by a ramp leading to the *1. Edge Potential*. In both cases the potentiostat is deactivated after the scan / Current record. Galvanostatic control cannot be used in CLV. It will be automatically changed to potentiostatic control.

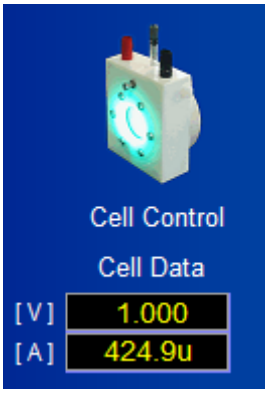


Fig. 6 Cell Control

5. Select Voltage Scan or Recording vs. Time

Use the mode selector (Fig. 7) to choose between linear voltage scan, current recording at constant polarization and OCP recording. The linear “voltage scan” choice is the most popular technique to get information about different photoelectric activity within the DC characteristic of a system under test.

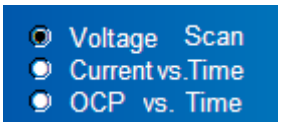


Fig. 7 Choose between linear voltage scan, current recording at constant polarization and OCP recording

Choose “Current vs. Time” if you intend to monitor the photocurrent response on chopped light at constant polarization voltage (potentiostat switched on at fixed potential). Application is for instance the investigation of ageing processes, drift with time or temperature or the reaction on external stimuli.
If you are interested on the photo voltage response on chopped light, choose “OCP vs. Time”. This method is performed with chopped light under OCP condition (potentiostat switched off).

5.1 Voltage Scan Control Parameters

Use the *Scan Control Parameters* (Fig. 8) to configure the settings of the voltage scan. Potential is swept from the 1st edge potential to the 2nd edge potential according to the *Scan Speed* setting. With *OCP referred* active as shown in Fig. 8 the edge potentials are understood as relative to the actual open circuit potential (OCP). By deselecting *OCP referred* the edge potentials are assumed as absolute (i.e. referred to 0 V) values. In case the 1st edge potential differs from the OCP, selecting *Starting Ramp* activates a voltage sweep from OCP to the 1st edge potential prior to the measurement in order to avoid a current transient.
The number of samples/s defines how many data points are recorded. The maximum is 100 samples/s. Light period time is considered as the sum of illumination time and dark time.

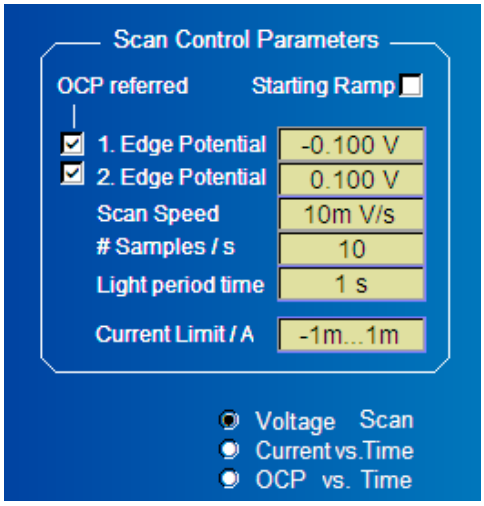


Fig. 8 Scan Control Parameters

During the scan the dynamic current limit function is active in order to protect sensitive samples against current overload. Use the *Current Limit / A* function to choose the appropriate current limit, which is used common to all voltage scanning programs within Thales.

5.2 Current vs. Time Control Parameters

Use the *Current vs. Time Control Parameters* (Fig. 9) to configure the settings of the current recording under constant polarization. The potential used is the “Set Potential”. With *OCP referred* active as

shown in Fig. 9 the polarization voltage is understood as relative to the actual open circuit potential (OCP). By deselecting *OCP referred* the set potential is assumed as absolute (i.e. referred to 0 V) values. In case the polarization potential differs from the OCP, selecting *Starting Ramp* activates a voltage sweep from OCP to the set potential prior to the measurement in order to avoid a current transient.
The number of samples/s defines how many data points are recorded per second. The maximum is 100 samples/s. Light period time is considered as the sum of illumination time and dark time. Different from the “Voltage Scan” mode, the recording time is not defined implicitly by the edge potentials and the scan speed. Therefore is has to be set directly by the input of “Recording time”.

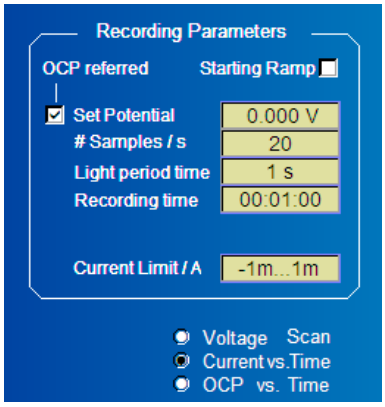


Fig. 9 Current vs. Time Recording Control Parameters

During the scan the dynamic current limit function is active in order to protect sensitive samples against current overload. Use the *Current Limit / A* function to choose the appropriate current limit, which is used common to all voltage scanning programs within Thales.

5.3 OCP vs. Time Control Parameters

Use the *OCP Recording Control Parameters* (Fig. 10) to configure the settings of the OCP mode of CLV. The number of samples/s defines how many data points are recorded. The maximum is 100 samples/s. Light period time is again considered as the sum of the illumination time and the dark time. The recording time must be set explicitly.

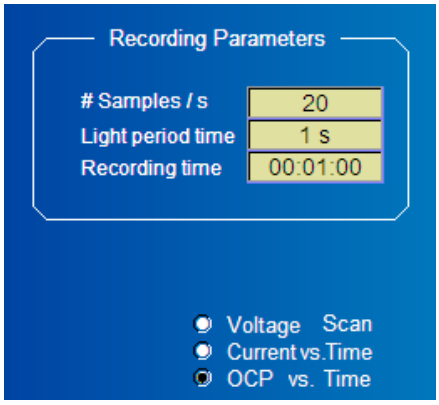


Fig. 10 OCP vs. Time Recording Control Parameters

6. Start Measurement

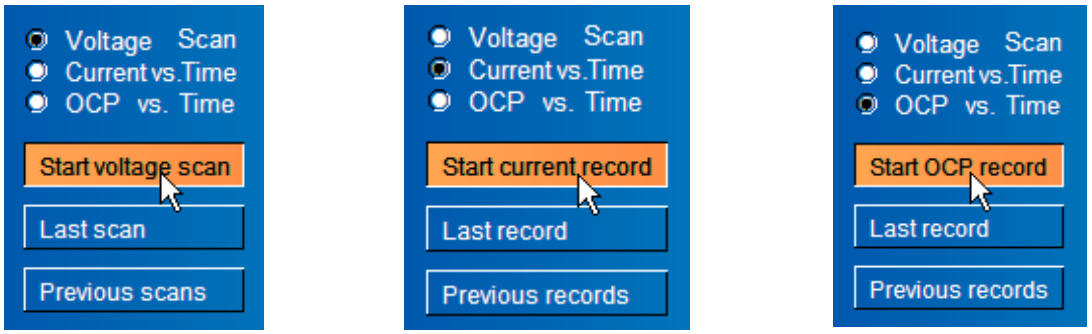


Fig. 11 The appearance of the start measurement button depends on the mode selection

The menu button (Fig. 11) actually starts the measurement procedure according to the settings. If the light intensity is still not set, you are automatically guided to the *set intensity* function (Fig. 4). In this case you are NOT asked for setting it in the on state (Fig. 5). Instead, the light off condition is assumed as the intended start condition for the first half light period and as default condition after the measurement completion. Complementary, if the light intensity was already set in on state prior to the measurement start, the light on condition is assumed as the intended start condition for the first half light period and as default condition after the measurement completion.
In “Voltage Scan” and “Current Recording” mode, depending on the state of the cell potentiostat and the *OCP referred* settings, you may enter an OCP settling phase after start (Fig. 12).

Fig. 12 OCP settling phase message

If the *Starting Ramp* function is activated, the system will now precede to the 1st edge potential respectively the polarization set voltage using a linear ramp (Fig. 13).

Fig. 13 Starting Ramp progress bar display

Fig. 14 CLV measurement display during scan

During the regular scan an online graphic will appear in the lower left corner of the CLV window (Fig. 14). The scan will proceed from the 1st edge potential to the 2nd edge potential, unless the measured current leaves the current limit window. In the case of a violation the potentiostatic loop is interrupted and a message (Fig. 15) is displayed.

Fig. 15 Current limit violation message

Besides, the scan can be stopped in the usual way also by pressing the *break* button or using the <esc> key or by pressing the middle mouse button. If the scan was started with the potentiostat in the on state at the 1st edge potential, the user has to decide, whether the actually reached voltage shall be kept or if the potentiostatic loop should be interrupted (Fig. 16).

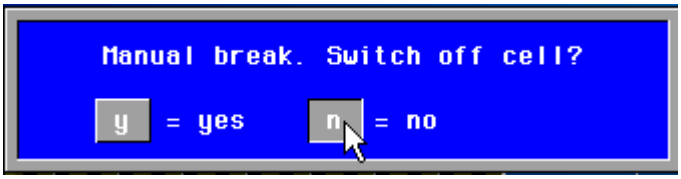


Fig. 16 Message after a manual break in the case of a default on state of the potentiostat.

6.1 Start Current Record

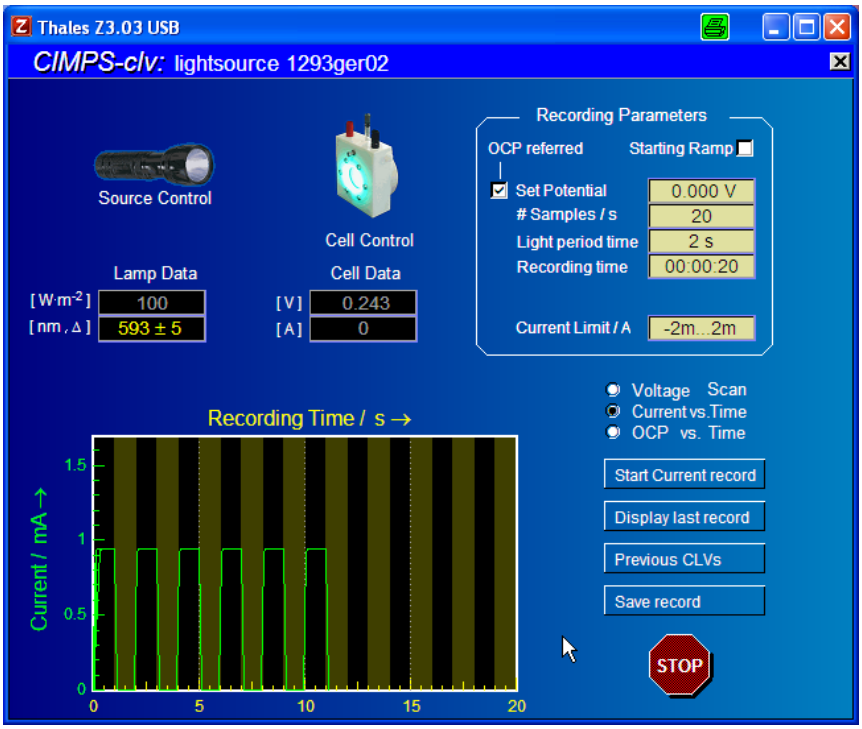


Fig. 17 CLV measurement display during current recording at constant polarization

If “Start Current recording” was chosen, X-axis of the immediate display is changed to time instead of voltage (Fig. 17). The considerations regarding the optionally starting ramp, the OCP reference of the set voltage and the OCP registration phase prior to starting are similar to the voltage scan mode.

6.2 Start OCP Record

Fig. 18 CLV measurement display during OCP recording

If “Start OCP record” was chosen, the X-axis of the immediate display is time like in the case of Current recording. The Y-axis is now Voltage (Fig. 18). Due to the OCP condition of the measurement neither starting ramp nor OCP reference are of relevance.

7. Last scan / record: visualize and export data

After a CLV scan is finished, the online graphic is refreshed and the user may enter the Last scan / record panel for more detailed graphic support (Fig. 19).

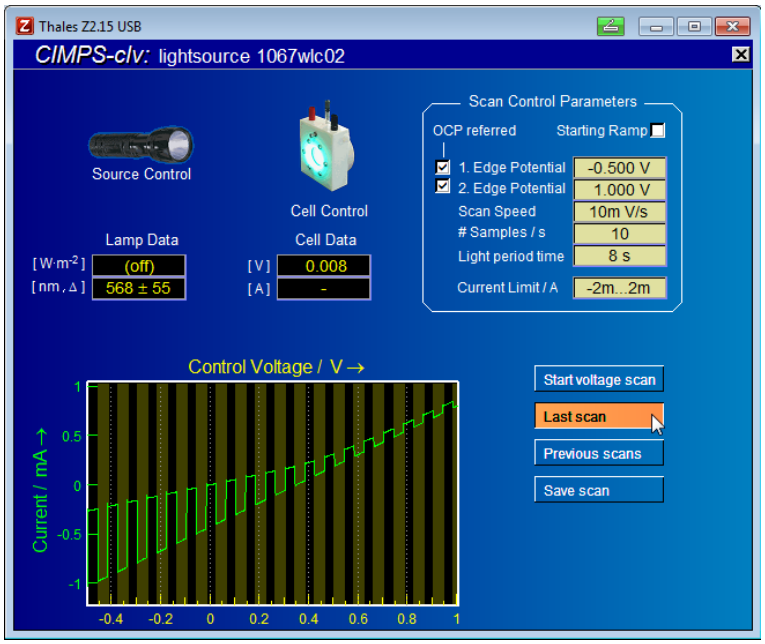


Fig. 19 The CLV display after a completed scan measurement. The *Last scan/record* button can be used in order to enter the *Last scan* menu.

Depending on the selected mode, the actual data are stored provisionally under the files
“c:\thales\cimps\sc_clv_last_vscan.isw”,
“c:\thales\cimps\sc_clv_last_crec.isw” or
“c:\thales\cimps\sc_clv_last_vrec.isw”
including the control parameters, even if the user does not save the data explicitly.

When entering the *Last scan/record* function, this data file is re-opened for display (Fig. 20). This will automatically reconfigure the parameter set to the last completed measurement. Intermediate changes of the *Scan Control Parameters* are overwritten.

The *Last scan* function can be used even if no actual measurement took place. By this, the user is enabled to parameterize CLV according to the last actual measurement instead of the default parameter set after start up.

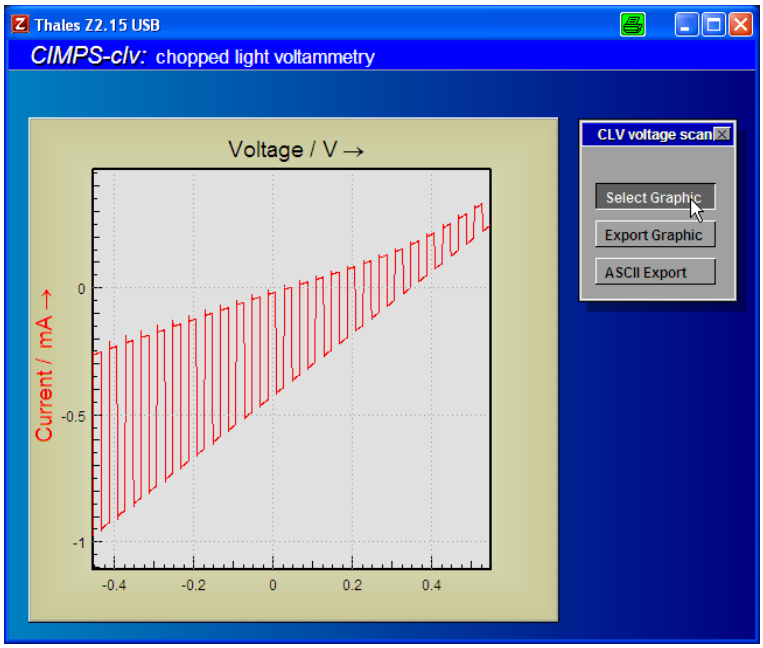


Fig. 20 Last scan menu

The user has the choice between different graphic representations (Fig. 21):

- Current vs. voltage
- Current vs. time
- Voltage vs. time
- Current and intensity vs. time (two y-axis)
- Current and voltage vs. time (two y-axis)
- Voltage and Intensity vs. time (two y-axis)
- POL format: Current in logarithmic scale and voltage vs. time (two separate plots, except after OCP recording Fig. 23)

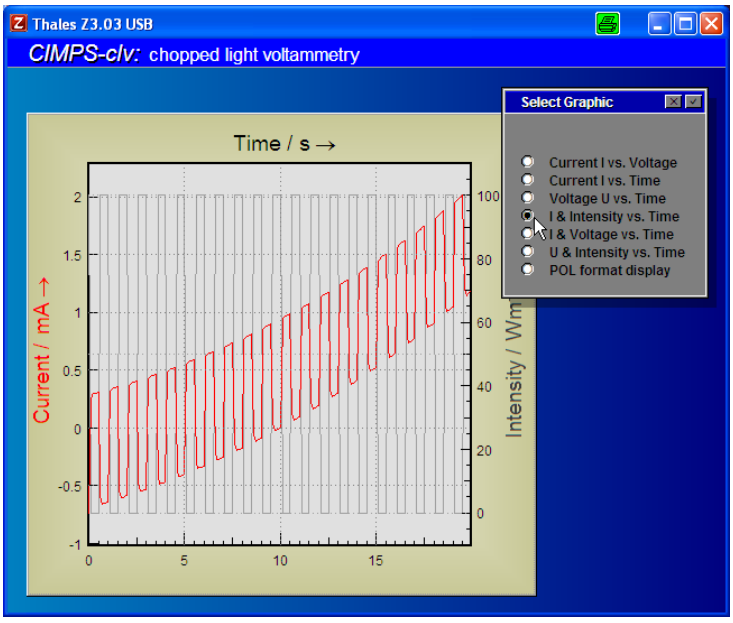


Fig. 21 Graphic selection panel

The currently displayed plot can be exported in the usual way of Thales to the Windows® clipboard, Thales CAD or saved as an enhanced metafile (emf) by means of the *Export Graphic* button (Fig. 20). The *ASCII Export* button (Fig. 20) creates a file with the columns voltage, current, time and intensity for use in third party software.

8. Save scan

After an actual CLV scan data can be stored using the *Save scan* button (Fig. 22).

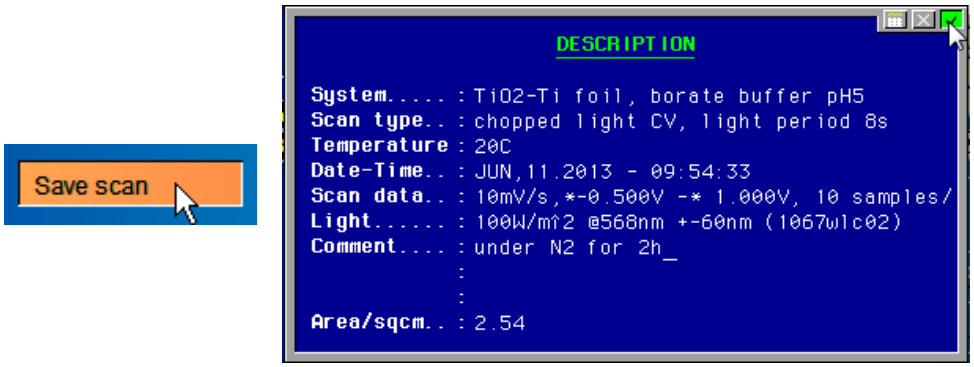


Fig. 22 Comment and save the data

Known measurement parameters are automatically provided by the *Scan comment* panel and most of the text is open for editing. The *Scan type…*, the *Scan data…* and the *Light…* line contain identification strings and the actual parameter settings for the configuration of CLV after re-opening. Changing these parameters by the user is ignored.
Confirming the *Scan comment* panel will open the Windows® file manager for the Thales binary POL/PVI.isw file format.
Alternatively, after selection of *POL format display* in the *Select Graphic* panel (Fig. 20 & Fig. 21), the data can be saved also in the *CorrPol* function environment (Fig. 23). Here the editing of CLV configuration parameters is not protected – do not alter the corresponding comment lines!

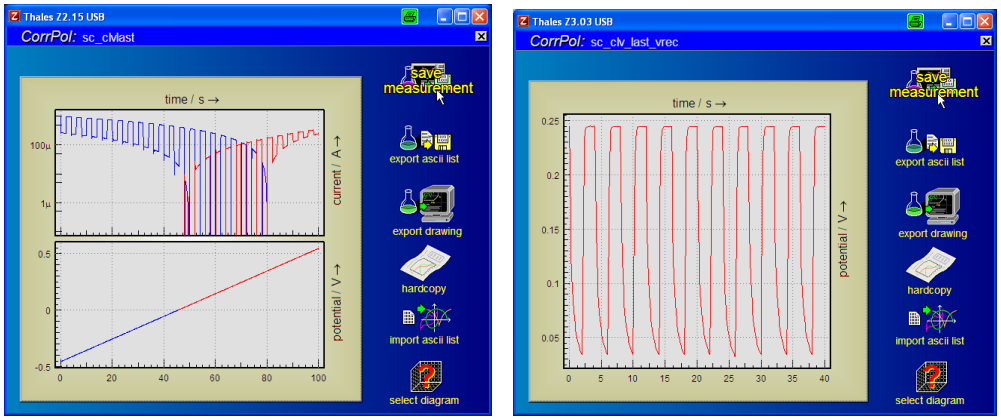


Fig. 23 POL display format displays and data save option

9. Previous CLVs

The function *Previous CLVs* enables the user to re-open previous explicitly saved CLV scans. Like the *Save scan* function (Fig. 24), *Previous scans* uses the POL/PVI data format and default directory.

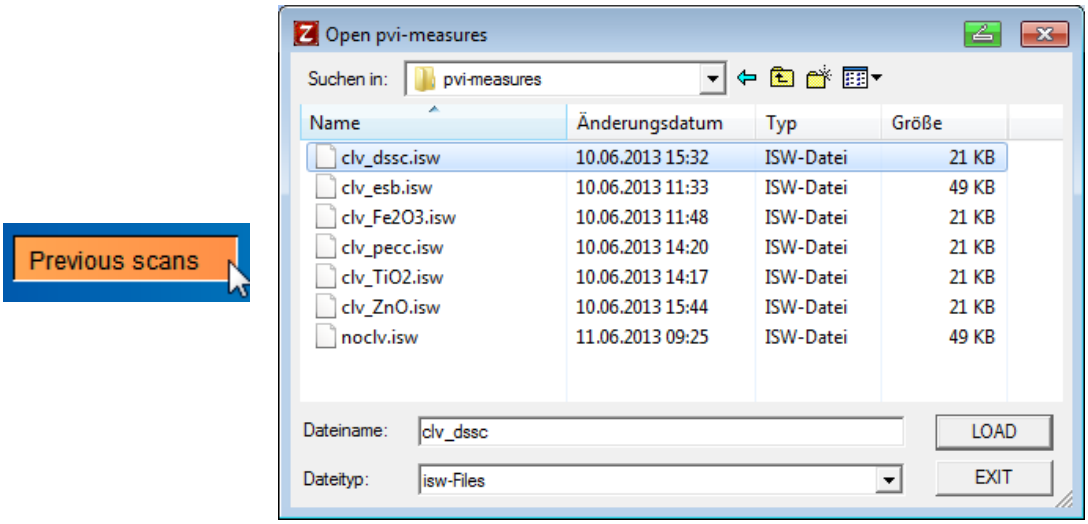


Fig. 24 Re-opening previous CLV scans by means of the *previous scans* data file dialog

Opening CLV data has a similar effect like described in the *last scan* chapter. Again, the actual measurement parameter settings are overwritten in order to configure the program for repetition of the previous experiment. The light intensity power is only overwritten, if the actual light source equals the light source used in the previous measurement. Like mentioned already in the chapter for the *Save scan* function, configuration parameters are stored in the first comment lines. If the keywords for identification of CLV data are not detected, a message (Fig. 25) will inform the user and the function will be aborted.

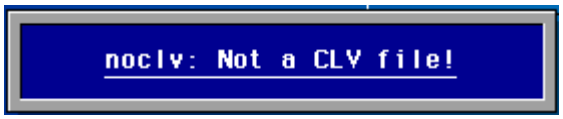


Fig. 25 This message will appear on an attempt to open a POL/PVI data file without CLV identity