C/E

Fixed Frequency Impedance Course
vs. Potential, Current, Time, Temperature, …

Introduction

The frequency response curve of the impedance of a physical object may always be described by a set of impedance elements being interconnected in a characteristic way by parallel and serial links. Rising pretensions to the concurrence between model and transfer functions increases the number of impedance elements being needed. The model becomes more complicated.

C/E Recording
Often only several selected impedance elements of a model are scientifically relevant, e.g. the components of an impedance describing the electrolytical conductivity or the double layer capacitance. In this case the response curve of selected parameters may be found by an analysis of a series of frequency response curves.

Recording the capacitance as a function of the potential may be done by measuring complete impedance spectra being fitted with the same model. The numerical value of the relevant impedance element (e.g. the double layer capacitance) may then be plotted as a function of the ordinal parameter (e.g. the potential). This way is named as way "A".

Under certain circumstances it is possible to find the parameter by measuring the impedance at a constant frequency instead of recording complete impedance spectra. This may be done in a frequency range where the real part or the imaginary part of the impedance is dominated by the investigated parameter within a given measuring accuracy. C/E curves are now recorded by measuring the impedance at varying potential and calculating the capacity either from the impedance or from the admittance. This way is named "B". Model "B" is fixed on either a parallel or a serial link of one resistor and one capacitor.

In comparison to way "B" way "A" may always be gone but takes a lot more time. In a third way "C" complete impedance spectra are needed as in way "A". "C" takes the same measuring time like "A" but saves time as fitting of a spectra series is not necessary. Instead of fitting the impedance is found by cutting the impedance at a certain frequency and calculating the capacity like in way "B". In contrary to "B" way "C" allows to check the significance of the found numerical value by additional cuts at other frequencies.

"A" and "C" result in files of data doublets of impedance and an additional parameter. Data coming from "A" and "C" or directly from "B" contain the potential as second parameter. To analyse a series of single spectra the program "SIM" offers the possibility to edit the second parameter and put in other quantities as ordinal parameter.

C/E files are the base of further reports supported by the program C/E, e.g. several different graphical representations. To analyse potential parameter curves to a chosen capacity (being put in either as an absolute capacity in F or as a relative capacity in %) the potential will be calculated via the C/E curve and forms a data doublet with the corresponding parameter. The generated potential parameter curves are subject of putting in the reference capacity the corresponding parameter (e.g. temperature, pH-value, concentration) may be put in, if not done while recording C/E curves via way "C".

Further information
C/E files as well as potential parameter files will be automatically smoothed while being loaded from a storage device. Manual smoothing is supported by functions in the different display subroutines. In addition to smoothing C/E allows to spline a curve. Smoothing is a equivalent to a filter with a limited bandwidth and makes sense in the case of spikes or noise being superimposed on a curve. By smoothing a data reduction will take place and the smoothed curve will not exactly fit to the measured points. Getting interpolated points in addition to the measured ones is an useful effect of smoothing but makes only sense if there is a minimum number of 15 to 20 points.

In contrast to smoothing there is no data reduction when splining. Splining will be used to get interpolations if there is only a small number of measured points. Splining is possible at a minimum

number of three measured points and exactly fits to these points. The default setting of smoothing operations is splining.

1. C/E Main Page

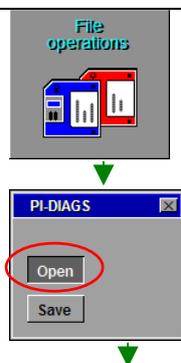Click on the   icons on the *Main Menu* page to open the C/E main page.
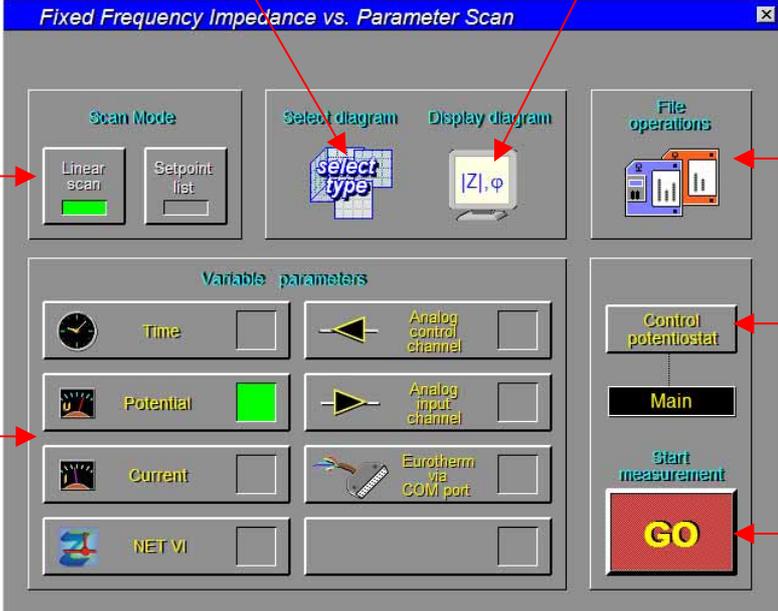
select diagram type   display resident C/E data as graphics

select scan mode →

load/save C/E data files

set U and I parameters

scanning variable or device →

start recording

1.1 File Operations

1.1.1 Open

This function allows you to load/save C/E data from/to the hard disk of your PC. Click on the icon and decide in the sub-menu, whether you want to open previously stored C/E data or save actual C/E data.

If there are no data in memory, this sub-menu is skipped.
After your decide to *Open,* a file browser will open displaying only C/E data files (file extension *.isp*).

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 C/E main page to display the data in a graphical form.
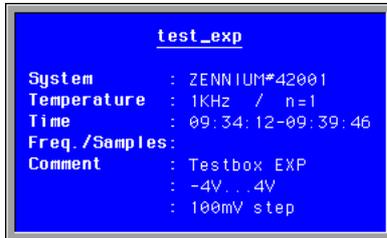
The next box shows the measurement parameters of the loaded data. Click on it if you want to close it.

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.**

1.1.2 Save

If there are data in memory, usually after an EIS spectrum measurement, you may want for *Save* them on hard disk for storage.
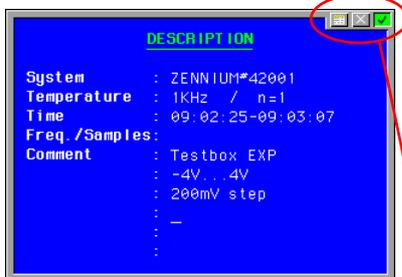
A *description* box opens where you may input your measurement parameters and comments. Some lines will be filled automatically by the software (e.g. potential, current and measuring time) others are free for the user to fill and are not used for any calculation.

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.
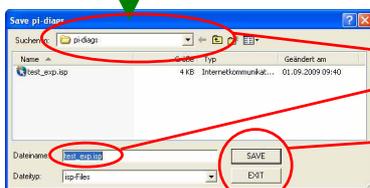
In the following browser navigate to the desired path,
Input a file name and
Click on the SAVE button to save the data.
Click on the EXIT button to cancel the saving.

1.2 Display Impedance vs. Parameter
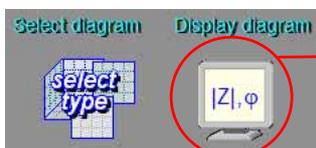
Click on this icon to display the diagram resident in memory. This may be measured or loaded data. The functions available in the display diagram page are described later in this chapter.

Click on this icon if you want to change the type of the diagram.

Select the type of the diagram type to be displayed here.

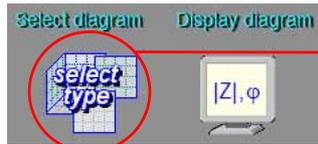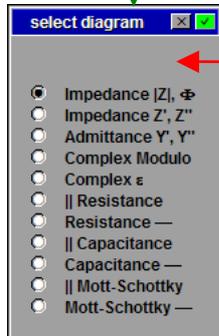|		
|Z|, Φ	Impedance modulus value Phase angle between AC voltage and AC current	Ω °
Z', Z''	Real part of the impedance Imaginary part of the impedance	Ω Ω
Y', Y''	Real part of the admittance Imaginary part of the admittance	Ω^{-1} Ω^{-1}
Complex Modulo	complex modulo	
Complex ε	complex dielectric constant	
parallel Resistor	mathematical calculated curve	Ω
Resistor serial	mathematical calculated curve	Ω
parallel Capacity	mathematical calculated curve	F
Capacity serial	mathematical calculated curve	F
parallel M.-S.	mathematical calculated curve	F^{-2}
M.-S. serial	mathematical calculated curve	F^{-2}

1.3 Scan Mode

1.3.1 Linear Scan
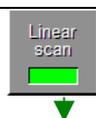
In *Linear Scan* Mode you scan through a range of the defined quantity in equidistant steps (linear).
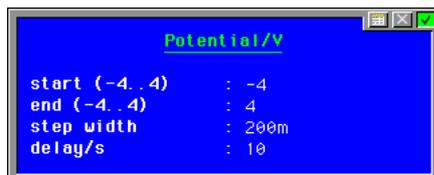
Start value : Value where the scan has to start
End value : Value where the scan is finished
Step width : Interval in which the measurements have to be carried out
Delay / s : Delay between reaching a scan-point and starting the measurement (settling time)

1.3.1.1 Linear Scan over Time

start time   Absolute time of the computer clock. The start time is set in units of hours, minutes and seconds. During definition of the time parameters the actual time is displayed in the input box.

duration	Starting at the start time the program will start impedance measurements until the total measurement time of *duration* has expired. The *duration* is set in units of hours, minutes and seconds.
delay	Delay time defines the time difference of the starting times of two successive impedance measurements.

> **!** **Set the delay time higher than the estimated measurement time shown on the *Recording Parameters* page. If measurements take longer than the delay time the equidistance of the spectra can not be guaranteed or less spectra will be measured.**

1.3.1.2 Linear Scan over Potential/Current

start value	Sets the potential or current at which the series measurement has to start. Potential and current will be given in units of V and A, respectively.
end value	Destination potential or current at which the series measurement is stopped.
step width	Step width of potential or current between two successive measurements. Setting the start value higher than the end value will require the input of a negative step width.
delay	After the new value of potential or current is reached the program waits for this number of seconds to ensure steady state conditions at the object.

> **!** **The delay time should not been defined too short because changes in potential and current may cause distortions of equilibrium. Allow the system to settle before continuing with measurements.**
> **The effect of the series control by DC-set-voltage or DC-set-current is related to the actual working mode of the potentiostat:**
> **Use DC-voltage only in potentiostatic mode.**
> **Use DC-current only in galvanostatic- or pseudo-galvanostatic mode.**

1.3.1.3 Linear Scans Controlled by Analogue I/O-Channels

Linear scans using additional analogue i/o-channels are working in a similar way as linear scans over potential or current do. The range parameters and the step width are given in the physical units defined for the corresponding channel on the *Data Acquisition Setup* page. The physical unit set there is displayed at the top of the appearing input box.

start value	Sets the value at which the series measurement has to start. Potential and current will be given in units of V and A, respectively.
end value	Destination value at which the series measurement is stopped.
step width	Step width between two successive measurements. Setting the start value higher than the end value will require the input of a negative step width.
delay	After the new value is reached the program waits for this number of seconds to ensure steady state conditions at the object.

> **!** **The delay time should be defined sufficiently high to offer the system some time to get settled.**
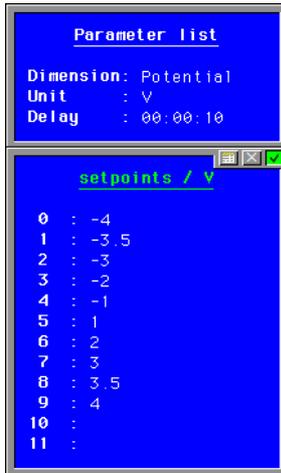
1.3.2 Setpoint List

Setpoint List mode lets you define a list of points at which the system has to measure. The list has not to be linear or steady.

In the first input box you define a delay time valid between the individual impedance measurements for settling. After reaching a set point, the software waits for the duration of the delay time before the

software waits for the duration of the delay time before the measurement is started.

```
Parameter list

Dimension: Potential
Unit      : V
Delay     : 00:00:10
```
```
setpoints / V

0  : -4
1  : -3.5
2  : -3
3  : -2
4  : -1
5  : 1
6  : 2
7  : 3
8  : 3.5
9  : 4
10 :
11 :
```

In the second box you may input the set points in the quality of the scan parameter set in the *Variable Parameters* box.

Up to 99 set points can be defined but only 12 points are displayed in the box. You can scroll through the list using the cursor keys or the RETURN key of your keyboard. The transition between two points always is a linear ramp.

1.4 Scan Variable or Device

In this section you set the parameters of the scan variable. This may be an internal signal (time, potential, current) or an external signal (analog input, analog output, interface control channel). For using external signals you may need an optional hardware such as *TEMP/U, FE42*, *DA4*, etc.

1.4.1 Internal Signals

Time	Impedance will be recorded at a fixed frequency over a certain interval of time, allowing studies of time dependent processes.
Potential	Impedance will be recorded at a fixed frequency in dependence of the DC potential, allowing studies of potential dependent processes.
Current	Impedance will be recorded at a fixed frequency in dependence of the DC current, allowing studies of processes dependent on the current density.

1.4.2 External Signals

Analog control channel — Four analogue outputs are provided by an optional *DA4* DA-converter module. The channels can be calibrated and correlated to any quantity to be controlled in the *Signal Acquisition Setup* page:

Analog input channel — Additional analogue input channels are provided by the optional modules FE42 and TEMP/U. In the *Signal Acquisition Setup* page the inputs can be calibrated and linked to one of the 'digital instrument displays' of the *Signal Acquisition & Output Control* page:

Generally, Thales is able to communicate via TCP/IP with external measurement and control units (NET-VIs) connected to any computer in the network. Besides this, an **Eurotherm 2404CG,** which is able to control the temperature of an oven, may be connected directly to the COM port of the PC controlling the IM instrument. This opens a cheap way to perform series measurements over controlled temperature.

2. Control Potentiostat

Control potentiostat The *Control Potentiostat* page is very useful for testing your external measurement setup, such as cabling, cell, electrodes, connections to the object, etc. Here you may apply different combinations of AC and DC voltages and currents at frequencies of interest. You may have a (first) look at the measurement values and signals at the selected frequency. Furthermore, the AC- and DC-parameters *DC voltage/current, AC amplitude* and potentiostat mode (potentiostatic or galvanostatic) are to be defined here for an C/E measurement to follow. And – very important – the potentiostat is switched on and off here. Please note, that the potentiostat is switched off automatically, when the potentiostat mode is changed.
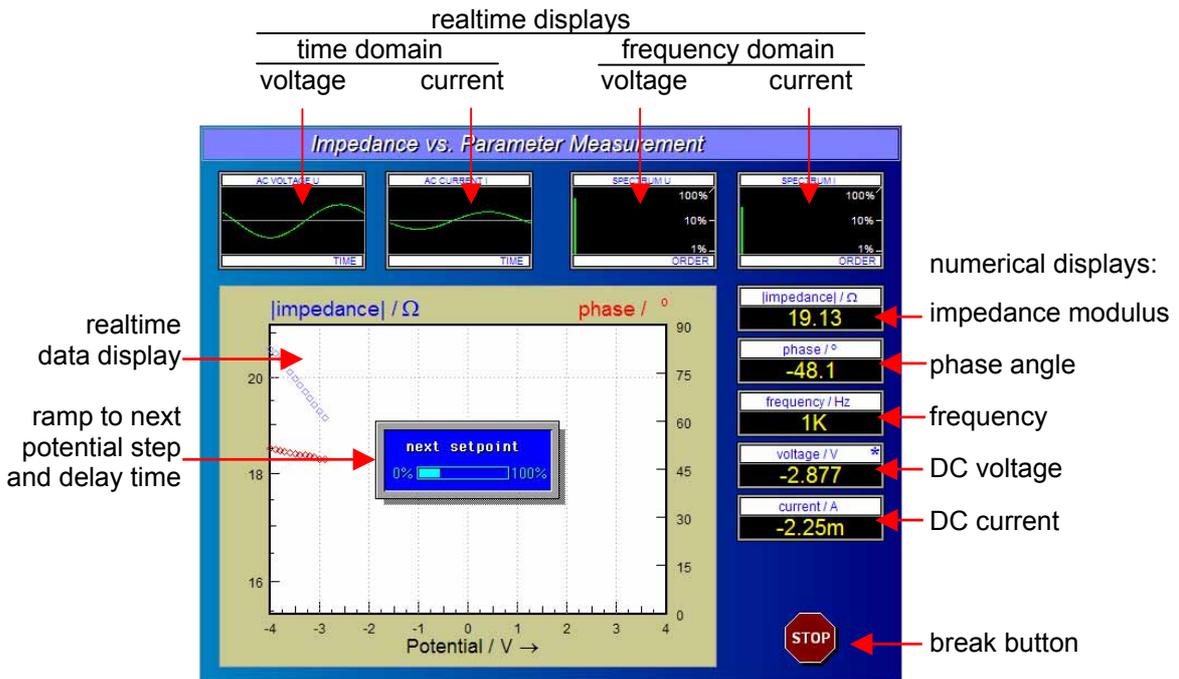
Also the final condition of the potentiostat can be selected here. If a C/E measurement is started with the potentiostat switched on, the potentiostat will remain operational after the C/E measurement has been completed. If the potentiostat has been switched off before starting a C/E measurement it will be switched off at the end of the measurement.

The potentiostat can be set to the C/E starting potential and switched on manually, what will avoid the automatic insertion of a start ramp between the actual potential and the C/E starting potential. The ramp speed may be altered in the general measurement setup under the point "DC-more".

3. Start Recording

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

realtime displays
time domain
voltage   current
frequency domain
voltage   current

numerical displays:

impedance modulus

phase angle

frequency

DC voltage

DC current

break button

realtime data display

ramp to next potential step and delay time

The measured impedance data is plotted online in the data window. At the top of the recording window four realtime displays shows the voltage and current signals in time and frequency domain. Five 'digital' instruments on the right side indicate the numeric values of the actually measured data. A running measurement can be terminated by using the <ESCAPE> function or by pressing the stop-button.

4. Display Diagram

The 'display diagram' function will be entered automatically after completion of a C/E measurement, and it may be recalled from the C/E main page if a the measurement is present. That C/E measurement will be displayed on the screen. Data can be exported to other programs by the standard i/o functions.
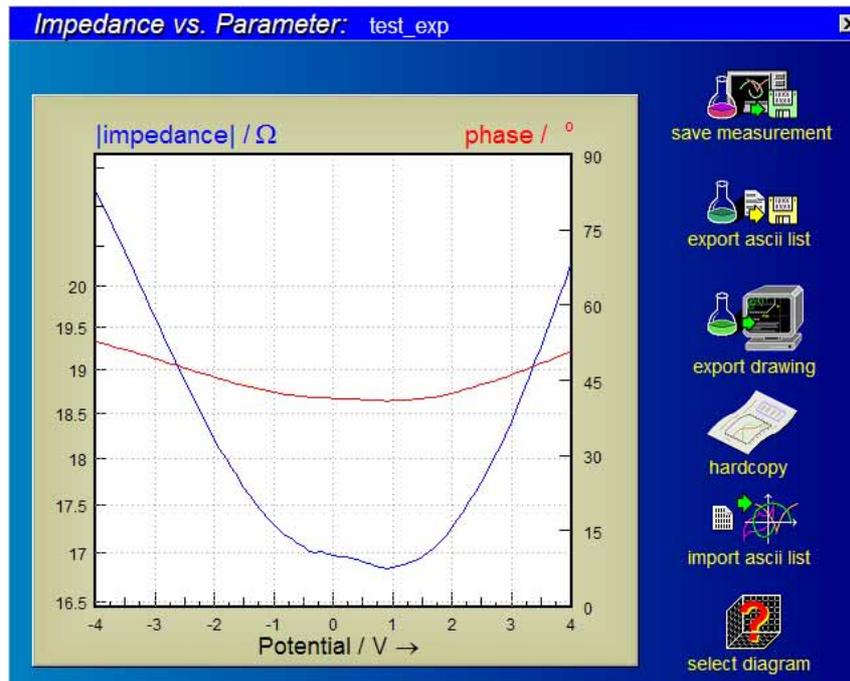
The C/E curve measured (or loaded by file) last is displayed as shown above after the 'display diagram' has been entered. The data window is situated in the middle of the screen. On the right, five i/o standard interfaces offer transfer functions of this data.

4.1 Save Measurement
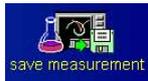
Save the
recorded data + the measurement parameters + the comments to the hard disk and return to the *C/E* page.
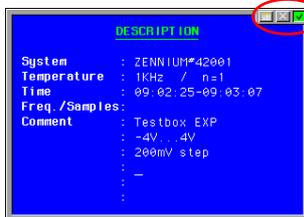
When clicking on either of the buttons a **description** box opens where you may input your measurement parameters and comments. Some lines will be filled automatically by the software (e.g. potential, current and measuring time) others are free for the user to fill. User parameters are not used by the 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.
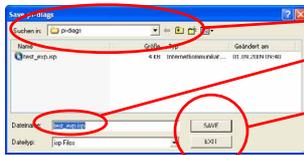
In the following browser navigate to the desired path,
input a file name and
click on the [SAVE] button to save the data or
click on the [EXIT] button to cancel the saving.

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.

4.2 Create Data List

Creates an ASCII list of the data:

and copies it to the Windows® clipboard

or saves it as plain text-file

or copies it to *ZEdit*
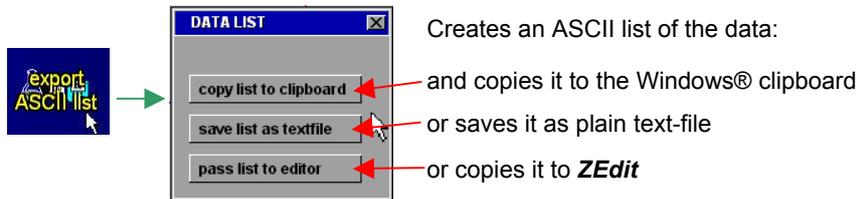
Example of an ASCII list of a C/E measurement

```
File.........:  test_exp - SEP,01.2009

System.......:  ZENNIUM#42001
Temperature..:  1KHz  /  n=1
Time.........:  09:34:12-09:39:46
Freq./Samples:
Comment......:  Testbox EXP
                -4V...4V
                100mV step



Impedance vs parameter

Lines:   81
Columns: 5

Number   Potential    Impedance/Ohm   Phase/deg   Signific.   Time/s
1        -4.000e+00   2.118e+01       -52.6       0.998        0.0
2        -3.900e+00   2.106e+01       -52.4       0.999        5.5
3        -3.800e+00   2.090e+01       -52.0       0.999       10.2
4        -3.700e+00   2.074e+01       -51.7       0.999       15.0
5        -3.600e+00   2.058e+01       -51.4       0.999       19.8
6        -3.500e+00   2.042e+01       -51.1       0.999       25.3
7        -3.400e+00   2.026e+01       -50.7       0.999       30.1
8        -3.300e+00   2.010e+01       -50.4       0.999       34.8
9        -3.200e+00   1.994e+01       -50.0       0.999       39.6
10       -3.100e+00   1.978e+01       -49.6       0.999       44.4
...       ...          ...             ...         ...         ...
...       ...          ...             ...         ...         ...
...       ...          ...             ...         ...         ...
76        3.500e+00   1.927e+01       -48.4       0.999      306.5
77        3.600e+00   1.946e+01       -48.8       0.999      311.3
78        3.700e+00   1.967e+01       -49.3       0.999      317.0
79        3.800e+00   1.985e+01       -49.7       0.999      321.8
80        3.900e+00   2.005e+01       -50.2       0.999      326.5
81        4.000e+00   2.027e+01       -50.7       0.999      331.31
```
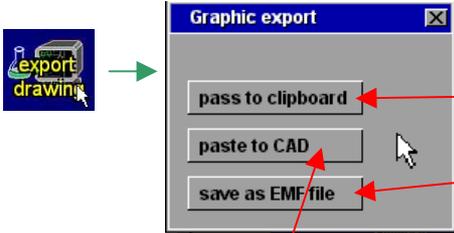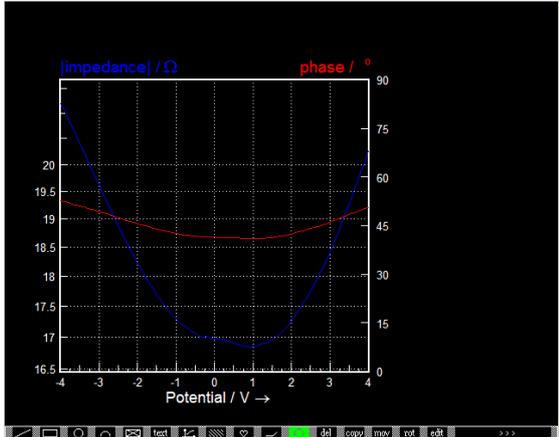
Note: Unlike to the save-functions the ECW state corresponding with the measurement is not content of the export data.

4.3 Export Drawing

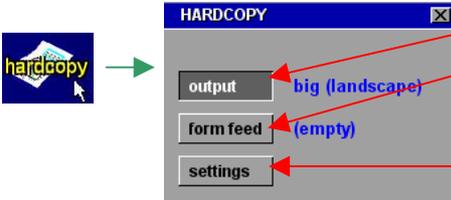Passes the actual graph as high quality vector graphic to the Windows clipboard

saves the graph as an EMF graphic file

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.

4.4 Hardcopy

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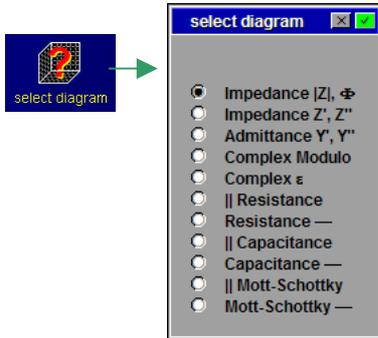
Do a form feed

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

4.5 Import Data List


- inactive within C/E -

4.6 Select Diagram

Select the type of the diagram type to be displayed here.

|Z|, Φ	Impedance modulus value Phase angle between AC voltage and AC current	Ω °
Z', Z''	Real part of the impedance Imaginary part of the impedance	Ω Ω
Y', Y''	Real part of the admittance Imaginary part of the admittance	Ω^{-1} Ω^{-1}
Complex Modulo	complex modulo	
Complex ε	complex dielectric constant	
parallel Resistor	mathematical calculated curve	Ω
Resistor serial	mathematical calculated curve	Ω
parallel Capacity	mathematical calculated curve	F
Capacity serial	mathematical calculated curve	F
parallel M.-S.	mathematical calculated curve	F^{-2}
M.-S. serial	mathematical calculated curve	F^{-2}

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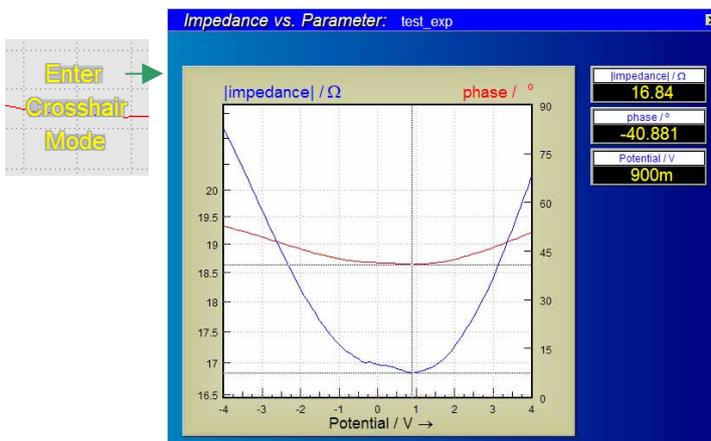
Move cursors through the curves with the mouse. The course leads through the history of the data source: moving from left to right means moving from the first samples recorded to later ones.

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.