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1. THE MAIN MENU

`POLAROGRAPHY` comes up with the main menu shown below.

The main menu roughly is divided into four sections.

- Selection of the applied method, editing of edge parameters, optional selection of pre treatment and enrichment phase
- Control of the used potentiostat, setting of current limits and potential range, check of cell connection, display of actual DC voltage/current
- Check of interfacing between IM6 and CGME
- Measurement and evaluation

The sub menus may easily be recognized by their titles and symbols being plotted within the button.

2. Selection of the applied method and parameter settings
To enter the method selecting menu activate the button

Polarography offers the following methods:

2.1. ‘Tast polarography’

2.2. ‘Differential Pulse Polarography’

2.3. ‘Differential Pulse Voltammetry’ (Stripping Voltammetry)
2.0. Global parameters of all methods

The global parameters for all methods are named `settling time` and `start ramp` and will be used during the starting phase of the IM6.

Similar to other DC methods of the THALES system a starting ramp and a settling phase have been prepared and can be used to reduce occurring oscillations or capacitive current overload when the potentiostat will be switched on.

The **starting ramp** will be used when the potentiostat is being switched on and a polarographic experiment will be started. Then the DC potential will be driven from the actual potential of the potentiostat to the defined starting potential. Setting the value of `start ramp` equal zero will disable the start ramp and the experiment will start immediately.

The **settling phase** may be used when the potentiostat will be switched on for a polarographic experiment. Switching on a potentiostat may cause some kind of instability of the investigated system.

The settling phase has been prepared

- to enable the system to return to a `steady state` and
- to wait until possible current fluctuations and oscillations will disappear.

When a settling time $t_{\text{set}}>0$ has been defined the system will be fixed at the starting potential for the fixed time period of length $t_{\text{set}}$ before the polarogramme will be started. Setting $t_{\text{set}}$ equal zero will disable the settling phase.
2.1. ‘TAST POLAROGRAPHY’

The potential will be swept between two edge potentials named ‘start potential’ and ‘end potential’. After a fixed waiting period (‘step width’) an abrupt potential step will be applied. The height of the potential step (‘step height’) must be put in positive. The sign of the potential step, however, will be defined by the setting of the edge potentials, i.e.

- \( E_{end} - E_{start} < 0 \) \( \Rightarrow \) negative potential steps
- \( E_{end} - E_{start} > 0 \) \( \Rightarrow \) positive potential steps

Simultaneously to the output of the potential step the knocker and the dispenser of the CGME will be triggered by the IM6. The drop size can be selected in two ways by the settings of the CGME:

- The dispenser is controlled by the CGME (CGME mode switch = SMDE). The drop size then is determined by the setting of the rotary size switch of the CGME (page 18 of CGME manual).
- The dispenser is controlled by the IM6 (CGME mode switch = CGME). The drop size is determined by the time interval being defined in the parameter named ‘Hg drop growth time’.

The current is sampled shortly before the next potential step will be applied. The sampling time will be defined by the parameter named ‘time of integration’.
2.2. ‘DIFFERENTIAL PULSE POLAROGRAPHY’

The base potential will be changed between two edge potentials named ‘start potential’ and ‘end potential’. After a fixed waiting period (‘step width’) a pulse will be applied. The pulse height is set in the parameter named ‘pulse height’, the pulse length in the parameter named ‘pulse width’. After the pulse the applied potential will return to the base potential +/- a small increment. The height of the potential step (‘step height’) must be put in positive. The sign of the potential step, however, will be defined by the setting of the edge potentials, i.e.

- \( E_{\text{end}} - E_{\text{start}} < 0 \) \( \Rightarrow \) negative potential steps
- \( E_{\text{end}} - E_{\text{start}} > 0 \) \( \Rightarrow \) positive potential steps

Simultaneously to the end of the applied pulse the knocker and the dispenser of the CGME will be triggered by the IM6. The drop size can be selected in two ways by the settings of the CGME:

- The dispenser is controlled by the CGME (CGME mode switch = SMDE). The drop size then is determined by the setting of the rotary size switch of the CGME (page 18 of CGME manual).
- The dispenser is controlled by the IM6 (CGME mode switch = CGME). The drop size is determined by the time interval being defined in the parameter named ‘Hg drop growth time’.

The first current sample will be measured shortly before the next pulse will be applied \( (t_1) \). The second sample will be measured shortly before the end of the pulse \( (t_2) \). The sampling time of both samples is being defined by the parameter named ‘time of integration’. The output current samples are the differences \( dl = I(t_2) - I(t_1) \).
2.3. `DIFFERENTIAL PULSE VOLTAMMETRY`

The parameter set of the DPV method is similar to the DPP method. However, the CGME will not be triggered by the IM6. The mercury drop must be dislodged and must be disposed manually. This offers the possibility to operate the CGME in the HMDE mode (Hanging mercury drop electrode).

The base potential will be changed between two edge potentials named `start potential` and `end potential`. After a fixed waiting period (`step width`) a pulse will be applied. The pulse height is set in the parameter named `pulse height`, the pulse length in the parameter named `pulse width`. After the pulse the applied potential will return to the base potential +/- a small increment. The height of the potential step (`step height`) must be put in positive. The sign of the potential step, however, will be defined by the setting of the edge potentials, i.e.

- \( E_{\text{end}} - E_{\text{start}} < 0 \) \( \Rightarrow \) negative potential steps
- \( E_{\text{end}} - E_{\text{start}} > 0 \) \( \Rightarrow \) positive potential steps

The first current sample will be measured shortly before the next pulse will be applied \( (t_1) \). The second sample will be measured shortly before the end of the pulse \( (t_2) \). The sampling time of both samples is being defined by the parameter named `time of integration`. The output current samples are the differences \( I(t) = I(t_2) - I(t_1) \).
3. `PRE TREATMENT & ENRICHMENT PHASE`  

Before a polarographic experiment a pre treatment phase and an enrichment phase can be activated independently.

3.1. `PRE TREATMENT PHASE`  

During the pre treatment phase the potentiostat will be fixed at its actual state for a certain period of time (`duration`). The stirrer and the purger can both be activated independently. To activate the pre treatment phase put in a duration t>0 and activate the main switch (`do pretreat`).

3.2. `ENRICHMENT PHASE`  

During the enrichment phase the potentiostat will be fixed at a certain potential (`potential`) for a certain period of time (`duration`). The stirrer and the purger can both be activated independently. To activate the enrichment phase put in a duration t>0 and activate the main switch (`do enrich`).
4. REMOTE CONTROL OF BAS CGME

The remote control of the BAS CGME offers 4 functions

- Stirrer
- Purger
- Dispenser
- Hammer

During a measurement the stirrer and the purger will both stay in the set state. The handling of dispenser and purger depend on the selected method.

4.1. STIRRER

The stirrer will be switched on/off by once activating the button named `stir`.

4.2. PURGER

The purger will be switched on/off by once activating the button named `purge`.

4.3. HAMMER

Activating the button named `knock` will once trigger the hammer.

4.4. DISPENSER

Activating the button named `dispense` will put out a pulse on the dispenser remote control line. The pulse length is the `Hg drop growth time`. In the DPV mode (no use of hammer) the pulse length will be set to 100ms.
5. CONTROL OF IM6 POTENTIOSTAT

The connection between CGME cell and IM6 potentiostat will be checked in the section ‘setup potentiostat’. This menu offers different entries to the tools of the EIS programme.

5.1. CHECK CELL CONNECTION

will call the menu ‘check cell connection’ of the EIS programme. In this menu the physical set up of the CGME cell must be defined.
- Usage of reference electrode
- Potential of reference electrode

5.2. SETUP ECW

will call the menu ‘test sampling & potentiostat control’. Here the potentiostat may be switched on and off and the DC conditions of the cell can be checked. For more detail kindly refer to the IM6 manual.

5.3. ILIM & ELIM

‘Elim’ will define a potential range that will be controlled by the software during measurement. The applied potential must not exceed the Elim settings otherwise the measurement will be interrupted and the potentiostat will be switched off.

‘Ilim’ will define the allowed current range during the measurement. The cell current must not exceed the set limits otherwise the measurement will be stopped and the potentiostat will be switched off.

The ‘instruments’ named ‘potential’ and ‘current’ will indicate the actual cell potential and the current actually flowing through the cell.
6. NEXT MEASUREMENT

A new scan will be started by activating the button named `start measurement`.

The checkbox shown below offers a last overview of the set parameters before the sequence will be started. If all settings are correct switch on the button named `start`.
6.1. PRE TREATMENT

If pre treatment has been selected the potentiostat will be switched off. The stirrer and the purger will be set to the defined states. Finally the OCP will be recorded during the time interval of the pre treatment phase.

6.2. ENRICHMENT PHASE

If an enrichment phase has been selected the potentiostat will be switched on and the chosen DC potential will be applied to the cell. The stirrer and the purger will be set to the defined states. Finally the cell current will be recorded during the time interval of the enrichment phase.
6.3. MEASUREMENT

The polarographic sequences will be controlled by a special system routine offering fast output of the DC signal and fast sampling of the flowing current. This routine, however, does not allow the switching of the shunt resistor. Like CV and PVI the measurement will be performed in the fix shunt mode. Consequently the optimum shunt resistor must be found. Therefore a short sequence at the start potential and at the ending potential will be put out starting at the highest shunt resistor being available. If no current overflow will occur that shunt will be used for the next measurement, otherwise the next lower one will be tested until the valid shunt has been found.

Finally the polarographic sequence will be started. The current samples I(E) will online be plotted in an I-E-diagram.
7. DISPLAY LAST MEASUREMENT

The present data will be plotted in an I(E)-diagram. The familiar THALES I/O interfaces will offer selective data output.

'export data'
An ASCII-data-list of the present data may be created and passed to other programs.

'activate crosshair'
The crosshair-functions allows the numerical output of the measured C/V-data.

'printer hardcopy'
The current displayed diagram will be put out to a printer hardcopy.
The analysis main menu offers entries to different submenus controlling the displayed data.

- Control plot     display settings
- Data output  data export functions
- Manipulation  smoothing & noise reduction
- Evaluation  peak search and peak integration
- Cursor control
8.1. THE CURSORS

Two cursors will offer numerical information of the measured data. Each cursor can be moved and may be activated individually.

**ENA C1** switches on/off cursor C1

**ENA C2** switches on/off cursor C2

To move a cursor activate the corresponding button `cursor1` or `cursor2`. To move the selected cursor push the mouse to the left or to the right. To set the cursor to the left/right end of the window use the keys

- `<s>` = start
- `<e>` = end

The cursors will be used to mark the interesting range for peak detection and integration or to zoom a defined range to a larger scaling.
8.2. CONTROL PLOT

Via `control plot` the display settings can be set to individual demands. The scaling of the displayed data can be done automatically (`auto`) or manually (`user`). By the options of the `drawing mode` the data representation and the colours of the selected graphs can be chosen individually.

8.2.1. SCALING

- **Auto** The displayed potential range will be set by use of the cursors C1 and C2. The current scale will be calculated automatically from the selected potential section, i.e. minimum and maximum of \( I(E) \) data \( I(E_{\text{left}}) \) to \( I(E_{\text{right}}) \). In the auto scaling mode the display can be stretched by use of the `ZOOM` button. By use of the `TOTAL` button the whole measurement will be redrawn.

- **User** The scaling limits will be set via two I/O windows.

These I/O functions will be active even in the auto scaling mode. To refresh the diagram any of the buttons `REDRAW`, `TOTAL` or `ZOOM` may be used.
8.2.2. DRAWING MODE

Three drawing modes can be activated individually:

- **Pixel**  The measured data set will be plotted in the pixel mode, i.e. each sample will be represented a small square.
- **Line**   The measured data set will be plotted in the line mode, i.e. all neighboured samples will be connected by a line.
- **Smooth** A second current data set may be displayed additionally. This data set will store the current samples after smoothing or filtering and will be used for integration and peak detection.

For each graph an individual colour can be selected by activating the button `colours` of the `drawing mode` menu.

To select the individual colours activate the corresponding button `pixel`, `line` or `smooth` and a colour selective menu will pop up. Consequently click to the desired colour. By use of the `REDRAW` button the graphical display will be redrawn using the newly defined colours.
8.2.3. REDRAW, TOTAL & ZOOM

- **REDRAW**  The data will be plotted with respect to the latest display settings (plotting colours, scaling mode, display limits).

- **TOTAL**   In the auto scaling mode the whole data set will be redrawn. Using the user scaling mode the plot will be refreshed with respect to the latest settings of X-range, Y-range and display colours.

- **ZOOM**    In the auto scaling mode the potential data between the two cursors will be stretched. The current scale will be calculated automatically from the selected potential section, i.e. minimum and maximum of I(E)-data I(E$_{\text{left}}$) to I(E$_{\text{right}}$). Using the user scaling mode the plot will be refreshed with respect to the latest settings of X-range, Y-range and display colours.
8.3. DATA OUTPUT

`data output` offers two export functions

- Output of the displayed graphic to a printer hardcopy
- Output of the displayed data to a MS-DOS formatted text list

8.3.1. HARDCOPY

8.3.2. ASCII LIST
The `export data` function of the `display last measurement` option will create a data list of all measured samples. In this section the range of the ASCII list can be set by use of the cursors C1 and C2, i.e. a certain interval can be defined for export.

After activating the button named `ASCII-List` the destination of the text list must be selected.

- **Print list** will usually not be used to put out a printed data list on the line printer.
- **Text editor** We recommend this option to take a look on the format of the THALES text lists. Finally the created header block may be removed before the data will be saved.
- **Direct to DOS** The data set will be written to an ASCII formatted text file in the defined subdirectory of the selected DOS-WIN device.

Example of an ASCII list
Selecting the option ‘direct to DOS’ an I/O box will prompt to put in filename and file extension. After a correct filename has been put in the file will be written to the subdirectory and storage device that has been defined in the global set up of the THALES system.

To set and control that path enter the section UTIL of the THALES main menu. The following sequence will describe the way how to check and how to redefine the DOS list path (for more details kindly refer to the section `disc ops` of the IM6 manual).

- **THALES main menu**
- **UTIL**
- **main setup**
- **Edit**
- **Data pathes**
- **Unit/Device**
- **PATH**

**NOTE:** All default data paths on the IM6 will be stored in the THALES main set up when the UTIL set up will be saved. That set up will be reinstalled during the next start up and all paths will be preset when the software will be started.
8.4. MANIPULATION

The section `manipulation` offers smoothing and filtering of the measured data. The manipulated data set will be stored in an additional array. Thus the evaluation can easily be reset to its original settings.
8.4.1. SMOOTHING

Smoothing will be done by a polynomial of 4\textsuperscript{th} degree

\[ SMOO(E) = I_0 + I_1 \cdot E + I_2 \cdot E^2 + I_3 \cdot E^3 \]

and uses the common regression algorithm

\[ \sum (I_n - SMOO(n))^2 = \text{min} \]

The smoothing window will be defined by the overall spectra length and the parameter named `smoothing window`.

Example:
- Dimension of data = 500
- Smoothing window = 2\% (2/100)
- Smoothing dimension = +/-5 samples

To vary the smoothing window call the I/O box named `WINDOW`. 
The smoothed data finally will be used for integration and peak detection in section `evaluation`. The graphics above show the influence of the smoothing operation on the data. Defining the smoothing window too broad (10%, 20%) will result in a clipping of the measured peaks. However, if the smoothing was too rough the data may easily be reloaded by `reset & reload measured data`.

8.4.2. NOISE REDUCTION
If the quotient \( Q \) of measured point over the mean value of its neighboured points will exceed an upper threshold \( I_{\text{upper}} \) or a lower threshold \( I_{\text{lower}} \) the corresponding measuring point \( I_n \) will be replaced by the mean value of its neighboured points \( I_{\text{mean}} \).

\[
Q = \frac{2 \cdot I_n}{I_{\text{mean}}} \quad I_{\text{mean}} = \frac{I_{n+1} + I_{n-1}}{2}
\]

\[
I_{\text{upper}} = I_{\text{mean}} + I_{\text{thresh}} \quad I_{\text{lower}} = I_{\text{mean}} - I_{\text{thresh}}
\]

The noise filtering routine can be repeated up to 25 times automatically.

To set the threshold and the repetitive count call the I/O box named ‘Threshold’.

8.4.3. NOISE REDUCTION BY USING A DIGITAL LOW PASS FILTER
The noise of the spectrum can be reduced by using a digital low pass filter of 1st order. Therefore the following restrictions must be considered:

The sampling frequency and the edge frequency are virtual magnitudes. The sampling frequency has been set equal to 10. To obtain a maximum stability of the filtering algorithm the edge frequency of the low pass is limited to a range \(0.1 \leq f_{min} \leq 1\).

The table below shows the result of digital low pass filtering in dependence of the chosen edge frequency.

<table>
<thead>
<tr>
<th>(F_{low, pass})</th>
<th>(F_{low, pass})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.6</td>
</tr>
<tr>
<td>0.2</td>
<td>0.1</td>
</tr>
</tbody>
</table>

To vary the edge frequency call the I/O box named ‘Fmax’.

8.5. RESET DATA MANIPULATION & RELOAD DATA
The original measuring data and the smoothed data are stored in different arrays IPOL(i) and IEVA(i). Each operation on the data manipulation will work on the second set IEVA(i). By this a simple copy operation can reset the data manipulation by overwriting IEVA() with the original data IPOL() without reloading the data from disk.

9. DATA EVALUATION

- BASE LINE SETTING
9.1. USAGE OF THE BASE LINE

Current integration and peak detection can both be done either

- absolutely (zero based)
- or relatively to a defined base line.

To select the absolute or the relative mode use the button named ‘use’.

9.2. SETTING THE BASE LINE

To call the base line editor activate the button named ‘set base’. Now the base line can be redefined by graphical or numerical input.

For numerical input activate the button named ‘Xbase Ybase’ and put in left and right end

For graphical input use the buttons named ‘left’ and ‘right’.
9.3. CURRENT INTEGRATION
To calculate the current integral activate the button named ‘calculate integral’. The result will be displayed and may be put out to either a hardcopy or may be appended to the actual text of the THALES text editor **ZEdit**.
9.4. PEAK DETECTION

The current peaks will be detected from the soothed data set. To reduce the noise nearly completely and to avoid erroneous peak detection an intermediate data set is being used. That set will be smoothed within a broad window and, if necessary that data set can be compressed to minimize the calculating time.

The smoothing window width and the compression factor will be put in by calling different I/O boxes.

Intermediate smooth

![Intermediate smooth interface]

Compression

![Compression interface]

By compression a loaded data set of dimension DATDIM may be compressed to a small set of at least 100 points. The maximum possible compression factor will be calculated dynamically and will define the upper limit of the corresponding I/O box. The compressed spectrum will be calculated from the smoothed spectrum by averaging n (=compression factor) measuring points. After measurement or after loading of a spectrum the compression factor will be set to a resulting compressed spectrum of 500 points in length. That compression factor will be stored as default and can be changed to the user’s demands.

To start the peak detection finally activate the button named ‘GO’.

A new peak search will be started

- after a new measurement
- after a measurement has been loaded
- if the parameters had been changed.

Otherwise the found peaks will be displayed with respect to the base line settings and the result may be put out either to a printer hardcopy or may be appended to an existing text of the text editor ZEdit.