

CV

*Cyclic Voltammetry*



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## Introduction

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Today linear potential scan methods are very useful tools for initial studies of new systems and proved to be reliable techniques to obtain information about fairly complicated electrode reactions. Cyclic voltammetric methods, in particular, have often been used in basic studies of electrochemical systems and in the field of analytical research.

Here follows a short overview on the features of the *Zennium* CV software:

Generally, CV is done under potentiostatic control. The control parameter is the applied potential, the response signal is the resulting time course of the current. The main feature is the application of cyclic linear voltage ramps with constant rise or changing sign between two voltage limits ("inverting potential"), where the slope of the scan is periodically inversed. Besides this, controlled starting and ending conditions are desirable. The *Zennium*-CV-software allows adjusting the potential and the duration of the start interval, the lower and the upper potential of reversion in the periodic part, as well as the potential and duration of the end interval independently. During the start interval the potentiostat forces the potential to a starting level. After expiration of the start interval the potentiostat will scan n-fold ( $1$  to  $10^6$ ) periodical between the two reversing potential. The voltage slew rate ranges from  $100 \mu\text{V/s}$  to at least  $100 \text{ V/s}$ . Note, that the *Zennium-pro* established with the optional ADF-extension and the *Zennium-X* allow higher rates, which is described in a separate chapter of this manual. At the end of the periodical part the potential may again be fixed to a certain end level for a certain period of time.

Anodic and cathodic current limiting can be selected separately. If one of these limits is exceeded, the corresponding potential of reversion will be corrected and the measurement can be restarted automatically. The technical data of the potentiostat has to be seen as the maximum selectable potentials and currents. IR compensation is carried out in the range of  $0$  to  $9\text{M}\Omega$  by means of calculated positive feedback. By means of the "recording window" functions a certain storage time interval for active data acquisition can be selected, allowing the suppression of unwanted recording, if a long pre-(or post-)treatment time is desired.

The application of CV as a dynamic measuring technique is based on the assumption of a clean linear rise/fall of the potential. In order to guarantee successful analysis, the electrochemical workstation has to treat the scan function with high priority and must avoid interruptions, for instance caused by auto-ranging functions. Therefore CV is performed in a fixed current measurement range, defined by the user through the limiting current input. It is important to select an appropriate current range to avoid restarting on current overdrive with shrunk voltage range on the one hand and a sufficient signal-to-noise ratio on the other hand. On demand the software supports the user with a comfortable ranging procedure, which scales the current range automatically after the first full transition between lower and upper reversing potential.

All CV measurement parameters can be entered through one CV panel and overseen on one glance. The meaning of each input will be shown by self-explanatory symbols of the calling buttons or comments within the corresponding input routine. Besides this, every button or active site on the panel will also display selective short hints on touch, and the context-sensitive help may be called by means of the alternate mouse button. When starting the experiment, a real time display will appear. After the completion (or on manual interrupt) of the measurement, data export and file management is provided.

Standard methods of CV

- Cyclic Voltammetry
- Cyclic Triangular Wave Voltammetry
- Chronoamperometry with Multiple Triangular Potential Sweeps

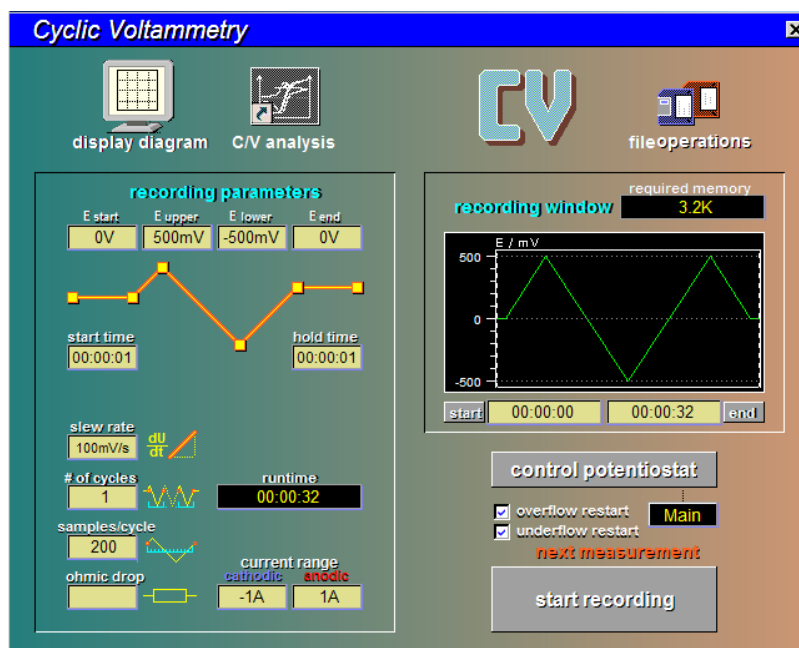
### Handling of the program CV

The menu technique common to all Thales functions is described in detail at the beginning of the general manual; also the course parameter as well as text input will take.

# CV Recording

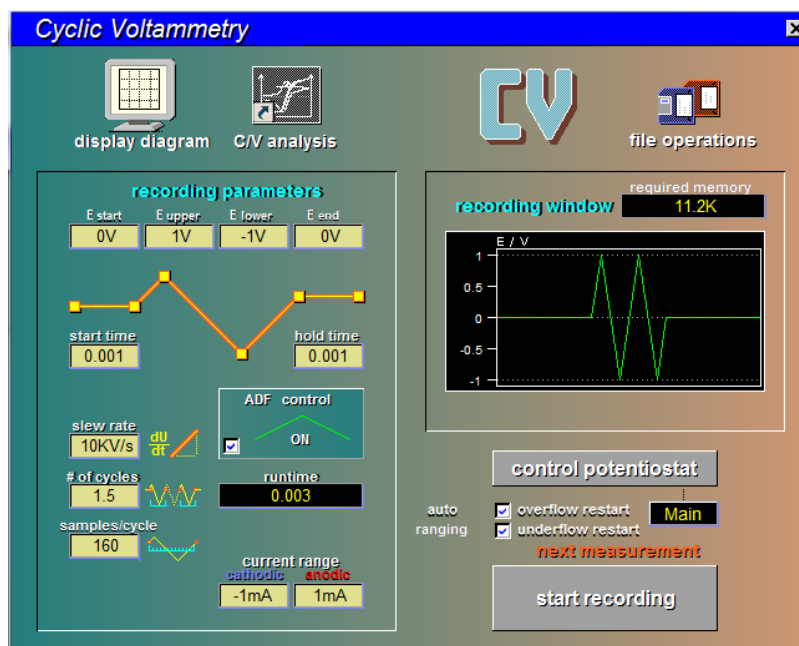
## 1. Recording Main Menu

CV starts with a graphical menu including a set of buttons and parameter input fields that can be activated by the user.

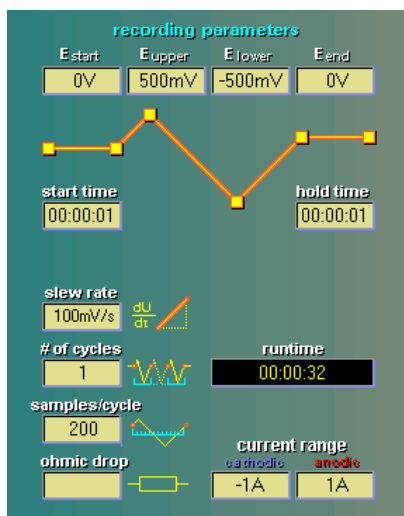


The functions can easily be recognized because of their titles and symbols which are plotted within the button. The main menu manages a group of sub-functions, which will be described briefly.

If the optional ADF function is present in the case of the *Zennium-pro* or the *Zennium-X*, the CV recording main menu appears a little different. The properties of ADF are described in detail in the chapter "Edit Parameters".



## 1.1 Edit Parameters



setting of control parameters

- start potential (holding potential prior to the cyclic part)
- start time (holding time prior to the cyclic part)
- end potential (holding potential after the cyclic part)
- end time (holding time after the cyclic part)
- upper and lower reversing potentials
- scan rate / resolution
- number of cycles of the periodic part
- etc.

## 1.2 Control Potentiostat



calls up the 'test sampling' panel, allowing the manual setting of the actual state of the ECW. For CV, the potentiostat has to be in the potentiostatic mode. An automatic starting ramp is encountered prior to the CV, if the actual set-potential of the potentiostat differs from the CV starting potential, or if the potentiostat is in the off-state. The ramp will then begin at the actual set-potential or at the actual OCP respectively.

## 1.3 Start Recording



starts the CV measurement under the condition displayed on the CV control panel.

## 1.4 Display Diagram



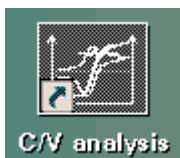
displays last CV measurement (no display, if no measurement was already performed or opened as data file from the storage).

## 1.5 File Operations



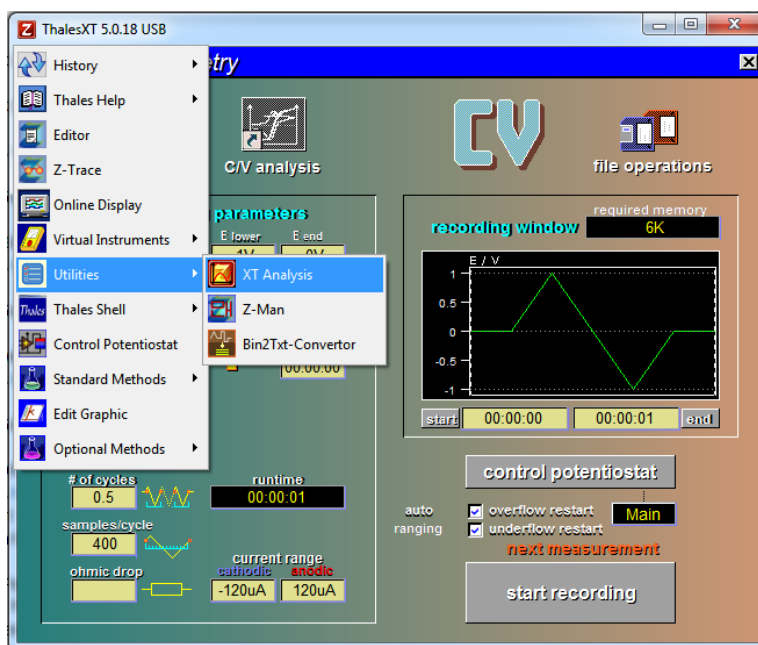
selects data file operations of CV data (save actual and load previous measurement, select i/o device and data path). Loading of a previous measurement will configure the ECW automatically according to the settings of this measurement.

## 1.6 Dynamic CV - Analysis



calls the CV evaluation program.

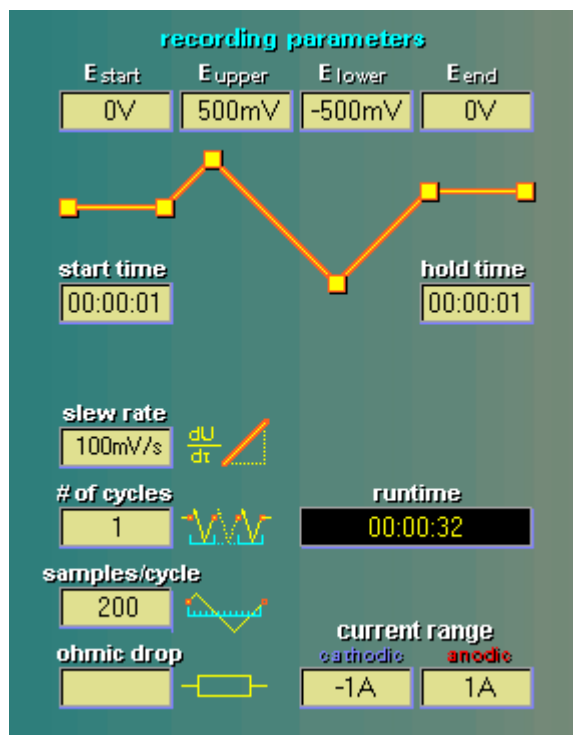
Alternatively Thales XT Analysis can be used for display and analysis of CV data. It can be started using the pulldown menu as shown below.



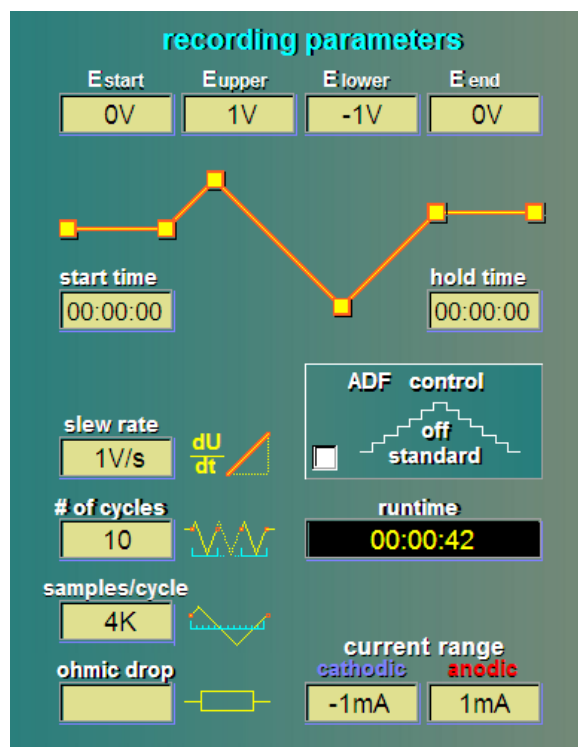


## 2. Edit Parameters

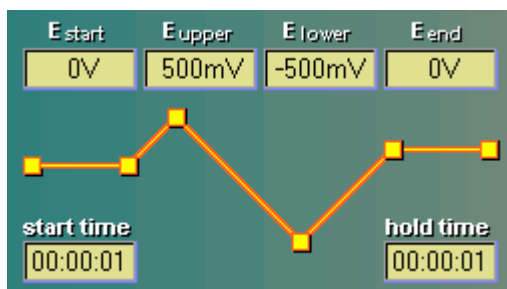
The actual control parameters in the CV control panel are indicated in the box called 'recording parameters'. See below.



The parameters can easily be modified by entering the input page of the control parameters. The „recording parameters“ section of the CV control panel comes up a little different if the optional ADF function is present in the case of the *Zennium-pro* or the *Zennium-X*.



## 2.1 Edge Potentials



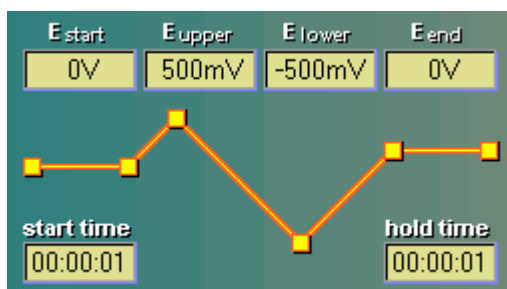
Four potentials can be defined independently. The 'start potential' offers the possibility to hold the probe at a certain potential before the cyclic part starts. 'Upper potential' and 'lower potential' define the upper and the lower reversing potentials. At the end of the measurement the potentiostat is fixed to the 'end potential'.

In order to change any of these potentials the corresponding button has to be activated and the new value has to be typed into the input box.

If one of the inverting potentials put is inadmissible in combination with the other one, the software will automatically enter the input routine for the other inverting potential successively (for instance, if the upper inverting potential is smaller or equal the lower one).

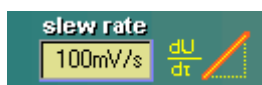
**Note:** Upper reversing potential must be more positive than the lower reversing potential. Use a negative slew rate for starting the CV scan in negative potential direction.

## 2.2 Starttime and Endtime



The duration of the starting phase and the final phase of the measurement are defined by the parameters 'start time' and 'end time'.

## 2.3 General Parameters

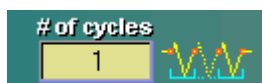


The potential is varied linearly with time. The speed of the voltage ramp is the 'slew rate' and is expressed in units of V/sec. Due to physical limits of the system the number of samples/s ("sampling rate")

$$\text{sampling rate} = \text{slew rate} \times \text{samples/cycle} / \text{cycle voltage span}$$

has to be less than 100 (IM6e/ex), 1000 (Zennium or IM6 with Coldfire signal processor) respectively 400000 if the optional ADF function is enabled in the case of the Zennium-pro or the Zennium-X. If the slew rate is put in beyond this limit, the count of samples/cycle is automatically reduced

**Note:** Use a negative slew rate for starting the CV scan in negative potential direction.

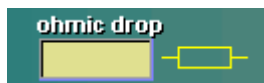


After the starting phase a ramp drives the applied potential from the start potential to the upper (lower) potential. Then the potentiostat swings n-fold ( $n = \text{\#cycles}$ ) between the reversing potentials. The sign of the 'slew rate' decides whether the upper- or the lower reversing potential is approached first. The cycle count definition may contain also half-cycles. Possible values are for instance 0.5, 1, 1.5, 10...



defines the sample data density of the acquired measuring points. Each sample results in a data triplet  $\langle U, I, t \rangle$ , with  $U$  being applied potential,  $I$  being measured current and  $t$  being actual runtime

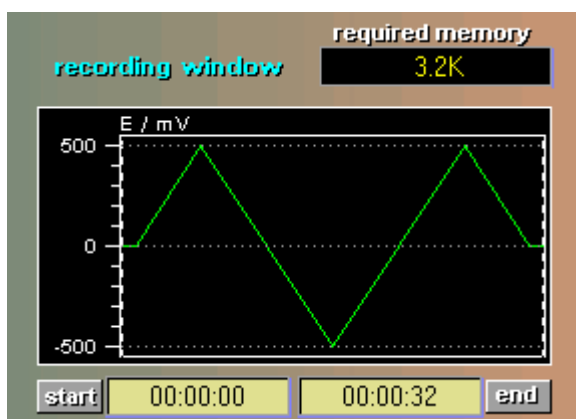
Like discussed in the previous remarks for the slew rate the maximum sample rate is considered by the software. If the count of samples/cycle is put in beyond the limit, the slew rate is automatically reduced.



Potential losses, e.g. caused by electrolyte resistance or ohmic resistances of the connecting lines can be compensated by positive feedback. By using the actual cell current, a drop potential is calculated. This potential is added to the actual ramp potential. Ohmic drop may be compensated up to a resistance of  $R_{\max}=9M\Omega$ . An input of a question mark instead of a numeric value will force an automatic ohmic drop determination cycle by the ECW.

**Note: Ohmic drop compensation has to be applied carefully. Any positive feedback will reduce the stability of the potentiostatic feedback loop. Best to compensate at maximum up to 90% of the estimated electrolyte resistance. Generally it is better to use a set-up avoiding excessive drop (for instance a micro electrode array instead of a standard working electrode) instead of compensation! If the optional ADF function is enabled, Ohmic drop compensation is not available.**

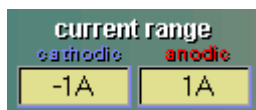
## 2.4 Recording Window



The function 'recording window' defines a time interval with active data acquisition. This interval covers the whole running time as default setting. The window is defined by 'start' and 'end' margin. The use of the 'recording window' offers the possibility to execute a pre-treatment of certain cycles without data acquisition before recording a certain interval of interest. The buttons <start> and <end> could be activated to change the recording window and to move the corresponding margin with help of the mouse or the cursor keys. The input fields will handle the direct input of the start- and end time of the active recording.

The 'recording window' function is disabled in the case, the ADF function is enabled.

## 2.5 Current Limiting



Anodic and cathodic current limiting can be selected independently. If one of these limits is exceeded, two kinds of action, depending on the setting of the 'auto restart' option, will be caused.

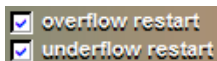
The absolute maximum value of both limits selects the shunt resistor and with that the current resolution (fixed range selection). The following table describes the effective current resolutions for the standard Zennium unit (and the IM6). The lines indicated with a \*\* are available only, if an HIZ probe is installed.

| Current range | shunt resistor | current resolution |
|---------------|----------------|--------------------|
| 2.5(3)A       | 10mΩ           | 1.2mA              |
| 2.5(3)A       | 0.1 Ω          | 120 μA             |
| 300mA         | 1 Ω            | 12 μA              |
| 110mA         | 10 Ω           | 1.2 μA             |
| 40mA          | 100 Ω          | 120 nA             |
| 4mA           | 1 kΩ           | 12 nA              |
| 400uA         | 10 kΩ          | 1.2 nA             |
| 40uA          | 100 kΩ         | 120 pA             |
| 4uA           | 1 MΩ           | 12 pA              |
| 400nA         | 10 MΩ          | 1.2 pA             |
| 40nA          | 100MΩ          | 120 fA**           |
| 4nA           | 1GΩ            | 12 fA**            |

The following table is valid for *Zennium-pro* and *Zennium-X* instruments:

| Current range | shunt resistor | current resolution |
|---------------|----------------|--------------------|
| 3(4)A         | 10mΩ           | 0.5 μA             |
| 3(4)A         | 0.1 Ω          | 500 nA             |
| 300mA         | 1 Ω            | 50 nA              |
| 110mA         | 10 Ω           | 5 nA               |
| 40mA          | 100 Ω          | 0.5 nA             |
| 4mA           | 1 kΩ           | 50 pA              |
| 400uA         | 10 kΩ          | 5 pA               |
| 40uA          | 100 kΩ         | 0.5 pA             |
| 4uA           | 1 MΩ           | 50 fA              |
| 400nA         | 10 MΩ          | 5 fA               |
| 40nA          | 100MΩ          | 0.5 fA             |
| 4nA           | 1GΩ            | 50 aA              |

## 2.6 Overflow / Underflow Restart Option

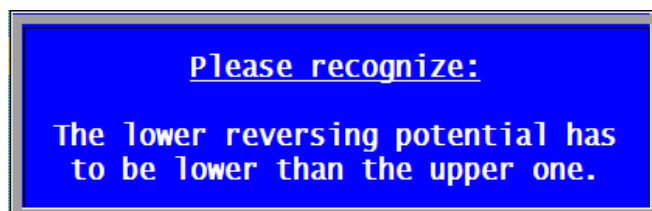


The Overflow / Underflow Restart Option provide an auto-range function for the CV measurement. The unavoidable interference of current range changes on the linearity excludes auto-ranging during a fast CV sweep. Therefore the Overflow / Underflow Restart function repeats the first cycle of a CV sweep, if a current overflow (violation of the current limit) or an underflow (the actual current range sensitivity is too small to provide accurate current data) occurs.

Restart on overflow or restart on underflow can be selected independently. The restart option check boxes work like toggle switches. Depending on the settings the following actions will be executed:

| overflow restart  | action on current limit violation                                                                          |
|-------------------|------------------------------------------------------------------------------------------------------------|
| off               | - measurement will be terminated<br>- potentiostat will be switched off                                    |
| checked           | - the correspondent edge potentials will be corrected<br>- the measurement will be restarted               |
| underflow restart | action on current underflow                                                                                |
| off               | - measurement will be continued                                                                            |
| checked           | - a new more appropriate current measurement range will be selected<br>- the measurement will be restarted |

**Note:** It is possible for the user to put in inadmissible parameter values and insist on those, by escaping from the input boxes, suggested by the software for correction purpose. Therefore CV checks the whole parameter set again when entering CV, if parameters are changed by the user or if a measurement shall be started. In order to inform the user on incorrect parameter settings, corresponding message boxes like the following one will appear:



## 2.7 Using the Analog Function Generator for CV

### 2.7.1 Introduction

Here follows a short overview on the features of the Zennium CV software: *Electrochemical Applications Zahner 1/96*

„When I'm examining objects dominated by double layer capacities, my cyclic voltammograms (CV) sometimes show strange effects. What is the reason for these effects?“

Seeming simple, capacities are not at all easy objects for an electrochemical measuring system. One reason for problems may be the instability of the feedback loop of the potentiostat used. The capacity adds phase shift to the loop. So undetected parasitic oscillations of the potentiostat may produce irregular results such as "starry skies" or severe current offsets.

Another problem arises with the measuring method itself used by certain equipment. In the era of computers it seems easy to change from the traditional analogue scan technique to its digital approximation by a small steps staircase technique. This task can be done by a software controlled

D/A-converter. The advantage of such a technique is the possibility to easily produce arbitrary waveforms, for instance stable slow signals (slew rate down to zero). The measurement itself too can be performed with the computer using A/D-converters. This is the base for flexible and user-friendly CV equipment - but the staircase-sweep-approximation idea is too simple to be good! Signals, created by a DA-converter remain discrete. Even if one tries to increase the resolution dramatically, it will stay finite. On the other hand the theories of CV techniques claim steady sweep signals. Regarding capacitive objects will help to focus on this important difference.

If one applies a voltage signal  $U(t)$  to a capacitor, the current  $I(t)=C \cdot dU/dt$  will flow. A constant slew rate results in a constant current. Discrete steps will cause current pulses with  $\delta$ -pulse shape - that means in theory infinite height for an infinite short time interval but with a well defined integral charge of  $Q=C \cdot \Delta U$ . In practice the  $\delta$ -pulse will be distorted to a short pulse of high amplitude. Its shape is determined by the pulse response of the potentiostat and parasitic effects. If the measurement technique samples the response signal after a short time delay relative to the step, the result must be wrong! The only way to get a correct current result is to measure the charge by integrating the total step interval and calculate the mean current. This calculated current value is identical with the one measured with the continuous method.

How can you find out, if your equipment uses this "clean" integrating CV technique? Take the enclosed aluminium electrolyte capacitor and perform a test measurement. Choose, for instance, a triangle scan of  $\pm 1$  V at  $\pm 100$  mV/s slewrate. The approximate capacitance value of  $1 \mu\text{F}$  should cause a square wave of  $\pm 0.1 \mu\text{A}$  current to flow. Consider the capacity tolerance of  $-5 \% / +25 \%$ . Check the correct capacity using an impedance measurement at low frequency (e.g. 1 Hz): Now the measured current should fit the calculated current exactly.

If not, call the service-hotline of your equipment's manufacturer!

## 2.7.2 Switching between digital and analog function generator

In case the ADF-option is enabled (standard in *Zennium-X*, optional in *Zennium-pro*), one can select either the digital function generator (ADF off, left hand side below) or analog function generator (ADF on, right hand side below).

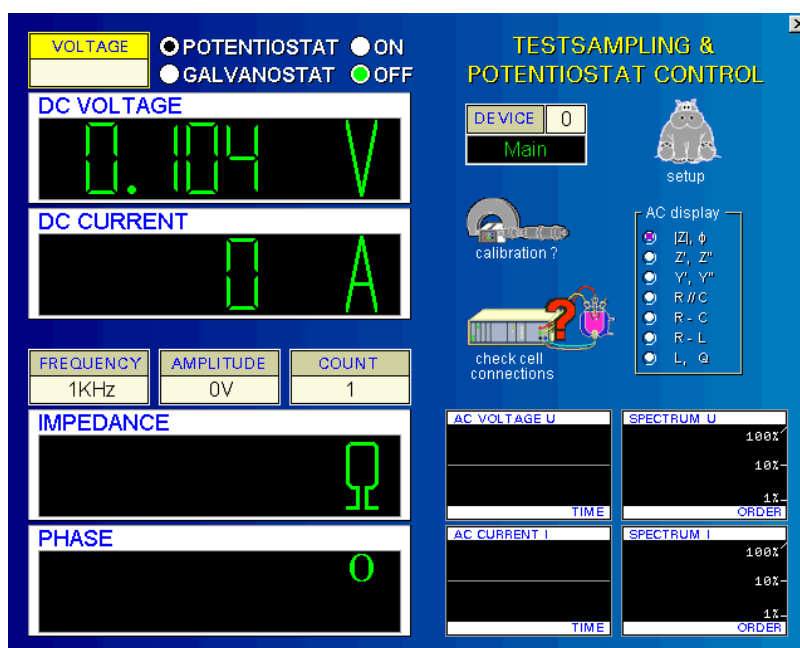


### 3. Control Potentiostat

#### control potentiostat

This option enters the potentiostat control panel of the ECW. The state of the potentiostat is set there. Here the potentiostat can be set to the CV starting potential and switched on manually, what will avoid the automatic insertion of a start ramp between the actual potential and the CV starting potential. The ramp speed may be altered in the general measurement set-up under the point "DC-more".

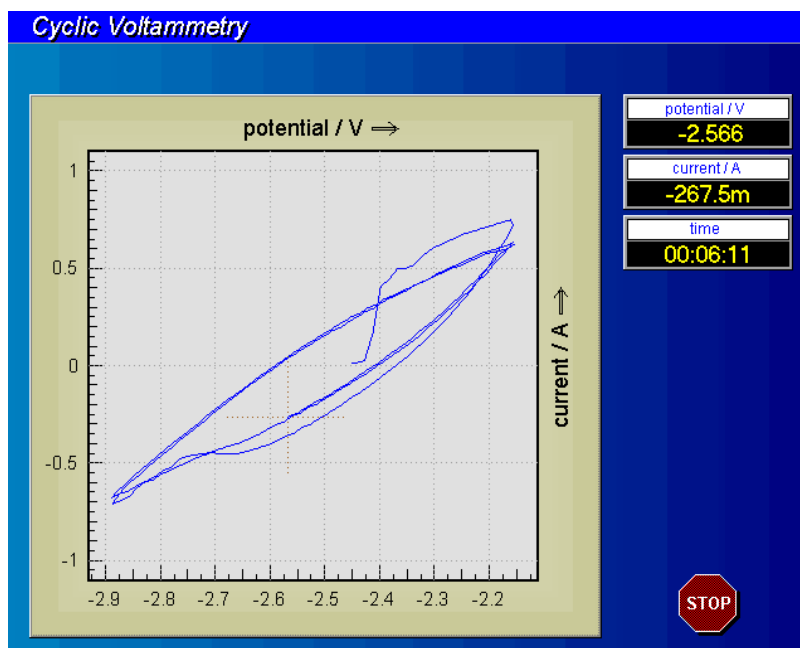
Also the final condition of the potentiostat can be selected here. If a CV measurement is started with the potentiostat switched on, the potentiostat will remain operational after the CV measurement has been completed. If the potentiostat has been switched off before starting a CV measurement it will be switched off at the end of the measurement.



## 4. Next Measurement

start recording

After all parameters have been set properly, a new measurement can be started by activating the button <start recording>. If a new measurement is started, the program will prompt the recording window shown below.



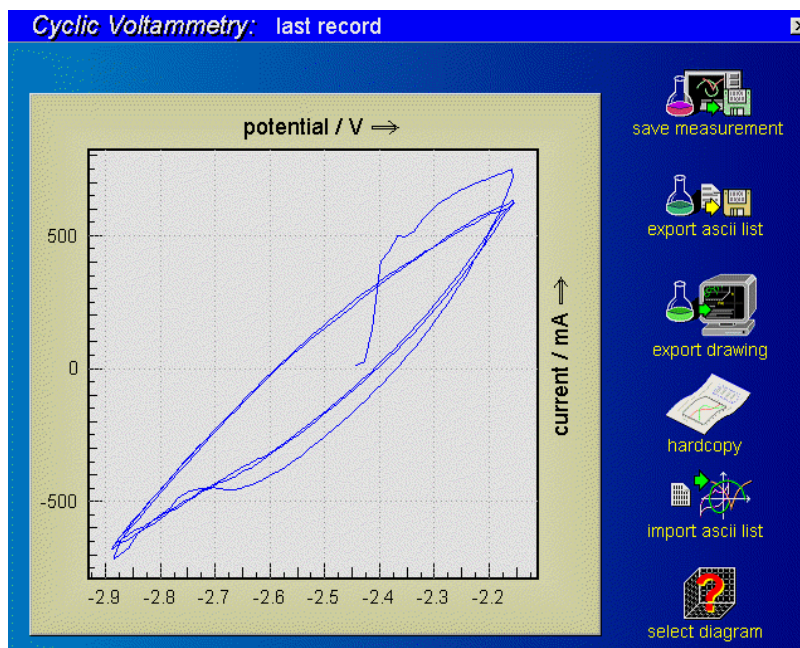
The measured U-I data is plotted online in the data window. At the upper right of the recording window three 'digital' instruments indicate the numeric values of the actually measured data triplett <U,I,t>. A running measurement can be terminated by using the <ESCAPE> function or by pressing the stop-button.



## 5. Display Diagram

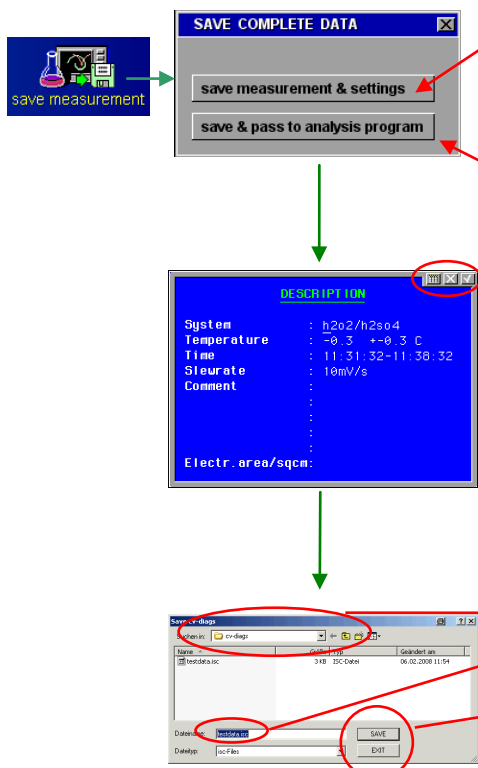


The 'display diagram' function will be entered automatically after completion of a CV, and it may be recalled from the CV control parameter as well as by means of the central pull-down menu, if a the measurement is present. That spectrum will be displayed on the screen. Data can be exported to other programs by the standard i/o functions.



The CV curve measured (or loaded by file) last is displayed as shown above after the 'display diagram' has been entered. The data window is situated in the middle of the screen. On the right, five i/o standard interfaces offer transfer functions of this data.

## 5.1 Save Measurement








The diagram illustrates the process of saving a measurement. It begins with a 'save measurement' icon, which leads to a 'SAVE COMPLETE DATA' dialog box. This dialog box has two options: 'save measurement & settings' and 'save & pass to analysis program'. Both options lead to a 'DESCRIPTION' dialog box where various parameters are entered. The 'DESCRIPTION' dialog box includes fields for System, Temperature, Time, Slope rate, Comment, and Electr. area/sqcm. After entering the data, the user can accept the inputs by clicking the green checkmark button or reject them by clicking the red X button. The 'DESCRIPTION' dialog box also has a calculator icon. Finally, the data is saved in a file browser, where the user can navigate to the desired path, input a file name, and click the 'SAVE' button to save the data or the 'EXIT' button to cancel the saving.

Save the recorded data + the measurement parameters + the comments to the hard disk and return to the CV page.

Save the recorded data + the measurement parameters + the comments to hard disk and pass them directly to the *SIM* software for analysis. You will end up in the *SIM* page.

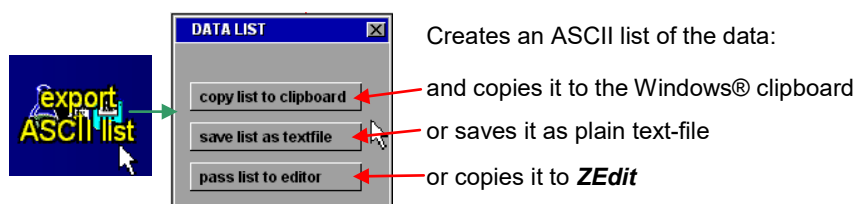
When clicking on either of the buttons a **description** box opens where you may input your measurement parameters and comments. Some lines will be filled automatically by the software (e.g. potential, current and measuring time) others are free for the user to fill. User parameters are not used by the software for any calculation. They are for the user's information only.

Accept the inputs by clicking on the  button in the upper right corner or reject the inputs by clicking on the  button. Click on the  button to call the calculator.

In the following browser navigate to the desired path, input a file name and click on the  button to save the data or click on the  button to cancel the saving.

**Note:** It is recommended to use one of the save-functions in order to store (and recall later) the ECW state corresponding with that measurement.

## 5.2 Create Data List



### Example of an ASCII list of a CV measurement

File.....: melectrode - FEB,06.2008

System.....: h2o2/h2so4  
 Temperature.....: -0.3 +-0.3 C  
 Time.....: 11:31:32-11:38:32  
 Slewrate.....: 10mV/s  
 Comment.....:

Electr.area/sqcm:

Cyclic voltammogram

Lines: 281  
 Columns: 3

| Number | Time/s | Potential/V | Current/A  |
|--------|--------|-------------|------------|
| 1      | 0.0    | -2.443      | 1.416e-02  |
| 2      | 0.7    | -2.428      | 2.413e-02  |
| 3      | 2.2    | -2.413      | 1.461e-01  |
| 4      | 3.7    | -2.398      | 4.056e-01  |
| 5      | 5.2    | -2.383      | 4.384e-01  |
| 6      | 6.7    | -2.368      | 4.986e-01  |
| 7      | 8.2    | -2.353      | 4.959e-01  |
| 8      | 9.7    | -2.338      | 5.155e-01  |
| 9      | 11.2   | -2.323      | 5.543e-01  |
| 10     | 12.7   | -2.309      | 5.889e-01  |
| ...    | ...    | ...         | ...        |
| ...    | ...    | ...         | ...        |
| ...    | ...    | ...         | ...        |
| ...    | ...    | ...         | ...        |
| 278    | 412.0  | -2.773      | -3.912e-01 |
| 279    | 413.5  | -2.758      | -3.524e-01 |
| 280    | 415.0  | -2.743      | -3.196e-01 |
| 281    | 416.5  | -2.728      | -2.868e-01 |

**Note:** Unlike to the save-functions the ECW state corresponding with the measurement is not content of the export data.

## 5.3 Export Drawing

**Graphic export**

- pass to clipboard → Passes the actual graph as high quality vector graphic to the Windows clipboard
- paste to CAD → saves the graph as an EMF graphic file
- save as EMF file

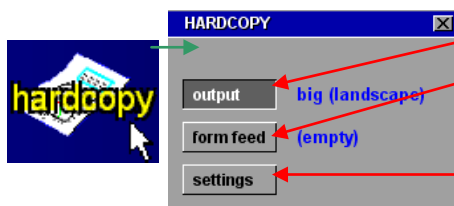
**Thales 4.05 USB**

- edit graphic
- file operations
- plot / export
- hardcopy
- new graphic

Transfers the graph to the CAD graphic editor section of Thales.

Edit the graph manually in the CAD section of Thales for later clipboard or EMF export.

## 5.4 Hardcopy



Create a bitmap copy of the screen for export or printing:  
Perform the selected output operation

Do a form feed

Select the output properties:

**landscape** = big format (DIN-A4) to printer

**upright** = small format (DIN-A5) to printer

**to clipboard** = sends screen to the Windows clipboard

**save as file** = saves the screen content as a bitmap file

## 5.5 Import Data List



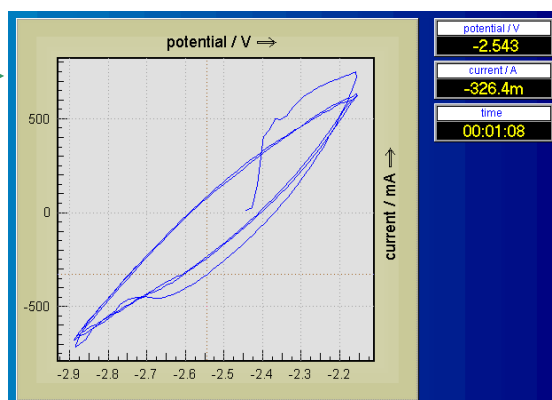
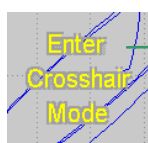
- inactive within CV -

## 5.6 Select Diagram



- inactive within CV -

## 5.7 Enter Crosshair Mode



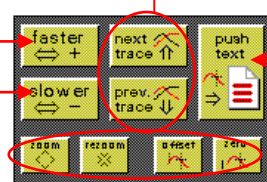
Move cursors through the curves with the mouse. The course leads through the history of the data source: moving from left to right means moving from the first samples recorded to later ones.

Use the cursor-left/right keys for fine steps. You leave the crosshair mode by clicking the middle mouse key or the <ESCAPE> button. If more than one data set is displayed, use the cursor-up/down keys to change from one curve to the next.

Click the right mouse button to open the *option box*:

Increase cursor key

Decrease cursor key



Set cursor to next / previous curve

Passes the data of the selected measurement point to *ZEdit*

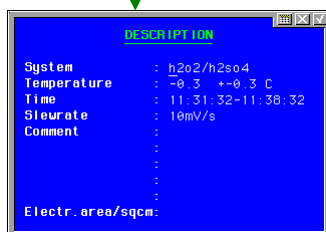
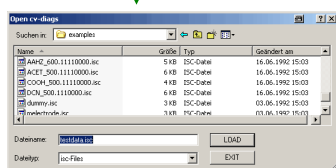
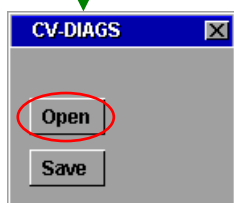
Not implemented, for future expansion

## 6. File Operations



The 'file operation' function will recall the last record or save the actual one. This function works like in all file menus within Thales.

### 6.1 Open



This function allows you to load/save CV data from/to the storage of your PC. Click on the icon and decide in the submenu, whether you want to open previously stored CV data or save actual CV data.

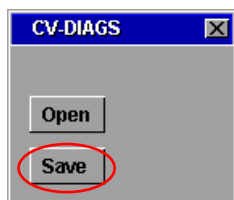
If there are no data in memory, this sub-menu is skipped. After you decide to **Open**, a file browser will open displaying only CV data files (file extension **.isc**).

Select a path and a file and click on the **LOAD** button to load the file to the *Thales* software. Click on the **Display Spectrum** icon on the CV main page to display the data in a graphical form.

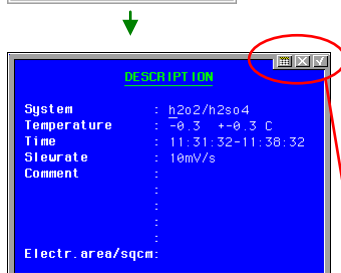
The next box shows the measurement parameters of the loaded data. Click on it if you want to close it.

**NOTE:** Opening a file will switch off the potentiostat and configures the potentiostat according to the loaded measurement-settings automatically. Loading a measurement file is an easy way to perform a new measurement with previously used settings.

## 6.2 Save

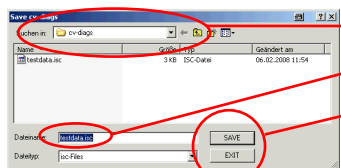


If there are data in memory, usually after a CV data measurement, you may want for **Save** them as data file on storage.



A **description** box opens where you may input your measurement parameters and comments. Some lines will be filled automatically by the software (e.g. potential, current and measuring time) others are free for the user to fill and are not used for any calculation. The last line is reserved to put in the area value of the working electrode under test in order to enable area relative calculations.

Accept the inputs by clicking on the button in the upper right corner or reject the inputs by clicking on the button. Click on the button to call the calculator.

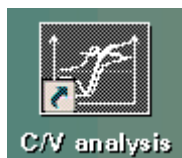


In the following browser navigate to the desired path, Input a file name and

Click on the button to save the data.

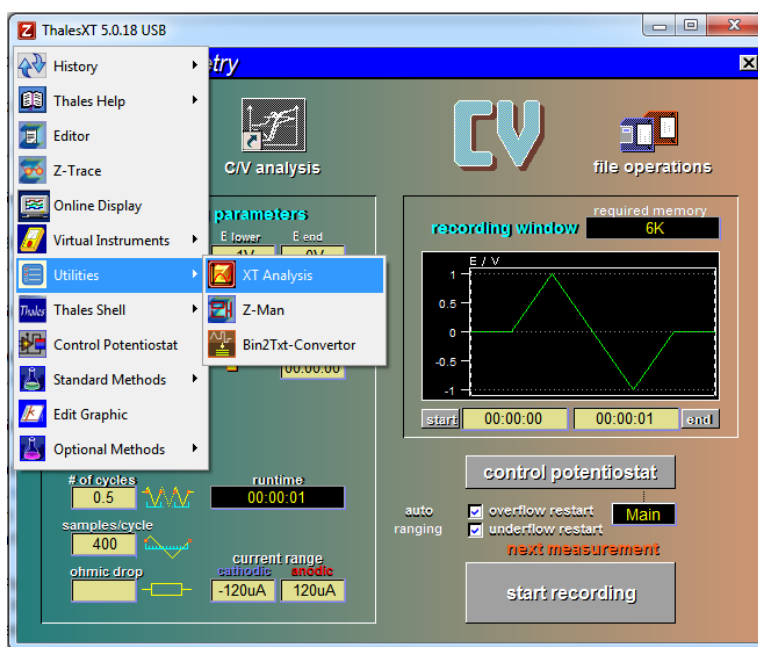
Click on the button to cancel the saving.

## 7. Dynamic CV - Analysis



The CV analysis software is called up by activating this button. The actual data is not present at the moment. In order to be on the safe side a measurement has to be saved in the recording program which should be loaded. Then it is evaluated in the analysis program. In the “display diagram” menu after a measurement you have the choice to save the data file and automatically pass it to the analysis program, if wanted.

Alternatively Thales XT Analysis can be used for display and analysis of CV data. It can be started using the pulldown menu as shown below.

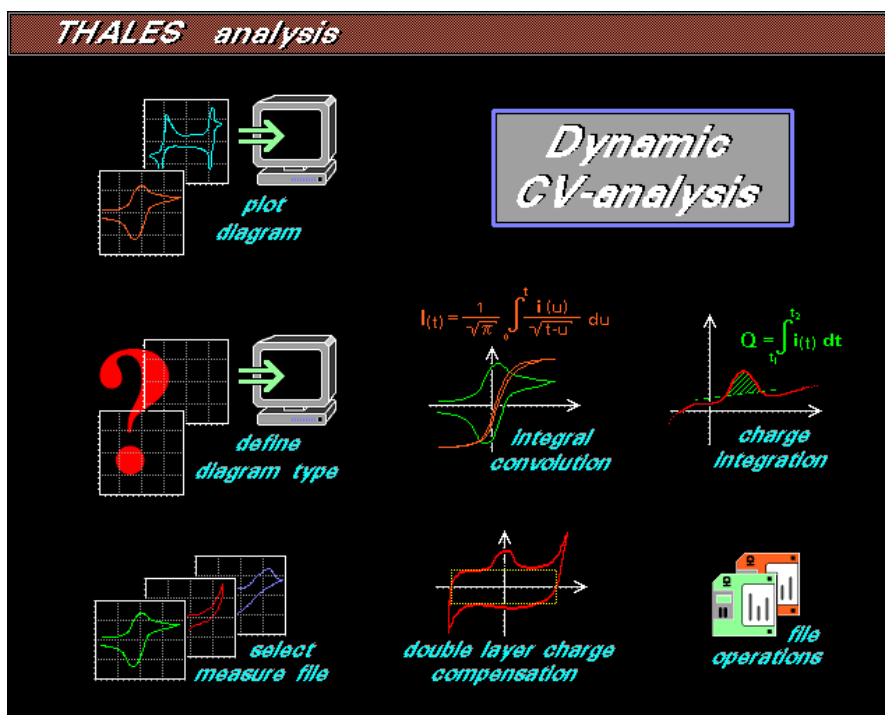




# CV Analysis

## 8. Analysis Main Menu

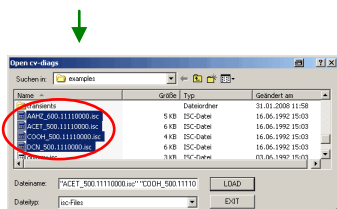
CV analysis starts with the menu shown below.



## 9. File Operations

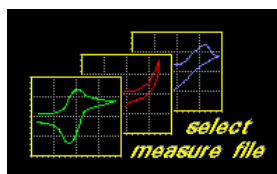


There are commonly known disc i/o functions to load measure data (see [CV recording chapter 6](#)) but with one restriction: The save option has been blocked. The reason is that it is possible to use the CV analysis to manipulate the original data through double layer charge compensation. If this data is saved, the original one will be overwritten.

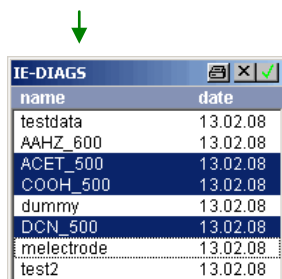


A file browser will open displaying only CV data files (file extension **.isc**). You can also select more than one data file to open.

## 10. Select Measure Files



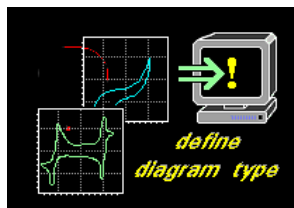
'select measure files' offers the possibility to select different sets of measurement for evaluation from a list of data sets already present in the program memory. When this function is activated a file list including all files which have already been loaded will be opened.



A blue background color indicate whether a file has been selected. To select or deselect a data file simply click on the file name.

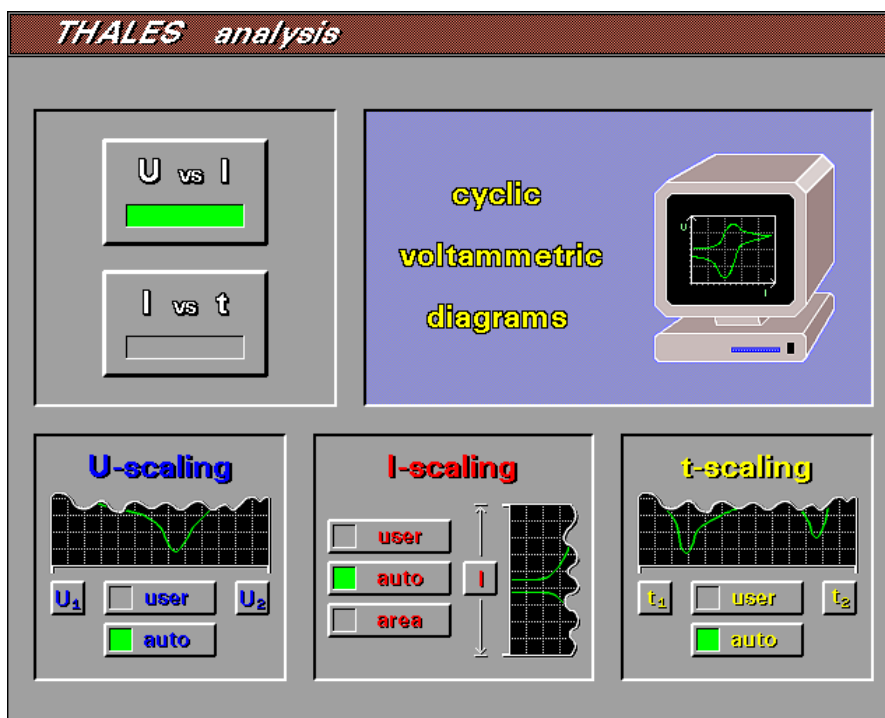
**NOTE:** Up to ten measurements can be loaded at the same time depending on the memory space available. If a loading operation fails because of an overflow message, the analysis program will have to be initialized with the 'INIT' function of the SIM program.

## 11. Define Diagram Type



CV measurements store data triplets of the format (U,I,t). This data can be plotted in different graphical representations. During the recording, the data can be plotted in the I(U) mode automatically. Another important mode is the I(t) plot. The 'define diagram' function allows to select between the two modes. Scaling can be done manually or automatically.

The function 'define diagram type' presents the menu shown below.



This submenu offers all definitions to create a plot of the data measured. The diagram can be affected

- by typing, **U vs. I** or **I vs. t** or
- by data ranges and display limits

The settings which are organized in a graphical control panel can be carried out by choosing the corresponding option and by entering some parameters.

### 11.1 Selection of Diagram Type



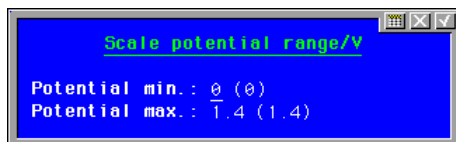
The diagram type is selected by activating the corresponding button. The activated mode is indicated by a green bar within this button and the symbolized terminal will change its graphic.

## 11.2 Setting of Display Limits

The display limits can be set in accordance with the selected diagram type. Each magnitude can be scaled automatically (auto) or manually (user) in order to redefine the display limits one of the buttons has to be selected



and the new values have to be input with help of the i/o box.



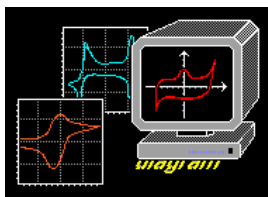
The values in brackets indicate the minimal/maximal values of the corresponding data track.

## 11.3 Plot Diagram

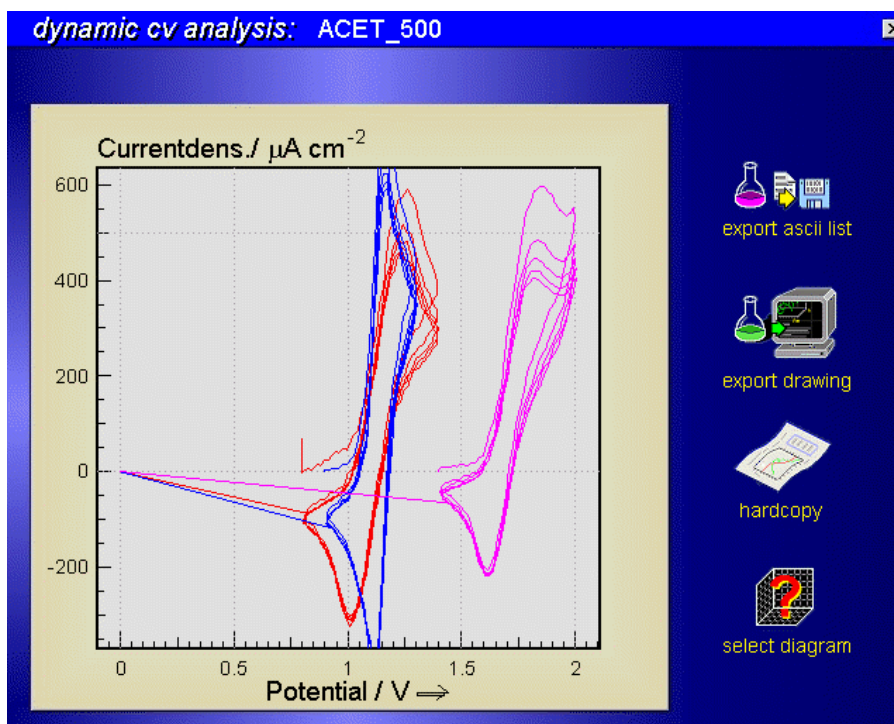


Redrawing the graphic is initiated by pressing this button. The next diagram will be plotted after the confirmation with <ENTER> or mouse click.

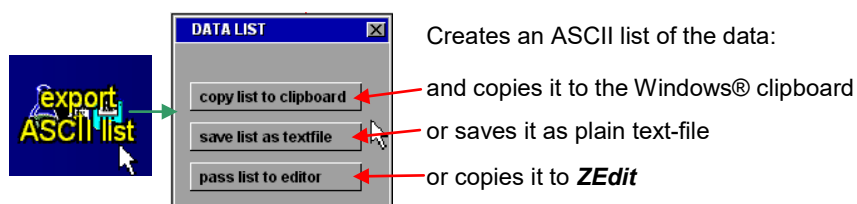
## 12. Plot Diagram



When all settings have been made, the diagram can be plotted. Output is initiated by activating the button 'plot diagram'. At the end of the plotting procedure five additional buttons on the right of the screen appear and offer the options.



## 12.1 Create Data List



### Example of an ASCII list of a CV measurement

File.....: melectrode - FEB,06.2008

System.....: h2o2/h2so4  
 Temperature.....: -0.3 +-0.3 C  
 Time.....: 11:31:32-11:38:32  
 Slewrate.....: 10mV/s  
 Comment.....:


Electr.area/sqcm:

Cyclic voltammogram

Lines: 281  
 Columns: 3

| Number | Time/s | Potential/V | Current/A  |
|--------|--------|-------------|------------|
| 1      | 0.0    | -2.443      | 1.416e-02  |
| 2      | 0.7    | -2.428      | 2.413e-02  |
| 3      | 2.2    | -2.413      | 1.461e-01  |
| 4      | 3.7    | -2.398      | 4.056e-01  |
| 5      | 5.2    | -2.383      | 4.384e-01  |
| 6      | 6.7    | -2.368      | 4.986e-01  |
| 7      | 8.2    | -2.353      | 4.959e-01  |
| 8      | 9.7    | -2.338      | 5.155e-01  |
| 9      | 11.2   | -2.323      | 5.543e-01  |
| 10     | 12.7   | -2.309      | 5.889e-01  |
| ...    | ...    | ...         | ...        |
| ...    | ...    | ...         | ...        |
| ...    | ...    | ...         | ...        |
| ...    | ...    | ...         | ...        |
| 278    | 412.0  | -2.773      | -3.912e-01 |
| 279    | 413.5  | -2.758      | -3.524e-01 |
| 280    | 415.0  | -2.743      | -3.196e-01 |
| 281    | 416.5  | -2.728      | -2.868e-01 |

## 12.2 Export Drawing



**Graphic export**


pass to clipboard

paste to CAD

save as EMF file

Passes the actual graph as high quality vector graphic to the Windows clipboard

saves graph as an EMF graphic file



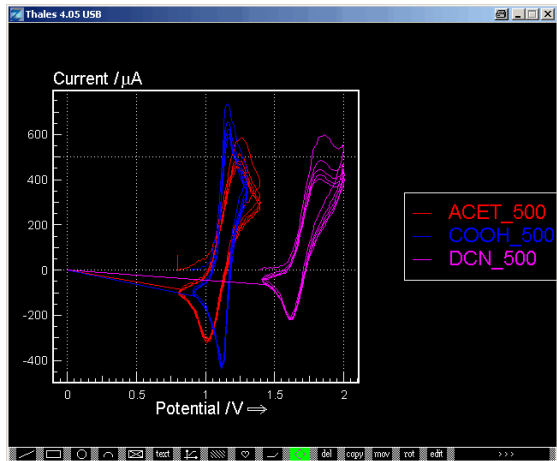
edit graphic

file operations

plot / export

hardcopy


new graphic



Transfer the graph to the CAD graphic editor section of Thales.

Edit the graph manually in the CAD section of Thales for later clipboard or EMF export.

## 12.3 Hardcopy



**HARDCOPY**

output

form feed

settings

Create a bitmap copy of the screen for export or printing:  
Perform the selected output operation

Do a form feed

Select the output properties:

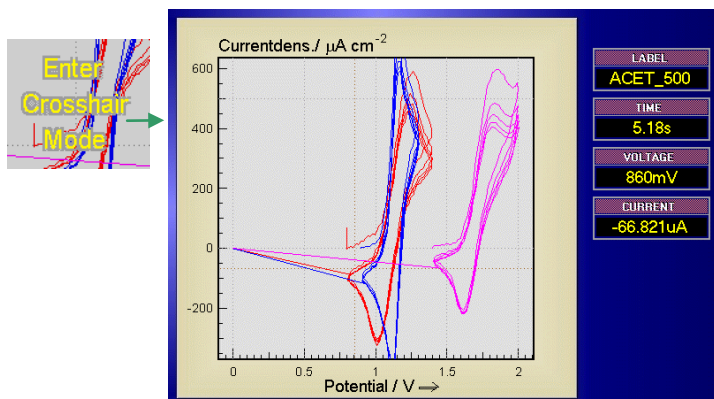
**landscape** = big format (DIN-A4) to printer  
**upright** = small format (DIN-A5) to printer  
**to clipboard** = sends screen to the Windows clipboard  
**save as file** = saves the screen as a bitmap file

## 12.4 Select Diagram



CV measurements store data triplets of the format (U,I,t). This data can be plotted in different graphical representations. During the recording, the data can be plotted in the I(U) mode automatically. Another important mode is the I(t) plot. The 'define diagram' function allows to select between the two modes. Scaling can be done manually or automatically (see [CV analysis chapter 11](#)).

## 12.5 Enter Crosshair Mode



Move cursors through the curves with the mouse. The course leads through the history of the data source: moving from left to right means moving from the first samples recorded to later.

Use the cursor-left/right keys for fine steps.

You leave the crosshair mode by clicking the middle mouse key.

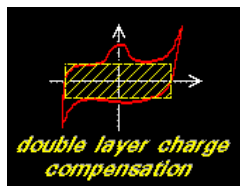
If more than one data set is displayed, use the cursor-up/down keys to change from one curve to the next.

Click the right mouse button to open the *option box*:

|                    |        |     |  |                                                            |
|--------------------|--------|-----|--|------------------------------------------------------------|
| Increase stepwidth | cursor | key |  | Set cursor to next / previous curve                        |
| Decrease stepwidth | cursor | key |  | Passes the data of the selected measurement point to ZEdit |
|                    |        |     |  | Not implemented, for future expansion                      |



## 13. Double Layer Charge Compensation



A resistor is the simplest object which is to be investigated by a CV measurement. The observed dependence of current and potential is linear. A voltage step  $\Delta E$  induces a current step  $\Delta I = \Delta E / R$ .

The investigation of an electro-chemical system with capacitive elements shows that a certain fraction of the induced current is charging these capacities. The Faradayic fraction of the flowing current can only be obtained when the measured data has been corrected. The studied system can be described with an equivalent circuit. Sometimes this circuit has a complex structure and corrections demand an even more complex numerical algorithm. CV analysis, however, provides for the best correction. The induced current is corrected with consideration of a capacitive double layer according to

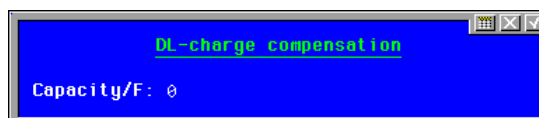
$$\Delta I = C \cdot dE/dt$$

with

$\Delta I$  being induced current  
 $C$  being capacity of double layer  
 $dE/dt$  being slewrate

The capacity of the double layer can be determined by an impedance measurement and subsequent modeling of the obtained spectrum.

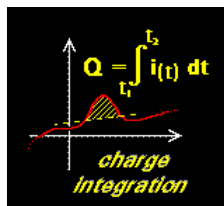
The double layer capacity has to be entered in order to activate the compensation routine.



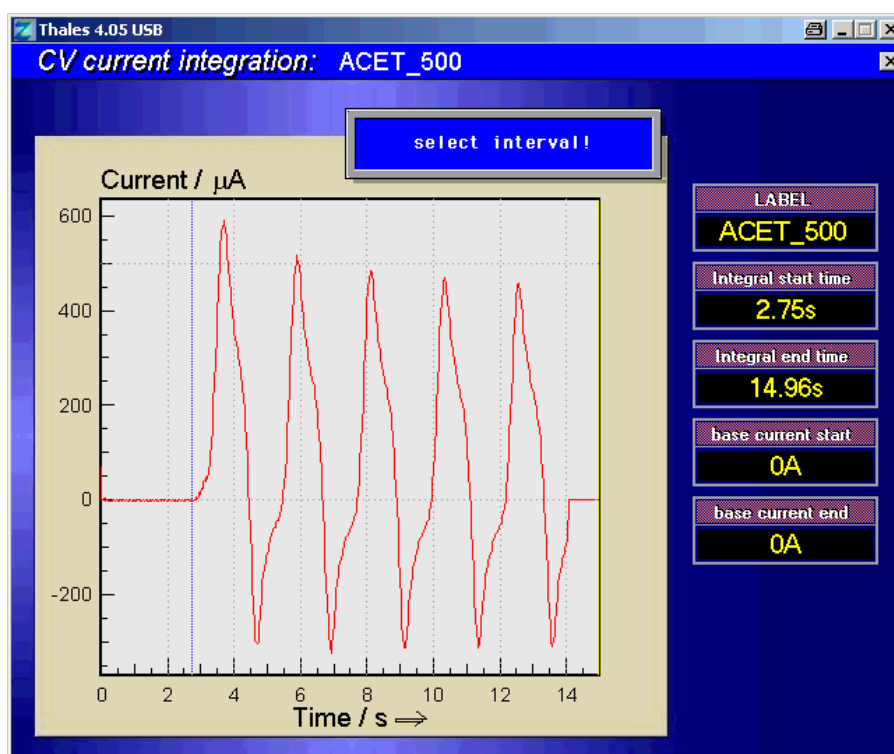
Corrections can be deleted by another compensation using the capacity

$$C_{\text{undo}} = -C_{\text{done}}$$

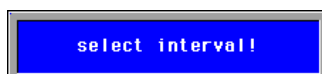
## 14. Charge Integration



When the I(t) plot mode has been chosen the Columb integral will be calculated. The boundaries of integration can be selected and a base line can be defined to obtain net results.



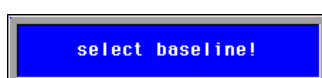
Calling up 'charge integration' results in an I(t) plot of the selected measurement. Five displays indicate the file name and the boundaries. An info box demands input of the interval of integration.



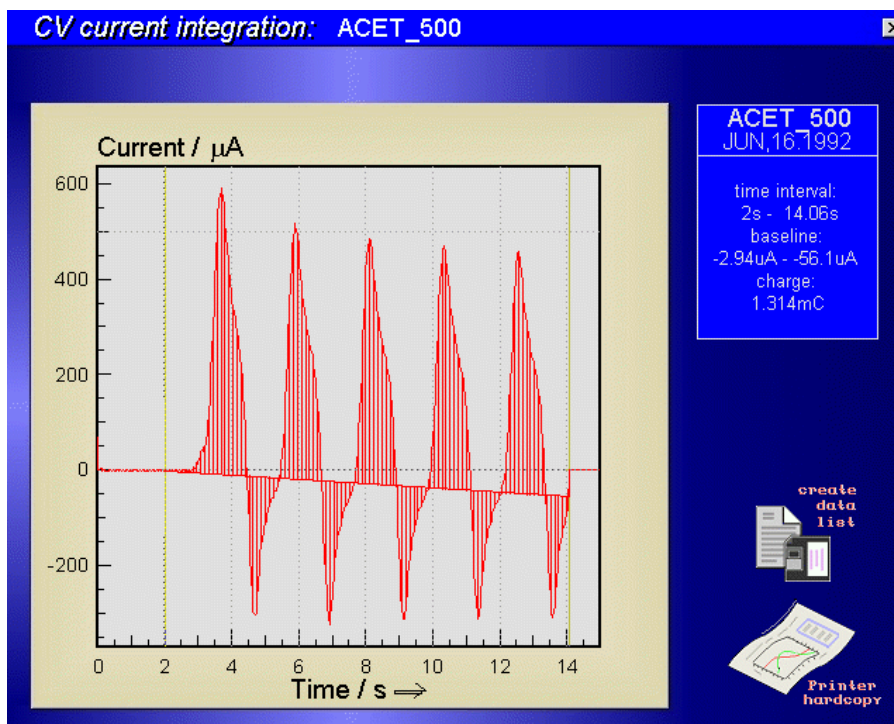
First, the left time marker is set by using the mouse or the cursor keys.

The start time is indicated by the instrument called 'integral start time'. The new value is entered by using the <ENTER> function. Eventually, the end time is entered in the same way.

A base line can be used, e.g., to integrate net peaks, after the time interval has been set. The info box



will then start the input of the base line. If no baseline is desired the <ENTER> function has to be used twice or the base start has to be set by moving the cursor and confirmation of this step. The base end is defined in the same way.



Finally the charge integral

$$Q = \int_{t_{start}}^{t_{end}} [I(t) - b(t)] \cdot dt \quad \text{with:} \quad b(t) = b_{start} + \frac{b_{end} - b_{start}}{t_{end} - t_{start}} (t - t_{start})$$

$I(t)$ : measured current data

will be calculated. The numeric values of integral and boundaries are printed out on the right of the data window. The standard output functions 'data list' and 'printer hardcopy' offer output to the text editor or the hardcopy. The 'data list' option appends the following lines to an existing text.

**File.....: melectrode - 10.JAN.1997**

**System.....: h2o2/h2so4**

**Temperature: 20**

**Time.....: 13:30:22**

**Charge integration**

**time interval: 0s - 00:03:39**

**baseline.....: -11.8 pA - -1.23 pA**

**charge.....: -555.2 nC f**