

PSTrace 5

Version 5.6

User Manual

In case of problems

Make sure your software and firmware are up-to-date.

Please do not hesitate to contact us at info@palmsens.com.

Try to describe the problem as detailed as possible, screenshots are often very helpful.

Alternatively, you can contact us one of the following ways:

Internet: <http://www.palmsens.com/en/contact/>

Telephone: +31 30 2459211

Please have your instrument model and serial numbers available, as well as any applicable software and firmware revisions.

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See Appendix A for a CE declaration of conformity.

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Contents

1	Getting Started	1
1.1	Requirements.....	1
1.2	Which model do I have?	1
1.3	Installation.....	2
1.4	Operating PalmSens1 or 2.....	3
1.5	Operating PalmSens3	4
1.6	Operating PalmSens4	5
1.7	Operating EmStat	5
1.8	Operating EmStat Blue	5
1.9	PSTrace basic principles	6
1.9.1	Methods	6
1.9.2	Measurement data.....	7
1.9.3	Curves	7
1.9.4	Saving your data.....	8
1.10	Configuring PSTrace.....	8
1.10.1	Program modes	9
1.10.2	Hardware configuration	10
1.10.3	Plot and data	12
1.11	Connecting	14
1.11.1	Connecting using Bluetooth	14
1.11.2	Using a USB to serial converter	17
2	First measurements	19
2.1	Which dummy cell do I have.....	19
2.2	First measurement on the TestSensor	19
2.3	First measurement on the Dummy Cell.....	21
2.4	First EIS measurement on the Dummy Cell	22
2.4.1	Fitting your data.....	23
2.5	Readings.....	25
3	Measuring	27
3.1	Setting up a measurement.....	27
3.2	Resolution and optimal current range selection	29
3.3	Running a measurement.....	31
3.3.1	Autosaving measured data.....	31
3.3.2	Recovery file in Simultaneous mode	33
3.4	Peaks and levels	33
3.5	Multiplexer	34
3.6	Recording an auxiliary input	36
3.7	Recording the cell potential	37
3.8	Using a BiPot	37
3.9	Using Blank subtraction.....	39
3.10	Using IR drop compensation	40

3.11	Noise.....	41
3.12	Measuring the noise level of the instrument	42
3.13	Available techniques	44
3.13.1	Linear Sweep Voltammetry (LSV)	44
3.13.2	47	
3.13.3	Differential Pulse Voltammetry (DPV).....	48
3.13.4	Square Wave Voltammetry (SWV)	51
3.13.5	Normal Pulse Voltammetry (NPV)	53
3.13.6	AC Voltammetry (ACV).....	56
3.13.7	Cyclic Voltammetry (CV)	59
3.13.8	Fast Cyclic Voltammetry (FCV)	62
3.13.9	Chronopotentiometric Stripping (SCP)	64
3.13.10	Chronoamperometry (CA).....	66
3.13.11	Pulsed Amperometric Detection (PAD).....	68
3.13.12	Fast Amperometry (FAM).....	71
3.13.13	Multiple Pulse Amperometry (MPAD)	72
3.13.14	Chronopotentiometry (CP).....	73
3.13.15	Open Circuit Potentiometry (OCP).....	75
3.13.16	Multistep Amperometry (MA).....	76
3.13.17	Multistep Potentiometry (MP)	77
3.13.18	Mixed Mode (MM).....	79
3.14	Measurement sequence	86
3.15	Measuring versus OCP	87
3.16	Advanced settings	88
3.16.1	Stop when E or I reaches specified value.....	88
3.16.2	Trigger at	88
3.16.3	On device storage	88
3.16.4	Use IR drop compensation.....	89
3.17	Limitations of the EmStat Pico	91
3.17.1	EmStat Pico modes.....	91
4	Electrochemical Impedance Spectroscopy	93
4.1	Introduction.....	93
4.2	Setting up an impedance measurement	97
4.3	Running an EIS measurement	102
4.4	Export for analysis and circuit fitting.....	104
4.4.1	Free EIS Spectrum Analyser.....	104
4.4.2	ZView	106
4.4.3	Origin	106
4.5	Limitations for EIS on EmStat Pico	107
5	Circuit Fitting	109
5.1	Overview	109
5.2	Opening the circuit editor	111
5.3	Switching between Edit mode and Fit mode	111
5.4	Building a circuit	112
5.5	Loading and saving circuits	119

5.6	Fitting or simulating a circuit.....	120
5.7	Overview of circuit components	125
5.8	Fitting Example	134
5.9	Fitting algorithm.....	145
6	Plot, curves and data	147
6.1	Handling curves	147
6.2	Session data	148
6.2.1	Measurement Tool window	149
6.2.2	Curve Tool window	150
6.3	Plot interactions	150
6.3.1	Marking peaks manually	151
6.3.2	Other calculations on the curve.....	156
6.4	Toolbars.....	158
6.5	Linear baseline subtraction.....	161
6.6	Non-linear baseline subtraction	162
6.7	Moving average baseline subtraction	164
6.8	Discarding data points	165
6.9	Separating overlapping peaks	167
6.9.1	Separating peaks.....	167
6.9.2	Advanced settings	169
6.10	Saving data.....	171
6.10.1	Legacy curve files.....	172
6.11	Exporting curves	172
7	Manual Control	175
7.1	Manual Control tab	175
8	Analytical mode	177
8.1	Supported techniques	177
8.2	Setting up parameters	178
8.3	Running a measurement.....	181
8.4	Result analysis	183
8.4.1	Standard Addition.....	183
8.5	Example data files.....	184
9	Corrosion mode	187
9.1	Supported techniques	187
9.2	Running a measurement.....	188
9.3	Result analysis	189
9.3.1	Setting up material parameters	189
9.3.2	Linear polarization	191
9.3.3	Impedance Spectroscopy	195
9.4	Exporting results	199
9.5	Example data files.....	200

10 Files	201
10.1 File types.....	201
10.2 Loading and saving data.....	202
10.3 Exporting data to other file formats	206
11 Scripting	207
11.1 Features.....	207
11.1.1 File menu	208
11.1.2 Composing a script	209
11.1.3 Changing parameters	209
11.1.4 Using the output file	210
11.2 Measure command.....	211
11.3 Fast Mode command.....	212
11.4 Cell command.....	212
11.5 Set current command	213
11.6 Read current command	214
11.7 Set potential command.....	215
11.8 Read potential command.....	215
11.9 Wait command.....	216
11.10 Repeat command	217
11.11 FindPeaks command	218
11.12 SetChannel command	219
11.13 NextChannel command	219
11.14 PrevChannel command	219
11.15 Stirrer command	219
11.16 SetAnalog command	219
11.17 ReadAuxiliary command	220
11.18 SetDigitalIO command.....	220
11.19 ReadDigitalIO command.....	220
11.20 Override parameter command.....	221
11.21 Run a script from the command line.....	222
12 CH8 Multiplexer	225
12.1 Sensor configurations.....	225
12.2 Changing the configuration.....	228
12.3 Pin layout	230
12.4 CH8 cable lay out	231
12.4.1 Belkin cable (dark grey) Colour codes	231
12.4.2 CH8 cable COPARTNER E119932-U Version 2 Colour codes	232
12.4.3 Specifications	233
13 MUX8 and MUX16 multiplexers	235
13.1 MUX8 multiplexer	235
13.1.1 Functional diagram	236
13.1.2 Specifications	236
13.1.3 Sensor configurations.....	237

13.1.4	Electrode connections	240
13.2	MUX16 multiplexer	241
13.2.1	Functional diagram	241
13.2.2	Specifications	241
13.2.3	Sensor configurations.....	242
13.2.4	Electrodes connections	244
14	MUX8-R2 multiplexer	245
14.1	MUX8-R2 Functional Diagram	245
14.2	Specifications	246
14.3	Configurations	246
14.4	Connections.....	247
14.5	MUX8-R2 Pin-outs.....	248
14.6	Stacking	249
15	PalmSens or EmStat firmware update	251
15.1	Firmware update	251
16	PalmSens instrument specifications	255
16.1	Description.....	255
16.2	PalmSens1 and 2 specifications	256
16.3	BiPot specifications for PalmSens1 and PalmSens2.....	257
16.4	PalmSens3 specifications	258
16.5	BiPot specifications for PalmSens3.....	259
16.6	PalmSens4 specifications	260
16.7	Auxiliary port pin-outs.....	262
16.8	Sensor connector pin-outs	264
16.9	Battery maintenance.....	267
17	EmStat instruments specifications	269
17.1	Description.....	269
17.2	EmStat and EmStat2 specifications	270
17.3	EmStat3 and EmStat3+ specifications	271
17.4	EmStat Blue auxiliary port pin-out	273
17.5	Sensor connector pin-outs	274
18	Multi-channel instruments specifications	275
18.1	MultiPalmSens4 specifications	275
18.2	MultiEmStat3 / 3+ specifications	275
18.3	EmStat-4WE specifications	276

19	Troubleshooting	279
19.1	Test procedure for PalmSens and EmStat.	279
19.2	Replacement of PalmSens1 or PalmSens2 battery	280
19.3	Restoring PalmSens3 in case of freeze	282
19.4	EIS Calibration	284
Appendix A – CE Certificate		285
20	Index	287

1 Getting Started

1.1 Requirements

PC requirements for PSTrace:

- Windows Vista, 7, 8, or 10 (32-bit or 64-bit)
- .NET 4.5.2 framework installed
- 1 GHz or faster 32-bit (x86) or 64-bit (x64) processor
- 1 GB RAM (32-bit) or 2 GB RAM (64-bit)
- Minimal screen resolution of 1024 x 768 pixels

Instrument requirements:

- Single channel instrument (or multiplexed) from PalmSens BV
- Connection by means of serial (RS232), USB cable, USB-to-serial adapter or Bluetooth

Required for test measurements:

- Sensor cable with crocodiles and PalmSens Dummy Cell

1.2 Which model do I have?

The following instruments can be used with PSTrace. Multi-channel instruments like MultiEmStat and EmStat4WE are used with the **MultiTrace** software.



EmStat1 (until 2010)



EmStat2 (until 2013)

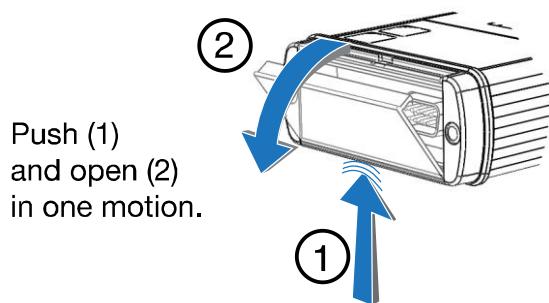
*EmStat3 or EmStat3+**EmStat3 or EmStat3+ Blue**EmStatMUX8 or EmStatMUX16**PalmSens1 or 2 (until 2013)**PalmSens3 (until 2017)**PalmSens4*

1.3 Installation

Install PSTrace by running Setup.exe from the media that came with the instrument or when downloaded; from the location where the downloaded ZIP file was extracted. After installation a folder ‘PSData’ is created in your ‘My Documents’ folder. This folder contains some example method and data files. A PSTrace shortcut is placed in the Start menu in ‘PalmSens\PSTrace’ and on the desktop.

1.4 Operating PalmSens1 or 2

Open the lid at the left-hand side of PalmSens by pressing the hinge upwards and then turning the lid.



Before PalmSens is used without the adapter, the batteries must be charged. Connect the adapter to the miniDIN-connector (PS1) or dc-in connector (PS2). Switch on PalmSens by pressing the power key until the display shows: "Selftest". During the self test the voltage range of the instrument is tested and shown. The normal range for PalmSens is approx. -2.035 V to +2.047 V.

After the test the display will show:

```
> PalmSens
Vs. #.#
E= #.### V
FsChg
```

As long as the display shows the text "FsChg", the batteries are being charged. As soon as the display shows "PwrOK", the batteries are full and the adapter can be disconnected. The batteries have to be recharged as soon as "LowBat" is shown and the corresponding beep is heard.

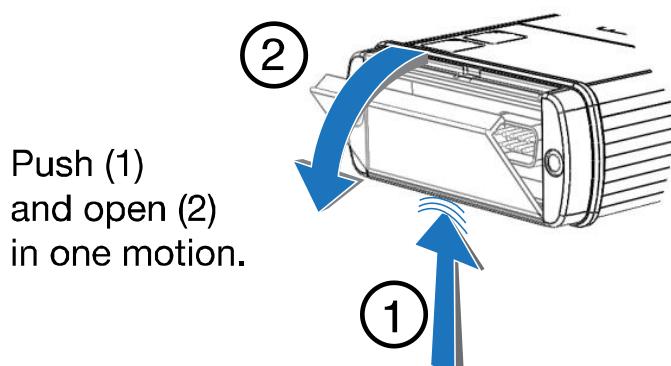
PalmSens can be used with the adapter connected and the batteries charged. The adapter however might increase the noise level.

The backlight of the LCD is switched on and off by using the key ▲. Please note that the backlight will reduce the battery-lifetime of PalmSens from approx. 8 hours to not more than 6 hours.

PalmSens is switched off by pressing the power key until the display shows "Shutting down".

1.5 Operating PalmSens3

Open the lid at the left-hand side of PalmSens by pressing the hinge upwards and then turning the lid.



Push (1)
and open (2)
in one motion.



Power button

PalmSens3 is switched on by pressing and holding the power button. If a PalmSens3 Bluetooth extension is used, make sure the Bluetooth extension is connected to the PalmSens3 auxiliary port BEFORE turning it on. PalmSens3 will detect any extensions during start-up.

PalmSens3 is switched off by pressing the power button twice. If PalmSens3 is not responding, press and hold the power button for a few seconds to force it to switch off.



Backlight button

The backlight of the LCD is switched on by using the backlight button next to the power button. Please note that the backlight will reduce the battery-lifetime of PalmSens3.

The backlight is turned off automatically after a while.



Charging icon

PalmSens3 is always charging when connected to a USB port. When charging the red battery icon will light up.



Stop button

Pushing the stop button will abort any running measurements immediately. If the instrument is in ‘fast mode’ it will return to normal mode.



Start button

Reserved for future updates.



Skip button

This button can be used to skip pretreatment stages and proceed to the next stage. See also section Measurement sequence

1.6 Operating PalmSens4



Power button

PalmSens4 is switched on by pressing and holding the power button.

PalmSens4 is switched off by pressing and holding the power for a couple of seconds. If PalmSens4 is not responding make sure to take out the USB connector and, press and hold the power button for a few seconds to force it to switch off.

1.7 Operating EmStat

EmStat is normally powered by means of the USB cable, which is shown by a (soft) green LED on EmStat1 and EmStat2 and a bright blue led on EmStat3 and EmStat3+. The red LED is shown when the cell is switched on (EmStat3 and EmStat3+). Certain laptops or PC's induce a high noise level. This can be eliminated using a USB-hub with its own ac-adapter or a Galvanic Isolation USB dongle, which is available from PalmSens BV.

1.8 Operating EmStat Blue

When connecting to the USB port of a PC, Bluetooth will switch off automatically unless there is Bluetooth a connection active. This allows the instrument to be charged via a PC while a Bluetooth connection is present.



Power button

EmStat Blue is switched on by pressing and holding the power button.

When device is on:

Press short to switch Bluetooth ON or OFF.



Bluetooth icon

Blinking: ready to connect

Steady: connected



Battery icon

Blinking red: battery low

Blinking green: charging battery

Steady green: battery fully charged

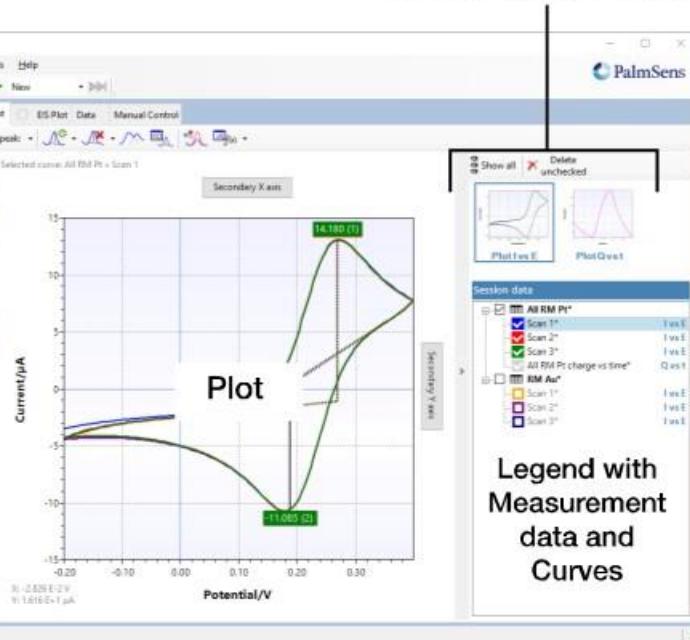
1.9 PSTrace basic principles

The main window of PSTrace shows a Method Editor on the left-hand side which contains all measurement parameters and related information and a Plot area on the right-hand side which contains everything post-measurement related, including measurement results and analytical tools.

Select current ranges for auto ranging and the starting current range.



Switch between plots if curves with different units are available.



PSTrace lay-out

1.9.1 Methods

PSTrace uses ‘Methods’ as a starting point for a measurement. A Method contains all measurement parameters like which *Technique* (Linear Sweep Voltammetry, Square Wave Voltammetry, Electrochemical Impedance Spectroscopy, etc.) is used and information about post-measurement actions like data smoothing and peak searching. All these parameters can be edited in the Method Editor which is found at the left-hand side of the PSTrace window.

The parameters can be saved to and loaded from a ‘.psmethod’ file using the menu: ‘Method’. These files do not include any data and only contain the measurement parameters settings as shown in the Method Editor.

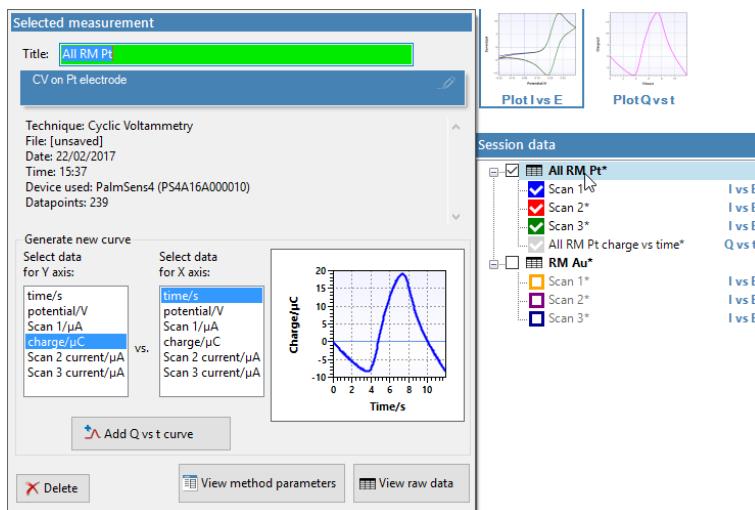
Switching between techniques or changes parameters in the Method Editor has no effect on anything that has already been measured and is displayed in the Plot.

1.9.2 Measurement data

As soon as a measurement is started a new ‘Measurement’ node appears in the Legend containing the default Curve for the corresponding technique. The Measurement contains the following information:

- Method parameters (as was defined in the Method Editor)
- Raw measurement data
- One or more curves

By clicking the Measurement in the Legend, the following window is shown:



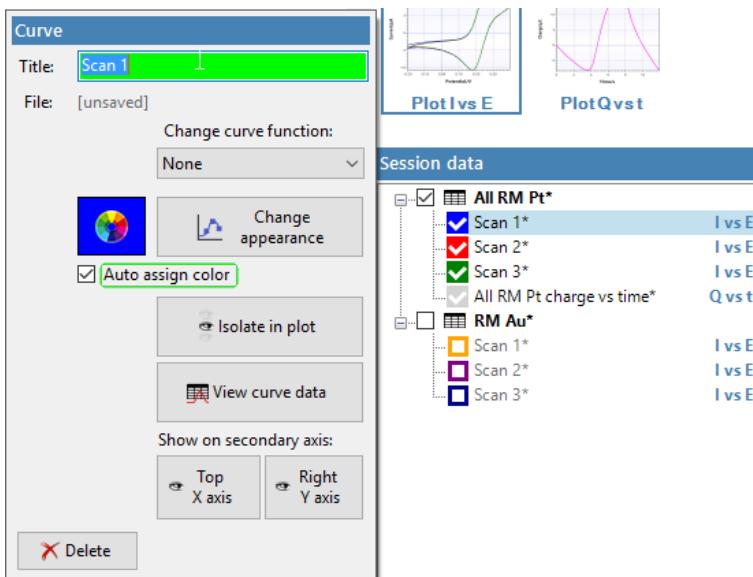
Pop-up window shown when clicking a Measurement in the Legend

The window allows to change the Measurement title and notes directly. The notes shown here are a copy from the original Method used for this measurement. Also, the window allows to add new curves to the Plot based on the available Measurement data.

The “View method parameters” button shows the original Method used for this Measurement. This Method is a copy from the original Method defined in the Method Editor before the measurement was started.

1.9.3 Curves

A measurement can contain one or more Curves. By clicking a Curve in the Legend a window is shown with information about the Curve. It allows you to directly change the title of the Curve as shown in the Legend or change its appearance or view the Data used for this curve.



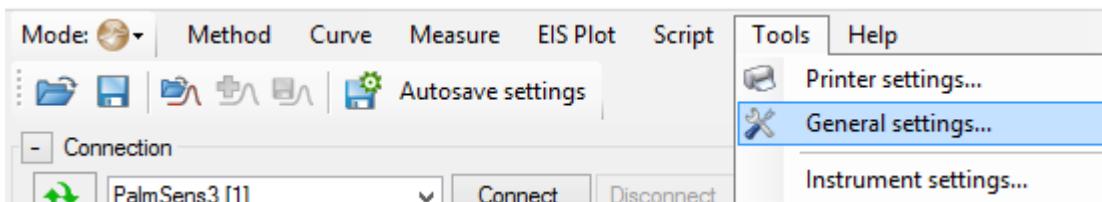
Pop-up window shown when clicking a Curve in the Legend

1.9.4 Saving your data

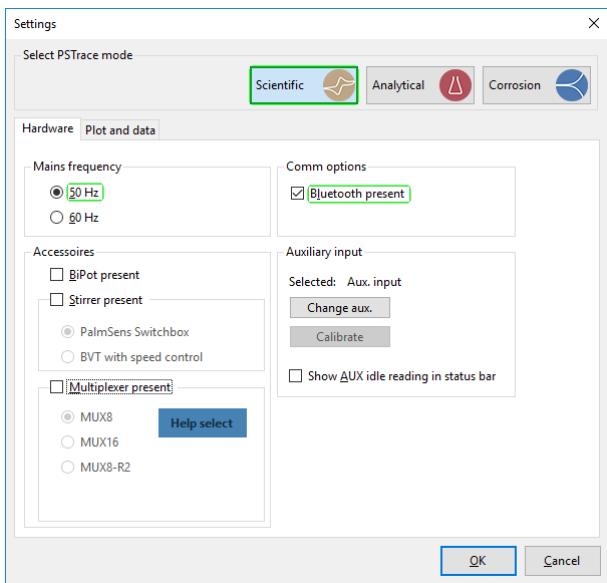
All available Measurement data and curves as well as the Method as shown in the Method editor can be saved to a single ‘Session’ file (.pssession). Use the menu ‘Data’ to save and load Sessions. Any titles changed or customised Curve appearances like colour and symbols used are saved as well.

1.10 Configuring PSTrace

Before you start using PSTrace it is important that all settings are determined. The Settings window is always shown at the first start of PSTrace.
The Settings window can also be found in the menu Tools → General settings.



General settings in the Tools menu

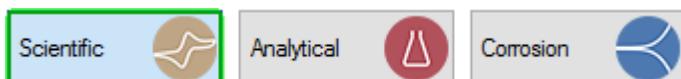


Settings window

1.10.1 Program modes

PSTrace can run in three different modes.

The mode can also be set using the button in the main window at the left corner.



Scientific mode

Scientific mode is the default mode of PSTrace. This mode supports all relevant measurements and generic tools for curve analysis. Automatic as well as manual peak search is available, for determining peak potential, peak height, peak area and peak width. It is also possible to subtract curves from each other and to perform linear regression on a marked part of a curve.

Analytical mode

The extension of program PSTrace for Voltammetric Analysis provides the possibility to do quantitative analysis by means of:

- Standard addition
- Using a calibration curve

For more information see section Analytical mode

Corrosion mode

The Corrosion mode of PSTRace translates the supported techniques to naming conventions generally used with Corrosion Analysis. Secondly a tab with analytical tools is added to the user interface for

- Linear polarization, from which the polarization resistance is obtained,
- Tafel plots, from which the corrosion rate is obtained.
- Impedance data analysis by means of equivalent circuit fitting for determining values like polarization resistance and corrosion rate.

For more information see section Corrosion mode

1.10.2 Hardware configuration

Mains frequency

The **Mains Frequency** is used by PalmSens or EmStat to eliminate noise induced by electrical appliances.

Accessories

PalmSens or EmStat can be used with a stirrer which is activated during the conditioning and deposition phase of a measurement. It can also be controlled manually in the Manual Control tab. The stirrer is normally controlled using a Switchbox from PalmSens BV. In case the BVT stirrer is used, its speed can be specified in the Manual Control tab.

If PalmSens is equipped with a BiPot module, a second WE (Working Electrode) can be used. This is supported in Manual Control as well as with several techniques. The BiPot **offset** can have a value between -0.05 and 0.05 V.

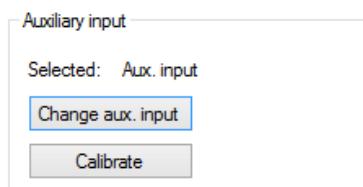
Check the ‘Multiplexer present’ checkbox if you are using a MUX multiplexer. All multiplexers can either be in the form as an accessory with the potentiostat or have an integrated EmStat potentiostat.

Use the button ‘Help select’ to see which model you are using.

Comm options

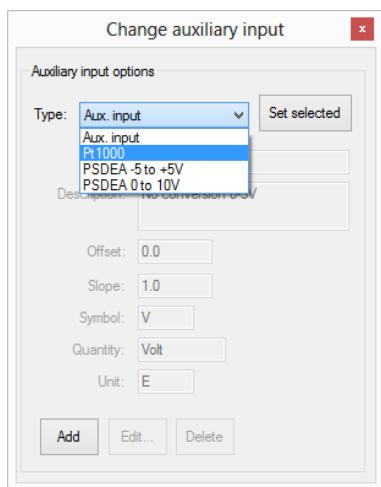
Check the ‘Bluetooth present’ checkbox if you are using an instrument that is Bluetooth enabled. See also section: [Connecting using Bluetooth](#) on page 14.

Auxiliary input



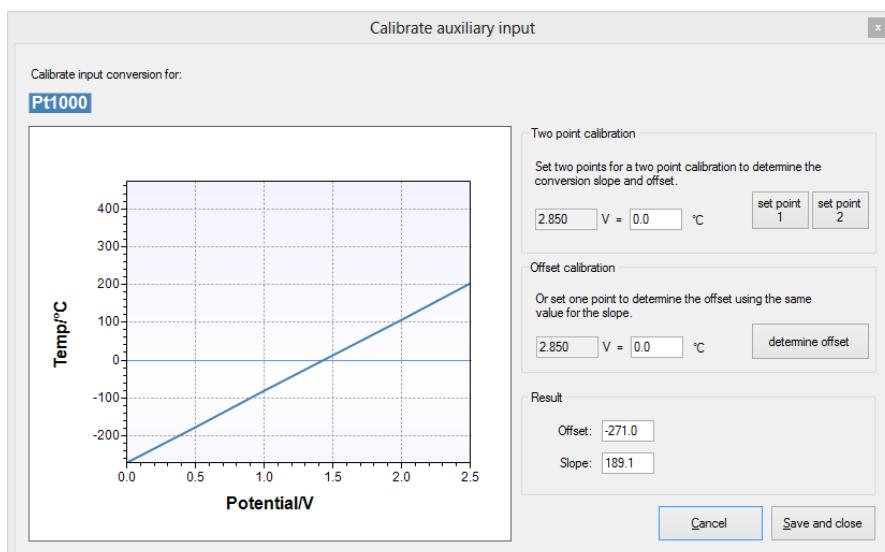
Auxiliary input options

Both EmStat and PalmSens have an auxiliary input that can be used to measure an external signal simultaneously with a measurement. The standard accessories provide by PalmSens BV that make use of the auxiliary port are listed when clicking the 'Change aux. input' button.



The auxiliary input selection window

A custom auxiliary input can also be added. If the analog output of any external device is linear, it can be translated to any given unit. Use the 'Calibrate' button for calibration.



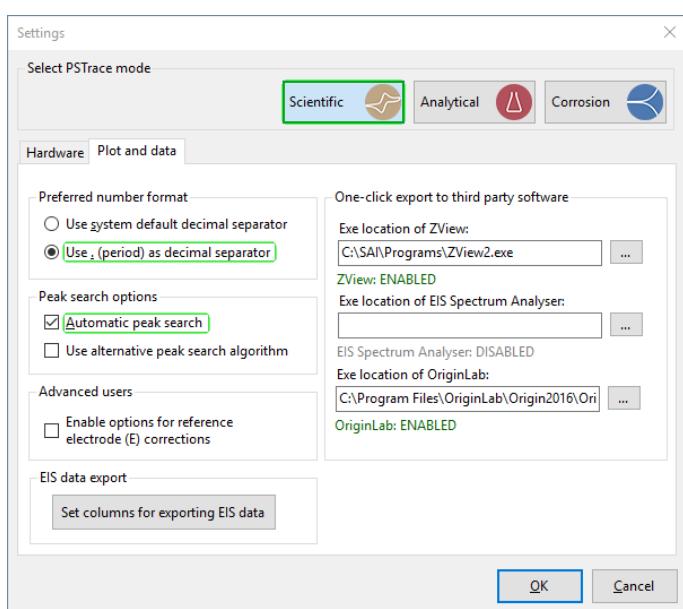
Calibrate the selected auxiliary input

Calibration can be done by setting two points to determine both offset and slope of the linear relation, or by just adjusting the offset.

The Pt1000 temperature sensor for example can be put in boiling water. Then 100 degrees can be entered in the field for Offset calibration to determine the offset.

A more precise two point calibration can also be used. In this case a high precision thermometer can be used in a low temperature and high temperature medium to enter two different values, e.g. room temperature and 100 degree Celsius by using the ‘set point 1’ and ‘set point 2’ buttons. This will determine both the offset and slope for the linear relation.

1.10.3 Plot and data



Settings window – Plot and data tab

Preferred number format

In case the local decimal separator is a comma instead of a point, the checkbox ‘Use local default decimal separator’ can be used to override this.

Peak search options

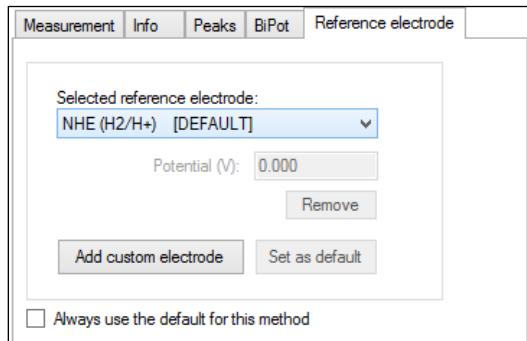
- ‘No automatic peak search’: If checked, no automatic peak search is done on measured data or when data is loaded from file.
- ‘Use alternative peak search algorithm’: If checked, a different peak search algorithm is used which performs better on curves on a steep slope with no clear valleys.



Peaks found with the Alternative Peak Search option enabled.

Advanced users

The checkbox ‘Enable options for E corrections’ adds a number of components to the user interface of PSTrace:



Set reference electrode used in the method editor



Extra toolbar added in plot with options to plot curves with potential values corrected for the reference electrode used.

Export data to ZView

Measured EIS data can be exported with one click to ZView. The location for ZView is detected automatically. If for some reason PSTTrace cannot detect the location of ZView automatically, browse to the location of the .exe file manually.

See also section ZView.

Export data to EIS Spectrum Analyser

Measured EIS data can be exported with one click to the free program EIS Analyser. In order to use the one-click-export button next to the plot, the location of this program needs to be set manually.

See also section EIS Spectrum Analyser.

Export data to Origin

Measured data can be exported with one click to Origin. To use the one-click-export button next to the plot, the location of this program needs to be set manually.

See also section Exporting Curves.

1.11 Connecting

Select the COM or USB port to which the instrument is connected and click ‘Connect’.

If a USB cable is plugged in after PSTTrace was started, use the ‘Refresh’ button: 

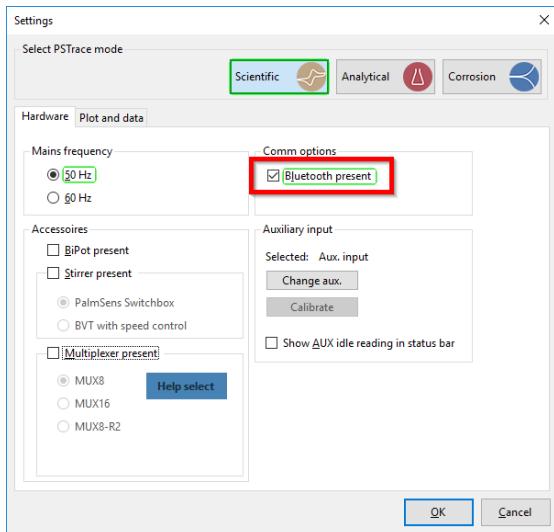


Connecting with a device

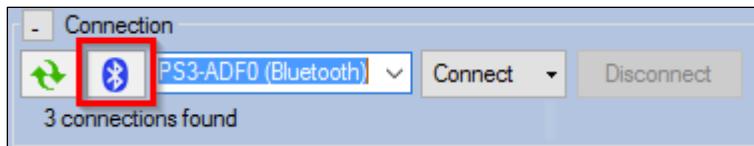
1.11.1 Connecting using Bluetooth

To make a connection using Bluetooth, please follow these steps:

1. In case of a PalmSens2; make sure your PalmSens2 is *Bluetooth ready*. This can be checked by a marking with ‘BT’ at the bottom of the instrument.
2. Connect the Bluetooth dongle to PalmSens or use an EmStat Blue or PalmSens4.
3. Make sure your PC is equipped with Bluetooth capabilities
4. Make sure the ‘Bluetooth present’ is checked in the Settings window of PSTTrace (see menu ‘Tools’ → ‘General settings...’)



5. Click the 'Bluetooth button':



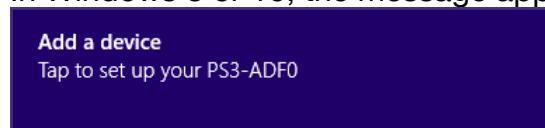
If the device is not listed, wait briefly and click the 'Refresh' button again. It can take some time before Windows has initialized all available Bluetooth devices.

6. Click 'Connect'. If this is the first time the PC is connecting to the Bluetooth extension, Windows will ask for pairing.

In Windows Vista or 7 the message appears:



In Windows 8 or 10, the message appears:



Click this message and when prompted for a code, enter 1234.

Use pairing code: 1234

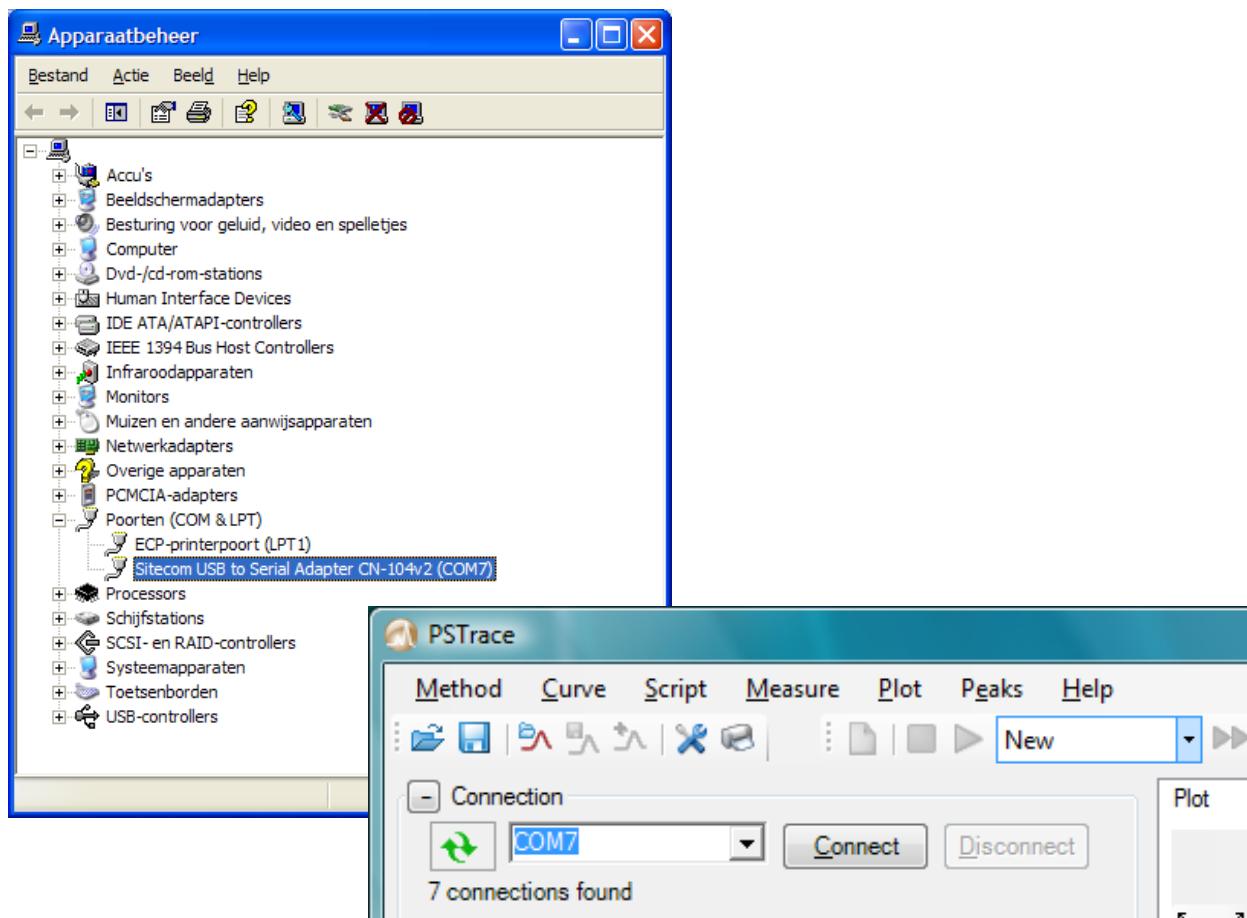
7. If the pairing procedure took too long, the connection might have timed out. In this case repeat the steps from step 4 on.

1.11.2 Using a USB to serial converter

In case a USB – RS232 adapter is used; the driver of the adapter has to be installed according to the manual of the adapter. The COM number used can be found in Windows' Device Manager. This adapter requires a null-modem adapter (female-female) between the cable and PalmSens.

To open the Device Manager quickly, press the Windows key  and the Pause/Break key on the keyboard of your computer simultaneously. Click the Hardware tab, and then click Device Manager. The installed COM port and its number are listed under Ports.

Specify this number in the COM textbox in PSTrace if necessary.



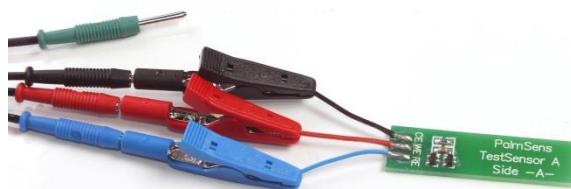
Make sure the right COM port is used in PSTrace

2 First measurements

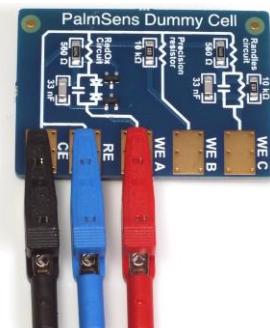
To get acquainted with the instrument, the PalmSens TestSensor or Dummy Cell (since late 2017) is supplied in order to perform reproducible measurements.

2.1 Which dummy cell do I have

Before proceeding, please make sure to verify which dummy cell you have:



PalmSens TestSensor A (shipped until late 2017)



PalmSens Dummy Cell

The following sections apply to either dummy cell.

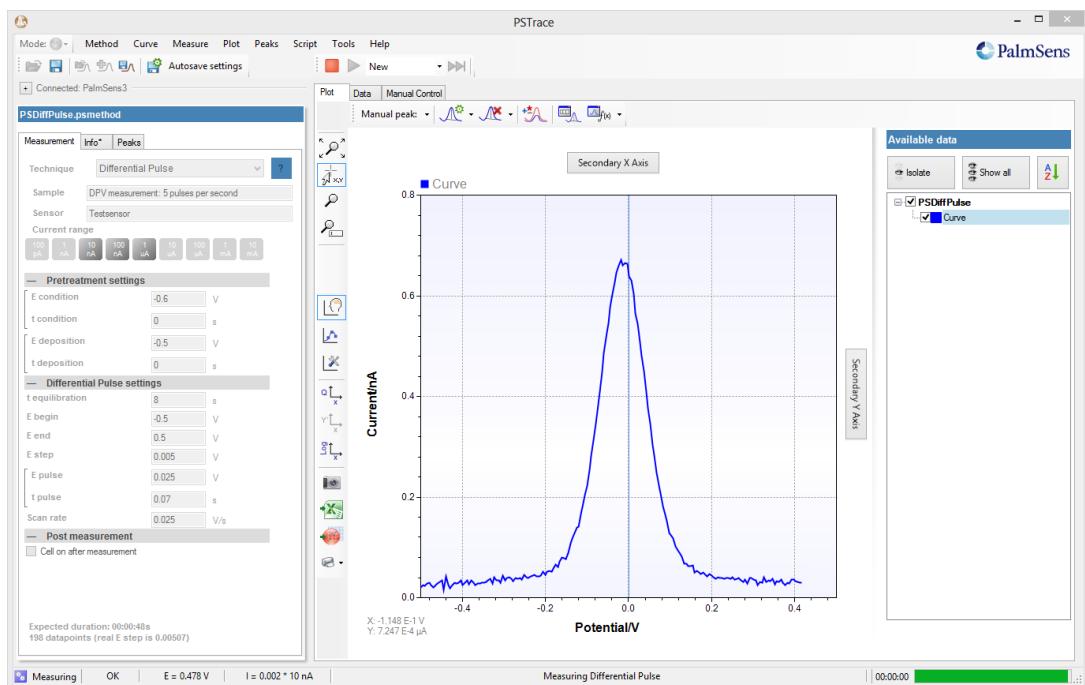
2.2 First measurement on the TestSensor

This section describes how to do a first Linear Sweep measurement with any PalmSens BV instrument (EmStat or PalmSens-series) using the PalmSens TestSensor.

Please follow these steps if you have a PalmSens TestSensor as shown here:



1. Make sure the instrument is on and connected to the PC
2. Open PSTrace and connect to the instrument
3. Load the following method file (menu: ‘Method’ → ‘Load’):
‘[USER]\Documents\PSData\PSDiffPulse.psmethod’
4. Connect the TestSensor using the croc clips as shown in the picture above.
5. Start measurement by clicking the start button in the toolbar.



Important:

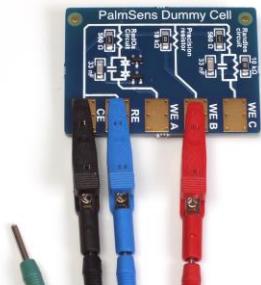
The TestSensor gives a current response in the order of nanoamperes. This means that proper shielding is of significant importance. In case the curve shows a different shape than the one shown in the picture above, make sure to use a Faraday cage and connect the green GND lead to the Faraday cage.

For more information see section Noise

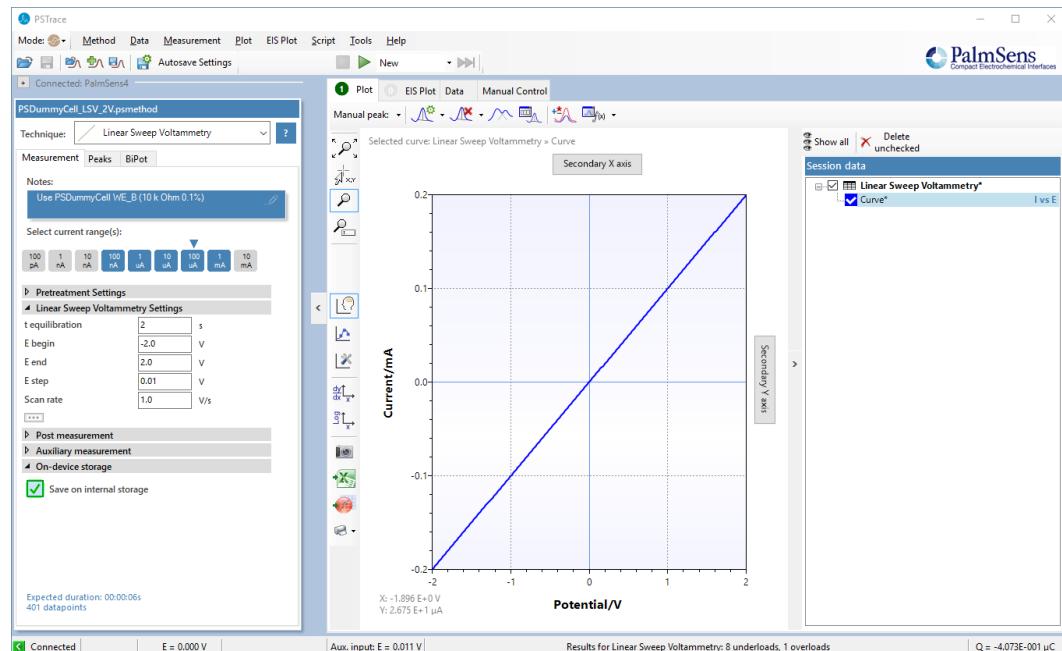
2.3 First measurement on the Dummy Cell

This section describes how to do a first Linear Sweep measurement with any PalmSens BV instrument (EmStat or PalmSens-series) using the PalmSens Dummy Cell.

Please follow these steps if you have a PalmSens Dummy Cell:



1. Make sure the instrument is on and connected to the PC
2. Open PSTrace and connect to the instrument
3. Load the following method file (menu: ‘Method’ → ‘Load’):
‘[USER]\Documents\PSData\PSDummyCell_LSV_2V.psmethod’
4. Connect the Dummy Cell using the croc clips as shown in the picture above: CE, RE to the corresponding pads and WE to pad WE_B (10k resistor).
5. Start measurement by clicking start in the toolbar:

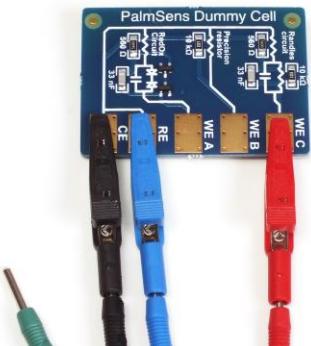


PSTrace in Scientific mode

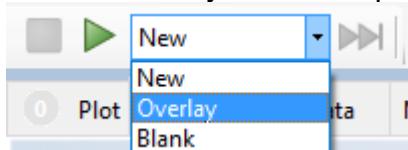
2.4 First EIS measurement on the Dummy Cell

This section describes how to do a first impedance measurement with any PalmSens-series instrument using the PalmSens Dummy Cell.

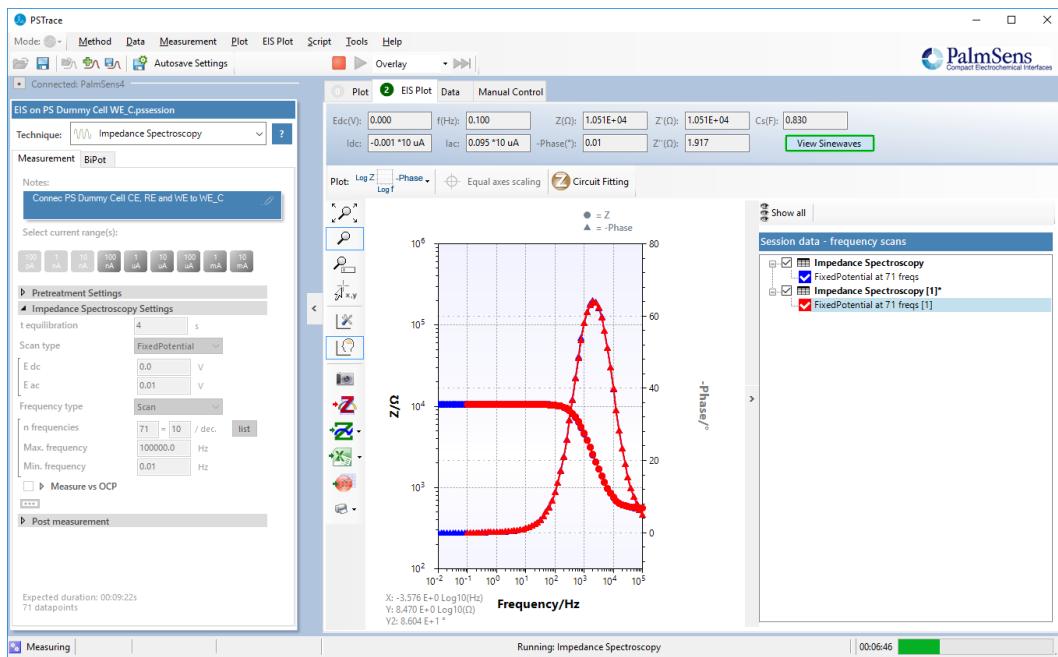
Please follow these steps if you have a PalmSens Dummy Cell:



1. Make sure the instrument is on and connected to the PC
2. Open PSTrace and connect to the instrument
3. Load the data file (menu: 'Data' → 'Load data file...'): '[USER]\Documents\PSData\EIS examples\EIS on PS Dummy Cell WE_C.pssession'
4. Connect the Dummy Cell using the croc clips as shown in the picture above: CE, RE to the corresponding pads and WE to pad WE_C (Randles Circuit).
5. Select 'Overlay' in the drop-down next to the green Start button:



6. Start measurement by clicking start in the toolbar.

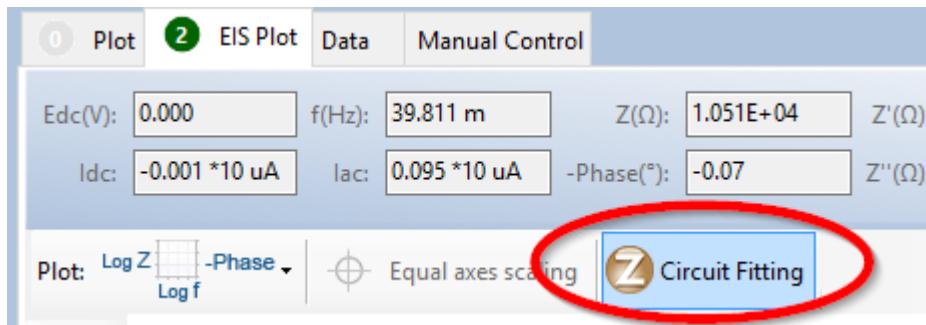


PSTrace in Scientific mode running EIS measurement

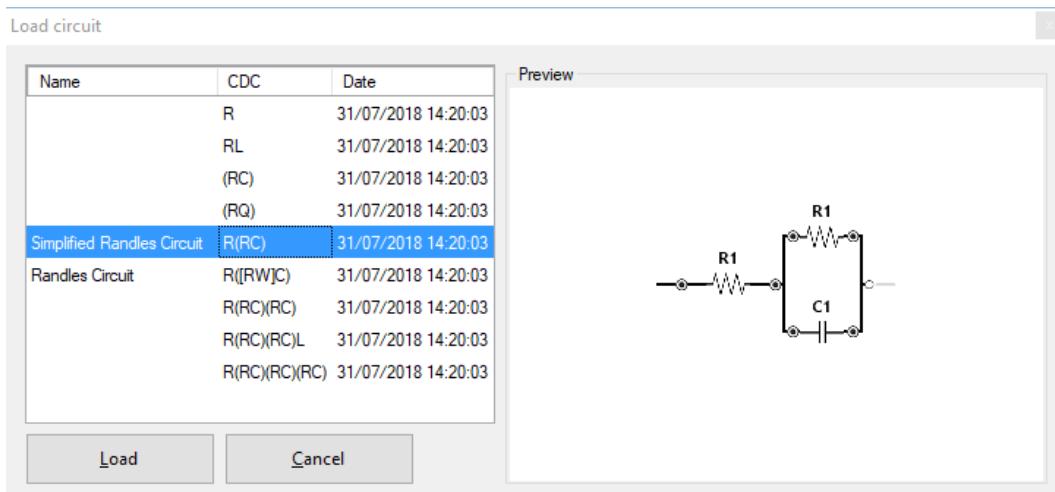
2.4.1 Fitting your data

Follow these additional steps to fit an equivalent circuit to your measurement data.

- When the EIS measurement is finished, click the Circuit Fitting button at the top of the plot:

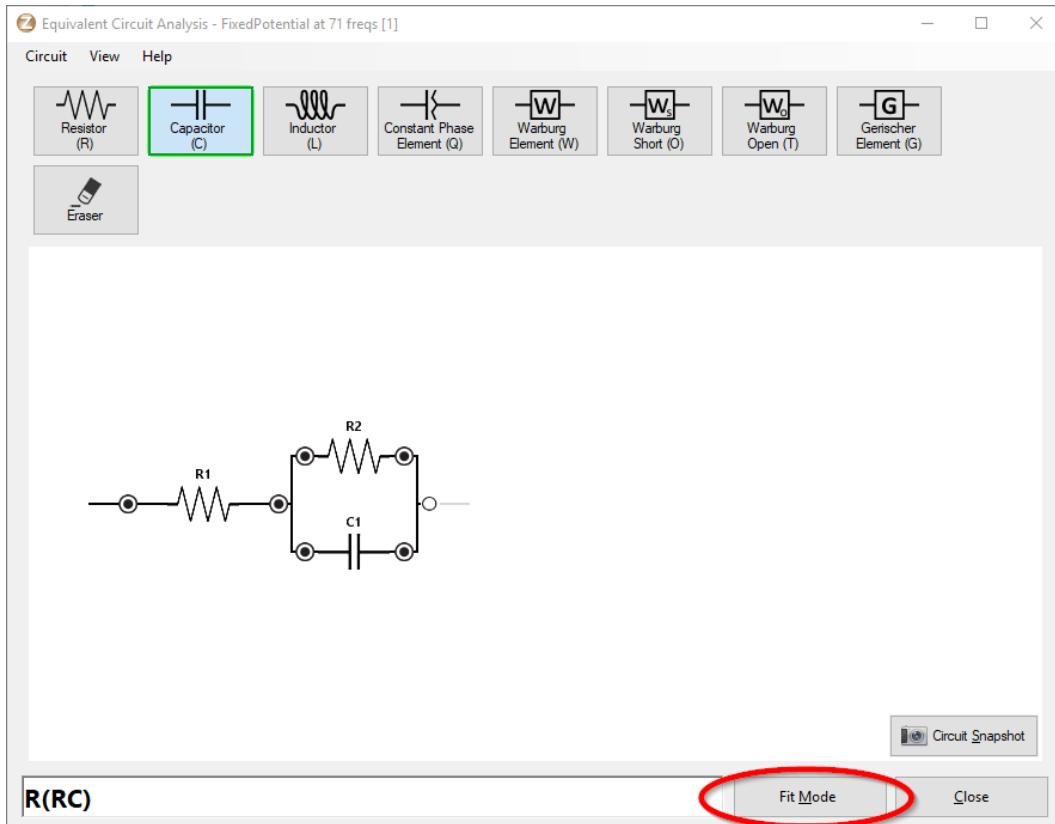


8. In the menu click ‘Circuit → Load’ and select the Simplified Randles circuit:



Click the ‘Load’ button.

9. Now click the ‘Fit Mode’ button:



10. Click the ‘Fit’ button:



11. The found results should be similar to this:

Element	Fitted Value	Min Value	Max Value	Unit	Error%
R 1	557.5	1.00E-6	1.00E+12	Ω	0.065
R 2	9966	1.00E-6	1.00E+12	Ω	0.035
C 1	0.033	1.00E-6	1.00E+3	μF	0.064
Chi-Squared:	4.60E-6	Iterations:	26		

For more information about impedance measurements (EIS) see section:
Electrochemical Impedance Spectroscopy

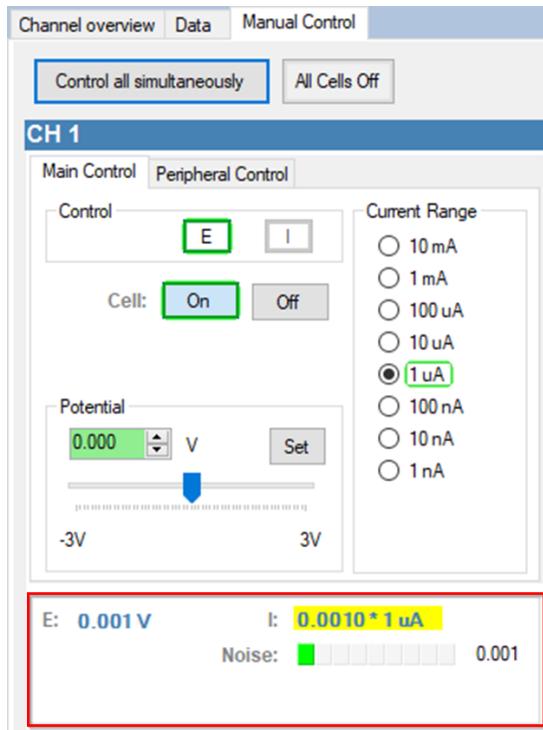
2.5 Readings

The status bar always shows the measured potential and the current as well as the noise if the cell is on.



Status bar

The measured potential, current (BiPot current if present) and noise readings are shown right at the bottom of each channel's Manual Control tab when the cell is set to ON.



Readings window

Underloads and overloads

The box showing the status is used to note whether the instrument does not show current overload, current underload or voltage overload.

Measured current values are wrong when a current overload warning is shown in red. This occurs when the current is out of the range of the selected current range. However, the warning is given already in orange at values that are close to overload.

If currents are below 5% of the selected current range, a current underload warning is given, since a lower current range can be applied. An underload will yield measurements with a low resolution. Select lower current ranges if available to increase the current resolution.

See section Resolution and optimal current range selection for more information.

The noise bar shows the noise level at the current range in use. In case the bar shows orange or red, it is advised to look for ways to limit the noise level. Please refer to section Noise.

Voltage overload means that the impedance between the counter and the reference electrode is too high. This can be found when:

- the counter or the reference electrode is not properly connected,
- the conductivity of the solution is too low, which is overcome by adding an electrolyte,
- an air bubble isolates the reference electrode from the solution.

3 Measuring

PSTrace provides not only the standard techniques as the voltammetric techniques or measuring current as a function of time but also complex methods like stripping chronopotentiometry (SCP) or PSA. Techniques are explained briefly in this chapter.

For information about impedimetric measurements, see chapter Impedance Spectroscopy (EIS).

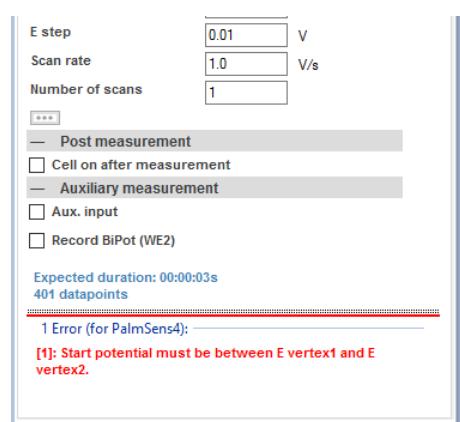
More theoretical background information can be found in:

- Christopher M.A. Brett and Ana Maria Oliveira Brett, *Electroanalysis* (Oxford Chemistry Printers, 64) Oxford Science Publications, ISBN-13: 978-0198548164
- Joseph Wang, *Analytical Electrochemistry* 3rd ed, John Wiley & Sons, ISBN-13 978-0471678793

3.1 Setting up a measurement

The ‘Measurement’ tab contains all the method parameters.

With each change of parameters, the validation of the method is checked. Errors or incompatibilities are shown instantly at the bottom of the measurement tab.



Method editor showing an error

Technique

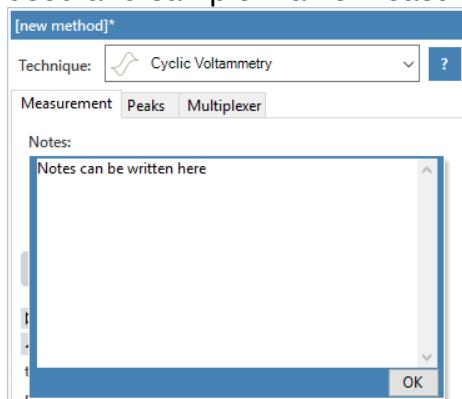
The techniques list shows the currently selected technique and allows the user to change the selected technique. If an instrument is connected, the techniques list will be

updated to show only the techniques supported by the instrument. Changing program mode will also filter out techniques that are not supported by the selected mode. If no device is connected and the Scientific Mode (see Program modes) is active, all techniques are shown in the list.

The parameters for each technique are saved when switching to another technique. This allows the user to switch between techniques without the need to change parameters each time.

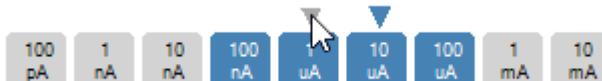
Sensor and sample

The Notes textbox can be used to describe information for example about the sensor used and sample that is measured.



The notes box in the Method editor.

Current range



The current range selection buttons determine which range(s) are used for the measurement. See for more information next section [Resolution and optimal current range selection](#) on page 29. The small arrow hovering above one of the selected ranges determines at which current range the measurement starts. The starting range can be changed by means of clicking above one of the other selected current ranges changes.

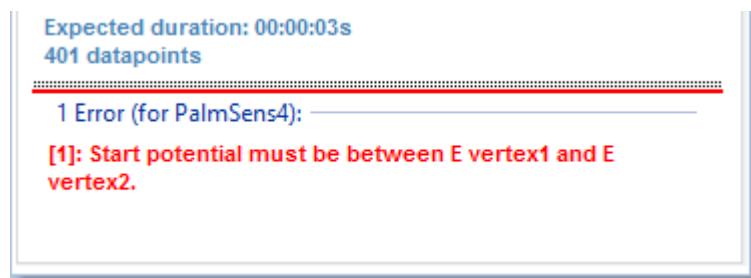
Method settings

Entered values for each method setting should be within the absolute limits any instrument by PalmSens BV can handle. If values are not supported by the instrument connected this is shown at the bottom of the method editor. See next chapter for a description and allowed values of each parameter.

Validation

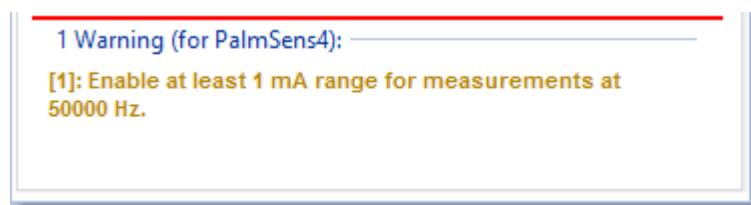
In case a value entered is invalid, an error message at the bottom is shown. Errors are shown in red and warnings are shown in orange. In case of a warning, this can be ignored by the user and the measurement can be started. In case of an error the values

need to be changed first to a value with the limits of the instrument to start the measurement.



Error shown in the method editor

A warning is shown in orange. Warnings can be ignored but, in most occasions, this will result a bad measurement due to wrong settings.



Warning shown in the method editor

In case a value for the step potential is given which cannot exactly be met by the instrument because of its hardware-determined resolution, the actual value is shown at the bottom as ‘real E step’.



Real E step shown in the method editor

3.2 Resolution and optimal current range selection

With the current range buttons shown at the top of the method editor, the applicable current range(s) during the measurement can be selected. If more than one button is selected, the instrument will select the most optimal current range automatically (auto ranging).

A measurement starts at the current range with the small arrow above it.



Selection of applicable current ranges

The starting range can be changed by means of clicking above one of the other selected current ranges changes.

Double-clicking a current range button will select only this range.

Automatic current ranging / auto ranging

During equilibration the most appropriate range will be selected. If during a measurement the current approaches a range limit, the instrument will switch automatically to a more suitable current range (lower or higher). When a measurement exceeds the upper threshold (80% of the range), a higher range is selected within the range of selected current ranges.

Likewise, when a measured current falls repeatedly below the lower threshold (5% of the range) repeatedly, a lower range is selected if enabled by the user.

Instrument	Max current per selected range
PalmSens1 and 2	$\pm 2 * \text{selected range}$
EmStat series (all)	$\pm 2 * \text{selected range}$
PalmSens3	$\pm 3 * \text{selected range}$
PalmSens4	$\pm 6 * \text{selected range}$

Because auto ranging takes some time (in the order of milliseconds) this feature is only available at lower scan rates. For techniques at very high scan rates automatic ranging is not available. This is always shown as an error in the Method Editor if this is the case.

Spikes and jumps

Please note that auto ranging can always cause spikes, especially during fast measurements and/or measurements with high Faradic currents. Spike or jumps may occur due to a short interruption or change in measurement interval when switching between the ranges.

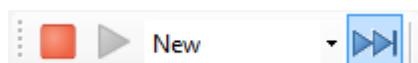
If auto ranging is not needed it is always better to enable a single current range to prevent from spikes or jumps in your curves.

If auto ranging is not needed it is always better to enable a single current range to prevent from spikes or jumps in your curves.

3.3 Running a measurement

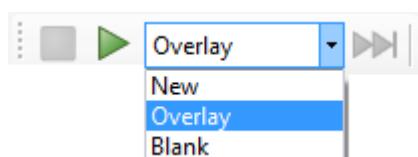
Measurements can be started and stopped with the buttons in the measurement tool strip or in the Measure menu.

The steps conditioning, deposition and equilibration can be skipped each using the skip button: ►►



Skip button

Next to the start button you can choose to make a ‘New’ graph for the measurement. If ‘Overlay’ is selected, the measured curve will be added to existing curves in the plot. Or measure a ‘Blank’ curve as a background scan to subtract it later.



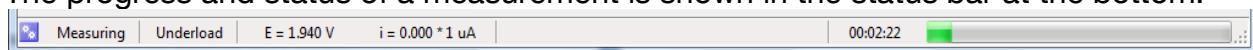
Options for the next measurement

If a blank curve is present an additional button is shown, see below. By enabling this button, the blank will be subtracted automatically after the measurement is finished.



Use blank button

The progress and status of a measurement is shown in the status bar at the bottom.



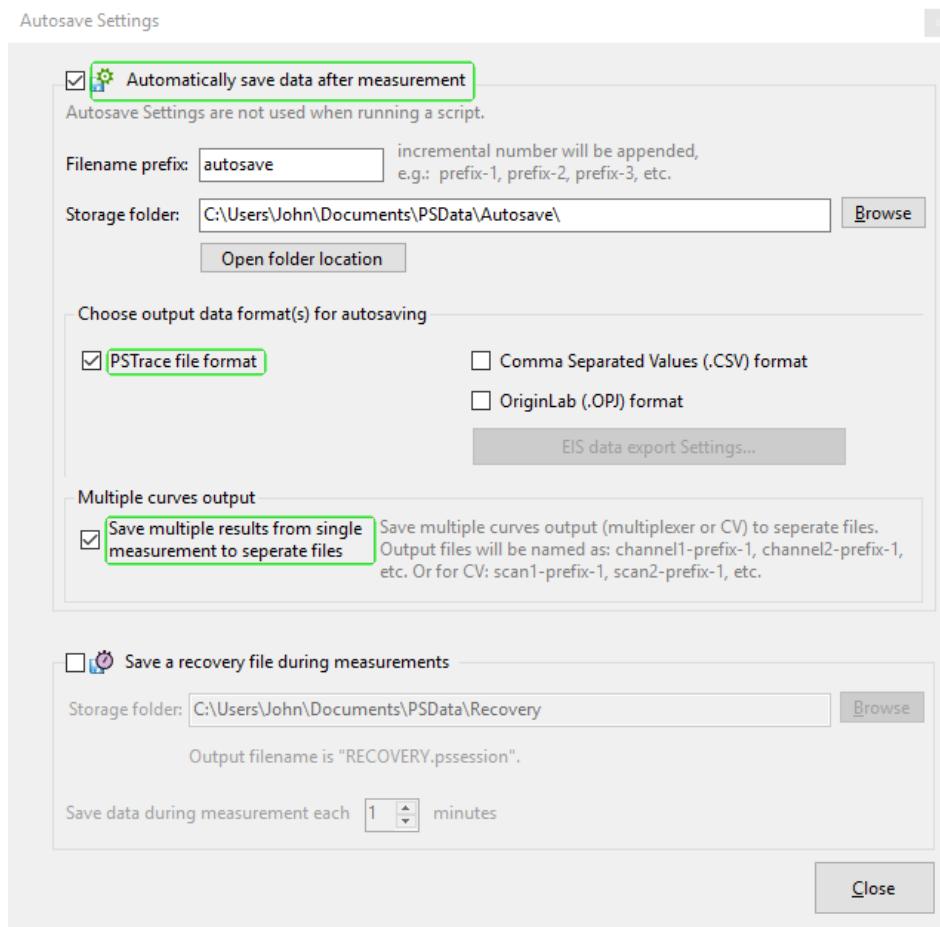
Status bar

3.3.1 Autosaving measured data

If autosave is enabled, every single measurement will be saved automatically in the corresponding format (see section Files) after the measurement has finished or is aborted.



The autosave output can be configured in the Autosave settings window.



The Autosave Settings window

Output settings

The output file gets the prefix followed by a sequential number. This number is based on the number of existing files with the given prefix in the storage folder specified and therefore increments with each new file added to the folder.

Output data formats

The output file can be stored in different formats. The PSTrace format will store the file in a format that can be loaded in PSTrace again. See also section File types.

A CSV file is a comma separated file and can easily be imported in third party programs like Excel and Origin.

As a third option it is possible to store the data in a native Origin file format. The latter will also include a graph (except for EIS data).

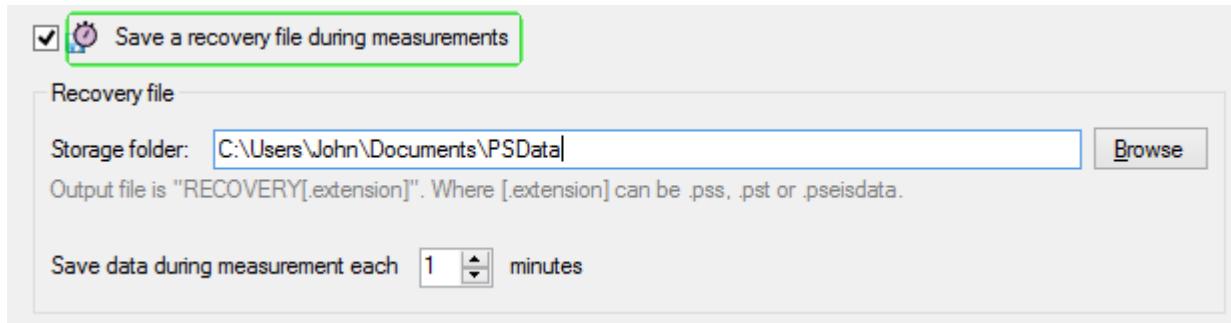
EIS data export settings

The button ‘EIS data export settings’ allows which columns are exported to the non-PSTrace file formats.

Multiple curves output

Some measurements produce multiple curves, like a Cyclic Voltammetry measurement with multiple scans or a measurement done with a multiplexer. Enabling the checkbox will save the output of each separate curve to a single file instead of to a single file containing the data of all curves.

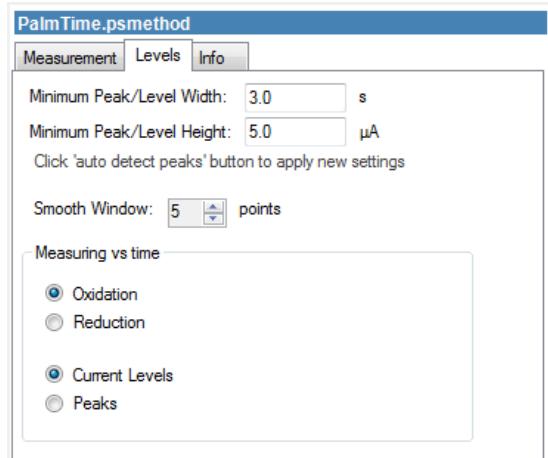
3.3.2 Recovery file in Simultaneous mode



Recovery file settings

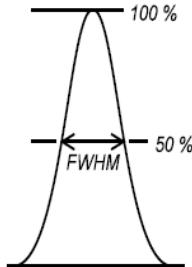
The ‘Autosave settings’ window also shows options for keeping a recovery file during measurements. This option can be useful for long term measurements. In case of a PC crash or power outage the most recent measurement data will still be available. The recovery file is overwritten for each new measurement.

3.4 Peaks and levels



Peak/Level parameters tab (showing options for a technique as a function of time)

Minimum Peak Width determines the minimum peak width. Peaks with a lower width may not be detected. The peak width is the Full Width at Half Maximum (FWHM).



Minimum Peak Height determines the minimum peak height. Peaks lower than this value are neglected.

Smooth Window determines to which degree the measured curve is smoothed. The specified number is used to smoothen the data by means of the Savitzky-Golay method. Please note that too many points will influence the shape of the curve

Extra options for time methods:

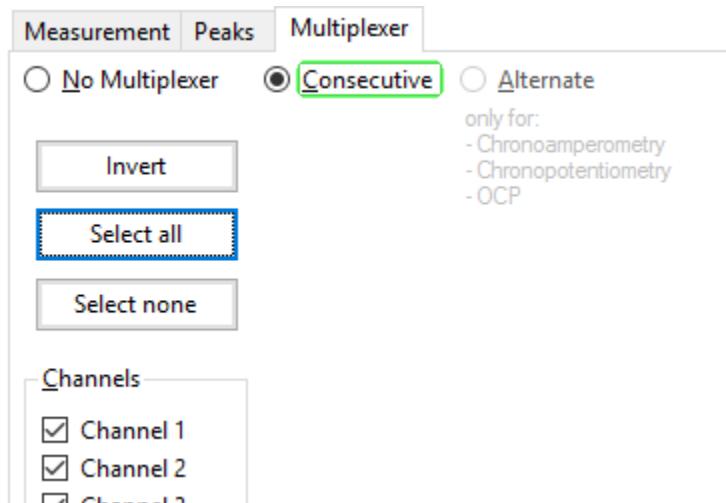
Oxidation or Reduction determines whether peaks or current levels are positive (Oxidation) or negative (Reduction).

Current Level or Peaks determines whether peaks or current levels are measured

3.5 Multiplexer

In the Multiplexer tab it can be specified which multiplexer channels are measured and whether they should be measured consecutive (one by one) or scanned alternately (all channels simultaneously).

When the Consecutive mode is chosen, any channel can be selected. In case Alternate is checked, manual selection of channels is limited to successive channels. So, it is possible to measure 2 to 8 or 2 to 16 successive channels, depending on the type of multiplexer in use.



Multiplexer parameters

Consecutive measurements

When doing Consecutive multiplexer measurements, the active multiplexer channel will switch to the next and be started after the entire measurement as defined in the Measurement tab has finished. This mode is available for every technique.

Alternate measurements

When doing Alternate multiplexer measurements all selected channels will be switched as fast as possible during each measurement interval. The switching time is ± 31 ms which means that the lower limit of the interval time is defined as (number of channels selected) * 0.031 s. So, for alternating between 8 channels the minimum interval time is 0.25 seconds.

The following techniques support the Alternate multiplexer mode:

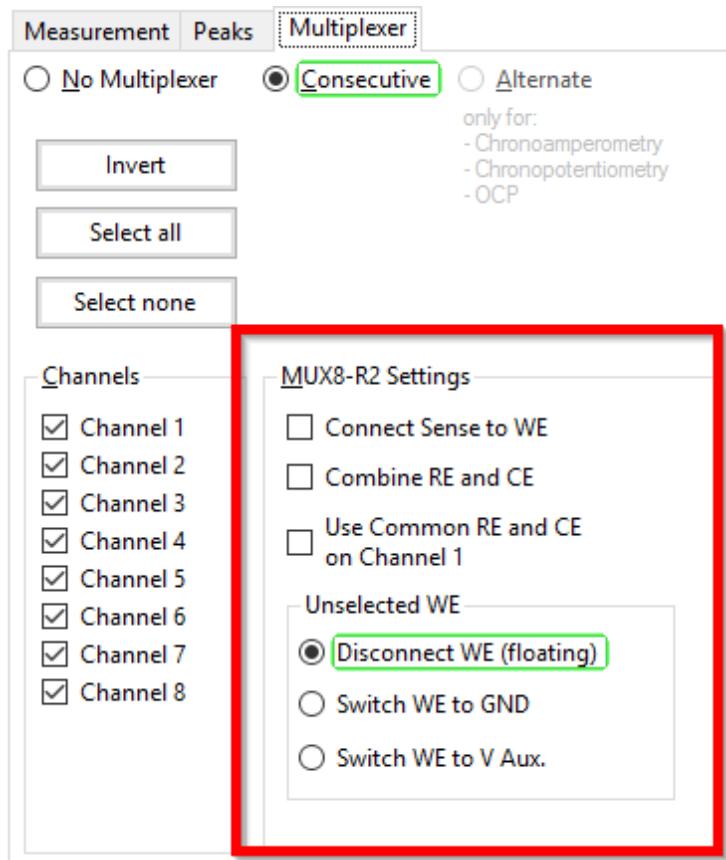
- Chronoamperometry;
- Chronopotentiometry;
- and Open Circuit Potentiometry.

MUX8 and MUX16 hardware settings

The multiplexer can be used in different configurations. For the older models, dip-switches are available on the bottom of the multiplexer to change the configuration. These settings are explained in section MUX8 and MUX16 multiplexers.

MUX8-R2 settings

The MUX8-R2 hardware configuration settings can be defined in software and will become visible in the multiplexer tab if the MUX8-R2 is either detected upon connection or selected in the General Settings window.
See also section MUX8-R2 multiplexer.



Multiplexer MUX8-R2 hardware configuration settings

When switching techniques, the initial MUX8-R2 settings will be taken from the Default settings as defined in the settings window of PSTrace. However when saving a method to either a .psmethod file or .pssession file the settings will be saved as present in the Multiplexer tab.

3.6 Recording an auxiliary input

To record an auxiliary value like WE2, temperature or cell potential, this needs to be enabled in the Method editor:

- Record additional data
- Record Aux. input

If the checkbox ‘Aux. input’ is checked, the voltage of the corresponding analog input pin on the physical AUX port is recorded.

The auxiliary input value can also be translated to another value, like temperature, RPM (For an RRDE) or pH, depending on what is connected. This can be set in the ‘General Settings’ window, see also section Hardware configuration.

For more information about the auxiliary input connector pins, see section Auxiliary port pin-outs.

3.7 Recording the cell potential

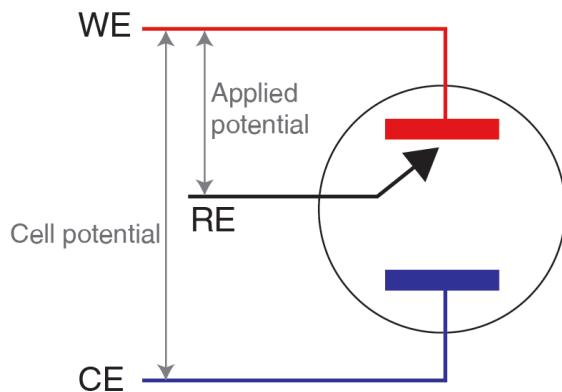
Recording cell potential is currently only supported by the PalmSens4 potentiostat.

◀ Record additional data

Record Aux. input

Record cell potential

The ‘cell potential’ is the potential between the working and the counter electrode and thus the potential applied to the whole cell. In other words, this is the working electrode’s potential versus the counter electrode’s potential.



Cell potential

Sometimes it is interesting to calculate the potential of the counter electrode versus the reference electrode. This can be easily calculated with the Applied potential and the Cell potential. As is visible from picture above the Cell potential is calculated by

$$\text{Cell Potential} = E(\text{WE}) - E(\text{CE})$$

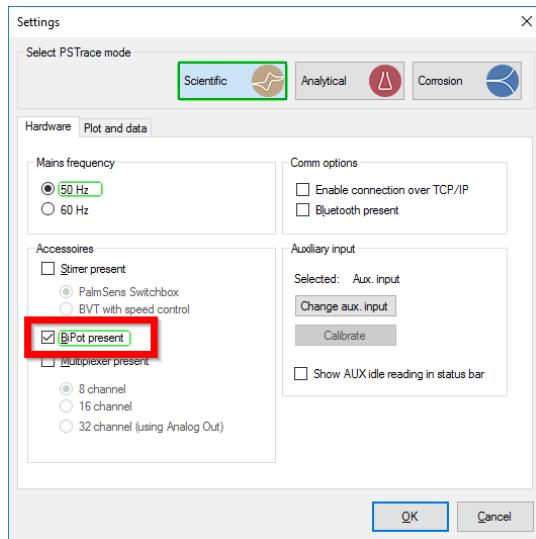
By rearranging it is clear that the potential of the counter electrode $E(\text{CE})$ can be calculated by

$$E(\text{CE}) = E(\text{WE}) - \text{Cell Potential}$$

3.8 Using a BiPot

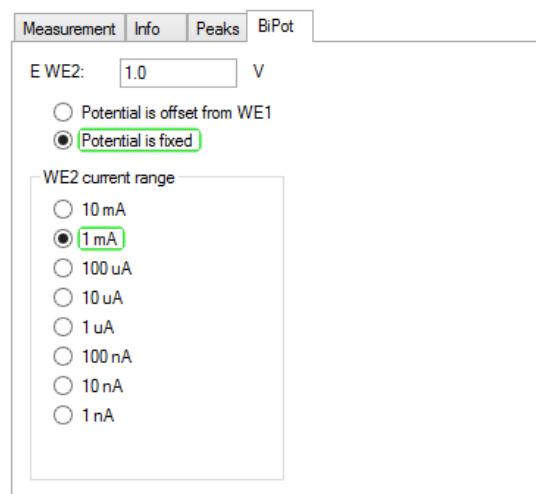
If a BiPot module is present and the BiPot module is enabled in the ‘Settings’ window, the second working electrode or WE2 can be used.

The Settings window can be found in the menu: ‘Tools’ → ‘General Settings...’



Select BiPot present in Settings window

An additional tab ‘BiPot’ will become visible in the method editor. This tab contains the settings for the use of the second working electrode (WE2).



The additional BiPot tab in the method editor.

The E WE2 is the potential set on the WE2. The options to choose if this potential is either an offset from WE1 or fixed is only shown for a BiPot with the PalmSens3 and PalmSens4.

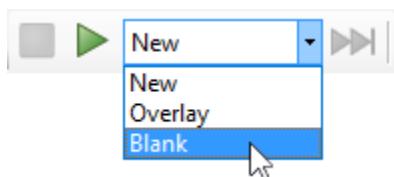
Both the BiPot and the auxiliary input can be used with the following methods:

- Linear Sweep Voltammetry
- Cyclic Voltammetry
- Amperometric Detection
- Multistep Amperometry
- Multistep Potentiometry

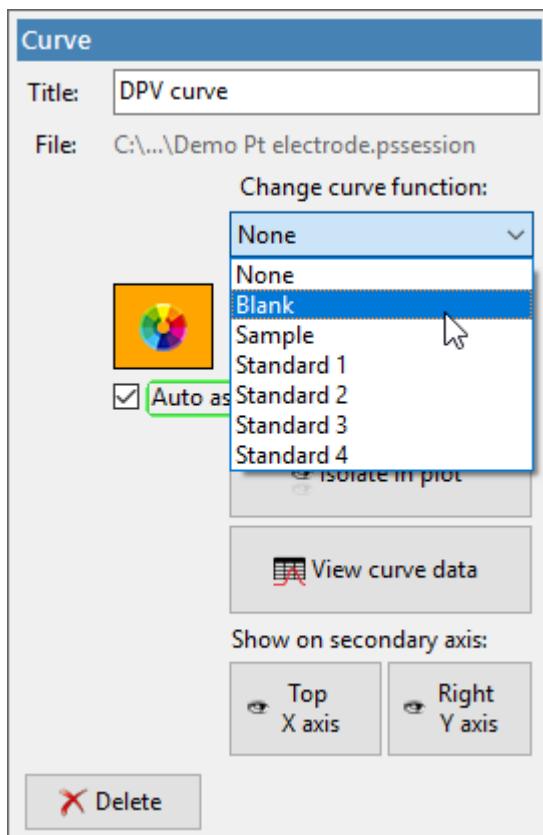
The plot window will show the current obtained for WE1 as well as for WE2 or Auxiliary.

3.9 Using Blank subtraction

When a Blank is measured a button appears next to the measurement controls in the bar on the top of the screen.

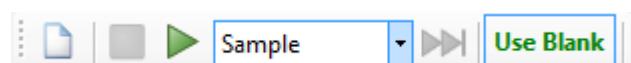


Select Blank to measure a Blank curve for Blank subtraction before clicking the Start button.



By changing the curve function in the curve tool window, which is accessed by clicking on a curve in the plot legend.

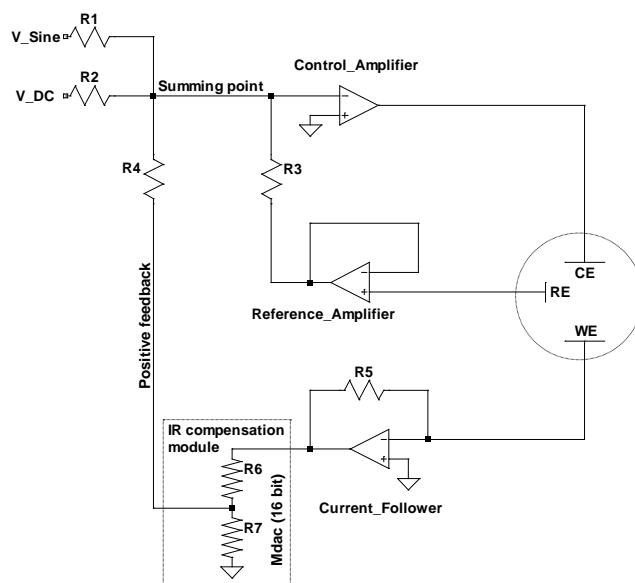
When enabling the Subtract Blank button, the available Blank curve is subtracted immediately from the measured curve. The Blank Curve is always shown in gray in the plot.



Button for automatic blank subtraction

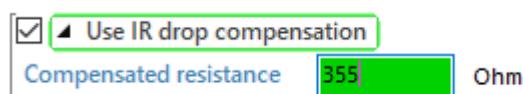
3.10 Using IR drop compensation

IR Compensation for PalmSens4 is available as an in-factory add-on module. The resistance between the reference electrode and the double layer of the specimen can cause a significant potential drop, decreasing the applied potential where it is required. The module provides positive feedback to compensate for the IR drop between Reference electrode and the outside of the double layer of the electrochemical cell. The PalmSens4 IR Compensation module works by means of Positive Feedback. This is achieved through the use of a 16 bit MDAC in the module which scales the output of the current follower opamp to provide a positive feedback voltage which is proportional to the current through the cell. The compensation voltage is added into the summing point before the control amplifier and thus increases the applied potential to counteract the IR drop.

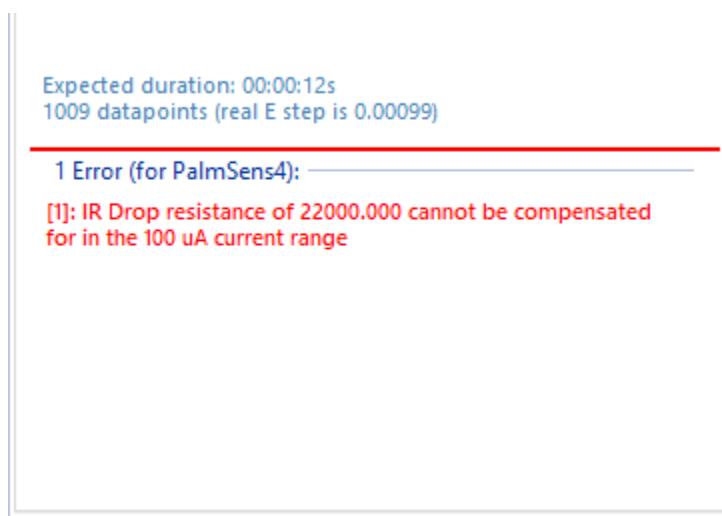


Positive feedback allows for fast scan rates up to 10 V/s, depending on the characteristics of the cell. If the potential error to compensate for becomes close to the value set for E applied, the system might become unstable. Using IR compensation limits the measurement bandwidth to 10 kHz.

The resistance to compensate for can be entered directly in the Method Editor in PSTrace:



If auto ranging is not allowed for the compensation used in combination with the selected current ranges, this is shown in the Method Editor:



Error message shown in the Method Editor

Make sure a single current range is selected in these circumstances.

Supported Techniques

The following techniques are supported for use with IR compensation:

- Linear Sweep Voltammetry
- Cyclic Voltammetry
- Square Wave Voltammetry
- Differential Pulse Voltammetry
- Normal Pulse Voltammetry
- ChronoAmperometry
- Multistep Amperometry

3.11 Noise

Electrochemical sensors and cells are susceptible to noise. The Readings window (shown during the time the cell is on) displays the potential and the current and shows the noise level. The background colour shows whether the noise might deteriorate the measurement. In case the noise level is higher than 0.1 times the selected current range, the bar will turn to orange. In case the noise level exceeds 0.5 times the selected current range, the bar turns to red. It is strongly advised to prevent measurements under such conditions.

Known sources of noise are:

- Unshielded or too long sensor- or cell cables. The connection between the instrument and the sensor or cell should not be extended. Especially unshielded cables used with many commercially available reference electrodes may result in high noise levels. Shorten the cables when possible.
- Bad cable connections. A bad connection for example due to corroded banana plugs or clips can be the cause of noisy or other kinds of bad readings.

- Ac-adapters. The adapter for charging PalmSens or also the laptop adapter may induce noise. Sensitive measurements can be performed without these adapters connected.
- Electrical equipment. Measurements near electrical equipment might be distorted by electrical interference. This might be eliminated by placing the cell in a faraday cage which is connected to earth or ground.
- A wrong setting for the mains frequency. It is important to specify the actual main frequency in the ‘General settings’ window.

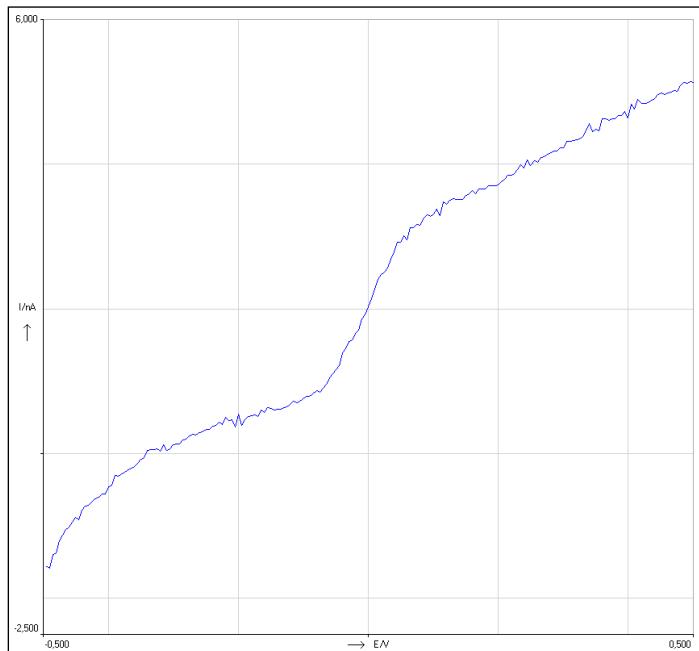
EmStat is powered from the USB bus. Some PC's or laptops have a noisy USB power supply. In this case it is advised to use a USB Hub with its own ac-adapter between the PC or laptop and EmStat.

In case the noise levels remain too high, the use of a Faraday cage (a simple metal cage or box may be sufficient) is required. Connect the metal cage or box to safety ground or to the green connector of the sensor cable. Place the cell or sensor together with the leads inside the cage.

3.12 Measuring the noise level of the instrument

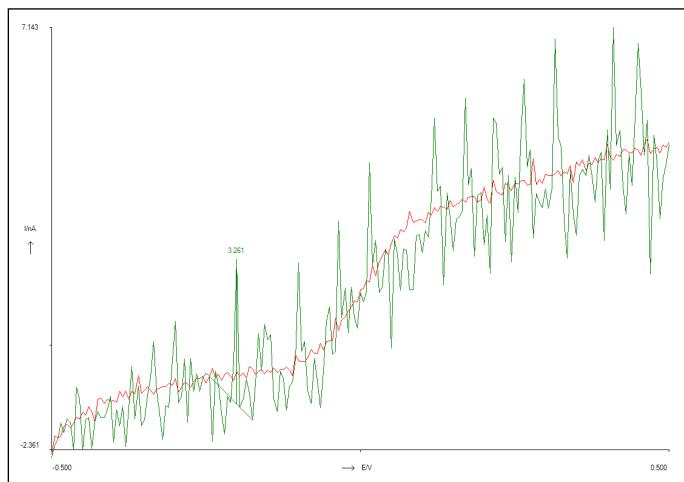
To determine the environmental noise levels, make sure the (green) test sensor is connected or the (blue) PS Dummy Cell is connected on pads RE, CE and WE A.

1. Load method file ‘PSNoiseTest.psmethod’.
2. Start measurement.
3. Repeat the measurement but with a scan rate of 0.05 V/s. Note that the noise level is lower, due to the fact that the current sampling time is longer now. This decreases the measured noise level.



The curve shown in the figure above is a typical curve measured using the unmodified PSNoiseTest method and a PalmSens2. The sensor and connections are housed inside a grounded Faraday Cage.

Curves measured with an EmStat may show higher noise levels than with a PalmSens. In case the noise level is too high this is due to a noisy power supply of the USB ports and therefore the use of a USB Hub with its own ac-adapter between the PC or laptop and EmStat is advised.



The green (noisy) and red curves are both measured with the same conditions as before and with the same EmStat. The red curve is obtained when EmStat is connected to a USB hub instead of directly to a USB port of the PC.

The instrument can be controlled manually using the ‘Manual Control’ tab.

To evaluate noise levels in the Manual Control tab click ‘Cell On’. Change the applied potential from $E = 0.000$ V to $E = 0.500$ V by manipulating the horizontal scrollbar or entering the value in the textbox. Select the current range 10 nA. The measured values of the potential and current as well as the noise are shown.

If the noise bar shows orange or red, the noise level is high. You are advised to see the effect of placing the test sensor in a Faraday cage.

Please refer to section [Noise](#) on page 41.

3.13 Available techniques

PSTrace supports the following techniques. Most of these techniques can be used in their stripping modes for trace analysis.

The applicable techniques (in Scientific Mode) are:

Voltammetric techniques:

▪ Linear Sweep Voltammetry	LSV
▪ Differential Pulse Voltammetry	DPV
▪ Square Wave Voltammetry	SWV
▪ Normal Pulse Voltammetry	NPV
▪ AC Voltammetry	ACV
▪ Cyclic Voltammetry	CV
▪ Fast Cyclic Voltammetry	FCV
▪ Stripping Chronopotentiometry (or PSA)	SCP

Techniques as a function of time:

▪ Chronoamperometry	CA
▪ Pulsed Amperometric Detection	PAD
▪ Fast Amperometry	FAM
▪ Multiple Pulse Amperometric Detection	MPAD
▪ Chronopotentiometry	CP
▪ Open Circuit Potentiometry	OCP
▪ Multistep Amperometry	MA
▪ Multistep Potentiometry	MP
▪ Mixed Mode	MM

Impedance spectroscopy / EIS:

- Potential scan
- Fixed potential
- Time scan

Scans can be done using on a fixed frequency or a frequency scan.

See chapter Electrochemical Impedance Spectroscopy for more information.

3.13.1 Linear Sweep Voltammetry (LSV)

Supported instruments: PalmSens series, EmStat3, EmStat3+, EmStat Pico

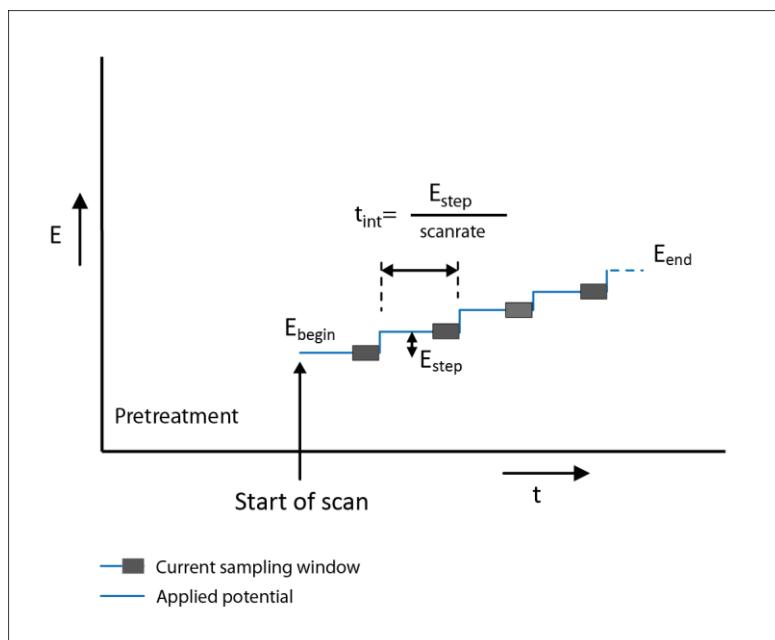
Description

In Linear Sweep Voltammetry a potential scan is performed from the begin potential, E_{begin} , to the end potential E_{end} . The scan is not really linear, but small potential steps (E_{step}) are made. The current is measured (sampled) during the last 25% interval period of each step. So the number of points in the curve of the current versus potential is $(E_{end} - E_{begin}) / E_{step} + 1$.

The scan rate is specified in V/s, which determines the time between two steps and thus the sampling time. The interval time is $E_{\text{step}} / \text{scan rate}$. So, when E_{step} is 0.005 V and the scan rate 0.1 V/s the interval time is 0.05 s.

Measuring

In some applications, it is important that the current does not get too high. This might ruin the working electrode. If the potential at which this will occur is not known, it is possible to specify a maximum current value at which the scan stops. In this case the end potential specified by the user is not reached.

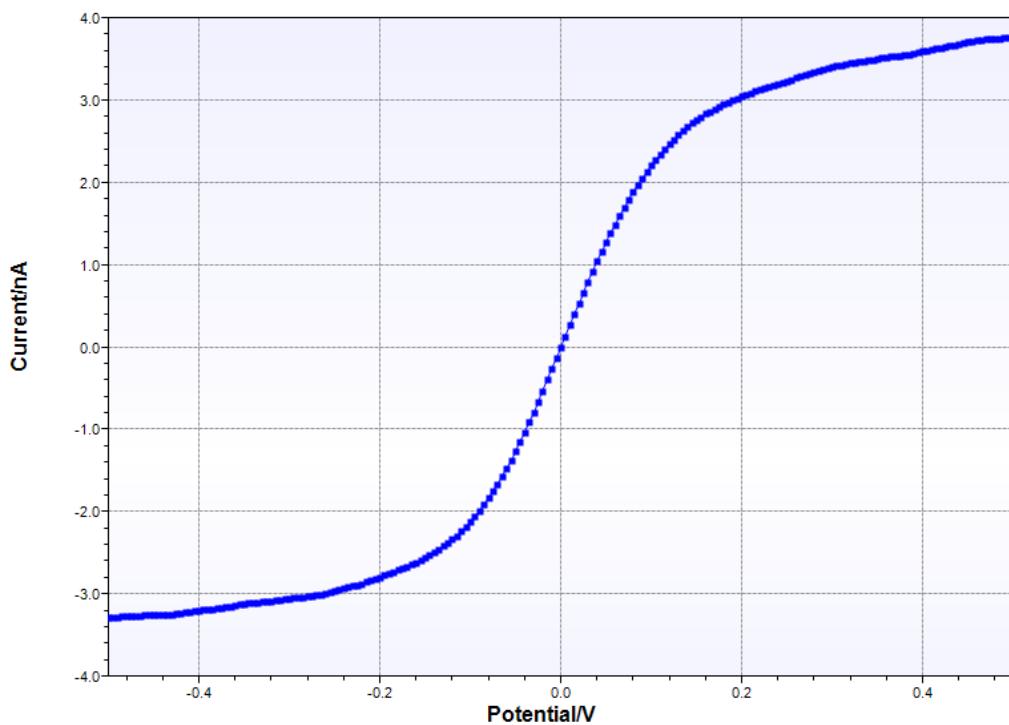


Potential applied during Linear Sweep Voltammetry

During the measurement, the curve is shown on the screen in real-time. It is possible to abort a measurement, by pressing the abort button above the plot.

During a measurement the use of the ‘Pause’ button will halt the scan until the same button is used again. This button is not available at higher scan rates.

See section [Measurement Sequence](#) on page 86 for information about the pretreatment and post measurement phases.



Typical LSV plot for a non-diffusion limited system

Technique specific parameters

E begin	Potential where scan starts.
E end	Potential where measurement stops. <i>The applicable potential range for each instrument:</i>
<i>PalmSens2 -2 V to +2 V PalmSens3 -5 V to +5 V PalmSens4 -10 V to +10 V EmStat2 -2 V to +2 V EmStat3 -3 V to +3 V EmStat3+ -4 V to +4 V EmStat Pico High Speed mode: -1.7 V to +2 V Low Speed mode: -1.25 V to +2 V</i>	
	<i>See also section Limitations of the EmStat Pico</i>
E step	Step potential <i>The applicable step range for all instruments</i>
	<i>PalmSens2 1 mV to 250 mV PalmSens3 0.15 mV to 250 mV PalmSens4 0.075 mV to 250 mV EmStat2 0.1 mV to 250 mV</i>

<i>EmStat3</i>	<i>0.125 mV to 250 mV</i>
<i>EmStat3+</i>	<i>0.125 mV to 250 mV</i>
<i>EmStat Pico</i>	<i>High Speed mode: 0.395 mV to 250 mV Low Speed mode: 0.537 mV to 250 mV</i>

Scan rate	The applied scan rate. The applicable range depends on the value of E step since the data acquisition rate is limited by the connected instrument. Max. data acquisition rates: EmStat3 series: 1000 points/sec PalmSens2: 4000 points/sec PalmSens3: 100,000 points/sec PalmSens4: 50,000 points/sec
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For PalmSens2:

In case the scan rate is so low that the time between two measured points is longer than approx. 0.05 s, the measured data points are displayed during the measurement. In other cases, the measurement is completed before the points are shown.

The applicable scan rates for each instrument:

<i>PalmSens2</i>	<i>1 mV/s (1 mV step) to 25 V/s (5 mV step)</i>
<i>PalmSens3</i>	<i>0.02 mV/s (0.15 mV step) to 500 V/s (5 mV step)</i>
<i>PalmSens4</i>	<i>0.02 mV/s (0.075 mV step) to 500 V/s (10 mV step)</i>
<i>EmStat2</i>	<i>0.02 mV/s (0.1 mV step) to 5 V/s (5 mV step)</i>
<i>EmStat3</i>	<i>0.025 mV/s (0.125 mV step) to 5 V/s (5 mV step)</i>
<i>EmStat3+</i>	<i>0.025 mV/s (0.125 mV step) to 5 V/s (5 mV step)</i>
<i>EmStat Pico</i>	<i>0.02 mV/s (0.280 mV step) to 5 V/s (10 mV step)</i>

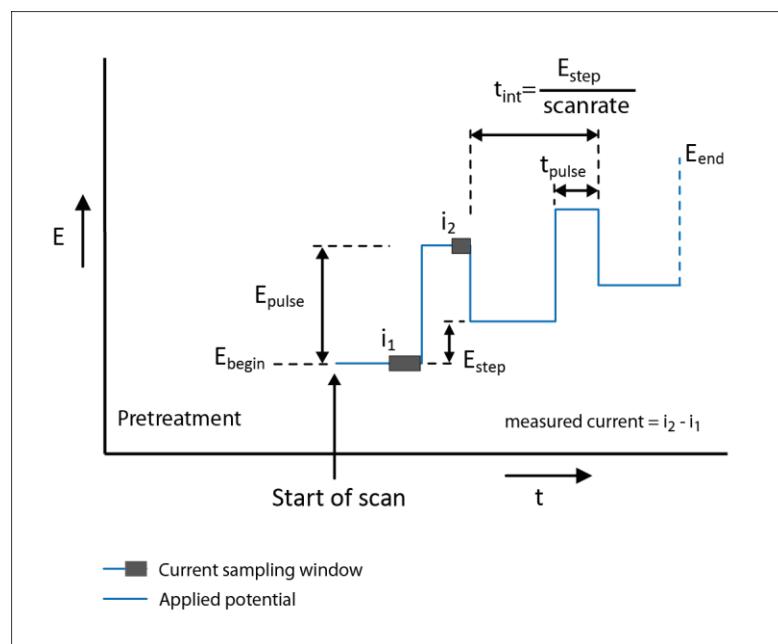
3.13.2

3.13.3 Differential Pulse Voltammetry (DPV)

Supported instruments: PalmSens series, EmStat3, EmStat3+, EmStat Pico

Description

In Differential Pulse Voltammetry a potential scan is made using pulses with a constant amplitude of E_{pulse} superimposed on the dc-potential. The amplitude is mostly in the range of 5 – 50 mV.



Potential applied during Differential Pulse Voltammetry

The interval time between the pulses is equal to $E_{step} / \text{scan rate}$.

The current is sampled twice in each step: one just before applying the pulse and one at the end of the pulse. The difference of these two current samples is plotted versus the potential.

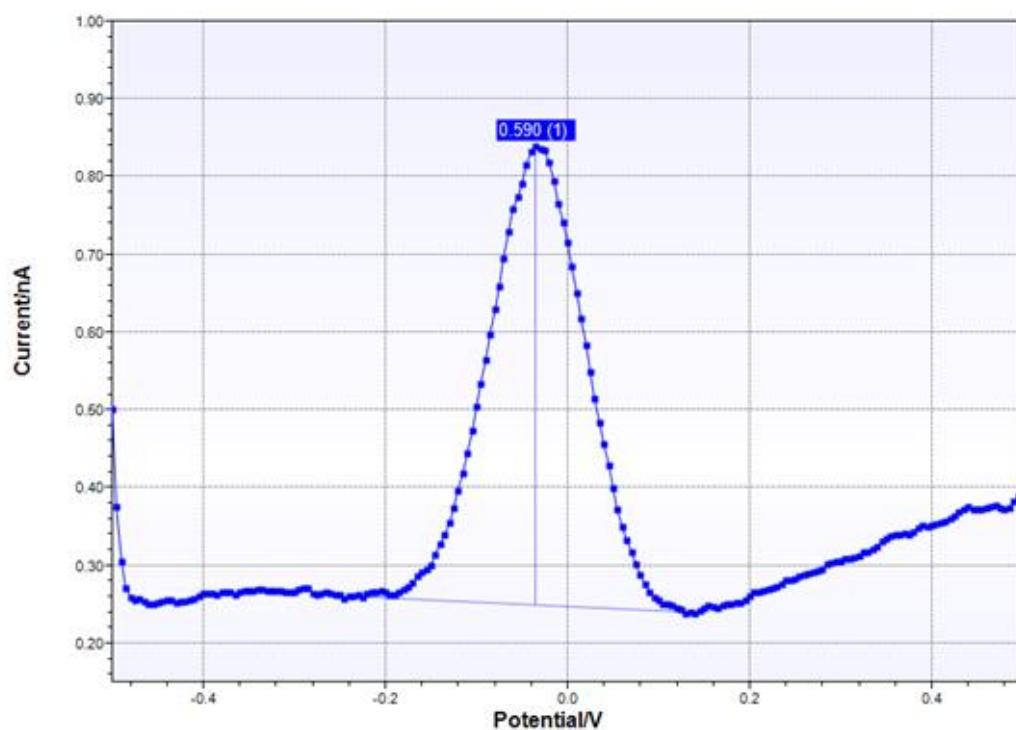
The obtained current is proportional to the derivative of the curve obtained using linear sweep or normal pulse voltammetry. A DPV thus has a peak shaped curve. The peak height is (normally) proportional to the concentration in the solution. Be aware that the peak is not the redox potential! $E_{peak} = E_{\frac{1}{2}} - \Delta E$

Measuring

As in Normal Pulse Voltammetry (NPV) the diffusion layer thickness increases with pulse time, the current will be lower when the pulse time is increased. However a short pulse time will result in an increased capacitive current and therefore give a higher (non-linear) baseline.

In trace analysis it is important to apply pulses with optimal pulse times. In general the optimal value must be found by varying the pulse time.

See section [Measurement Sequence](#) on page 86 for information about the pretreatment and post measurement phases.



Typical DPV plot

Technique specific parameters

E begin	Potential where scan starts.
E end	Potential where measurement stops. <i>The applicable potential range for each instrument:</i>
<i>PalmSens2</i> -2 V to +2 V <i>PalmSens3</i> -5 V to +5 V <i>PalmSens4</i> -10 V to +10 V <i>EmStat2</i> -2 V to +2 V <i>EmStat3</i> -3 V to +3 V <i>EmStat3+</i> -4 V to +4 V <i>EmStat Pico</i> <i>High Speed mode:</i> -1.7 V to +2 V <i>Low Speed mode:</i> -1.25 V to +2 V	
	<i>See also section Limitations of the EmStat Pico</i>
E step	Step potential <i>The applicable step range for all instruments</i>
	<i>PalmSens2</i> 1 mV to 250 mV

	<i>PalmSens3</i> 0.15 mV to 250 mV <i>PalmSens4</i> 0.075 mV to 250 mV <i>EmStat2</i> 0.1 mV to 250 mV <i>EmStat3</i> 0.125 mV to 250 mV <i>EmStat3+</i> 0.125 mV to 250 mV <i>EmStat Pico</i> <i>High Speed mode:</i> 0.395 mV to 250 mV <i>Low Speed mode:</i> 0.537 mV to 250 mV
Scan rate	The applied scan rate. The applicable range depends on the value of E step. <i>For PalmSens2:</i> <i>In case the scan rate is so low that the time between two measured points is longer than approx. 0.05 s, the measured data points are displayed during the measurement. In other cases the measurement is completed before the points are shown.</i> <i>The applicable scan rate for each instrument:</i>
	<i>PalmSens2</i> 0.2 mV/s (0.1 mV step) to 50 mV/s (5 mV step) <i>PalmSens3</i> 0.02 mV/s (0.15 mV step) to 25 V/s (0.25 V step) <i>PalmSens4</i> 0.02 mV/s (0.07 mV step) to 25 V/s (0.25 V step)
	<i>EmStat2</i> 0.02 mV/s (0.1 mV step) to 5 V/s (5 mV step) <i>EmStat3</i> 0.025 mV/s (0.125 mV step) to 5 V/s (5 mV step) <i>EmStat3+</i> 0.025 mV/s (0.125 mV step) to 5 V/s (5 mV step) <i>EmStat Pico</i> 0.02 mV/s (0.280 mV step) to 5 V/s (10 mV step)
E pulse	Pulse potential
t pulse	The pulse time <i>The applicable step range for all instruments</i>
	<i>PalmSens2</i> 1 mV to 250 mV <i>PalmSens3</i> 0.15 mV to 250 mV <i>PalmSens4</i> 0.075 mV to 250 mV <i>EmStat2</i> 0.1 mV to 250 mV <i>EmStat3</i> 0.125 mV to 250 mV <i>EmStat3+</i> 0.125 mV to 250 mV <i>EmStat Pico</i> <i>High Speed mode:</i> 0.395 mV to 250 mV <i>Low Speed mode:</i>

0.537 mV to 250 mV

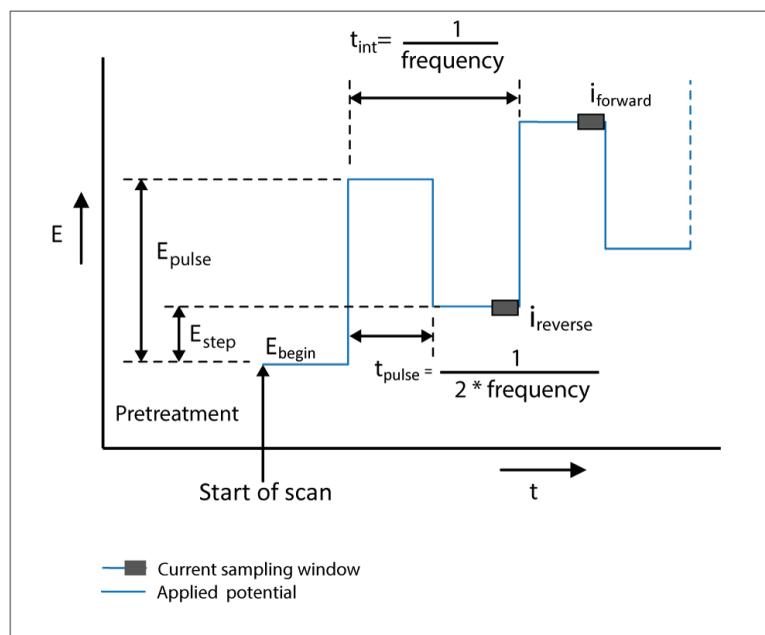
3.13.4 Square Wave Voltammetry (SWV)

Supported instruments: PalmSens series, EmStat3, EmStat3+, EmStat Pico

Description

Square wave Voltammetry is in fact a special version of DPV.

DPV is SWV when t pulse is equal t interval/2 (see DPV). The interval time is the inverse of the frequency (Freq): $t_{interval} = 1 / \text{Freq}$. As in DPV the pulse amplitude is also normally in the range of 5 - 25 or 50 mV.



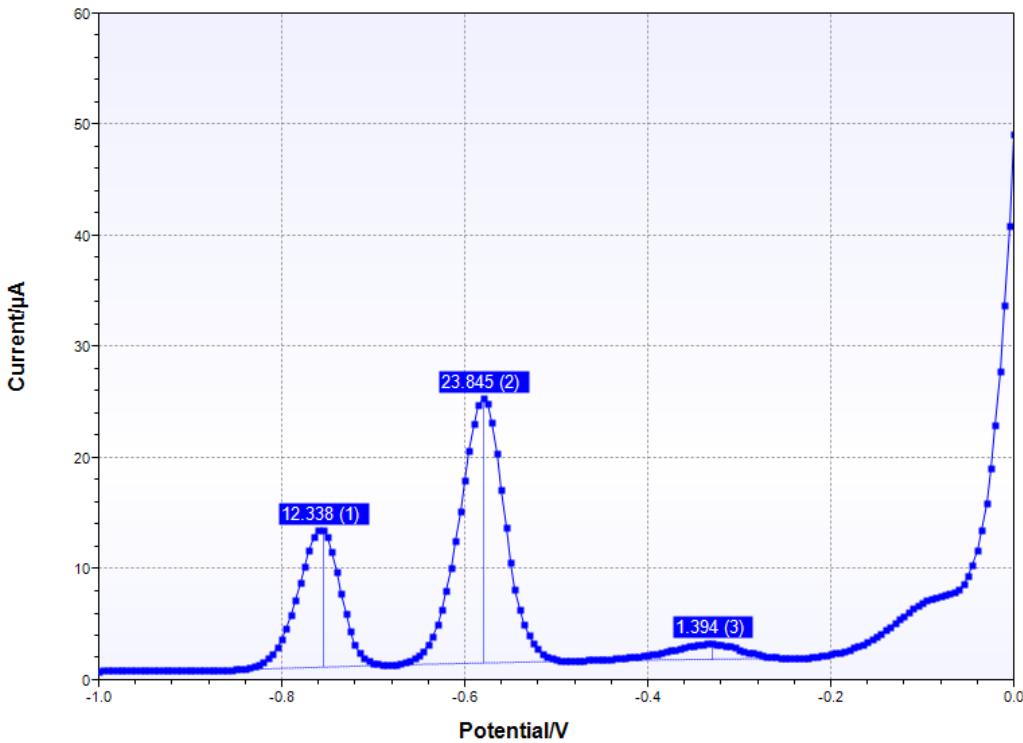
Potential applied during Square Wave Voltammetry

Measuring

In trace analysis it is important to apply a frequency with optimal values. As in DPV the optimal value must be found by varying the frequency.

SWV is sometimes used to measure the reaction rate of the electrode reaction. In this case, a plot of the currents observed in the positive potential pulses are plotted next to the currents measured in the negative potential pulses (forward and reverse currents). The shape of these curves shows how reversible or how fast the electrode reaction is.

See section [Measurement Sequence](#) on page 86 for information about the pretreatment and post measurement phases.



Typical SWV plot

Technique specific parameters

E begin	Potential where scan starts.
E end	Potential where measurement stops. <i>The applicable potential range for each instrument:</i>
<i>PalmSens2</i> -2 V to +2 V <i>PalmSens3</i> -5 V to +5 V <i>PalmSens4</i> -10 V to +10 V <i>EmStat2</i> -2 V to +2 V <i>EmStat3</i> -3 V to +3 V <i>EmStat3+</i> -4 V to +4 V <i>EmStat Pico</i> <i>High Speed mode:</i> -1.7 V to +2 V <i>Low Speed mode:</i> -1.25 V to +2 V <i>See also section Limitations of the EmStat Pico</i>	
E step	Step potential <i>The applicable step range for all instruments</i>
<i>PalmSens2</i> 1 mV to 250 mV <i>PalmSens3</i> 0.15 mV to 250 mV <i>PalmSens4</i> 0.075 mV to 250 mV <i>EmStat2</i> 0.1 mV to 250 mV	

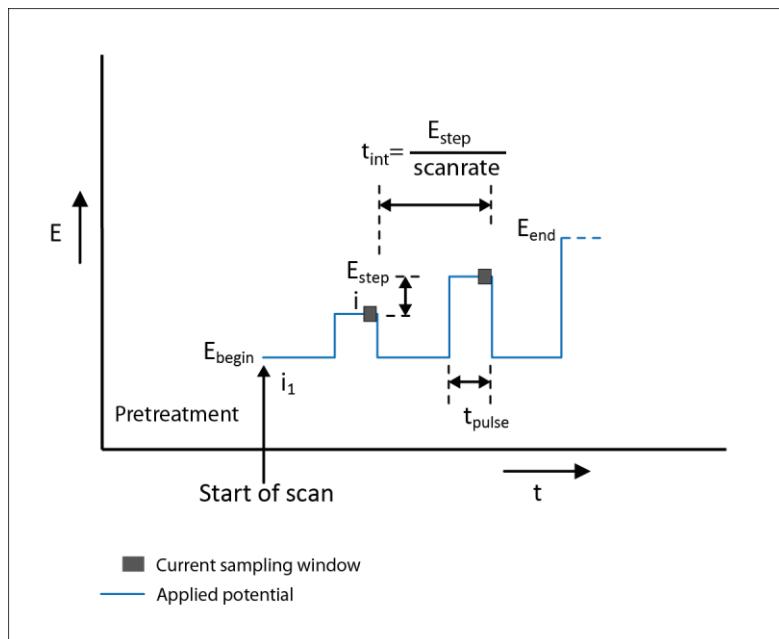
	<i>EmStat3</i>	0.125 mV to 250 mV
	<i>EmStat3+</i>	0.125 mV to 250 mV
	<i>EmStat Pico</i>	<i>High Speed mode:</i> 0.395 mV to 250 mV <i>Low Speed mode:</i> 0.537 mV to 250 mV
Amplitude	Amplitude of square wave pulse Values are half peak-to-peak	
	<i>The amplitude range for all instruments: 0.1 mV to 250 mV</i>	
Frequency	The frequency of the square wave <i>Frequency range for each instruments:</i>	
	<i>PalmSens2</i>	1 Hz to 400 Hz
	<i>PalmSens3</i>	1 Hz to 2000 Hz
	<i>PalmSens4</i>	1 Hz to 2000 Hz
	<i>EmStat2</i>	1 Hz to 500 Hz
	<i>EmStat3</i>	1 Hz to 500 Hz
	<i>EmStat3+</i>	1 Hz to 500 Hz
	<i>EmStat Pico</i>	1 Hz to 500 Hz

3.13.5 Normal Pulse Voltammetry (NPV)

Supported instruments: PalmSens series, EmStat3, EmStat3+, EmStat Pico

Description

With Normal Pulse Voltammetry the influence of diffusion limitation on your I-E curve (Cottrel behavior) is removed. In Normal Pulse Voltammetry (NPV) a potential scan is made by making constantly larger potential steps of pulse. NPV is normally more sensitive than LSV, since the diffusion layer thickness will be smaller, resulting in a higher faradaic current.



Potential applied during Normal Pulse Voltammetry

At the first potential step the pulse is equal to E_{step} , at next twice the value E_{step} , until the end where the pulse is $E_{begin} + n * E_{step}$ is equal to E_{end} , where $n = (E_{end} - E_{begin}) / (E_{step} + 1)$.

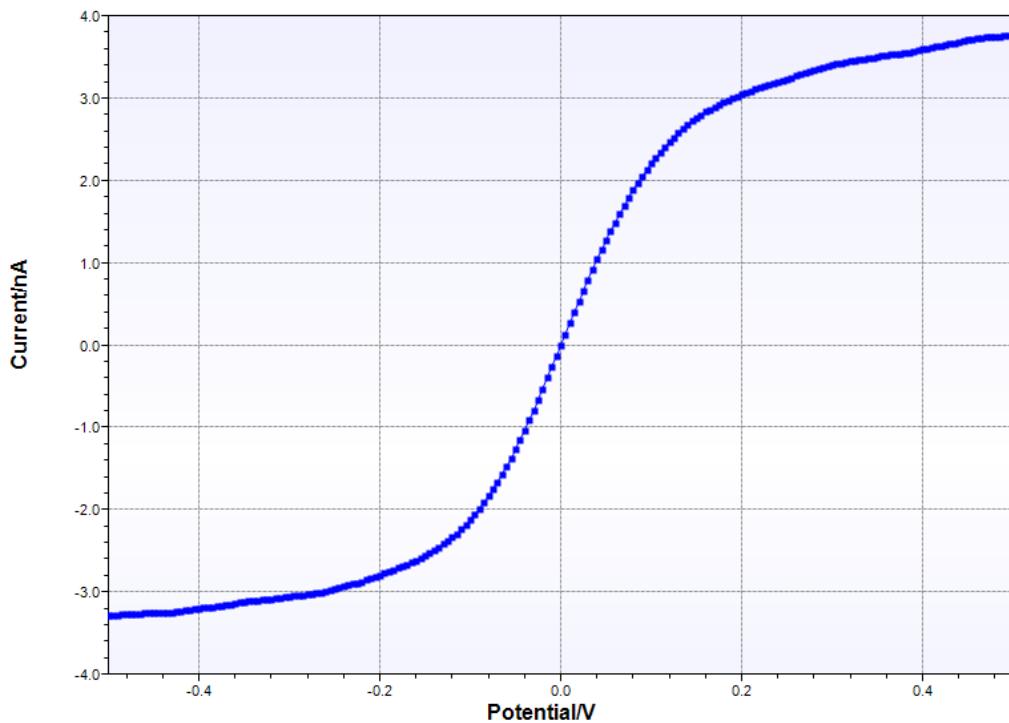
The pulse time t_{pulse} is specified by the user, but must not exceed half the interval time.

So the $t_{pulse} \leq (E_{step} / \text{scan rate} / 2)$.

Measuring

Since the diffusion layer thickness increases with time, the current will be lower when the pulse time is increased. However, a short pulse time will result in an increased capacitive current and therefore give a higher (non-linear) baseline.

See section [Measurement Sequence](#) on page 86 for information about the pretreatment and post measurement phases.



Typical NPV plot

Technique specific parameters

E begin	Potential where scan starts.
E end	Potential where measurement stops. <i>The applicable potential range for each instrument:</i>
<i>PalmSens2 -2 V to +2 V PalmSens3 -5 V to +5 V PalmSens4 -10 V to +10 V EmStat2 -2 V to +2 V EmStat3 -3 V to +3 V EmStat3+ -4 V to +4 V EmStat Pico High Speed mode: -1.7 V to +2 V Low Speed mode: -1.25 V to +2 V</i>	
	<i>See also section Limitations of the EmStat Pico</i>
E step	Step potential <i>The applicable step range for all instruments</i>
	<i>PalmSens2 1 mV to 250 mV PalmSens3 0.15 mV to 250 mV PalmSens4 0.075 mV to 250 mV EmStat2 0.1 mV to 250 mV</i>

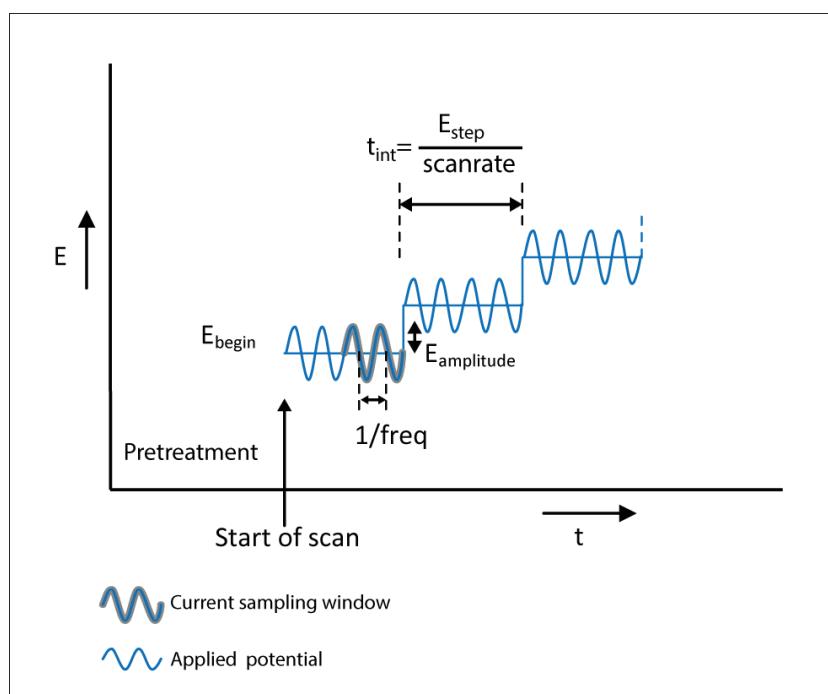
	<i>EmStat3</i> 0.125 mV to 250 mV <i>EmStat3+</i> 0.125 mV to 250 mV <i>EmStat Pico</i> <i>High Speed mode:</i> 0.395 mV to 250 mV <i>Low Speed mode:</i> 0.537 mV to 250 mV														
t pulse	The pulse time <i>Pulse time for each instrument: 5 ms to 300 ms</i>														
Scan rate	The applied scan rate. The applicable range depends on the value of E step. <i>For PalmSens2:</i> <i>In case the scan rate is so low that the time between two measured points is longer than approx. 0.05 s, the measured data points are displayed during the measurement. In other cases the measurement is completed before the points are shown.</i> <i>The applicable scan rate for each instrument:</i> <table> <tbody> <tr> <td><i>PalmSens2</i></td> <td>0.2 mV/s (0.1 mV step) to 50 mV/s (5 mV step)</td> </tr> <tr> <td><i>PalmSens3</i></td> <td>0.02 mV/s (0.15 mV step) to 25 V/s (0.25 V step)</td> </tr> <tr> <td><i>PalmSens4</i></td> <td>0.02 mV/s (0.07 mV step) to 25 V/s (0.25 V step)</td> </tr> <tr> <td><i>EmStat2</i></td> <td>0.02 mV/s (0.1 mV step) to 5 V/s (5 mV step)</td> </tr> <tr> <td><i>EmStat3</i></td> <td>0.025 mV/s (0.125 mV step) to 5 V/s (5 mV step)</td> </tr> <tr> <td><i>EmStat3+</i></td> <td>0.025 mV/s (0.125 mV step) to 5 V/s (5 mV step)</td> </tr> <tr> <td><i>EmStat Pico</i></td> <td>0.02 mV/s (0.280 mV step) to 5 V/s (10 mV step)</td> </tr> </tbody> </table>	<i>PalmSens2</i>	0.2 mV/s (0.1 mV step) to 50 mV/s (5 mV step)	<i>PalmSens3</i>	0.02 mV/s (0.15 mV step) to 25 V/s (0.25 V step)	<i>PalmSens4</i>	0.02 mV/s (0.07 mV step) to 25 V/s (0.25 V step)	<i>EmStat2</i>	0.02 mV/s (0.1 mV step) to 5 V/s (5 mV step)	<i>EmStat3</i>	0.025 mV/s (0.125 mV step) to 5 V/s (5 mV step)	<i>EmStat3+</i>	0.025 mV/s (0.125 mV step) to 5 V/s (5 mV step)	<i>EmStat Pico</i>	0.02 mV/s (0.280 mV step) to 5 V/s (10 mV step)
<i>PalmSens2</i>	0.2 mV/s (0.1 mV step) to 50 mV/s (5 mV step)														
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<i>PalmSens4</i>	0.02 mV/s (0.07 mV step) to 25 V/s (0.25 V step)														
<i>EmStat2</i>	0.02 mV/s (0.1 mV step) to 5 V/s (5 mV step)														
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<i>EmStat3+</i>	0.025 mV/s (0.125 mV step) to 5 V/s (5 mV step)														
<i>EmStat Pico</i>	0.02 mV/s (0.280 mV step) to 5 V/s (10 mV step)														

3.13.6 AC Voltammetry (ACV)

Supported instruments: PalmSens series

Description

In AC Voltammetry a potential scan is made with a superimposed sine wave which has a relatively small amplitude (normally 5 – 10 mV) and a frequency of 10 – 250 Hz. The AC signal superimposed on the DC-potential results in an AC current response (Iac).



Signal applied during AC Voltammetry

See section [Measurement Sequence](#) on page 86 for information about the pretreatment and post measurement phases.

Technique specific parameters

E begin	Potential where scan starts.
E end	Potential where measurement stops.
<i>The applicable potential range for each instrument:</i>	
<i>PalmSens2</i>	-2 V to +2 V
<i>PalmSens3</i>	-5 V to +5 V
<i>PalmSens4</i>	-10 V to +10 V
<i>EmStat2</i>	-2 V to +2 V
<i>EmStat3</i>	-3 V to +3 V
<i>EmStat3+</i>	-4 V to +4 V
<i>EmStat Pico</i>	<i>High Speed mode:</i> -1.7 V to +2 V <i>Low Speed mode:</i> -1.25 V to +2 V
<i>See also section Limitations of the EmStat Pico</i>	

E step	<p>Step potential</p> <p><i>The applicable step range for all instruments</i></p> <table> <tbody> <tr><td><i>PalmSens2</i></td><td>1 mV to 250 mV</td></tr> <tr><td><i>PalmSens3</i></td><td>0.15 mV to 250 mV</td></tr> <tr><td><i>PalmSens4</i></td><td>0.075 mV to 250 mV</td></tr> <tr><td><i>EmStat2</i></td><td>0.1 mV to 250 mV</td></tr> <tr><td><i>EmStat3</i></td><td>0.125 mV to 250 mV</td></tr> <tr><td><i>EmStat3+</i></td><td>0.125 mV to 250 mV</td></tr> <tr><td><i>EmStat Pico</i></td><td><i>High Speed mode:</i> 0.395 mV to 250 mV <i>Low Speed mode:</i> 0.537 mV to 250 mV</td></tr> </tbody> </table>	<i>PalmSens2</i>	1 mV to 250 mV	<i>PalmSens3</i>	0.15 mV to 250 mV	<i>PalmSens4</i>	0.075 mV to 250 mV	<i>EmStat2</i>	0.1 mV to 250 mV	<i>EmStat3</i>	0.125 mV to 250 mV	<i>EmStat3+</i>	0.125 mV to 250 mV	<i>EmStat Pico</i>	<i>High Speed mode:</i> 0.395 mV to 250 mV <i>Low Speed mode:</i> 0.537 mV to 250 mV
<i>PalmSens2</i>	1 mV to 250 mV														
<i>PalmSens3</i>	0.15 mV to 250 mV														
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<i>EmStat3+</i>	0.125 mV to 250 mV														
<i>EmStat Pico</i>	<i>High Speed mode:</i> 0.395 mV to 250 mV <i>Low Speed mode:</i> 0.537 mV to 250 mV														
Scan rate	<p>The applied scan rate. The applicable range depends on the value of E step.</p> <p><i>For PalmSens2:</i></p> <p><i>In case the scan rate is so low that the time between two measured points is longer than approx. 0.05 s, the measured data points are displayed during the measurement. In other cases the measurement is completed before the points are shown.</i></p> <p><i>The applicable scan rate for each instrument:</i></p> <table> <tbody> <tr><td><i>PalmSens2</i></td><td>1 mV/s (1 mV step) to 25 mV/s (5 mV step)</td></tr> <tr><td><i>PalmSens3</i></td><td>0.2 mV/s (1mV step) to 50 mV/s (5 mV step)</td></tr> <tr><td><i>PalmSens4</i></td><td>0.2 mV/s (1mV step) to 50 mV/s (5 mV step)</td></tr> </tbody> </table>	<i>PalmSens2</i>	1 mV/s (1 mV step) to 25 mV/s (5 mV step)	<i>PalmSens3</i>	0.2 mV/s (1mV step) to 50 mV/s (5 mV step)	<i>PalmSens4</i>	0.2 mV/s (1mV step) to 50 mV/s (5 mV step)								
<i>PalmSens2</i>	1 mV/s (1 mV step) to 25 mV/s (5 mV step)														
<i>PalmSens3</i>	0.2 mV/s (1mV step) to 50 mV/s (5 mV step)														
<i>PalmSens4</i>	0.2 mV/s (1mV step) to 50 mV/s (5 mV step)														
E ac	<p>Amplitude of sine wave. Values are RMS Values are half peak-to-peak</p> <p><i>The amplitude range for PalmSens2: 1 mV to 250 mV</i></p>														
Frequency	<p>The frequency of the AC signal</p> <p><i>The applicable frequency range for each instrument:</i></p> <table> <tbody> <tr><td><i>PalmSens2</i></td><td>0.12 Hz to 250 Hz</td></tr> <tr><td><i>PalmSens3</i></td><td>1 Hz to 2000 Hz</td></tr> <tr><td><i>PalmSens4</i></td><td>1 Hz to 2000 Hz</td></tr> </tbody> </table>	<i>PalmSens2</i>	0.12 Hz to 250 Hz	<i>PalmSens3</i>	1 Hz to 2000 Hz	<i>PalmSens4</i>	1 Hz to 2000 Hz								
<i>PalmSens2</i>	0.12 Hz to 250 Hz														
<i>PalmSens3</i>	1 Hz to 2000 Hz														
<i>PalmSens4</i>	1 Hz to 2000 Hz														

3.13.7 Cyclic Voltammetry (CV)

Supported instruments: PalmSens series, EmStat3, EmStat3+, EmStat Pico

Description

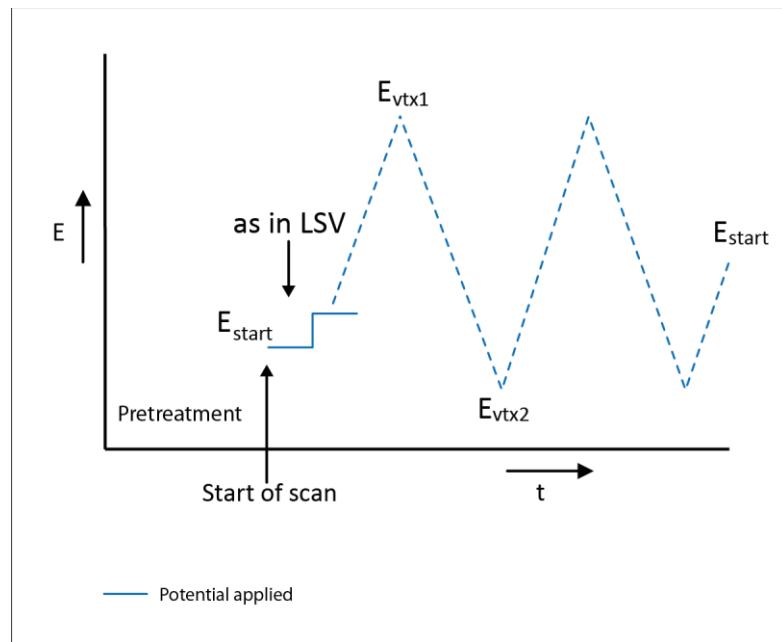
In Cyclic Voltammetry a cyclic potential scan is performed between two vertex potentials $E_{\text{vertex}1}$ and $E_{\text{vertex}2}$. The scan might start (E_{start}) at one of these vertex potentials or anywhere in between.

The scan is again not really linear, but small potential steps (E_{step}) are made. The current is measured (sampled) during the 25% interval period of each step. So the number of points per scan of the current versus potential curve is $2 * (E_{\text{end}} - E_{\text{begin}}) / (E_{\text{step}} + 1)$.

The scan rate is specified in V/s, which determines the time between two steps and thus the sampling time. The interval time is (scan rate) / E_{step} . So when E_{step} is 0.005 V and the scan rate 0.1 V/s the interval time is 0.05 s.

Fast CV

A CV becomes a Fast CV if the scan rate in combination with E_{step} results in a rate of over 2500 points / second ($E_{\text{step}} / \text{scan rate} > 2500$). See next section for more information.



Potential applied during Cyclic Voltammetry

Measuring

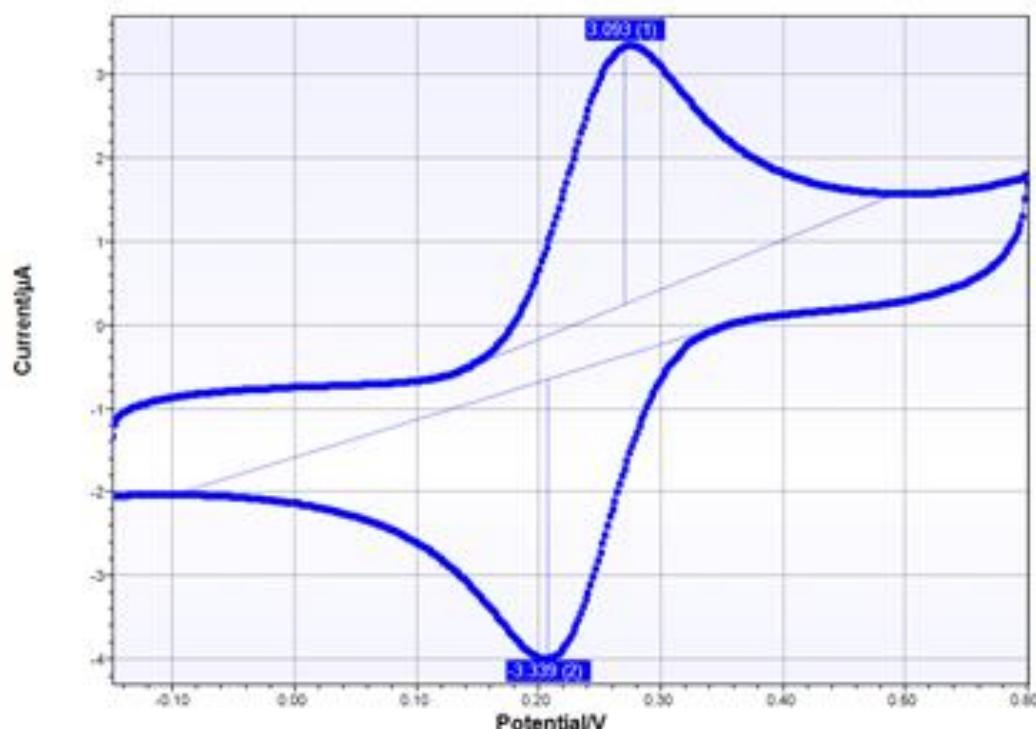
As in LSV it is sometimes important that the current does not get too high. This might ruin the working electrode. If the potential at which this will occur is not known, it is possible to specify a maximum current value at which the scan direction will reverse.

The user can also interactively determine where the scan direction is reversed, using the button 'Reverse'. In these cases the specified vertex potential by the user is not reached.

During the measurement, the curve is shown on the screen in real-time. It is possible to abort a measurement, by pressing the abort button above the plot.

During a measurement the use of the 'Pause' button will halt the scan until the same button is used again. This button is not available at higher scan rates.

See section [Measurement Sequence](#) on page 86 for information about the pretreatment and post measurement phases.



Typical CV plot for a free diffusing redox species

Technique specific parameters

E start	Potential where scan starts and stops.
E vertex1	First potential where direction reverses.
E vertex2	Second potential where direction reverses.

The applicable potential range for each instrument:

PalmSens2	-2 V to +2 V
PalmSens3	-5 V to +5 V
PalmSens4	-10 V to +10 V
EmStat2	-2 V to +2 V

	<p><i>EmStat3</i> -3 V to +3 V <i>EmStat3+</i> -4 V to +4 V <i>EmStat Pico</i> <i>High Speed mode:</i> -1.7 V to +2 V <i>Low Speed mode:</i> -1.25 V to +2 V</p> <p><i>See also section Limitations of the EmStat Pico</i></p>
E step	<p>Step potential</p> <p><i>The applicable step range for all instruments</i></p> <p><i>PalmSens2</i> 1 mV to 250 mV <i>PalmSens3</i> 0.15 mV to 250 mV <i>PalmSens4</i> 0.075 mV to 250 mV <i>EmStat2</i> 0.1 mV to 250 mV <i>EmStat3</i> 0.125 mV to 250 mV <i>EmStat3+</i> 0.125 mV to 250 mV <i>EmStat Pico</i> <i>High Speed mode:</i> 0.395 mV to 250 mV <i>Low Speed mode:</i> 0.537 mV to 250 mV</p>
Scan rate	<p>The applied scan rate. The applicable range depends on the value of E step.</p> <p><i>For PalmSens2:</i> <i>In case the scan rate is so low that the time between two measured points is longer than approx. 0.05 s, the measured data points are displayed during the measurement. In other cases the measurement is completed before the points are shown.</i></p> <p><i>The applicable scan rates for each instrument:</i></p> <p><i>PalmSens2</i> 1 mV/s (1 mV step) to 25 V/s (5 mV step) <i>PalmSens3</i> 0.02 mV/s (0.15 mV step) to 500 V/s (5 mV step) <i>PalmSens4</i> 0.02 mV/s (0.075 mV step) to 500 V/s (10 mV step) <i>EmStat2</i> 0.02 mV/s (0.1 mV step) to 5 V/s (5 mV step) <i>EmStat3</i> 0.025 mV/s (0.125 mV step) to 5 V/s (5 mV step) <i>EmStat3+</i> 0.025 mV/s (0.125 mV step) to 5 V/s (5 mV step) <i>EmStat Pico</i> 0.02 mV/s (0.280 mV step) to 5 V/s (10 mV step)</p>
Number of scans	The number of repetitions for this scan.

3.13.8 Fast Cyclic Voltammetry (FCV)

Supported instruments: PalmSens series

Description

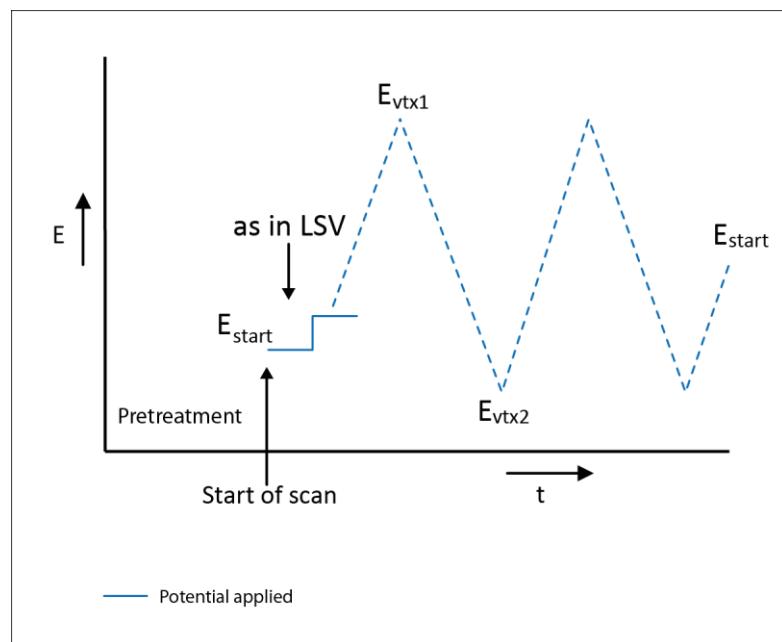
(see also previous section: *Cyclic Voltammetry*)

In Cyclic Voltammetry a cyclic potential scan is performed between two vertex potentials $E_{\text{vertex}1}$ and $E_{\text{vertex}2}$. The scan might start (E_{start}) at one of these vertex potentials or anywhere in between.

A CV becomes a Fast CV if the scan rate in combination with E step results in a rate of over 2500 points / second (E step / scan rate > 2500).

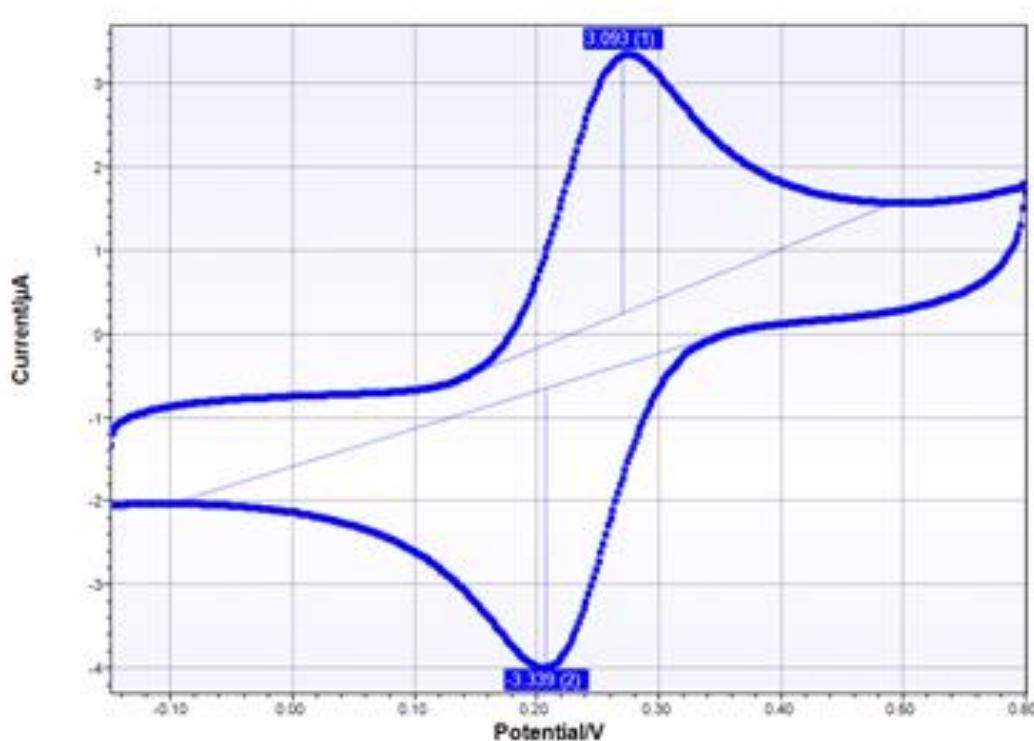
Additional options for Fast CV compared to a normal CV include averaging multiple scans and using equilibration scans. This technique can be particularly useful for very noisy measurements. Of course, it would be preferable to eliminate noise at the source first.

Auto ranging cannot be used at these high speeds, so only one current range should be selected.



Potential applied during (Fast) Cyclic Voltammetry

See section [Measurement Sequence](#) on page 86 for information about the pretreatment and post measurement phases.



Typical CV plot for a free diffusing redox species

Technique specific parameters

E start	Potential where scan starts and stops.
E vertex1	First potential where direction reverses.
E vertex2	Second potential where direction reverses.
<i>The applicable potential range for each instrument:</i>	
<i>PalmSens2</i>	-2 V to +2 V
<i>PalmSens3</i>	-5 V to +5 V
<i>PalmSens4</i>	-10 V to +10 V
<i>EmStat2</i>	-2 V to +2 V
<i>EmStat3</i>	-3 V to +3 V
<i>EmStat3+</i>	-4 V to +4 V
<i>EmStat Pico</i>	<i>High Speed mode:</i> -1.7 V to +2 V <i>Low Speed mode:</i> -1.25 V to +2 V
<i>See also section Limitations of the EmStat Pico</i>	
E step	Step potential
<i>The applicable step range for all instruments</i>	
<i>PalmSens2</i>	1 mV to 250 mV
<i>PalmSens3</i>	0.15 mV to 250 mV

	<i>PalmSens4</i> 0.075 mV to 250 mV <i>EmStat2</i> 0.1 mV to 250 mV <i>EmStat3</i> 0.125 mV to 250 mV <i>EmStat3+</i> 0.125 mV to 250 mV <i>EmStat Pico</i> <i>High Speed mode:</i> 0.395 mV to 250 mV <i>Low Speed mode:</i> 0.537 mV to 250 mV
Scan rate	The applied scan rate. The applicable range depends on the value of E step. <i>The applicable scan rates for each instrument:</i>
	<i>PalmSens2</i> 1 mV/s (1 mV step) to 25 V/s (5 mV step) <i>PalmSens3</i> 0.02 mV/s (0.15 mV step) to 500 V/s (5 mV step) <i>PalmSens4</i> 0.02 mV/s (0.075 mV step) to 500 V/s (10 mV step) <i>EmStat2</i> 0.02 mV/s (0.1 mV step) to 5 V/s (5 mV step) <i>EmStat3</i> 0.025 mV/s (0.125 mV step) to 5 V/s (5 mV step) <i>EmStat3+</i> 0.025 mV/s (0.125 mV step) to 5 V/s (5 mV step) <i>EmStat Pico</i> 0.02 mV/s (0.280 mV step) to 5 V/s (10 mV step)
Number of scans	The number of repetitions for this scan.
n averaged scans	The number of scans to be averaged.
n equil. scans	The number of equilibration scans. These are not used for measurement results.

3.13.9 Chronopotentiometric Stripping (SCP)

Also known as: Potentiometric Stripping Analysis (PSA)

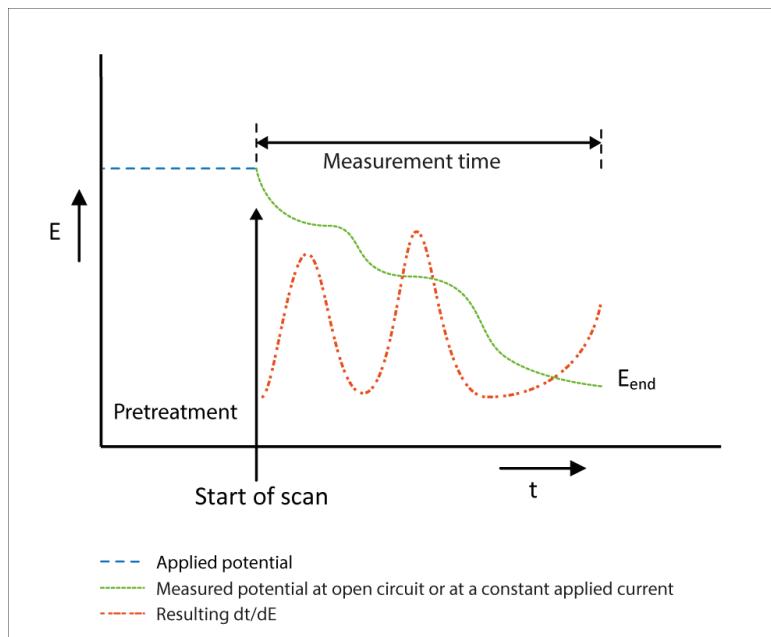
Supported instruments: PalmSens2 and PalmSens3 only

Description

Chronopotentiometric Stripping or Stripping chronopotentiometry is a sensitive analytical technique.

Before the SCP measurement starts a deposition stage at the deposition potential E dep is required.

After this stage the potential versus time is recorded. In this stage the potentiostat is switched off and the measurement starts.



Constant current stripping chronopotentiometry (CCSCP).

Measuring

The actual measurement can be done in two modes:

1. Chemical stripping, using a chemical oxidant (or reductant)
2. Using the instrument as a galvanostat and applying a constant stripping current.

In both cases the potential versus time (E vs t) is measured. The resulting curve is recalculated to the inverse derivative, so dt/dE (in s/V) vs E .

In case a component was deposited at the electrode surface, it requires current to oxidize or reduce. The higher the amount of absorbed component, the more electrical charge (time integral of the current) it requires, so the longer it takes to change the electrode potential.

The plot of dt/dE vs E therefore will show a peak the potential where the oxidation or reduction occurs.

See section [Measurement Sequence](#) on page 86 for information about the pretreatment and post measurement phases.

Technique specific parameters

E end

Potential where measurement stops.

The applicable potential range for PalmSens series:

<i>PalmSens2</i>	-2 V to +2 V
<i>PalmSens3</i>	-5 V to +5 V
<i>PalmSens4</i>	-10 V to +10 V

Stripping Current If specified as 0, the method is called chemical stripping otherwise it is constant current stripping.
Stripping current and potential ranges for each instruments:

PalmSens2 $\pm 0.001 \mu\text{A}$ to $\pm 2 \text{ mA}$.
 Potential is -2 V to +2 V.

PalmSens3 $\pm 0.001 \mu\text{A}$ to $\pm 2 \text{ mA}$.
 Potential is -5 V to +5 V.

Measurement time The maximum measurement time. This value should always exceed the required measurement time. It only limits the time of the measurement. When the potential response is erroneously and E end is not found within this time, the measurement is aborted.

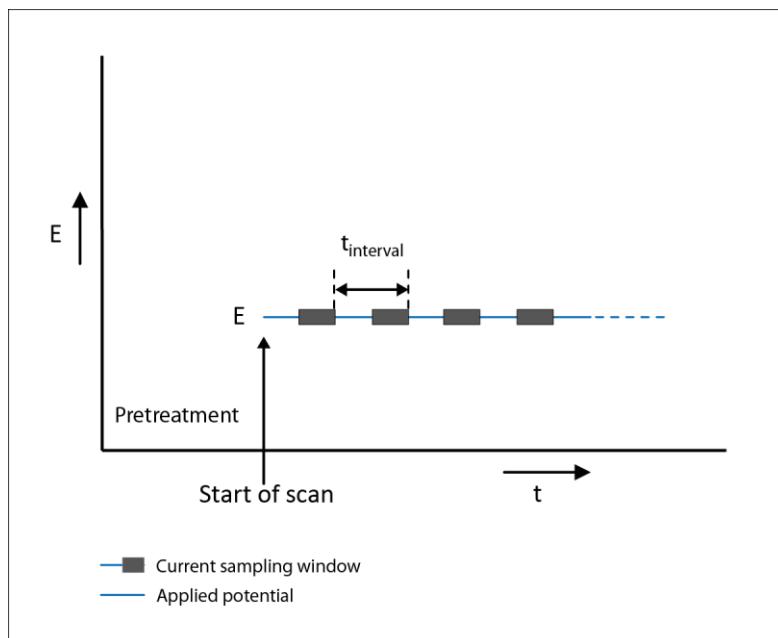
3.13.10 Chronoamperometry (CA)

Also known as: Amperometric Detection

Supported instruments: PalmSens series, EmStat3, EmStat3+, EmStat Pico

Description

The simplest, but widely used measurement technique is Chronoamperometry (or Amperometric Detection). Many sensors, like those for glucose or oxygen, require this technique.



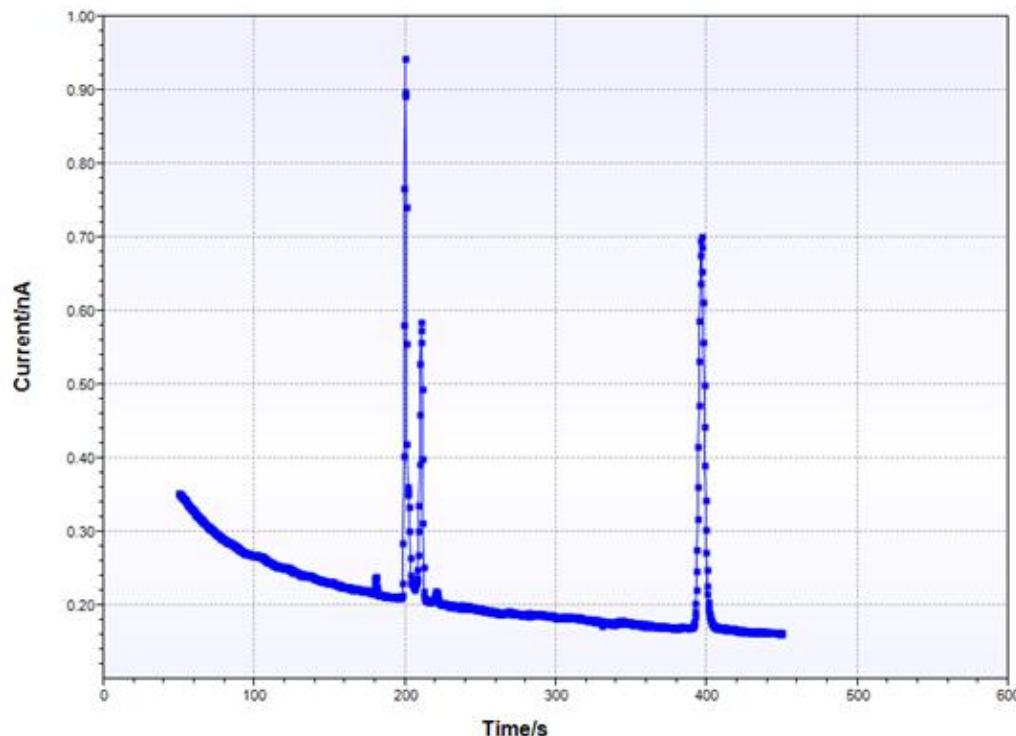
Signal applied during Chronoamperometry

Measuring

The instrument applies a constant dc-potential (E_{dc}) and the current is mostly measured with constant interval times. For most sensors, the current sampled at a fixed time after switching the potential on. By dividing the obtained current by a calibration factor the concentration of a specific analyte in the sample is calculated. Such applications allow the design of a very compact instrument like the ‘glucose pen’, with disposable sensors.

The technique is also applied when electrochemical detection is used with a flow cell or flow injection cell (FIA). FIA results in peaks instead of current levels with flow cells.

See section [Measurement Sequence](#) on page 86 for information about the pretreatment and post measurement phases.



Typical CA curve obtained using capillary electrophoresis.

Technique specific parameters

E dc	Potential during measurement. <i>The applicable potential range for each instrument:</i>
	<i>PalmSens2 -2 V to +2 V</i>
	<i>PalmSens3 -5 V to +5 V</i>
	<i>PalmSens4 -10 V to +10 V</i>
	<i>EmStat2 -2 V to +2 V</i>
	<i>EmStat3 -3 V to +3 V</i>
	<i>EmStat3+ -4 V to +4 V</i>
	<i>EmStat Pico High Speed mode: -1.7 V to +2 V Low Speed mode: -1.25 V to +2 V</i>
	<i>See also section Limitations of the EmStat Pico</i>
t interval	Time between two current samples. <i>Interval range for each instruments:</i>
	<i>PalmSens2 1 ms to 300 s</i>
	<i>PalmSens3 0.2 ms to 300 s</i>
	<i>PalmSens4 0.4 ms to 300 s</i>
	<i>EmStat2 1 ms to 300 s</i>
	<i>EmStat3 1 ms to 300 s</i>
	<i>EmStat3+ 1 ms to 300 s</i>
	<i>EmStat Pico 1 ms to practically infinite</i>
t run	Total run time of scan. <i>Run time for each instrument: 10 s to 100,000 s (+/-27 hours)</i>

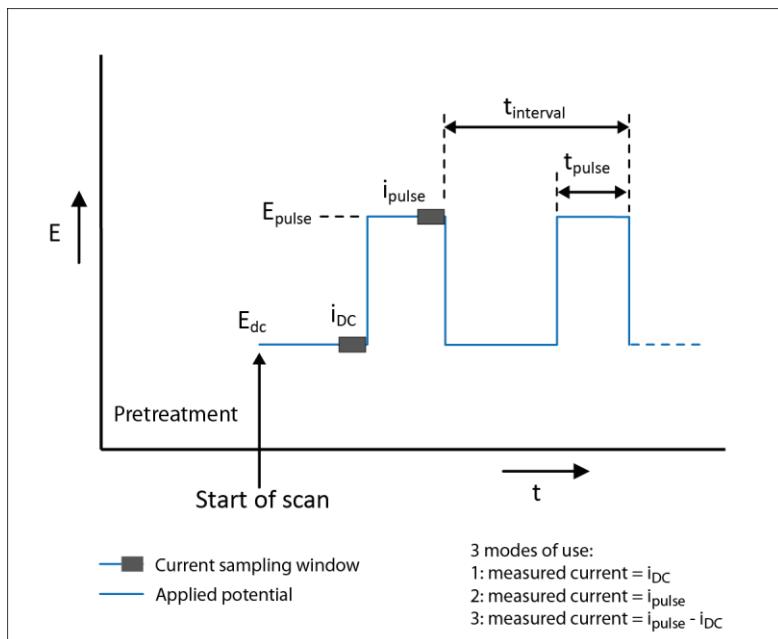
3.13.11 Pulsed Amperometric Detection (PAD)

Also known as: Pulsed Amperometry

Supported instruments: PalmSens series, EmStat3, EmStat3+

Description

With Pulsed Amperometric Detection a series of pulses (pulse profile) is periodically repeated. Pulsed Amperometric Detection can be used when a higher sensitivity is required. Using pulses instead of a constant potential might result in higher faradic currents. PAD is also used when the electrode surface has to be regenerated continuously, for instance to remove adsorbents from the electrode surface.



Signal applied during Pulsed Amperometric Detection

See section [Measurement Sequence](#) on page 86 for information about the pretreatment and post measurement phases.

Technique specific parameters

E dc

The dc or base potential.

The applicable potential range for each instrument:

PalmSens2	-2 V to +2 V
PalmSens3	-5 V to +5 V
PalmSens4	-10 V to +10 V
EmStat2	-2 V to +2 V
EmStat3	-3 V to +3 V
EmStat3+	-4 V to +4 V
EmStat Pico	<i>High Speed mode:</i> -1.7 V to +2 V <i>Low Speed mode:</i> -1.25 V to +2 V

See also section Limitations of the EmStat Pico

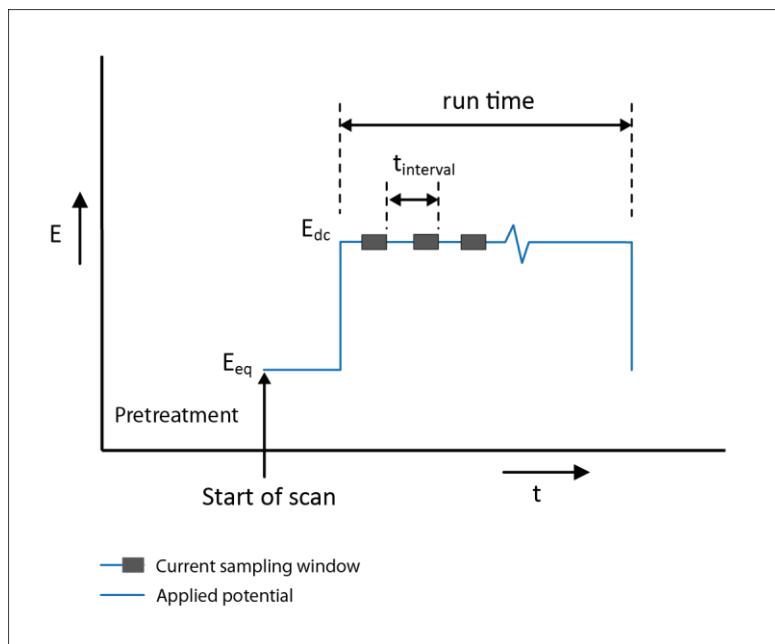
E pulse	Potential in pulse. Note that this value is not relative to E dc, given above.																
t pulse	<p>The pulse time.</p> <p><i>Pulse potential ranges for each instrument:</i></p> <table> <tr><td><i>PalmSens2</i></td><td>-2 V to +2 V</td></tr> <tr><td><i>PalmSens3</i></td><td>-5 V to +5 V</td></tr> <tr><td><i>PalmSens4</i></td><td>-10 V to +10 V</td></tr> <tr><td><i>EmStat2</i></td><td>-2 V to +2 V</td></tr> <tr><td><i>EmStat3</i></td><td>-3 V to +3 V</td></tr> <tr><td><i>EmStat3+</i></td><td>-4 V to +4 V</td></tr> </table> <p><i>Pulse time ranges:</i></p> <table> <tr><td><i>PalmSens series</i></td><td>10 ms to 1 s</td></tr> <tr><td><i>EmStat series</i></td><td>5 ms to 1 s</td></tr> </table>	<i>PalmSens2</i>	-2 V to +2 V	<i>PalmSens3</i>	-5 V to +5 V	<i>PalmSens4</i>	-10 V to +10 V	<i>EmStat2</i>	-2 V to +2 V	<i>EmStat3</i>	-3 V to +3 V	<i>EmStat3+</i>	-4 V to +4 V	<i>PalmSens series</i>	10 ms to 1 s	<i>EmStat series</i>	5 ms to 1 s
<i>PalmSens2</i>	-2 V to +2 V																
<i>PalmSens3</i>	-5 V to +5 V																
<i>PalmSens4</i>	-10 V to +10 V																
<i>EmStat2</i>	-2 V to +2 V																
<i>EmStat3</i>	-3 V to +3 V																
<i>EmStat3+</i>	-4 V to +4 V																
<i>PalmSens series</i>	10 ms to 1 s																
<i>EmStat series</i>	5 ms to 1 s																
Mode	<p>DC: i(dc) measurement is performed at potential E</p> <p>pulse: i(pulse) measurement is performed at potential E pulse</p> <p>different: i(dif) measurement is i(pulse) - i(dc)</p> <p>ial:</p>																
t run	<p>Total run time of scan.</p> <p><i>Run time for each instrument: 10 s to 100,000 s (+/-27 hours)</i></p>																
t interval	<p>Time between two current samples.</p> <p><i>Interval time for each instrument: 0.05 s to 10 s</i></p>																

3.13.12 Fast Amperometry (FAM)

Supported instruments: PalmSens series only

Description

Fast amperometry is a form of amperometric detection with very high scan rates.



Signal applied during Fast Amperometry

Technique specific parameters

E equilibration

Equilibration potential at which the measurement starts.

The applicable potential range for each instrument:

PalmSens2	-2 V to +2 V
PalmSens3	-5 V to +5 V
PalmSens4	-10 V to +10 V
EmStat2	-2 V to +2 V
EmStat3	-3 V to +3 V
EmStat3+	-4 V to +4 V
EmStat Pico	<i>High Speed mode:</i> -1.7 V to +2 V <i>Low Speed mode:</i> -1.25 V to +2 V

See also section Limitations of the EmStat Pico

E dc

Potential of pulse. Note that this value is not relative to E dc, given above.

The current is continuously sampled during this stage.

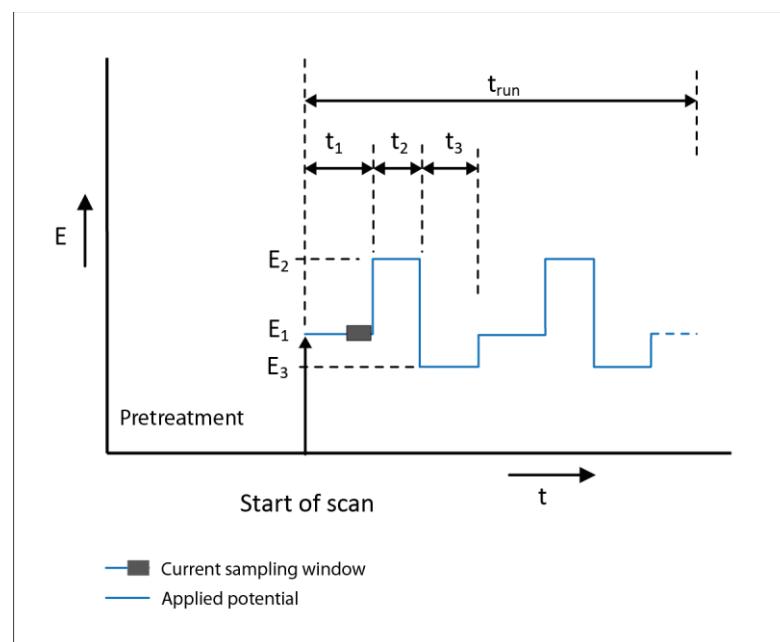
t run	Total run time of scan. <i>Run time for each supporting instrument: 1 ms to 30 s</i>
t interval	Time between two current samples. <i>Interval time for each supporting instrument: 0.01 ms to 1 s</i>

3.13.13 Multiple Pulse Amperometry (MPAD)

Supported instruments: PalmSens series, EmStat3, EmStat3+

Description

Multiple Pulse Amperometry can be used when a higher sensitivity is required. Using pulses instead of a constant potential might result in higher faradaic currents. MPAD is used when the electrode surface must be regenerated continuously, for instance to remove adsorbents from the electrode surface.



Signal applied during Multiple Pulse Amperometry

See section [Measurement Sequence](#) on page 86 for information about the pretreatment and post measurement phases.

Technique specific parameters

E1(measure)	first potential level in which the current is recorded
E2	second applied potential level
E3	third applied potential level <i>The applicable potential range for each instrument:</i>
<i>PalmSens2</i>	-2 V to +2 V
<i>PalmSens3</i>	-5 V to +5 V
<i>PalmSens4</i>	-10 V to +10 V
<i>EmStat2</i>	-2 V to +2 V
<i>EmStat3</i>	-3 V to +3 V
<i>EmStat3+</i>	-4 V to +4 V
<i>EmStat Pico</i>	<i>High Speed mode:</i> -1.7 V to +2 V <i>Low Speed mode:</i> -1.25 V to +2 V
<i>See also section Limitations of the EmStat Pico</i>	
t1	The duration of the first applied potential
t2	The duration of the second applied potential
t3	The duration of the third applied potential
<i>Values t1, t2 and t3 can be 0.1 to 2 s</i>	
t run	Total run time of scan. <i>Run time for each instrument: 10 s to 100,000 s (+/-27 hours)</i>

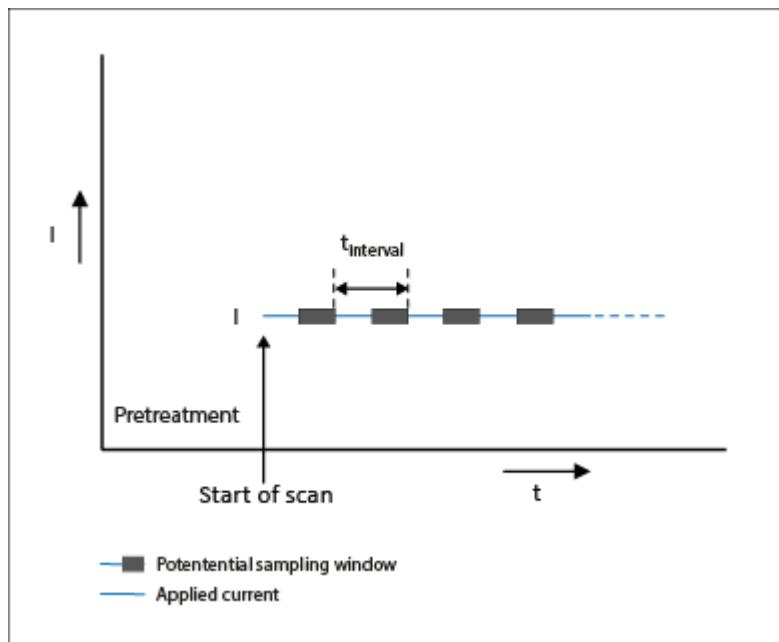
3.13.14 Chronopotentiometry (CP)

Supported instruments: PalmSens series only

Description

In this technique the potential versus time is recorded. The PalmSens instruments can be used as a galvanostat. With a galvanostat it is possible to specify the current to be applied while recording the potential response.

See section [Measurement Sequence](#) on page 86 for information about the pretreatment and post measurement phases.



Signal applied during Chronopotentiometry

Technique specific parameters

I applied

The current to apply. The unit of the value is the selected current range at the top. So if 10 μA is selected and 1.5 is given as value, the applied current will be 15 μA .

Applied current range for each instruments:

PalmSens2	1 μA to 10 mA
PalmSens3	1 μA to 10 mA
PalmSens4	1 nA to 10 mA

Applied current range for each instruments:

PalmSens2	1 μA to 10 mA
PalmSens3	1 μA to 10 mA
PalmSens4	1 nA to 10 mA

t run

Total run time of scan.

Run time for each instrument: 10 s to 100,000 s (+/-27 hours)

t interval	Time between two potential samples.
-------------------	-------------------------------------

Interval range for each instruments:

<i>PalmSens2</i>	<i>1 ms to 300 s</i>
<i>PalmSens3</i>	<i>0.2 ms to 300 s</i>
<i>PalmSens4</i>	<i>0.4 ms to 300 s</i>
<i>EmStat2</i>	<i>1 ms to 300 s</i>
<i>EmStat3</i>	<i>1 ms to 300 s</i>
<i>EmStat3+</i>	<i>1 ms to 300 s</i>
<i>EmStat Pico</i>	<i>1 ms to practically infinite</i>

3.13.15 Open Circuit Potentiometry (OCP)

Supported instruments: PalmSens series, EmStat3, EmStat3+, EmStat Pico

Description

For Open Circuit Potentiometry the current is zero and the so-called open circuit potential (OCP) is obtained.

See section [Measurement Sequence](#) on page 86 for information about the pretreatment and post measurement phases.

Technique specific parameters

t run	Total run time of scan.
--------------	-------------------------

*Run time for each instrument: 5*t interval to 100,000 s (+/-27 hours)*

t interval	Time between two potential samples.
-------------------	-------------------------------------

Interval range for each instruments:

<i>PalmSens2</i>	<i>1 ms to 300 s</i>
<i>PalmSens3</i>	<i>0.2 ms to 300 s</i>
<i>PalmSens4</i>	<i>0.4 ms to 300 s</i>
<i>EmStat2</i>	<i>1 ms to 300 s</i>
<i>EmStat3</i>	<i>1 ms to 300 s</i>
<i>EmStat3+</i>	<i>1 ms to 300 s</i>
<i>EmStat Pico</i>	<i>1 ms to practically infinite</i>

3.13.16 Multistep Amperometry (MA)

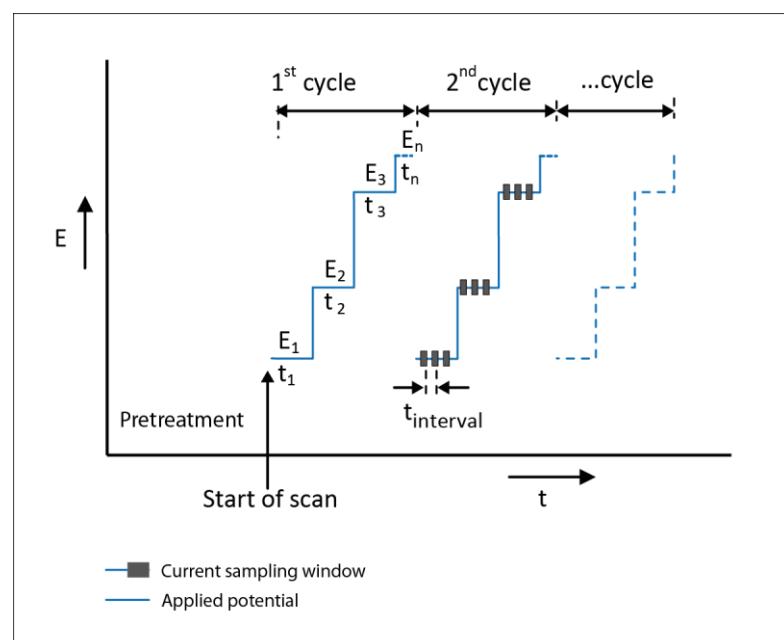
Supported instruments: PalmSens series, EmStat3, EmStat3+, EmStat Pico

Description

Multistep amperometry simply allows the user to specify the number of potential steps they want to apply and how long each step should last. The current is continuously samples with the specified interval.

A whole cycle of steps can be repeated a number of times.

(Note: if only one potential step is use, this technique is identical to Chronoamperometry, which provides a larger range of measurement rates.)



Signal applied during Multistep Amperometry

See section [Measurement Sequence](#) on page 86 for information about the pretreatment and post measurement phases.

Technique specific parameters

t interval	Time between two current samples. <i>Interval range for each instruments:</i>
	<i>PalmSens2</i> 1 ms to 300 s <i>PalmSens3</i> 0.2 ms to 300 s <i>PalmSens4</i> 0.4 ms to 300 s <i>EmStat2</i> 1 ms to 300 s <i>EmStat3</i> 1 ms to 300 s <i>EmStat3+</i> 1 ms to 300 s <i>EmStat Pico</i> 1 ms to practically infinite
Cycles	The number of repetitions.
Levels	The number of potentials to apply within a cycle. Switching between levels adds an overhead time of +/- 80 ms.
E level [n]	Potential level at which the current is recorded. <i>The applicable potential range for each instrument:</i>
	<i>PalmSens2</i> -2 V to +2 V <i>PalmSens3</i> -5 V to +5 V <i>PalmSens4</i> -10 V to +10 V <i>EmStat2</i> -2 V to +2 V <i>EmStat3</i> -3 V to +3 V <i>EmStat3+</i> -4 V to +4 V <i>EmStat Pico</i> <i>High Speed mode:</i> -1.7 V to +2 V <i>Low Speed mode:</i> -1.25 V to +2 V
	<i>See also section Limitations of the EmStat Pico</i>
t [n]	The duration of the applied potential.

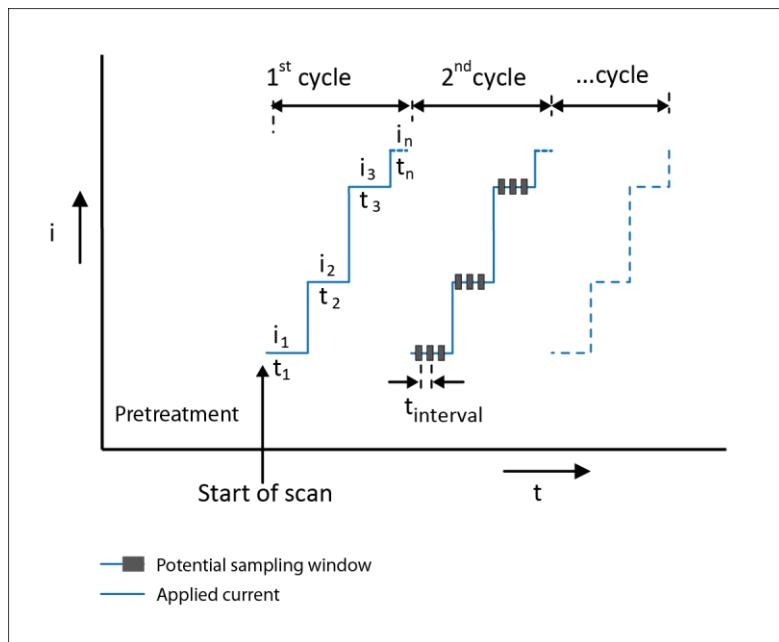
3.13.17 Multistep Potentiometry (MP)

Supported instruments: PalmSens series, EmStat3, EmStat3+

Description

Multistep Potentiometry simply allows the user to specify the number of current steps they want to apply and how long each step should last. The potential response is continuously sampled with the specified interval.
A whole cycle of steps can be repeated several times.

(Note: if only one current step is used, this technique is identical to Potentiometry which provide a larger range of measurement rates.)



Signal applied during Multistep Potentiometry

See section [Measurement Sequence](#) on page 86 for information about the pretreatment and post measurement phases.

Technique specific parameters

t interval	Time between two potential samples.
-------------------	-------------------------------------

Interval range for each instruments:

PalmSens2	1 ms to 300 s
PalmSens3	0.2 ms to 300 s
PalmSens4	0.4 ms to 300 s
EmStat2	1 ms to 300 s
EmStat3	1 ms to 300 s
EmStat3+	1 ms to 300 s
EmStat Pico	1 ms to practically infinite

Cycles	The number of repetitions.
---------------	----------------------------

Levels	The number of potentials to apply within a cycle. Switching between levels adds an overhead time of +/- 80 ms.
---------------	---

I level [n]	Current level at which the potential is recorded. The current is specified in the selected current range (the bar above pretreatment settings)
-------------	---

Applied current range for each instruments:

PalmSens2	1 µA to 10 mA
PalmSens3	1 µA to 10 mA
PalmSens4	1 nA to 10 mA

The applicable potential range for each instrument:

PalmSens2	-2 V to +2 V
PalmSens3	-5 V to +5 V
PalmSens4	-10 V to +10 V
EmStat2	-2 V to +2 V
EmStat3	-3 V to +3 V
EmStat3+	-4 V to +4 V
EmStat Pico	<i>High Speed mode:</i> -1.7 V to +2 V <i>Low Speed mode:</i> -1.25 V to +2 V

See also section Limitations of the EmStat Pico

t [n]	The duration of the applied current.
-------	--------------------------------------

3.13.18 Mixed Mode (MM)

Supported instruments: PalmSens and partly supported by EmStat3 and EmStat3+

Description

Mixed Mode is a flexible technique that allows for switching between potentiostatic, galvanostatic and open circuit measurements during a single run.

See section [Measurement Sequence](#) on page 86 for information about the pretreatment and post measurement phases.

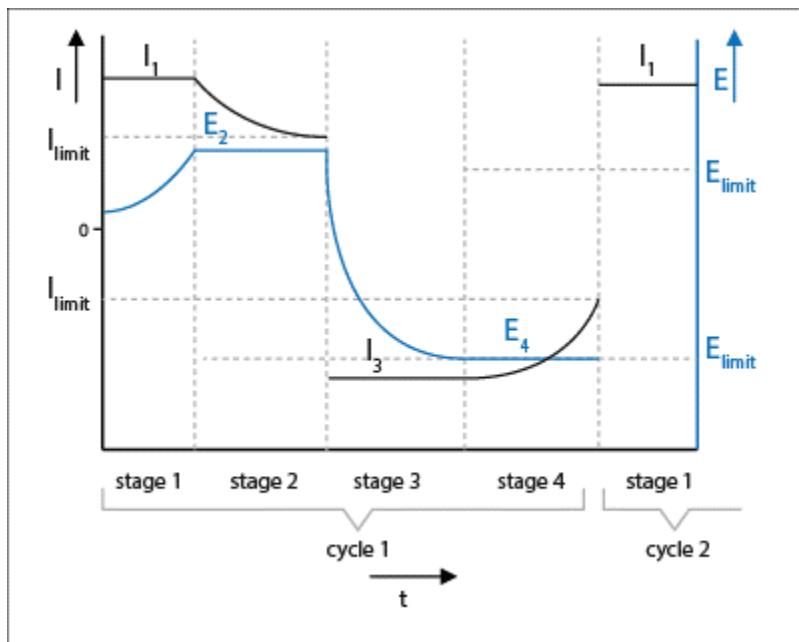
The Mixed Mode uses different stages similar to the levels during Multistep Amperometry or Potentiometry, but each stage can be galvanostatic or potentiostatic independent of the previous stage.

The available stage types are ConstantE, Constant I, SweepE, OpenCircuit and Impedance. SweepE offers a linear sweep of the potential. During an Impedance stage the impedance is measured by applying a small AC potential superimposed with a DC potential. This corresponds to EIS with a single frequency.

Each stage can use the previous stage's potential as reference point, for example a constant current is applied for a fixed period and afterwards the reached potential is kept constant for a fixed period.

Furthermore, each stage can end, because a fixed period has elapsed or certain criteria are met. At the moment, available criteria are reaching a maximum current, minimum current, maximum potential and minimum potential.

These modes are useful especially for energy conversion and storage research, i.e. battery, solar cell or super capacitors research. A classic test for batteries is to charge and discharge them in several cycles. A constant current is applied and the potential change is recorded. If a certain potential is reached, the next stage is triggered, which is usually applying the inverted constant current. This is repeated for multiple cycles. While this method could be performed with Multistep Potentiometry, as soon as further steps are introduced the Mixed Mode is necessary. For example to determine the capacity you would like to discharge a battery but you need to take care that the terminal potential isn't crossed. First the battery is charged. You can apply a constant current until a set potential is reached, e.g. the termination potential. After that the termination potential is kept constant until a current limit is reached or time has elapsed. Then this process is repeated with a negative current to discharge the battery.



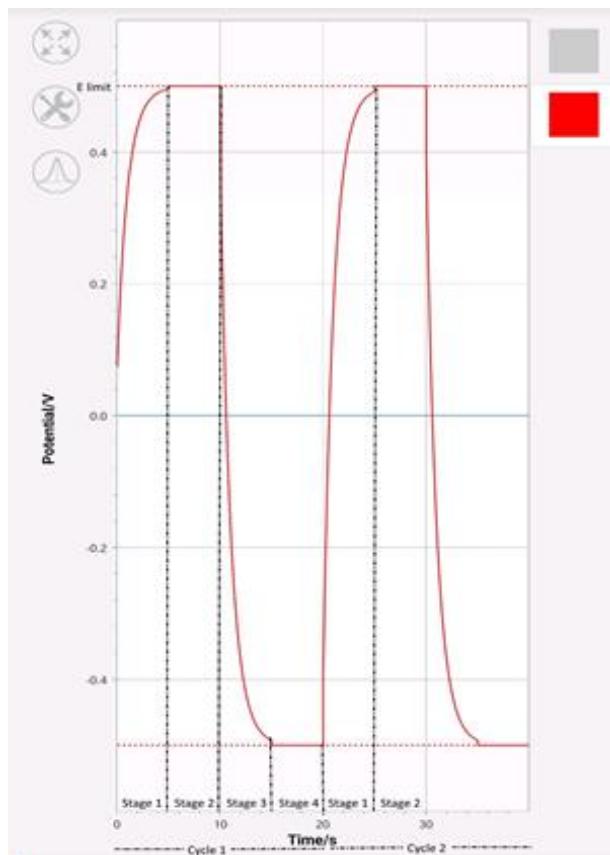
Scheme of potential and current profile during the above described example.

Mixed Mode Settings

t interval	60.0	s
Cycles	3	
Stage 1: Constant I		
I applied	1.0	100 mA
t run	86400.0	s
<input type="button" value="..."/>		
<input type="checkbox"/> Proceed when E <	0.0	V
<input checked="" type="checkbox"/> Proceed when E >	1.7	V
Stage 2: Constant E		
E dc	1.7	V
t run	3600.0	s
<input type="button" value="..."/>		
<input type="checkbox"/> E vs previous E		
<input checked="" type="checkbox"/> Proceed when I <	50000.0	uA
<input type="checkbox"/> Proceed when I >	0.0	uA
Stage 3: Constant I		
I applied	-1.0	100 mA
t run	86400.0	s
<input type="button" value="..."/>		
<input type="checkbox"/> I vs previous I		
<input checked="" type="checkbox"/> Proceed when E <	0.2	V
<input type="checkbox"/> Proceed when E >	0.0	V
Stage 4: Constant E		
E dc	0.2	V

Expected duration: 50:04:00s
3004 datapoints

Part of the Method needed to perform the above described method.



Another example is to study how well a supercapacitor stores charge. First the capacitor is charged with a fixed current followed by observing the OCP of the supercapacitor.

Technique specific parameters

t interval	Time between two current samples.
-------------------	-----------------------------------

Interval range for each instruments:

<i>PalmSens2</i>	<i>1 ms to 300 s</i>
<i>PalmSens3</i>	<i>0.2 ms to 300 s</i>
<i>PalmSens4</i>	<i>0.4 ms to 300 s</i>
<i>EmStat2</i>	<i>1 ms to 300 s</i>
<i>EmStat3</i>	<i>1 ms to 300 s</i>
<i>EmStat3+</i>	<i>1 ms to 300 s</i>
<i>EmStat Pico</i>	<i>1 ms to practically infinite</i>

Cycles	The number of repetitions.
---------------	----------------------------

Parameters for Constant E stage

E dc	Potential during measurement. <i>The applicable potential range for each instrument:</i>
	<i>PalmSens2</i> -2 V to +2 V
	<i>PalmSens3</i> -5 V to +5 V
	<i>PalmSens4</i> -10 V to +10 V
	<i>EmStat2</i> -2 V to +2 V
	<i>EmStat3</i> -3 V to +3 V
	<i>EmStat3+</i> -4 V to +4 V
	<i>EmStat Pico</i> <i>High Speed mode:</i> -1.7 V to +2 V <i>Low Speed mode:</i> -1.25 V to +2 V
	<i>See also section Limitations of the EmStat Pico</i>
t run	Total run time of the stage. <i>Run time for each instrument: 10 s to 100,000 s (+/-27 hours)</i>

Parameters for Constant I stage

I applied	The current to apply. The unit of the value is the selected current range at the top. So if 10 uA is selected and 1.5 is given as value, the applied current will be 15 uA. <i>Applied current range for each instruments:</i>
	<i>PalmSens2</i> 1 μ A to 10 mA
	<i>PalmSens3</i> 1 μ A to 10 mA
	<i>PalmSens4</i> 1 nA to 10 mA
	<i>Applied current range for each instruments:</i>
	<i>PalmSens2</i> 1 μ A to 10 mA
	<i>PalmSens3</i> 1 μ A to 10 mA
	<i>PalmSens4</i> 1 nA to 10 mA
t run	Total run time of the stage. <i>Run time for each instrument: 10 s to 100,000 s (+/-27 hours)</i>

Parameters for Sweep E stage

E begin	Potential where scan starts.
E end	Potential where measurement stops. <i>The applicable potential range for each instrument:</i>
<i>PalmSens2 -2 V to +2 V PalmSens3 -5 V to +5 V PalmSens4 -10 V to +10 V EmStat2 -2 V to +2 V EmStat3 -3 V to +3 V EmStat3+ -4 V to +4 V EmStat Pico High Speed mode: -1.7 V to +2 V Low Speed mode: -1.25 V to +2 V</i>	
	<i>See also section Limitations of the EmStat Pico</i>
E step	Step potential <i>The applicable step range for all instruments</i>
	<i>PalmSens2 1 mV to 250 mV PalmSens3 0.15 mV to 250 mV PalmSens4 0.075 mV to 250 mV EmStat2 0.1 mV to 250 mV EmStat3 0.125 mV to 250 mV EmStat3+ 0.125 mV to 250 mV EmStat Pico High Speed mode: 0.395 mV to 250 mV Low Speed mode: 0.537 mV to 250 mV</i>
Scan rate	<p>The applied scan rate. The applicable range depends on the value of E step since the data acquisition rate is limited by the connected instrument.</p> <p>Max. data acquisition rates:</p> <ul style="list-style-type: none"> EmStat3 series: 1000 points/sec PalmSens2: 4000 points/sec PalmSens3: 100,000 points/sec PalmSens4: 50,000 points/sec <p><i>For PalmSens2:</i></p> <p><i>In case the scan rate is so low that the time between two measured points is longer than approx. 0.05 s, the measured data points are displayed during the measurement. In other cases the measurement is completed before the points are shown.</i></p>

The applicable scan rates for each instrument:

<i>PalmSens2</i>	<i>1 mV/s (1 mV step) to 25 V/s (5 mV step)</i>
<i>PalmSens3</i>	<i>0.02 mV/s (0.15 mV step) to 500 V/s (5 mV step)</i>
<i>PalmSens4</i>	<i>0.02 mV/s (0.075 mV step) to 500 V/s (10 mV step)</i>
<i>EmStat2</i>	<i>0.02 mV/s (0.1 mV step) to 5 V/s (5 mV step)</i>
<i>EmStat3</i>	<i>0.025 mV/s (0.125 mV step) to 5 V/s (5 mV step)</i>
<i>EmStat3+</i>	<i>0.025 mV/s (0.125 mV step) to 5 V/s (5 mV step)</i>
<i>EmStat Pico</i>	<i>0.02 mV/s (0.280 mV step) to 5 V/s (10 mV step)</i>

t interval

Time between two current samples.

Interval range for each instruments:

<i>PalmSens2</i>	<i>1 ms to 300 s</i>
<i>PalmSens3</i>	<i>0.2 ms to 300 s</i>
<i>PalmSens4</i>	<i>0.4 ms to 300 s</i>
<i>EmStat2</i>	<i>1 ms to 300 s</i>
<i>EmStat3</i>	<i>1 ms to 300 s</i>
<i>EmStat3+</i>	<i>1 ms to 300 s</i>
<i>EmStat Pico</i>	<i>1 ms to practically infinite</i>

Cycles

The number of repetitions.

Levels

The number of potentials to apply within a cycle.

Switching between levels adds an overhead time of +/-.

E level [n]

Potential level at which the current is recorded.

The applicable potential range for each instrument:

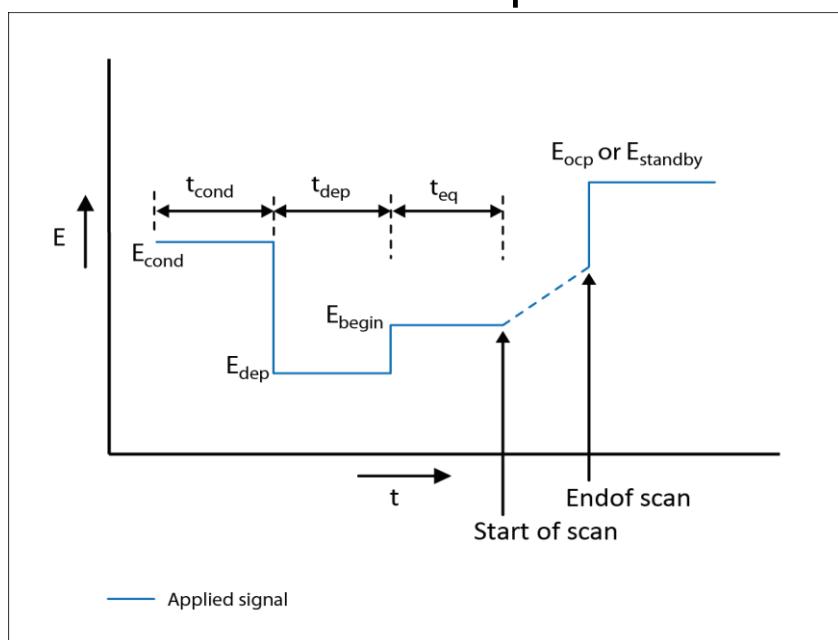
<i>PalmSens2</i>	<i>-2 V to +2 V</i>
<i>PalmSens3</i>	<i>-5 V to +5 V</i>
<i>PalmSens4</i>	<i>-10 V to +10 V</i>
<i>EmStat2</i>	<i>-2 V to +2 V</i>
<i>EmStat3</i>	<i>-3 V to +3 V</i>
<i>EmStat3+</i>	<i>-4 V to +4 V</i>
<i>EmStat Pico</i>	<i>High Speed mode: -1.7 V to +2 V Low Speed mode: -1.25 V to +2 V</i>

See also section Limitations of the EmStat Pico

t [n]

The duration of the applied potential.

3.14 Measurement sequence



Normal measurement sequence

The sequence of a voltammetric measurement (except for stripping chronopotentiometry) is:

1. In case Measure vs OCP is enabled: determine the OCP.
2. Apply E cond, the conditioning potential, if t cond is not zero.
3. Apply E dep, the deposition potential, if t dep is not zero.
4. Apply E begin and wait t eq seconds
5. Start measurement at E start and continue until E end with steps E step, with the specified scan rate. In CV the scan is continued by reversing the scan direction. The current range is set automatically however with the constraints as specified.
6. If the measurement rate is less then approximately 25 points per second the points are displayed on-line. During the measurement the plot can be re-scaled automatically. If the scan rate is higher the points are plotted after completing the scan. (PalmSens only)
7. If the cell must remain switched on, E stby is applied; otherwise the cell is switched off.

The sequence of a measurement as a function of time:

1. (in case Measure vs OCP is used) Determine the OCP.
2. Apply E cond the conditioning potential, if t cond is not zero.
3. Apply E dep the deposition potential, if t dep is not zero.
4. Apply E or E eq and wait t eq seconds
5. Start the measurement. The measured points are displayed on-line.
6. If the cell must remain switched on, E standby is applied, otherwise the cell is switched off.

The sequence of stripping chronopotentiometry (SCP or PSA) is:

1. Apply E cond, the conditioning potential, if t cond is not zero.

2. Apply E dep, the deposition potential, if t dep is not zero.
3. Apply E dep and wait t equilibration seconds.
4. If I strip = 0 then the cell is switched off, otherwise a constant current I strip is applied. The measurement with a rate of 40 kHz starts. The measurement stops when either the measured potential is below E end or the run time is exceeded.
5. If the cell must remain switched on, E standby is applied, otherwise the cell is switched off. If 'Limit to' is checked, the cell is switched off after the specified time.

For PalmSens2 and PalmSens3:

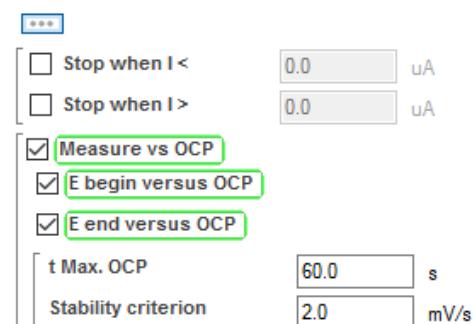
During the conditioning, deposition and equilibration stages two keys of the keypad are active. When the stop button is pressed the measurement is ended. The skip key is used to step to the next stage. During a measurement only the ESC or ■ key is active.

	Old model (green LCD)	PalmSens3 (blue LCD)
Skip key	▶	▶▶
Stop key	ESC	■

3.15 Measuring versus OCP

Voltammetric measurements can be done by specifying the potential scan with respect to the Open Circuit Potential (OCP) or with absolute values versus the reference electrode.

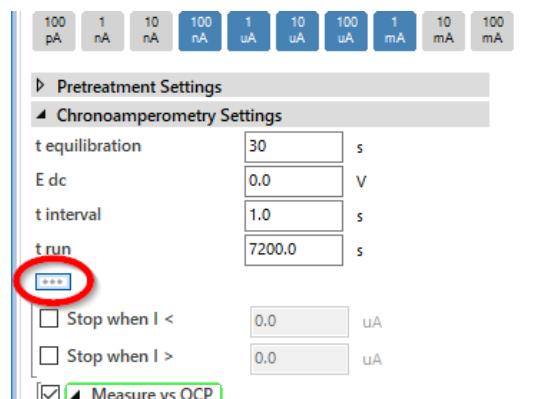
In case one or more potentials are specified with respect to the OCP, the open circuit potential must be determined before the actual measurement is done. This OCP measurement requires a variable time, which is determined by the drift of the open circuit potential and the maximum time to measure the OCP value. The OCP value is set as soon as the drift is lower than the specified value for the 'Stability criterion' or when the 't Max. OCP' has elapsed.



OCP parameters

3.16 Advanced settings

Additional settings for each technique can be found under the [...] button.

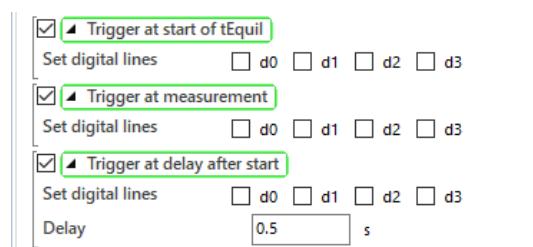


The more button found in the Method Editor.

3.16.1 Stop when E or I reaches specified value

The limits entered here apply to the entire measurement excluding the pretreatment stages.

3.16.2 Trigger at ...



In case “Trigger at ...” is set, the selected digital line(s) on the AUX port of the instrument will be set high when triggered. They will remain high until the end of the measurement. Refer to section Auxiliary port pin-outs for more information about the position of the digital pins on your instrument’s auxiliary port.

In case “Trigger at delay after start” is used, the delay will be rounded to the applicable interval time between each measured data point.

3.16.3 On device storage



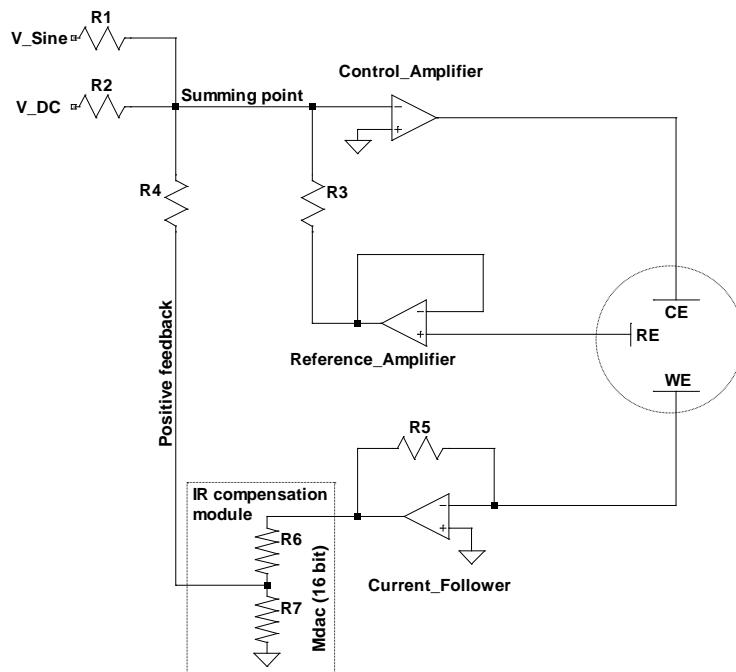
The PalmSens4 is equipped with internal data storage of 4 or 8 GB (depending on the date of purchase). In case the option “Save on internal storage” is enabled, the measurement will be stored on-board the PalmSens4 in a folder with the name of the day’s date.

The on-board data can be browsed and downloaded using the menu: “Data” → “Load data from PalmSens4 internal storage...”.

The following techniques are not supported for this functionality:
EIS, MultiStep and MixedMode.

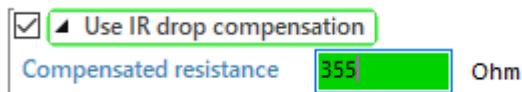
3.16.4 Use IR drop compensation

IR Compensation for PalmSens4 is available as an in-factory add-on module. The resistance between the reference electrode and the double layer of the specimen can cause a significant potential drop, decreasing the applied potential where it is required. The module provides positive feedback to compensate for the IR drop between Reference electrode and the outside of the double layer of the electrochemical cell. The PalmSens4 IR Compensation module works by means of Positive Feedback. This is achieved through the use of a 16 bit MDAC in the module which scales the output of the current follower opamp to provide a positive feedback voltage which is proportional to the current through the cell. The compensation voltage is added into the summing point before the control amplifier and thus increases the applied potential to counteract the IR drop.



Positive feedback allows for fast scan rates up to 10 V/s, depending on the characteristics of the cell. If the potential error to compensate for becomes close to the value set for E applied, the system might become unstable. Using IR compensation limits the measurement bandwidth to 10 kHz.

The resistance to compensate for can be entered directly in the Method Editor in PSTrace:



If auto ranging is not allowed for the compensation used in combination with the selected current ranges, this is shown in the Method Editor:



Error message shown in Method Editor

Make sure a single current range is selected in these circumstances.

Supported Techniques

The following techniques are supported for use with IR compensation:

- Linear Sweep Voltammetry
- Cyclic Voltammetry
- Square Wave Voltammetry
- Differential Pulse Voltammetry
- Normal Pulse Voltammetry
- ChronoAmperometry
- Multistep Amperometry

3.17 Limitations of the EmStat Pico

The EmStat Pico module has some limitations for each technique which are explained in this section.



EmStat Pico on development board

3.17.1 EmStat Pico modes

The EmStat Pico can be used in two different (PGStat) modes; Low Speed and High Speed.

Each mode has different limitations for potential ranges. The table below shows which ranges are applicable for each mode.

High Speed mode		
Mode property	Value min	Value max
Bandwidth	0.016 Hz	100 Hz
Potential range	-1.25 V	2.0 V
Dynamic potential window*	2.2 V	2.2 V
Low Speed mode		
Mode property	Value min	Value max
Bandwidth	0.016 Hz	200 kHz
Potential range	-1.7 V	2.0 V
Dynamic potential window*	1.214 V	1.214 V

*Dynamic potential window

The dynamic potential window is the available range that can be used during a single scan/sweep within the available potential range. In the High Speed mode, a Linear Sweep Voltammetry scan can for example have the following parameters:
 E Begin = -1 V and E End = 1.2 V, or E Begin = -0.2 V and E End = 2 V

which both are within the maximum dynamic potential window of 2.2 V.

The same limitations apply to the Low Speed mode which has a more limited dynamic potential window.

4 Electrochemical Impedance Spectroscopy

PSTrace provides the possibility to do electrochemical impedance measurements with the PalmSens3 or PalmSens4 instrument. The impedance measurements are done in potentiostatic mode. A sine wave is superimposed on the specified dc-potential, so $E = E_{dc} + E_{ac}$. This results in a dc-current with a superimposed ac-current, $I = I_{dc} + I_{ac}$.

An introduction can be found in for instance the textbook **Electrochemical Methods: Fundamentals and Applications**, written by Allen J. Bard and Larry R. Faulkner, ISBN-13: 978-0471043720

4.1 Introduction

The program provides different modes of measurements:

- a frequency scan at a fixed dc-potential
- frequency scans at each potential in a potential scan
- frequency scans at specified time intervals (time scan)
- a single frequency applied at each potential in a potential scan
- a single frequency at specified time intervals

The measured data can be presented in different plot formats.

For EIS data analysis, see section [Export for analysis and circuit fitting](#) on page 104.

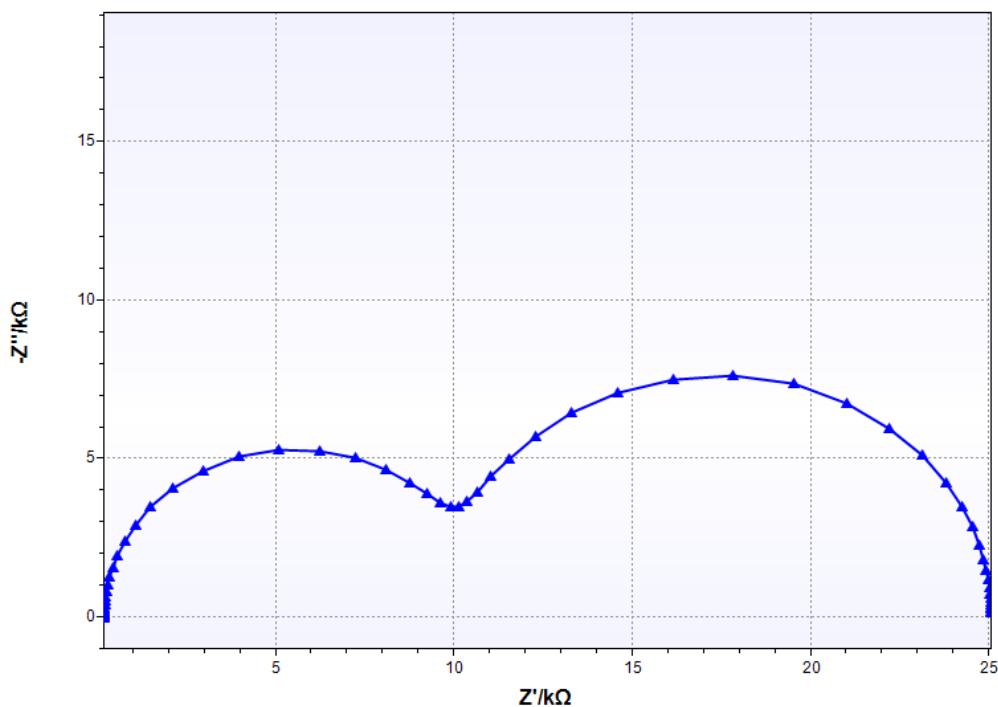
The measurements yield the impedance defined by $Z(\omega) = E_{ac}(\omega) / I_{ac}(\omega)$.

The impedance is a complex number $Z(\omega) = Z'(\omega) - jZ''(\omega)$, where Z' is the real part and Z'' the imaginary part of the impedance and $\omega = 2\pi f$, where f is the applied frequency. The phase shift ϕ is defined as $\tan(\phi) = -Z'' / Z'$. (Note: we do not use (ω) from here anymore)

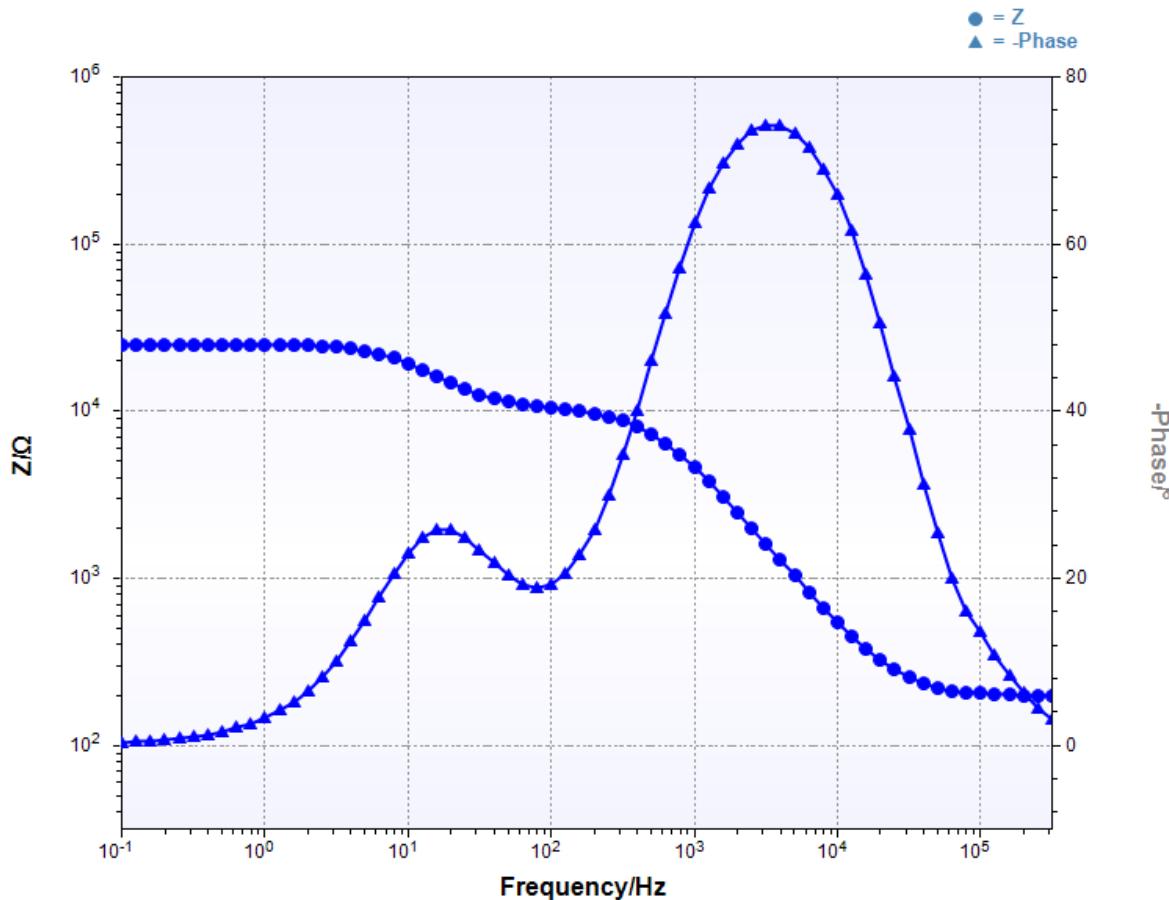
The impedance data are often presented in the Nyquist plot, with Z'' vs Z' or in a Bode plot, with the decimal logarithm of the magnitude of Z and phase shift versus the logarithm of the frequency.

The magnitude Z is defined as

$$|Z|^2 = (Z')^2 + (-Z'')^2.$$



Example of a Nyquist plot.

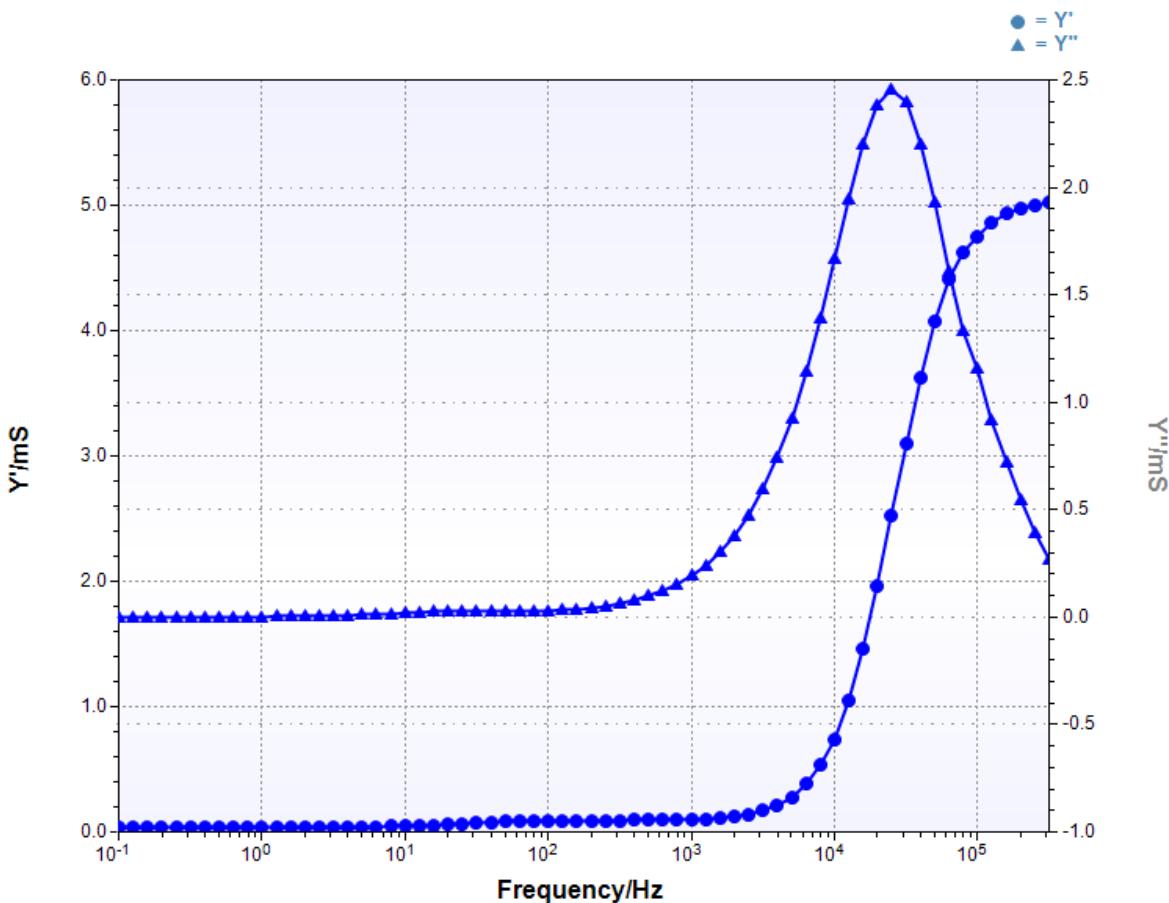


Example of a Bode plot.

The inverse of the impedance is the admittance, which is also a complex number $Y = Y' + jY''$,

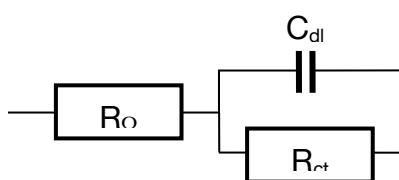
where $Y = 1 / Z$, $Y' = Z' / (Z'^2 + Z''^2)$ and $Y'' = Z'' / (Z'^2 + Z''^2)$.

Sometimes impedance measurements are represented in a plot of Y vs $\log(f)$ or Y'' vs Y' .



Example of an admittance plot.

The example shown in the plots above represents a measurement of an ideal working electrode at which a faradaic reaction occurs. The equivalent circuit for such a simple system is shown in the figure below.



Equivalent circuit

Where R_Ω is the ohmic resistance of the electrolytic solution, C_{dl} the capacitance of the double layer of the working electrode and R_{ct} is the resistance due to the electron transfer of the faradic reaction.

At high frequencies the impedance is dominated by the value of R_Ω , so $Z = R_\Omega$, with a phase shift of 0°.

At low frequencies the impedance of the double layer is so high that it can be neglected, so the impedance is equal to $R_\Omega + R_{ct}$ and the phase shift is again 0°.

At intermediate frequencies the influence of the capacitance of the double layer (which has an impedance of $Z = -j / (\omega C_{dl})$) results in a phase shift and a measured impedance between the two limits of R_Ω and $(R_\Omega + R_{ct})$.

4.2 Setting up an impedance measurement

The Measurement tab contains all the method parameters. The Notes textbox can be used to describe the sensor used and sample that is measured.

Current ranges



With the current range buttons at the top, the applicable current range(s) during the measurement can be selected. If more than one button is selected (blue), the instrument will select the most optimal current. The highest current to be enabled is determined by the lowest impedance value and equal to $1 / Z$ (lowest value) as well as the highest obtained value for the dc-current. The lowest enabled current range is determined by the highest impedance to be measured and equal to $1 / Z$ (highest) and again the lowest value to the dc-current.

So, if the lowest impedance is in the order of 100 Ohm or lower, enable 10 mA and if the highest impedance is in the order of MOhm, enable current ranges down to 1 μ A or 100 nA.

In general, it is best to enable all current ranges for EIS. The instruments can select the proper current range automatically.

A measurement starts at the highest selected current range.

Pretreatment settings

Before a measurement starts, the working electrode or sensor can be pretreated according to the specified values for E condition1 and 2 and related times. Each time a new dc-potential is applied, the equilibration time is used before the impedance measurements start.

Impedance Spectroscopy (EIS) parameters

- | | |
|------------------|--|
| Scan type | <ul style="list-style-type: none"> ▪ Potential scan: defined by the E begin, E end and Estep values. At each dc potential, a single, fixed frequency is applied or a frequency scan is made. ▪ Time scan: defined by E dc and t run and interval values ▪ Fixed potential: defined by the E dc value. |
|------------------|--|

Parameters for Scan type = PotentialScan:

E begin Potential where scan starts.

The applicable potential range for each instrument:

PalmSens3 -5 V to +5 V

PalmSens4 -10 V to +10 V

EmStat Pico -1.25 V to +2 V

See also section Limitations of the EmStat Pico

E step Step potential

The applicable step range for all instruments

PalmSens3 0.15 mV to 250 mV

PalmSens4 0.075 mV to 250 mV

EmStat Pico 0.537 mV to 250 mV

E end Potential where scan ends.

The applicable potential range for each instrument:

PalmSens3 -5 V to +5 V

PalmSens4 -10 V to +10 V

EmStat Pico -1.25 V to +2 V

See also section Limitations of the EmStat Pico

Parameters for Scan type = TimeScan:

t run Total run time of scan.

Run time for each instrument: <1 s to 1,000,000 s

t interval The minimum interval time between each datapoint (Frequency type=Fixed) or between each frequency scan (Frequency type=Scan). The interval time cannot be lower than the required time to measure the data point or perform the frequency scan + overhead time.

Parameters for all scan types:

E dc	The dc potential applied during the EIS scan.
E ac	The amplitude of the E ac signal has a range of 0.0001 V to 0.25 V (rms). In many applications a value of 0.010 V (rms) is used. The actual amplitude must be small enough to prevent a current response with considerable higher harmonics of the applied ac frequency.
Frequency type	Fixed: a single frequency is applied for the given duration or at each potential step or time interval. Scan: a frequency scan is performed starting at the given Max. frequency to the given Min. frequency.
Frequency	The applied frequency (in case Frequency type=Fixed).

Parameters for *Frequency type = Scan*:

n frequencies	The number of frequencies to apply between the given Max. frequency and Min. frequency. <i>See also section “Frequency scan settings”, below.</i>
Max. frequency	The frequency to start the frequency scan on. <i>See also section “Frequency scan settings”, below.</i>
Min. frequency	The frequency to end the frequency scan on. <i>See also section “Frequency scan settings”, below.</i>
Measure vs OCP	If enabled, the Open Circuit Potential will be determined first as reference point for applied dc potentials. <i>See also section Measuring versus OCP</i>

Advanced parameters under [...] button:

Pretreat each scan	The potentials set in the “Pretreatment Settings” will be applied before each frequency scan is started
Force max stability filter	Applies to PalmSens4 only. Overrides the frequency dependent stability filter to its maximum value, can prevent shift in impedance due to 100uA to 10uA CR switch.
t. Min. sampling	Each measurement point of the impedance spectrum is performed during the period specified by minimum sampling time ‘t Min sampling’. This means that the number of measured sine waves is equal to t Min sampling * frequency. If this value is less than 1 sine wave, the sampling is extended to 1 / frequency. So, for a measurement at a frequency, at least one complete sine wave is measured. Reasonable values for the sampling are in the range of 0.1 to 1 s.
t. Max equilibration	The impedance measurement requires a stationary state. This means that before the actual measurement starts, the sine wave is applied during ‘t Max equilibration’ only to reach the stationary state. The maximum number of equilibration sine waves is however 5. The minimum number of equilibration sines is set to 1, but for very low frequencies, this time is limited by ‘t Max equilibration’. The maximum time to wait for stationary state is determined by the value of this parameter. A reasonable value might be 5 seconds. In this case this parameter is only relevant when the lowest frequency is less than 1/ 5 s so 0.2 Hz.

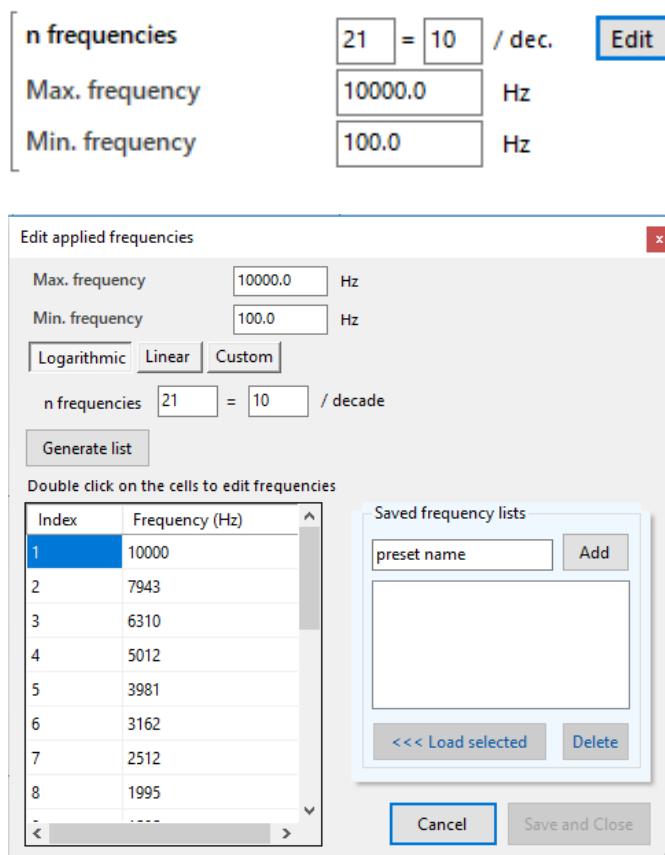
Parameters applicable for PalmSens3 only:

Allow AC coupled measurements > 200 Hz	Enables the use of ac-coupled measurements when reading the current during measurements above 200 Hz. This option increases accuracy, but also increases sensitivity to noise and might introduce a ‘jump’ around 200 Hz.
Disable use of High Stability mode	The High Stability Mode is enabled by default for measurements at frequencies below 400 Hz. This mode filters out high frequency noise and increases the stability of the measurement. If a small jump in phase shift is observed in a measurement around 400 Hz, it is advised to disable this mode.
Sensitivity mode	Determines the maximum gain used and therefore resolution in the measurements. If measured signals in the scope window seem too noisy, a lower sensitivity might be helpful.

With each change the validation of the method is checked. Errors or incompatibilities are shown instantly at the bottom of the measurement tab.

Frequency scan settings

A frequency scan starts at the highest specified frequency and ends at the lowest frequency. The frequency distribution can be logarithmic, linear or custom. If frequency distribution is logarithmic, a fixed number of frequencies per decade are applied. In general a suitable number of frequencies is 10 per decade (order of magnitude). So if a scan to be made from 10 kHz down to 100 Hz, the number of frequencies can be 2 decades times $10 + 1$, so 21 frequencies. The actual applied number of frequencies can be entered or the number of frequencies per decade.



Edit applied frequencies window

The list of frequencies is shown by clicking the Edit button in the method editor. It opens up a dialog which allows the user to choose a mode (Logarithmic, linear or custom) to generate the frequency list. Any edits made to the frequency list turns it in to a custom list which is written back to the method. The modified list can also be saved in the application settings to be used later if needed.

4.3 Running an EIS measurement

The sequence of the measurement depends of course on the specified parameters.

1. In case Measure vs OCP is enabled: determine the OCP.
2. If 't condition 1' > 1 apply E condition1 and wait the specified time
3. If 't condition 2' > 1 apply E condition2 and wait the specified time
4. Apply the dc-potential at which the impedance has to be measured and wait 't equilibration' seconds.
5. Apply sine wave and wait for stationary state, using the parameters as described above.
6. Sample the impedance value by measuring at least one complete sine wave, but during at least the specified 't Min. sampling'.
7. Perform the necessary calculations and present them in the 'EIS Plot' window.
8. The next measurement is now done by stepping back to step 1, step 3 or step 4:
 - step1: if the checkbox 'Pretreat each frequency' or 'Pretreat each scan'
 - step 3: if the next dc-potential has to be applied
 - step 4: if another frequency has to be applied and the checkbox 'Pretreat each frequency' has NOT been checked.
 - Note: In case a 'Time scan' is made, the program waits until, the 't interval' has been completed.

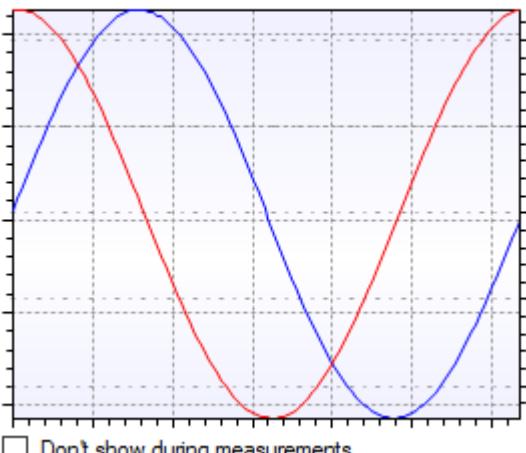
This sequence can be preceded by the measurement of the open circuit potential E OCP.

Measurement results

During the measurement the measured response is presented. The rough measurement yields a sinewave which is displayed in the 'Scope' window.

The EmStat Pico does not support the Scope window.

Sinewaves



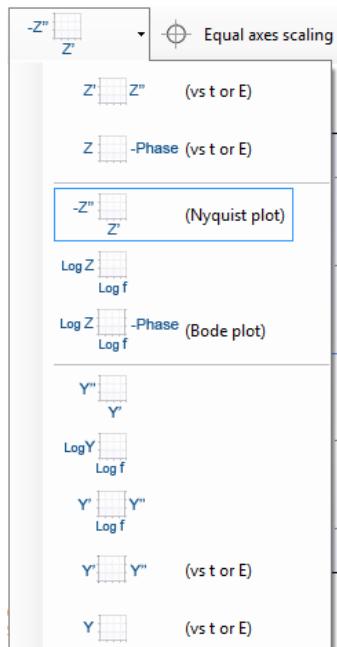
Scope window

This window is used to check that the response is not distorted by higher harmonics or noise (especially 50/60 Hz from mains) and also whether the current is not measured in an overload situation.

The presented numerical results are:

- dc current
- ac current, both in units of the applied current range
- Impedance amplitude Z and phase shift in degrees
- Real or in-phase impedance Z' and imaginary or out-of-phase impedance Z''

The measured data can be graphically presented as in different ways.



Impedance plot options

For a frequency scan:

- $-Z''$ vs Z' , or Nyquist plot
- Log $|Z|$ vs log f
- Log $|Z|$ and Phase (shift) vs log f, or Bode plot
- Y'' vs Y'
- Log Y vs Log f

For a time or potential scan:

- Z' and Z'' vs time (t) or potential (E)
- Z and -Phase (shift) vs t or E
- Y' and Y'' vs t or E
- Y vs t or E

Please note that if a plot of Y vs potential is made, the plot in fact is an ac-voltammogram.

The numerical values of impedance, phase shift and admittance are shown in the Data tab.

Index	Frequency/Hz	Z/Ohm	ZRe/Ohm	ZIm/Ohm	-Phase/Degr	Cs/F	CR
1	10000	669.882	661.115	-108.025	9.28	1.473E-07	1 mA
2	7943.28	769.209	707.219	-302.53	23.16	6.623E-08	1 mA
3	6309.57	909.844	750.994	-513.639	34.37	4.911E-08	1 mA
4	5011.87	1101	800.139	-756.39	43.39	4.198E-08	1 mA
5	3981.07	1354	873.853	-1034	49.8	3.866E-08	1 mA
6	3162.28	1680	971.615	-1371	54.67	3.672E-08	1 mA
7	2511.89	2080	1104	-1763	57.93	3.595E-08	1 mA
8	1995.26	2585	1319	-2223	59.33	3.588E-08	1 mA
9	1584.89	3206	1641	-2754	59.22	3.646E-08	1 mA
10	1258.93	3962	2122	-3346	57.61	3.779E-08	1 mA

Data tab showing the raw measured data

4.4 Export for analysis and circuit fitting

PSTrace offers next to the integrated circuit fitting functionalities integrated export functionalities with Scribner's ZView and the free program EIS Spectrum Analyser. Measured data in PSTrace can be opened or added to ZView with a one-click action. A combination of PSTrace and ZView is available from PalmSens BV.

4.4.1 Free EIS Spectrum Analyser

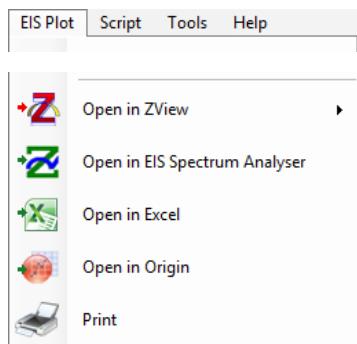
Data can be saved in a file which is loaded in the third party program (free of charge) EIS Spectrum Analyzer, written by Alexander S. Bondarenko and Genady A. Ragoisha and is available from <http://www.palmsens.com/eisspectrumanalyser>.

This program allows users to fit the measured data to specific equivalent circuits and for instance obtain the best values of the elements in the equivalent circuit, for instance R_{Ω} , R_{ct} and C_{dl} .

The file can be saved using the button in the toolbar left from the plot:



Or from the EIS Plot menu:

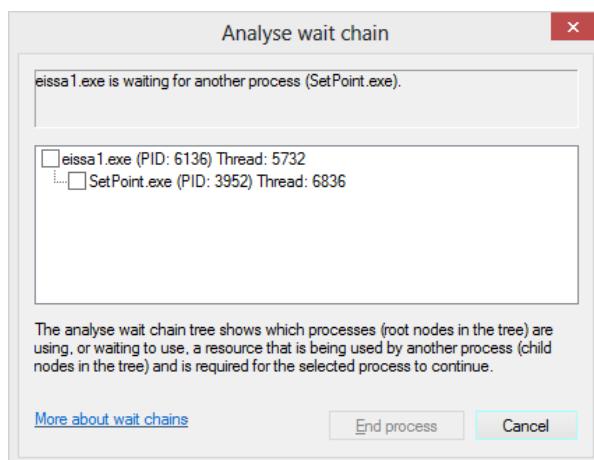


EIS plot menu

For detailed instructions consider the manual of EIS Spectrum Analyser.

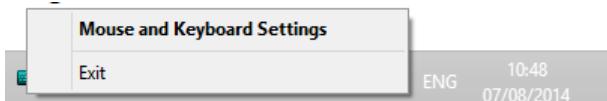
Known issue with exporting to EIS Spectrum Analyser

If the EIS Spectrum Analyser doesn't show and you are sure you have pointed to the eissa1.exe file in the settings window, this might be due to the process 'SetPoint.exe' running. This software by Logitech somehow prevents opening the EIS Spectrum Analyser.



eissa1.exe waiting for SetPoint.exe

To solve the issue: right mouse click on the SetPoint icon in the notification area of the Task Bar and click 'Exit'



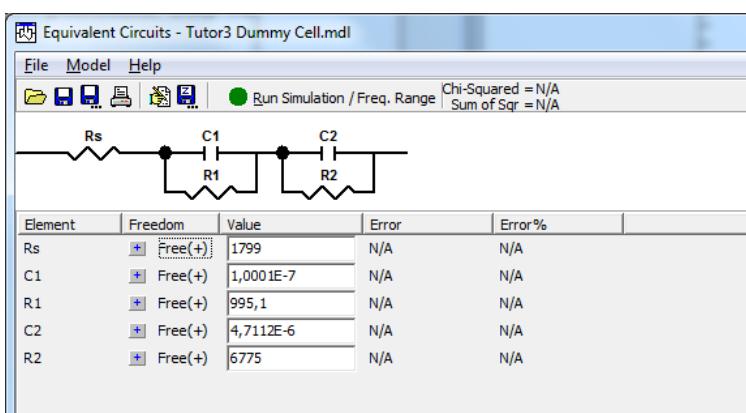
Close SetPoint, preventing exporting to EIS Spectrum Analyser

4.4.2 ZView

If ZView 3.3 or later is installed, PSTrace will detect this automatically. A one-click-export button will appear next to the plot. The measurement selected in the Legend will be exported to ZView.



ZView one-click-export button



Equivalent circuit model in ZView

Multiple measurements can be run from PSTrace and fitted on the active circuit model in ZView with a single click from PSTrace.

For detailed instructions consider the manual of ZView.

4.4.3 Origin

Origin from OriginLab is scientific graphing and data analysis software widely used at universities.

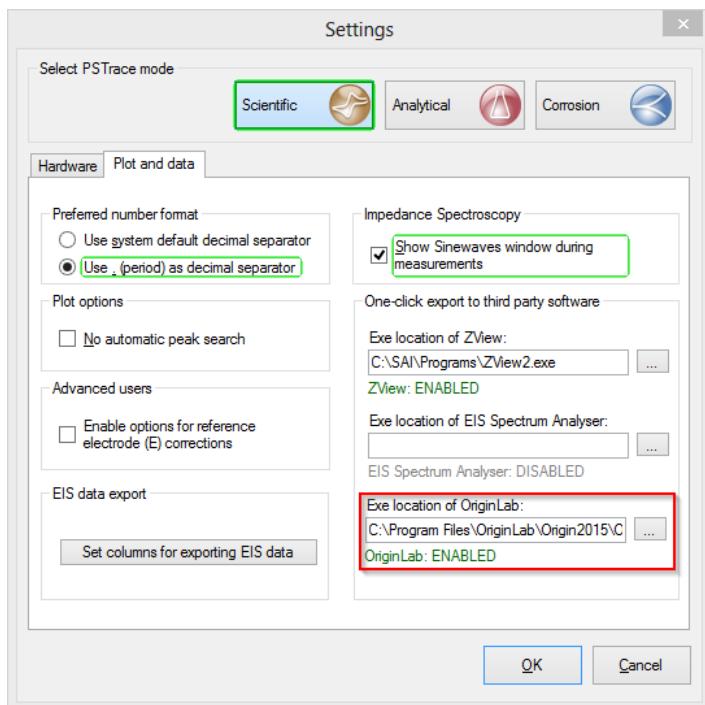
See for more information: <http://www.originlab.com/>

If Origin is installed on the PC where PSTrace is running an extra button appears in the toolbar next to the plot:



When clicking this button, Origin will be opened showing the selected EIS data directly in a Work sheet.

If the button is not showing and Origin is installed, open the General settings window in the menu (Tools → General settings...) and check in the ‘Plot and data’ tab if the location for Origin is properly set.



Location for Origin specified in the Settings window.

To change the exported columns for EIS data, click the button ‘Set columns for exporting EIS data’ on the left-hand side of the Settings window.

4.5 Limitations for EIS on EmStat Pico

Electrochemical Impedance Spectroscopy (EIS) measures the change of the complex impedance over a frequency range (spectrum). The common way to calculate the complex impedance is by dividing the complex voltage by the complex current. The ADUCM355 has only 1 ADC so it is not possible to measure both signals (voltage and current) at the same time, the proposed solution to enable EIS measurement using only the current signals is a 3-stage measurement. The total EIS measurement for one single frequency point is split up into three measurements on three different impedances:

1. Zcell + Rload
2. Rload (load resistor in the WE signal path)
3. Rcall (calibration reference resistor)

Since all three measurements are performed under the same conditions and Rcall is a reference resistor of known value, the final complex impedance of Zcell can be calculated having only the complex currents of the three measurements.

Complex voltage correction

For the plain ADuCM355 the conditions for the 3 measurements are equal, for the Emstat Pico the measurement on the Zcell + Rload is performed using external RE-

buffers introducing a complex transfer function for the applied AC voltage on the Zcell +Rload. This complex voltage transfer function is modeled by an electronic circuit simulation the gain and phase behavior of the transfer function.

Time-domain sinewave

The Emstat Pico integrates a DFT calculation block enabling onboard complex current calculations. In contrast to other Palmsens devices having the EIS feature, the raw ADC signal is not available and therefore the time-domain signal cannot be shown in a host application (PSTrace, PStouch)

Measurement duration

The accuracy of the complex current depends on the number of the applied frequency cycles presented to the DFT process. For higher frequencies the time to measure multiple cycles is relatively short in contrast to the lower frequencies. For example, measuring 8 cycles of 1Hz takes 8 seconds resulting in a 24 seconds measurement duration for a complete 3-stage measurement.

Current ranges

Since the conditions must be the same, all 3 measurements must be performed using the same current range. Rload ($\sim 100 \Omega$) and the Rcall (1k Ω or 100k Ω) are fixed values, however the complex current measurements are frequency depended due to parasitic effects of the signals path. The changes of Zcell vs frequency can be so large that it cannot be covered by staying in the same current range. Auto current ranging dynamically changes the current range (in combination with the PGA) to cover the frequency range in the EIS measurement.

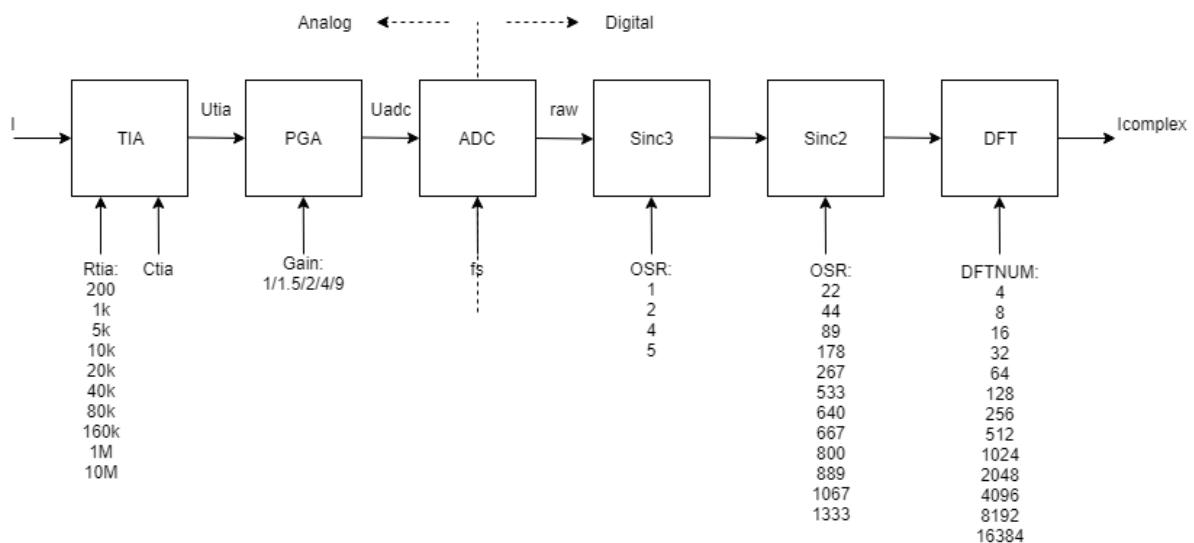


Figure 1; DFT signal path block diagram

More details can be found in the ADuCM355 Hardware Reference Manual- UG-1262 p137-p143.

5 Circuit Fitting

The Circuit Editor can be used to build, simulate and fit equivalent circuits on your Electrochemical Impedance Spectroscopy data. The following chapters present an overview of the circuit editor's options and features.

For more detailed information on fitting equivalent circuits electrochemical impedance spectroscopy measurement the following literature is recommended:

Electrochemical Impedance Spectroscopy. Chapter 23: An Integrated Approach to Impedance Spectroscopy. Mark E. Orazem & Bernard Tribollet, ISBN: 978-0-470-04140-6.

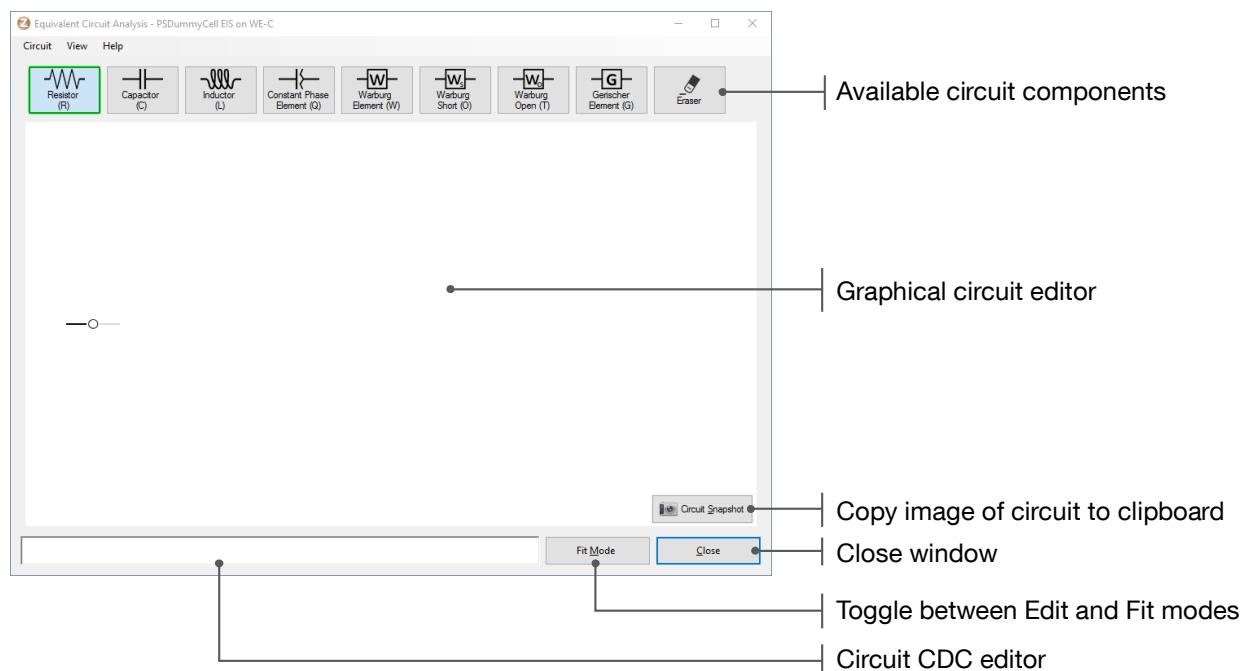
Electrochemical Impedance Spectroscopy and its Applications. Chapter 14: Modeling of Experimental Data. Andrzej Lasia, ISBN: 978-1-4614-8932-0.

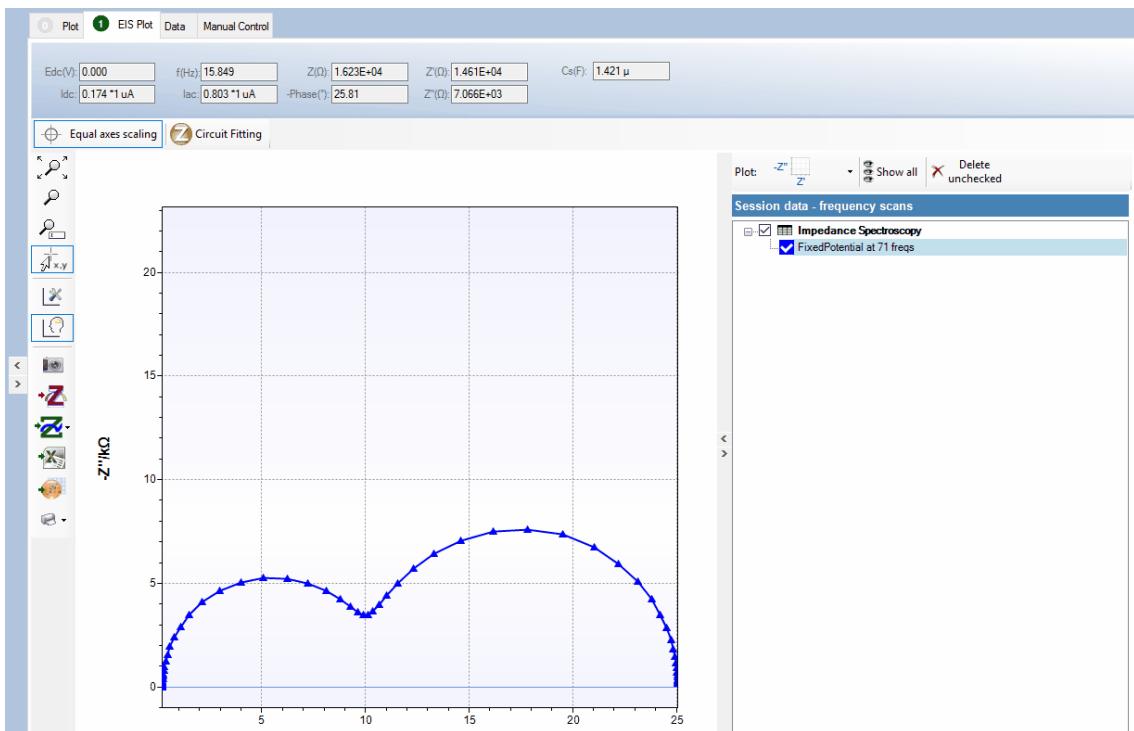
5.1 Overview

The circuit editor can be used in two different modes;

- Edit mode; draw the circuit or type CDC circuit
- Fit mode; fit the EIS data on the circuit or simulate the circuit

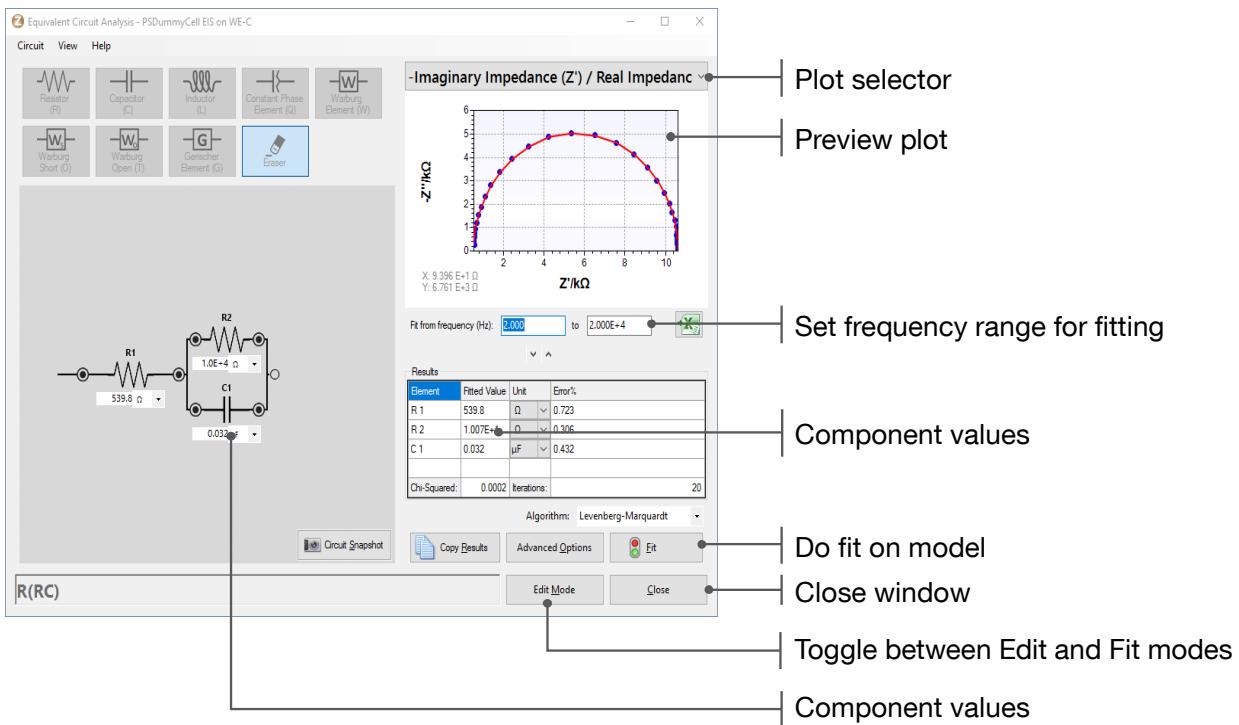
Circuit Edit Mode





Circuit Editor main window in Edit Mode.

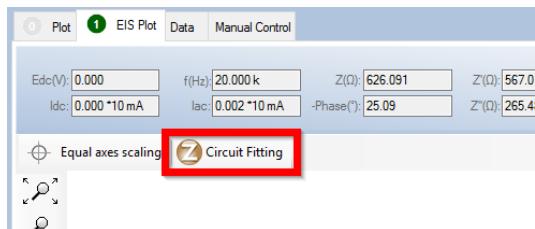
Circuit Fit Mode



Circuit Editor main window in Fit Mode.

5.2 Opening the circuit editor

The circuit editor can be opened from the EIS Plot tab in PSpice. To fit a circuit the measurement to fit on must be selected from the Session Manager first. When no measurement is selected it is only possible to simulate circuits.



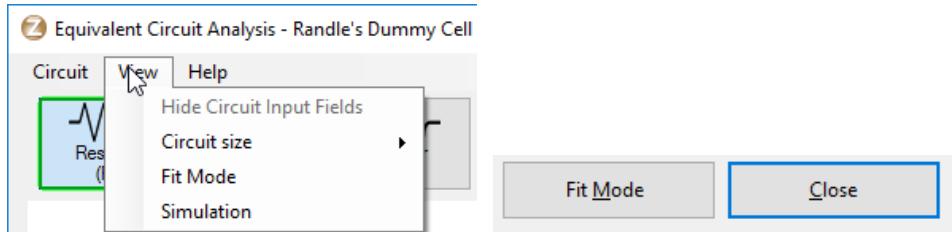
Button for opening Circuit Fitting window

5.3 Switching between Edit mode and Fit mode

The circuit editor has two modes.

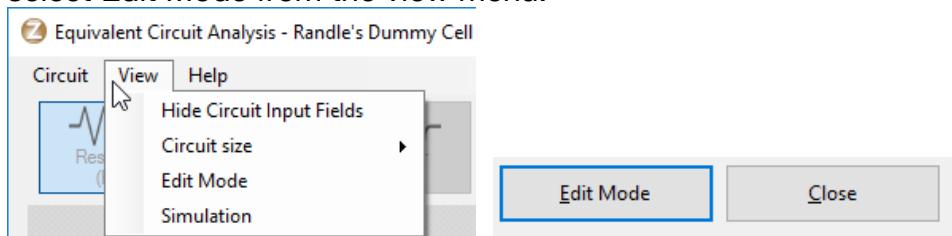
1. **Edit mode:** In Edit Mode circuits can be built, edited, loaded and saved.
2. **Fit mode:** In Fit Mode the circuit built in the Edit Mode can be simulated or fit on the electrochemical impedance spectroscopy data. (Note: Fitting is only possible when a measurement was selected in the Session Manager while opening the circuit editor.)

To switch from the edit mode to the switch mode either press the Fit Mode button or select Fit Mode from the view menu.



Switching between the two modes

To switch from the fit mode to the edit mode either press the Edit Mode button or select Edit Mode from the view menu.



Switching between the two modes

5.4 Building a circuit

There are two ways to build an equivalent circuit.

1. Using the graphical circuit editor.
2. Using the CDC editor.

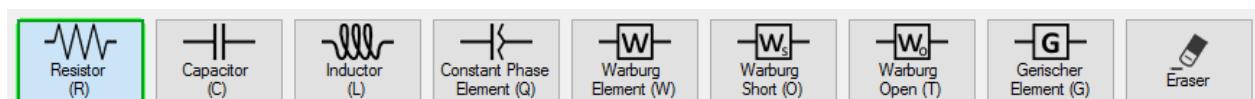
To build a circuit the circuit editor must be in edit mode.

Graphical circuit editor

Circuits can be built graphically using the circuit components and the graphical circuit editor.

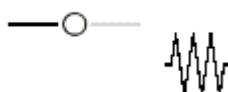
Selecting a circuit component

By default the resistor is selected. To select another circuit component click on it. The eraser is used to remove components from the circuit.



Adding a component to the circuit

Components can be added in series or in parallel with other components. The first component is added by hovering the mouse cursor over the open connector in the graphical circuit editor and clicking the left mouse button.



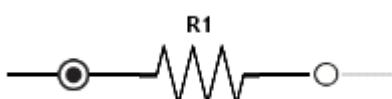
The open connector

When hovering the mouse cursor over a connector it will turn green and a grey preview of the component is displayed.



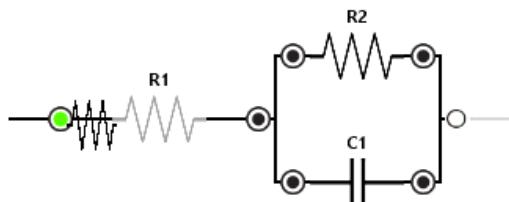
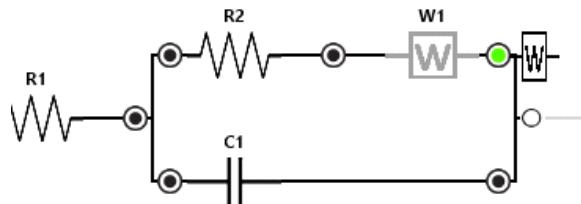
Preview of the component

By clicking the left mouse button the component is added to the circuit.



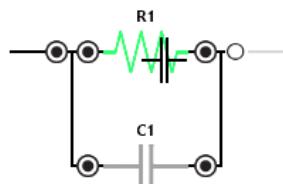
The inserted component.

To add components in serial the mouse cursor must hover over a connector. Clicking on the left mouse confirms the placement of the component.

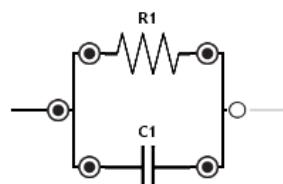


Adding components in series

Components can be added in parallel to other components by hovering the mouse cursor over the component it must be placed parallel to. When hovering the mouse cursor over another component it will turn green to indicate that it is selected and a preview parallel component is shown in grey. Click the left mouse button to confirm the placement of the component in the circuit.



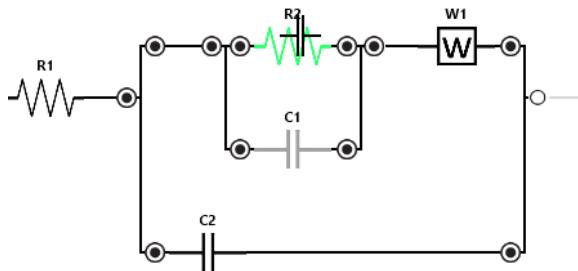
Preview of a parallel component



Component added in parallel

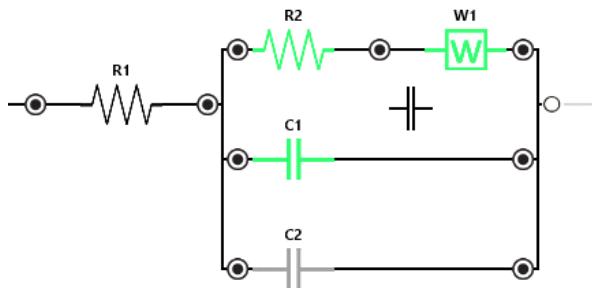
When creating larger circuits it is useful to know that components can be added in parallel within or over a parallel group in the circuit.

To place a component in parallel to a component within a parallel group directly hover the mouse cursor over the other component and click on the left mouse button.



Placing a component in parallel to a component within a parallel group

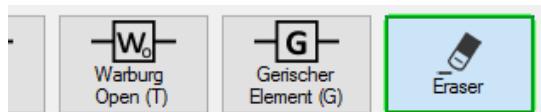
To place a component in parallel to the entire group hover the mouse cursor over the group. This will select the entire group (i.e. all its components will turn green). Clicking on the left mouse button will confirm the placement of the component.



Placing a component in parallel to the entire parallel group

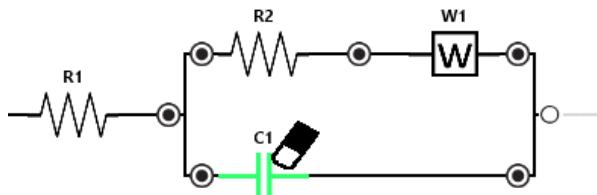
Removing components from the circuit

Components can be removed from the circuit using the eraser tool. To remove a component select the eraser tool.

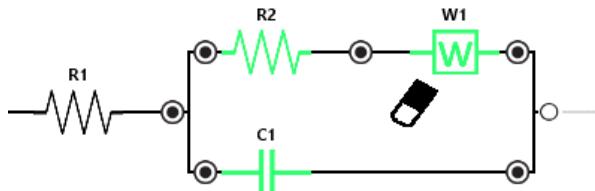


Eraser tool

To remove a component or a group of parallel components hover the mouse cursor over it. The component(s) will turn green indicating that they are selected. Clicking the left mouse button will remove the selected components from the circuit.



Removing a single component



Removing a group of components

CDC circuit editor

The CDC circuit editor is located at the bottom of the circuit editor. To build a circuit using the CDC circuit editor click on it and type the circuits CDC code. If the CDC code is valid the circuit is updated directly in the graphical circuit editor. The CDC code is described by Boukamp in:

Boukamp BA (1986) A package for impedance/admittance data analysis. *Solid State Ionics* 18 & 19, 136-40.

R(RC)

Field for entering CDC directly

Supported CDC characters

The following characters and controls are supported by the CDC circuit editor.

R

Inserts a resistor.

C

Inserts a capacitor.

L

Inserts an inductor.

W

Inserts a Warburg impedance.

Q

Inserts a constant phase element.

Shift
↑

(
9

Inserts a parenthesis defining the beginning of a parallel group.

Shift
↑

)
0

Inserts a parenthesis defining the end of a parallel group.

{
[

Inserts a bracket defining the beginning of a series group.



Inserts a bracket defining the end of a series group.

Supported CDC controls

The following controls are supported by the CDC circuit editor.

The mouse cursor places the text cursor in the CDC editor by clicking the left mouse button. It can also be used to select text in the CDC editor by holding down the left mouse button and dragging the cursor over the CDC characters it should select.



The arrow keys move the text cursor left and right respectively. In



combination with they select CDC code.



Home and end move the cursor to the beginning or end of the CDC code



respectively. In combination with they select CDC code.



Backspace removes the CDC character to the left. Backspace cannot be used to remove a selection of CDC characters.



Delete removes the CDC character to the right. Backspace cannot be used to remove a selection of CDC characters.



A

Control + A selects all of the CDC code.



C

Control + C copies the selected CDC code to the clipboard.



X

Control + X cuts the selected CDC code and sends it to the clipboard.

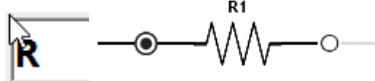


V

Control + V pastes the contents of the clipboard to the location of the text cursor.

Adding components

Components are added to the circuit by typing the keys of the supported characters.



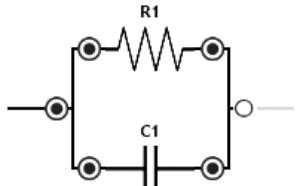
Pressing R will add a resistor to your circuit

To add components in parallel parenthesis must be used. After opening the parenthesis the CDC editor will turn red indicating the CDC code is invalid at the moment. Ignore this and add the components that should be placed parallel to each other.

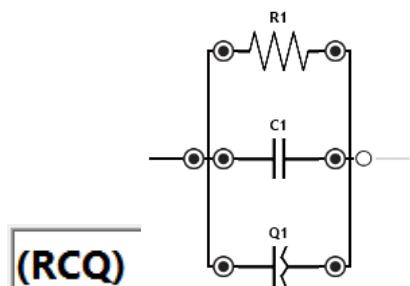
- 1.
- 2.
- 3.

Entering CDC code for components parallel to each other

As soon as the parenthesis are closed the CDC code will become valid again and the graphical circuit editor will display the circuit as well.



Graphical representation of the (RC) circuit in the graphical circuit editor

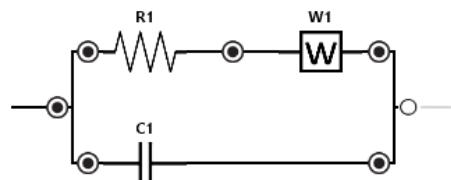


Example of a CDC code with three components parallel to each other

Within a group of components parallel to each other brackets must be used to add a component in series to one of the components. After opening the brackets the CDC editor will turn red indicating the CDC code is invalid at the moment. Ignore this and add the components that should be placed series to each other.

- 1.
- 2.
- 3.

Entering CDC code for components in series within a parallel group



Graphical representation of the ([RW]C) circuit in the graphical circuit editor

In some cases it is easier to copy and paste parts of the CDC code to quickly build a large circuit. This can be done using the supported CDC controls.

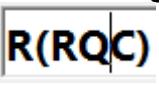
- 1.
- 2.
- 3.

Copying and pasting in the CDC editor

Removing components

Components can be removed from the circuit with the CDC circuit editor by placing the text cursor next to the component that should be removed and using the supported

CDC circuit editor controls. Pressing backspace or delete removes the CDC character to the left or right of the text cursor respectively. The changes to the circuit are directly visible in the graphical circuit editor.

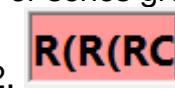
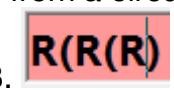
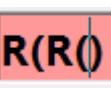
1.  2. 

Backspace removes the constant phase element to the left of the text cursor

1.  2. 

Delete removes the capacitor to the right of the text cursor

Removing a parenthesis or bracket from a valid CDC code will invalidate it. The CDC circuit editor will indicate this by turning red. This happens typically when you want to remove a parallel or series group from a circuit.

1.  2.  3.  4.  5. 

Removing a parallel group from a circuit using backspace

In this example the parentheses around the second resistor are removed as they no longer have any meaning.

A selection of CDC characters can be removed by cutting or deleting it with control + x, backspace or delete. The selection can also be replaced by pasting data from the clipboard, control + v, or replacing it with any of the supported characters.

1.  2. 

Invalid CDC code

In the case of an invalid CDC code the CDC circuit editor indicates this by turning red. The graphical circuit editor is not updated until the CDC code is valid again, this is indicated by the CDC circuit editor turning white again.

When adding or removing a parallel or series group from a circuit using the CDC circuit editor ignore that the code is invalid, as it will be valid again once the entire parallel or series group has been added or removed.

Important! When using the graphical circuit editor in combination with the CDC circuit editor hovering the mouse over the graphical representation will remove any invalid CDC code in the CDC circuit editor.



Invalid placement of closing parenthesis

Here the invalid CDC code can be resolved by removing the closing parenthesis between the resistor and Warburg impedance and placing it at the end of the CDC code.

R(C[RW])RC)

Unbalanced amount of opening and closing parentheses or brackets

Here the invalid CDC code can be resolved by adding an opening parenthesis or removing a closing parenthesis, as the amount of opening and closing parenthesis is unbalanced in this example.

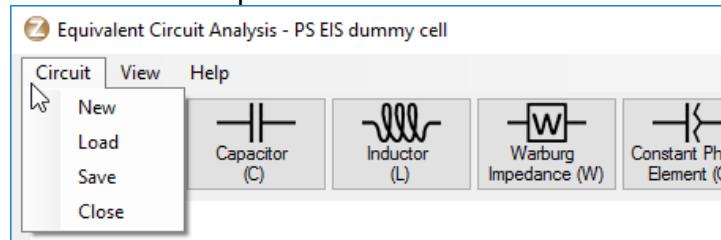
R(RCfewfe)

Unsupported CDC characters have been pasted into the CDC circuit editor

This code is invalid because unsupported CDC characters were pasted into the CDC circuit editor from the clipboard. To resolve this the unsupported CDC characters must be removed.

5.5 Loading and saving circuits

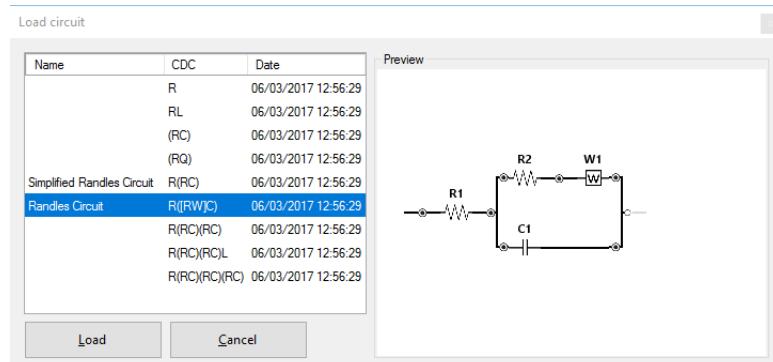
Circuits can be stored in and retrieved from the circuit database on your computer. The load and save options are located in the Circuit menu.



To load or save a circuit the circuit editor must be in edit mode.

Loading a circuit

To load a circuit open the load circuit screen by selecting load in the Circuit menu. In this screen the available circuits stored on your computer are listed in the circuit browser on the left. A preview of the selected circuit is presented in the preview panel on the right.

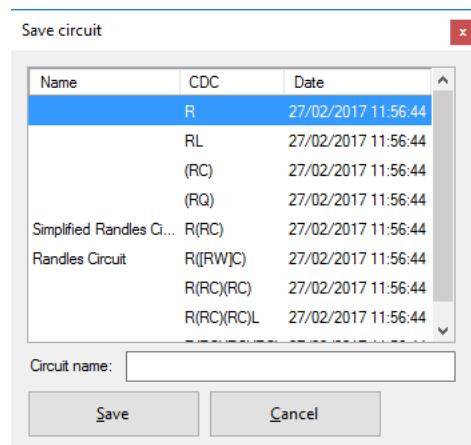


Load circuit window

The selected circuit can be loaded by pressing on the Load button or double clicking on the circuit.

Saving a circuit

Circuits can be saved using the save circuit screen. To open the save circuit screen select save in the Circuit menu. The option to save a circuit is only available if there is a circuit containing at least one component in the editor. The save circuit screen contains a circuit browser and a field to input the name of circuit that is being saved.

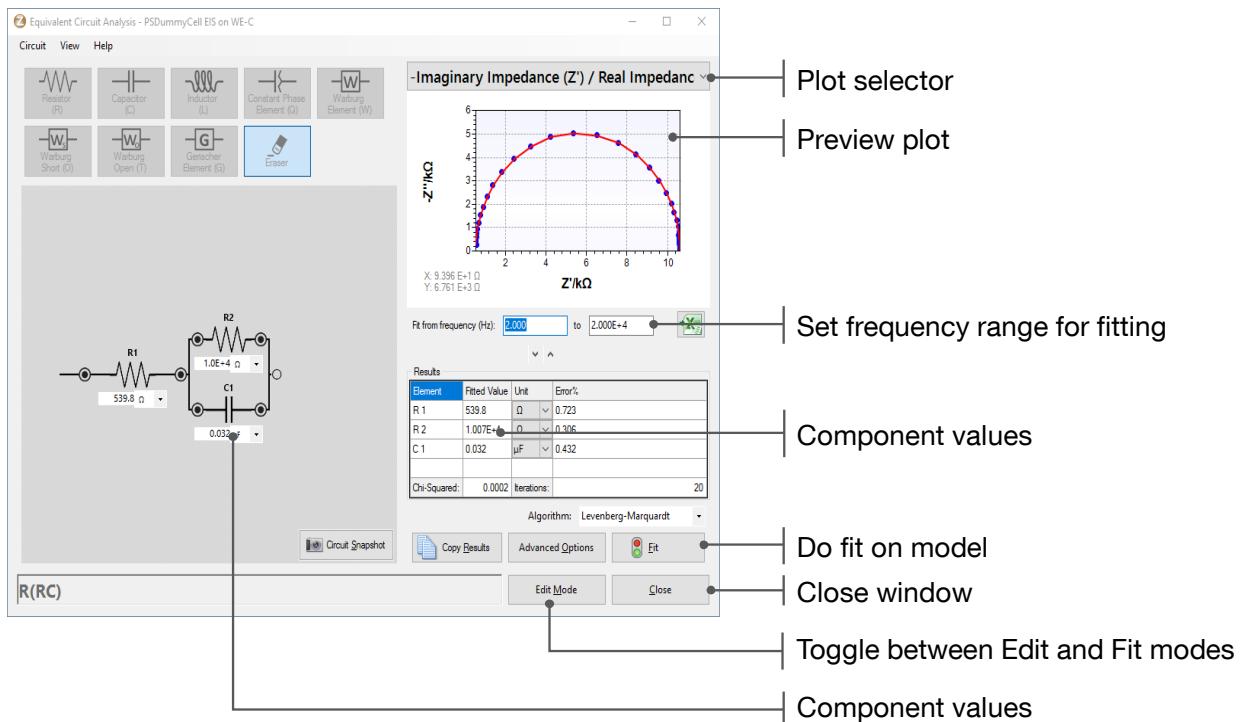


Save circuit window

To save the circuit press the save button. Optionally a name can be assigned to the circuit in the circuit name input field.

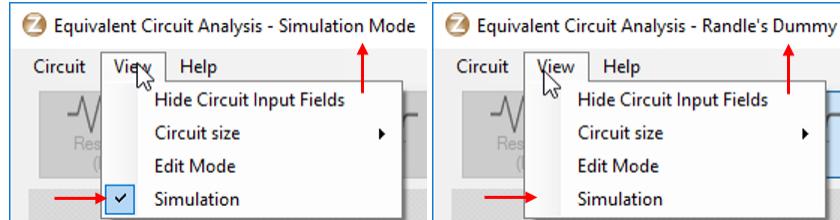
5.6 Fitting or simulating a circuit

After an equivalent circuit has been built or loaded into the circuit editor in Edit Mode it can be simulated or fit onto the data of the electrochemical impedance spectroscopy measurement.



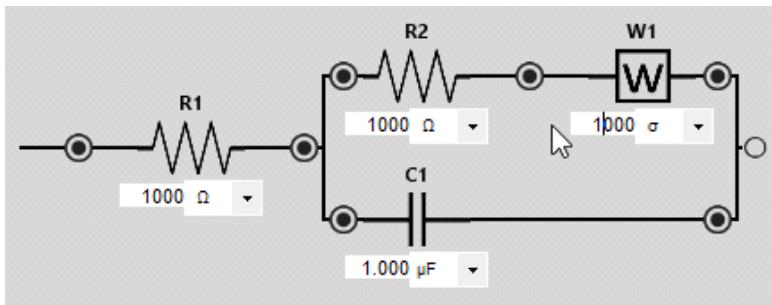
Simulating a circuit

The impedance of circuits can be simulated using the circuit editor. When simulating the fit options are disabled. Check the title of the circuit editor or the view menu to see whether the circuit editor is set to simulation mode.



Circuit editor set to simulation mode and fit mode. In fit mode the name of the measurement is visible in the title bar and the simulation is not checked in the view menu.

Values of the components can be changed in the circuit table and the graphical circuit editor. Changing the value of a component in either the graphical circuit editor or the table will automatically update the value in the other. The effects of these changes will appear directly in the preview plot.

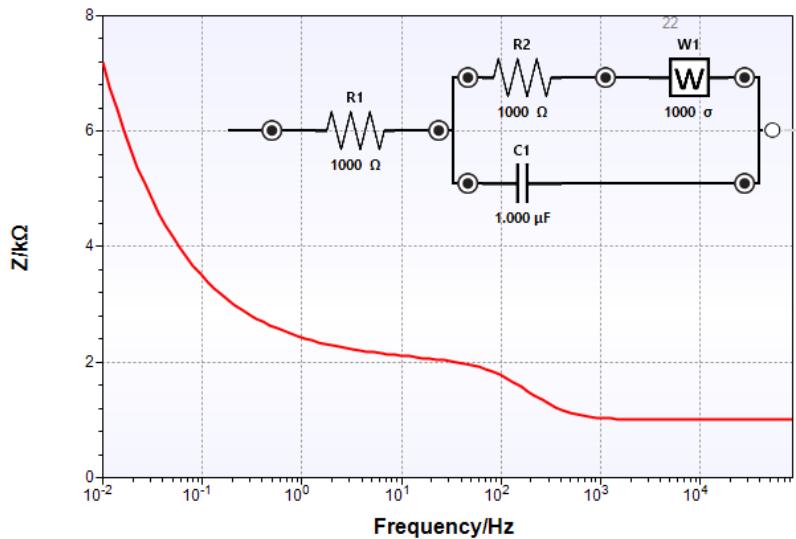


Changing the value of the Warburg Coefficient for a Warburg Impedance in the graphical circuit editor.

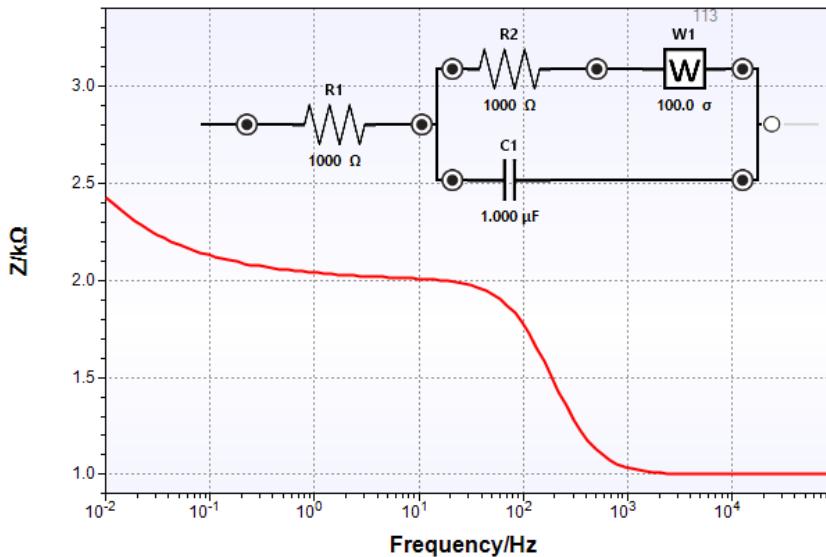
Element	Fitted Value	Unit	Error%
R 1	1000	Ω	
R 2	1000	Ω	
W 1	1000	σ	
C 1	1.000	μF	

Changing the value of the Warburg Coefficient for a Warburg Impedance in the circuit table.

For example changing the value of the Warburg Coefficient to 100 will lower the impedance at the lower frequencies.

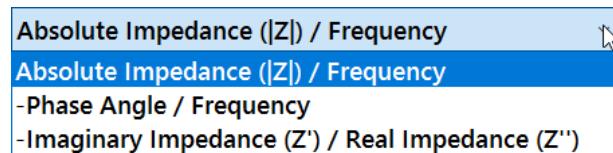


Simulation of the absolute impedance over frequency of a Randle's circuit using the default values.



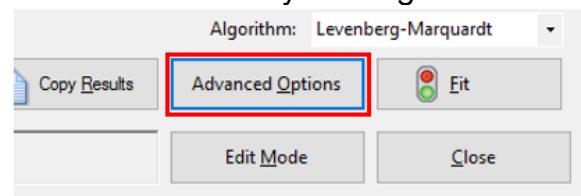
Simulation of the absolute impedance over frequency of a Randle's circuit with the value of the Warburg Coefficient lowered to 100.

Using the plot selector it is possible to view the effects of lowering the Warburg Coefficient to 100 on the negative phase angle over frequency and the Nyquist plot as well.

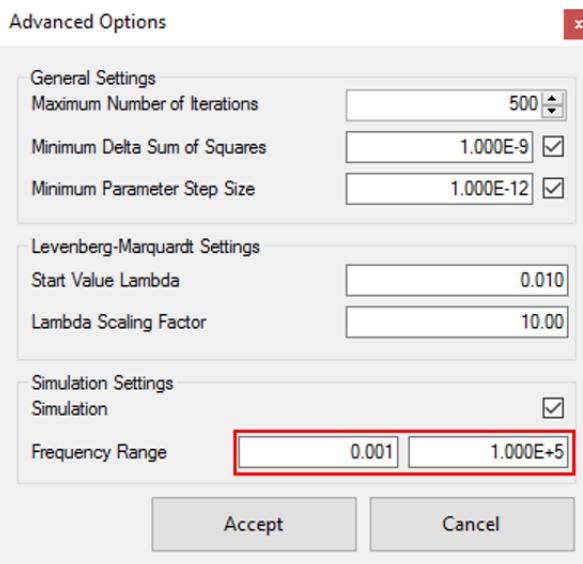


Setting the simulation's frequency range

The frequency range of the simulation can be set in the Advanced Options menu which can be accessed by clicking on the Advanced Options button.

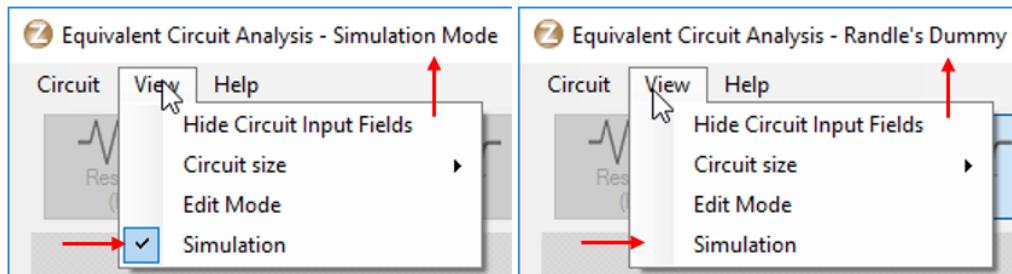


The simulations frequency range (Hz) can be specified in the simulation settings, by default this is 0.01 to 100000 Hz.



Fitting a circuit

Before fitting the circuit it is important to check whether the circuit editor is in simulation or fit mode. Check the title of the circuit editor or if the simulation option is checked in the view menu.



Circuit editor set to simulation mode and fit mode. In fit mode the name of the measurement is visible in the title bar and the simulation is not checked in the view menu.

To ensure a good fit on a measurement it is important to build the right equivalent circuit. It is often possible to achieve a good fit with different but similar circuits. Although these other circuits can provide a good fit they are not necessarily an accurate representation of the cell that was measured. Selecting appropriate initial values for the components in the models is also recommended, as in some cases the fitting algorithm will get stuck in a local minimum and the quality of the fit is not optimal.

In the next chapter and the example brief instructions are given on selecting the components for the circuit. However, further reading on the topic is recommended: <http://www.consultrsr.net/resources/eis/index.htm>

Electrochemical Impedance Spectroscopy. Chapter 23: An Integrated Approach to Impedance Spectroscopy. Mark E. Orazem & Bernard Tribollet, ISBN: 978-0-470-04140-6.

Electrochemical Impedance Spectroscopy and its Applications. Chapter 14: Modelling

of Experimental Data. Andrzej Lasia, ISBN: 978-1-4614-8932-0.

5.7 Overview of circuit components

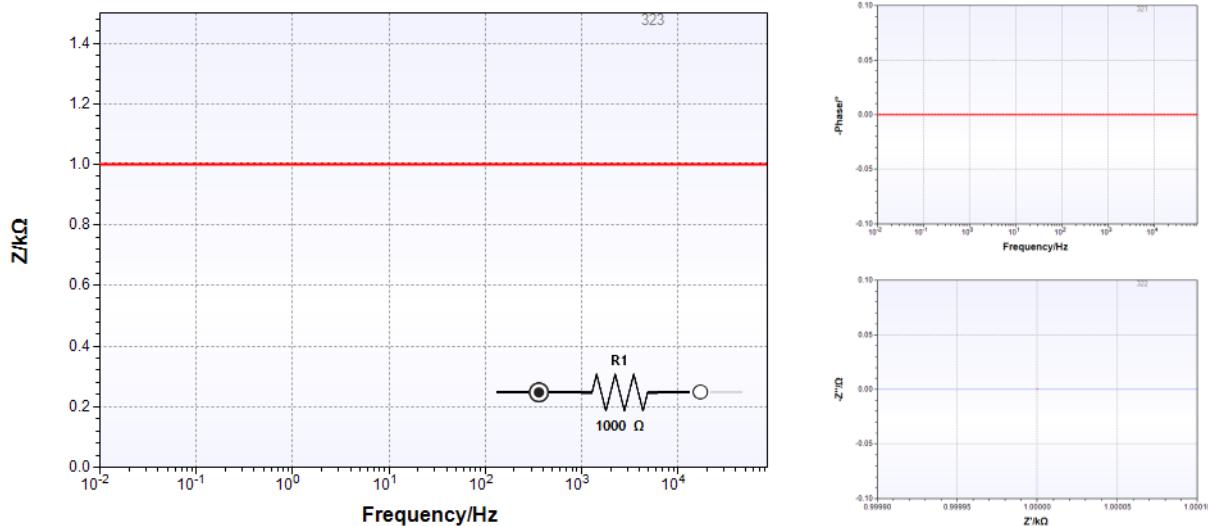
The following components can be used to build equivalent circuits in the circuit editor. The two chapters after this chapter provide two examples of selecting the components for an equivalent circuit, setting/adjusting their values to obtain a good fit and interpreting the quality of the fit.

Resistor

$$Z_R = R$$

The impedance of a resistor is independent of frequency and it only contributes to the real component of impedance. Hence it does not affect phase shift and it is represented by a single dot in the Nyquist plot. By default resistors are 1000 Ω in the circuit editor.

When modelling an electrochemical impedance measurement on a cell a resistor can be used to model the solution resistance (resistance between the working electrode's surface and the tip of the reference electrode).

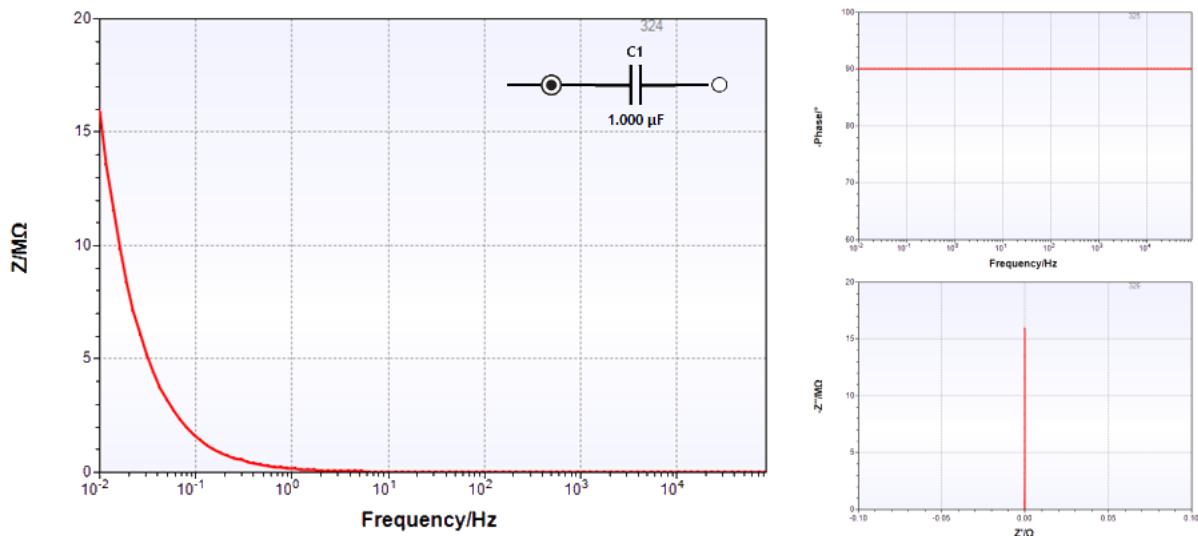


Left: The absolute impedance of a resistor plotted against frequency. Top right: Phase shift of a resistor over frequency. Bottom right: In the Nyquist plot a resistor is seen as a single dot (little red dot in the center of the plot).

Capacitor

$$Z_C = 1/j\omega C$$

A capacitor's effect on impedance pertains to its imaginary component and decreases with increasing frequency. On its own a capacitor causes a phase shift 90° independent of frequency. As it only effects the imaginary component of impedance it is represented by a vertical line in the Nyquist plot. The default value of a capacitor is 1 μF in the circuit editor.



Left: The absolute impedance of a capacitor plotted against frequency. Top right: Phase shift of a capacitor over frequency. Bottom right: Nyquist plot of capacitor.

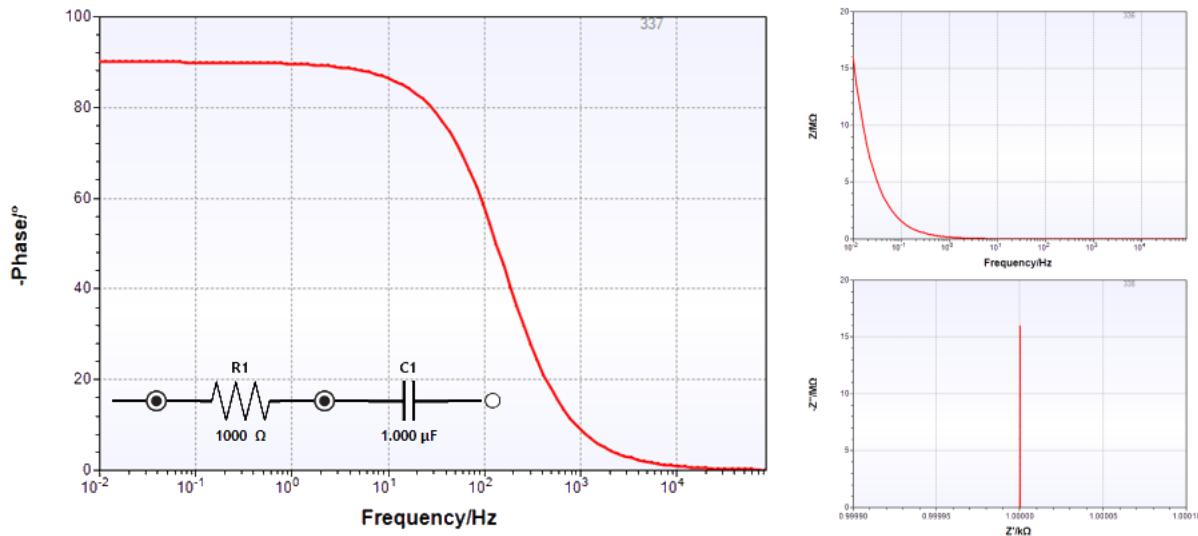
When a capacitor is placed in series with a resistor the circuit's phase shift becomes frequency dependent. At low frequencies it approaches 90° and at high frequencies it approaches 0° . Thus, at high frequencies the capacitor's effect on the circuit's impedance and phase shift becomes negligible and the circuit effectively behaves as a single resistor. The Nyquist plot below shows that real component of the impedance remains $1\text{ k}\Omega$ regardless of frequency.

A resistor and capacitor in series model the impedance of an ideally polarized liquid electrode / blocking electrode, i.e. an electrode that does not transfer charge with the surrounding solution. In this model the resistor represents the solution resistance and the capacitor represents product of the real surface area of the electrode and its double layer capacitance. With increasing frequency there is less time for the electrochemical double layer to charge and its effects on impedance and phase shift diminish.

Another application of a resistor and capacitor in series is modelling an ideal coating. Again the resistor represents the solution resistance. But in this model the capacitor represents the coating capacity. A coating's capacity depends on the coating's thickness, surface area and its dielectric constant.

For more information on modelling corrosion we recommend reading:

Electrochemical Impedance Spectroscopy and its Applications. Chapter 11: Coatings and Paints. Andrzej Lasia, ISBN: 978-1-4614-8932-0.



Left: The phase shift of a resistor and capacitor in series plotted against frequency. Top right: Absolute impedance over frequency. Bottom right: Nyquist plot.

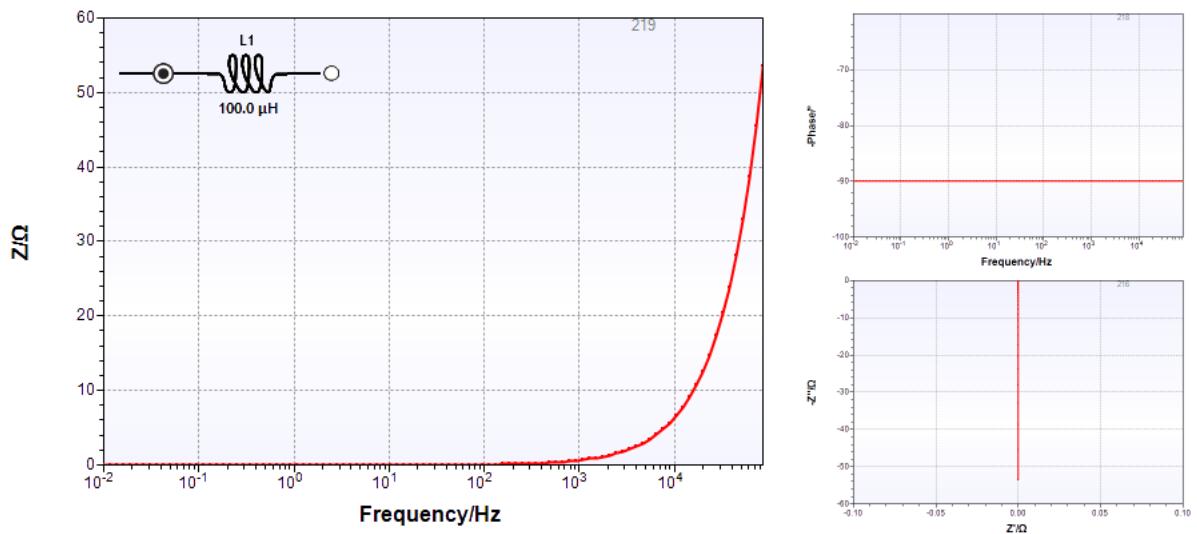
Inductor

$$Z_L = j\omega L$$

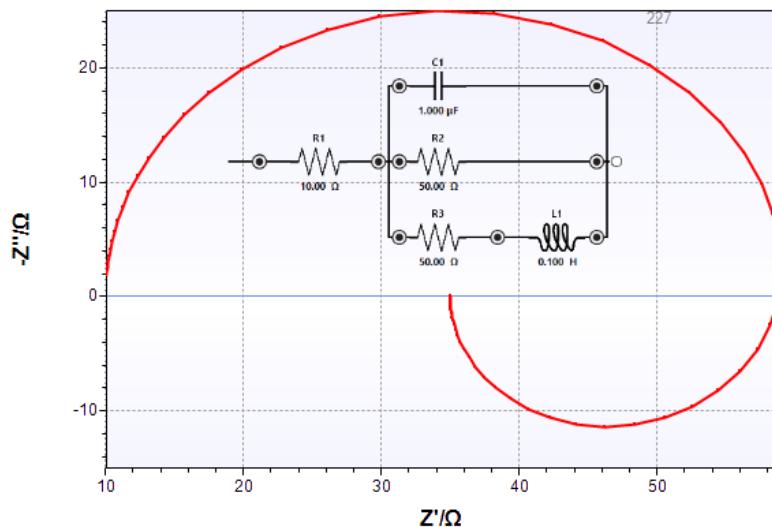
A inductor is the reciprocal of a capacitor its effect also pertains to the imaginary component of impedance. However, in contrast to a capacitor the impedance of a inductor increases with frequency and its phase shift is -90° . It is also represented by a vertical line in the Nyquist plot, but in the opposite direction. In the circuit editor the default value of a inductor is 100 μH .

An example of a model where an inductor is used is a model of a faradaic reaction involving adsorption of one or more species. In certain cases on the Nyquist plot inductive loops can be observed together with capacitive loops and it is possible to model inductance as the product of the resistance of the charge transfer squared and the absorption pseudocapacitance. For further reading see:

Electrochemical Impedance Spectroscopy and its Applications. Chapter 5: Impedance of the faradaic reactions in the presence of adsorption. Andrzej Lasia, ISBN: 978-1-4614-8932-0.



Left: The absolute impedance of a inductor plotted against frequency. Top right: Phase shift of a inductor over frequency. Bottom right: Nyquist plot of Inductor.

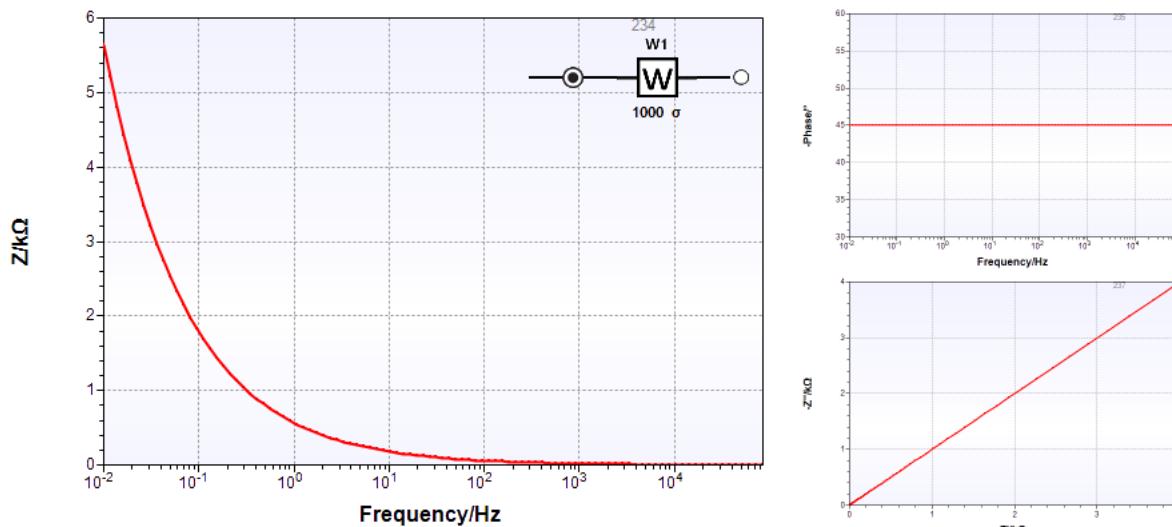


Nyquist plot of a circuit that can model faradaic reactions involving adsorption and subsequent desorption of a species.

Warburg impedance

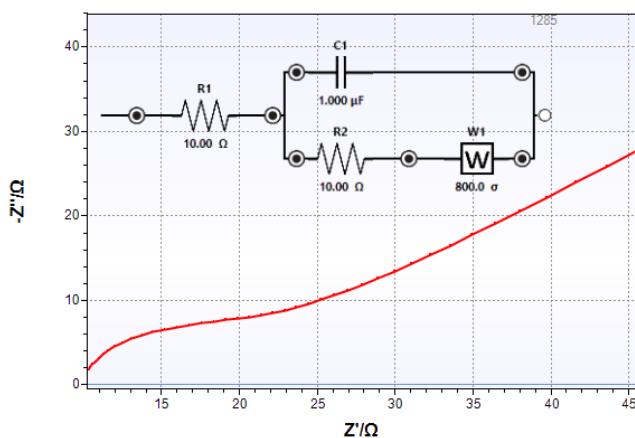
$$Z_W = \frac{\sigma}{\sqrt{\omega}} - j \frac{\sigma}{\sqrt{\omega}}$$

A Warburg element is a component used to model the transfer of charge between the electrode and a redox species in the solution and the depletion of the diffusion layer's inner layer. This Warburg element assumes there is a semi-infinite linear diffusion layer. Both the real and imaginary components of impedance increase equally with frequency. The equal decrease in real and imaginary impedance can be seen in the Nyquist plot and results in a constant phase shift of 45°. The default value of the Warburg element in the circuit editor is 1000 σ.

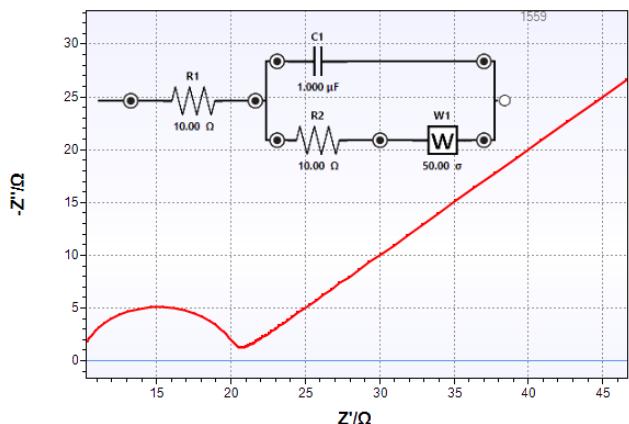


Left: The absolute impedance of a Warburg element plotted against frequency. *Top right:* Phase shift of a Warburg element over frequency. *Bottom right:* Nyquist plot of Warburg element.

The Randle's circuit is often used to model the transfer of charge between the electrode and a redox species a solution. The Randle's circuit consists of two resistors, a capacitor and a Warburg element. The first resistor is in series and represents the solution resistance. The electrode's double layer capacitance is represented by a capacitor parallel to a resistor that represents the charge transfer resistance and the Warburg element. At high concentrations of the oxidant the semicircle and the diffusion are separated and a low concentrations they overlap.



Nyquist plot of a Randle's circuit with a large value for the Warburg coefficient of the Warburg element. This represents the transfer of chare between the electrode and redox species with a low concentration of the oxidant (overlap of semicircle and diffusion).



Nyquist plot of a Randle's circuit with a small value for the Warburg coefficient of the Warburg element. This represents the transfer of charge between the electrode and redox species with a high concentration of the oxidant (no overlap of semicircle and diffusion).

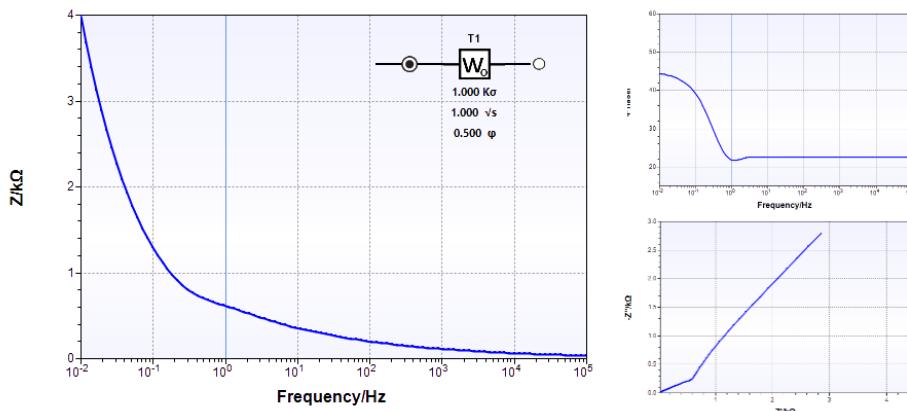
Warburg Short/Open

In contrast to the Warburg element the Warburg open/short do not assume semi-infinite diffusion.

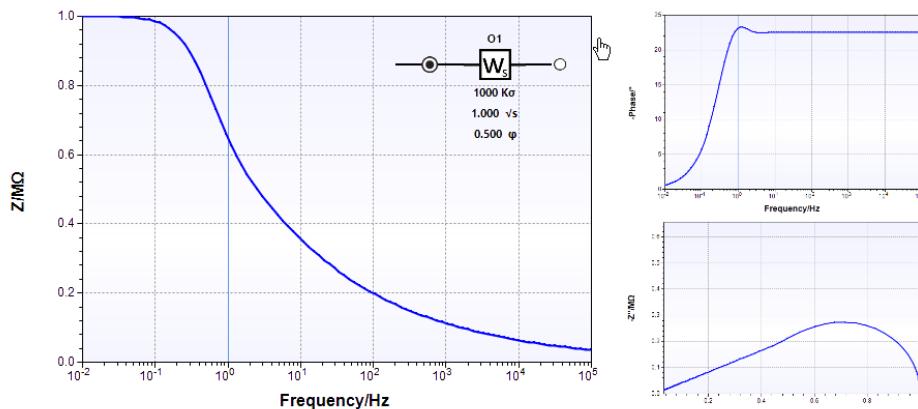
$$Z_o = \frac{\sigma B}{(B\sqrt{j\omega})^\phi} \tanh(B\sqrt{j\omega})^\phi$$

$$Z_T = \frac{\sigma B}{(B\sqrt{j\omega})^\phi} \coth(B\sqrt{j\omega})^\phi$$

Respectively the Warburg short (O) and Warburg open (T) model the transmissive and reflective boundaries of a diffusion layer. B represents the thickness (l) in metres (m) and the diffusion coefficient (D) of the diffusion layer in square metres per second (m^2/s), $B = l/\sqrt{D}$. The experimental parameter (ϕ) has a maximum value of 1 when diffusion is uniform and is smaller when diffusion is nonuniform. The default values for the Warburg coefficient, B and the experimental parameter are 1000 σ, 1 √s and 0.5 respectively.

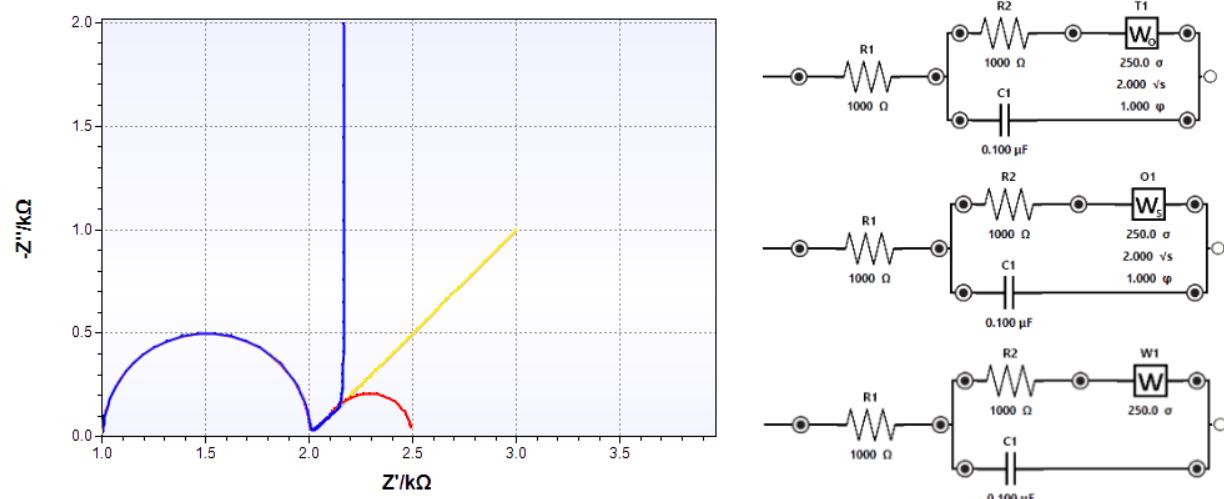


Left: The absolute impedance of a Warburg short plotted against frequency. Top right: Phase shift of a Warburg short over frequency. Bottom right: Nyquist plot of Warburg short.



Left: The absolute impedance of a Warburg open plotted against frequency. *Top right:* Phase shift of a Warburg open over frequency. *Bottom right:* Nyquist plot of Warburg open.

The circuits in the figure below model show the differences in the transfer of charge between the electrode and a redox species a solution, assuming finite diffusion transmissive/reflective boundary or semi-infinite diffusion.

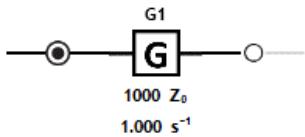
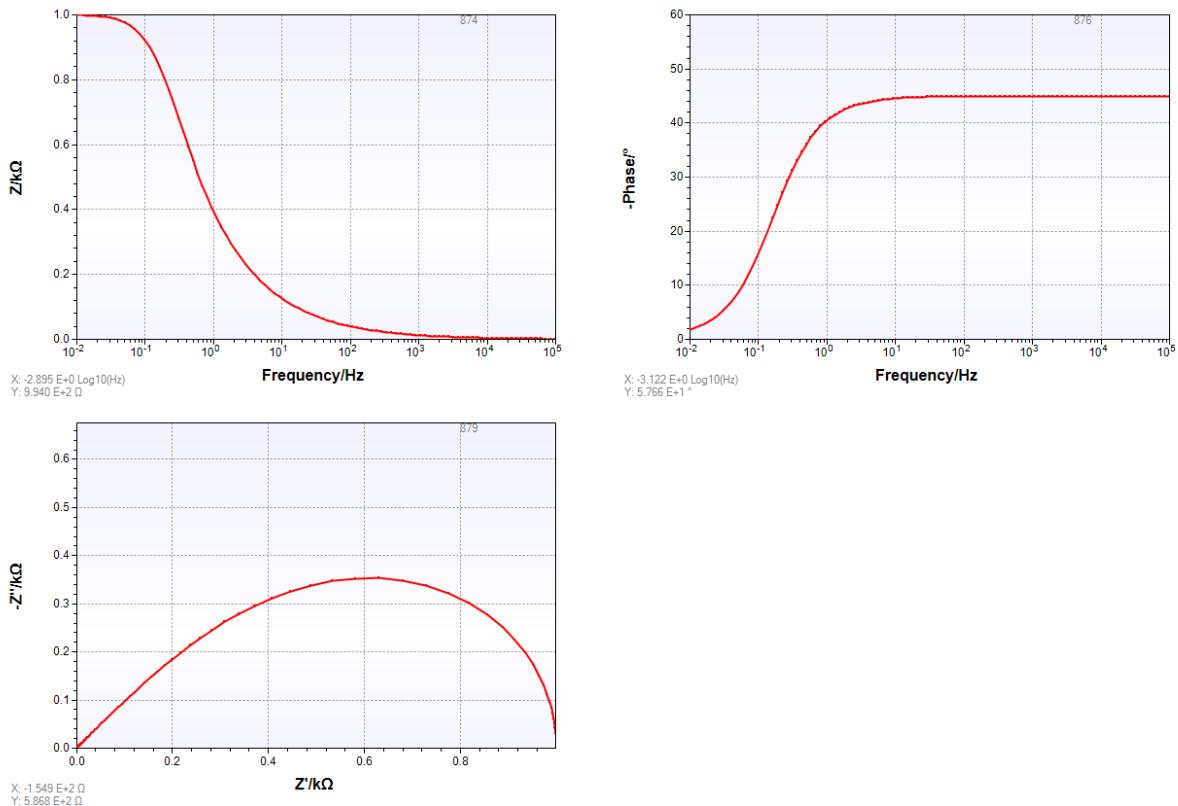


Nyquist plot demonstrating the differences in diffusion at low frequencies for a Randle's circuit (yellow line and bottom circuit), an electrode with a transmissive boundary (blue line and top circuit) and an electrode with a reflective boundary (red line and middle circuit).

Gerischer element

$$Z_G = \frac{Z_0}{\sqrt{k + \omega}}$$

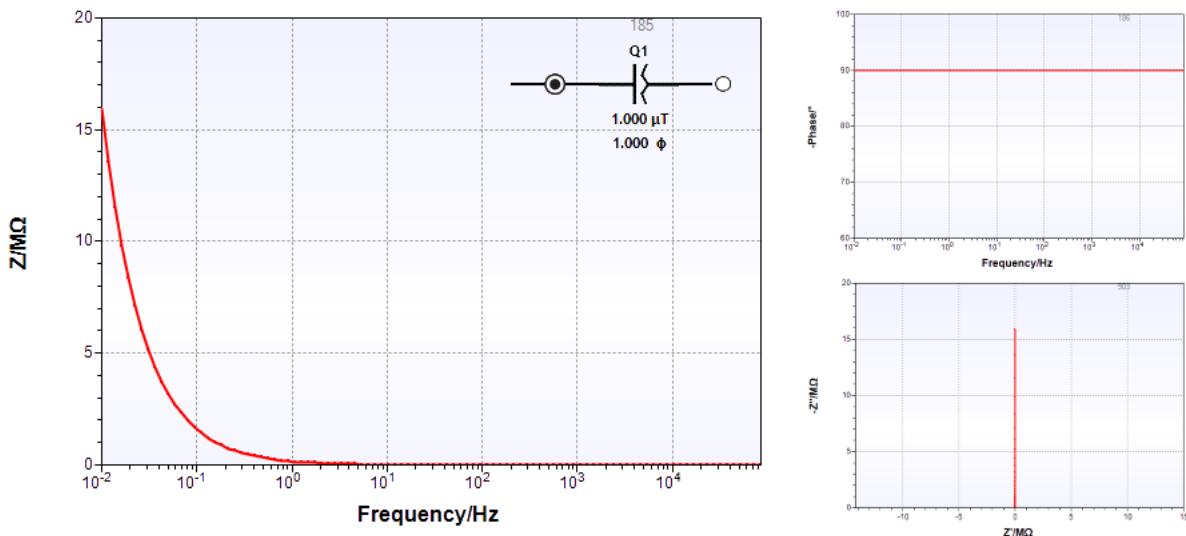
The effects of a Gerischer element are similar to those of a Warburg open. However, the parameters of the model are different, Z_0 is the magnitude of the impedance at $\omega = 1$ rad/s and k is a rate constant. It is designed to model the effect of an electrochemical species reacting with something to form an inactive substance or absorbed species during the diffusion process.



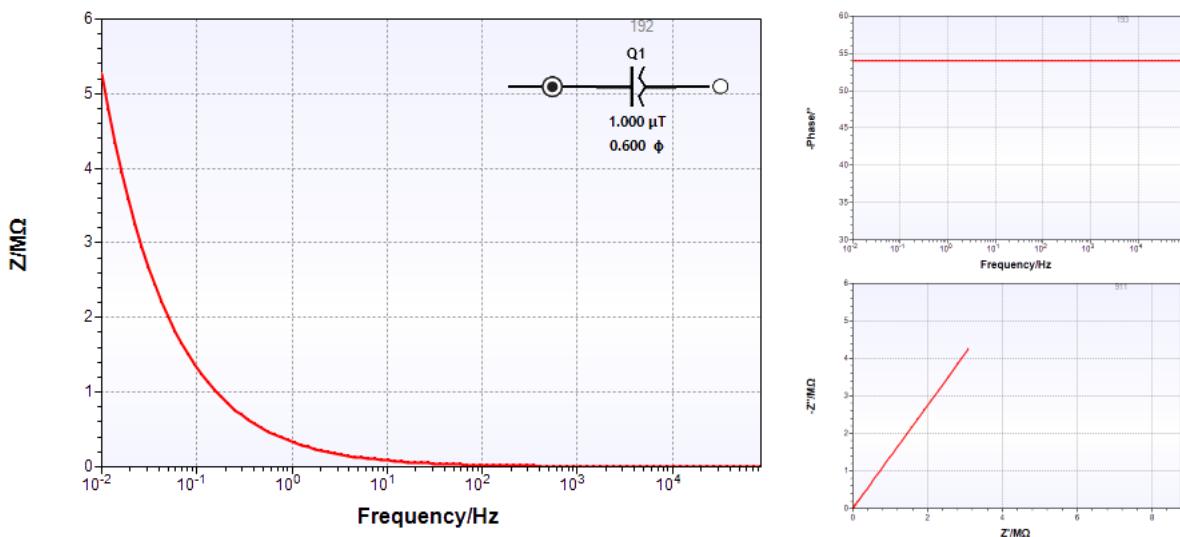
Constant phase element

$$Z_{CPE} = \frac{1}{T(j\omega)^\phi}$$

A constant phase element is similar to a capacitor, but unlike a capacitor it can also model frequency dispersion and affects both the real and imaginary components of impedance. The constant phase element has two parameters: T is related to its capacitance and ϕ is the constant phase exponent which is related to the deviation from a regular capacitor. The value of the constant phase exponent should be between 0 and 1; values of the phase exponent correspond with the phase shift of approaching 90° for values close to 1 and 0° for values close to 0. At a ϕ of 1 the behavior of a constant phase element is the same as that of a capacitor and for a ϕ of 0.5 its behavior resembles that of a Warburg element. The phase shift of a constant phase element is independent of frequency, the slope of the line in the Nyquist plot corresponds to the magnitude of the phase shift specified by ϕ . The default values of the constant phase element in the circuit editor are 1 μT and 1 ϕ .

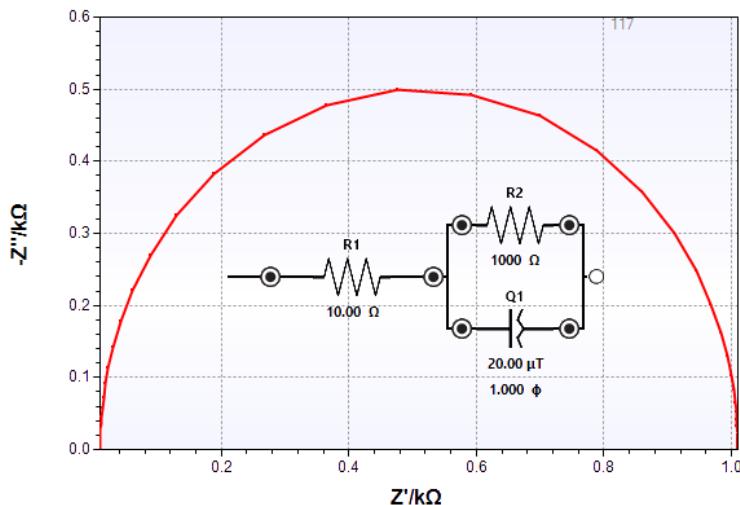


Left: The absolute impedance of a constant phase element with a constant phase exponent of 1 ϕ (i.e. a capacitor) plotted against frequency. *Top right:* Phase shift of a constant phase element over frequency. *Bottom right:* Nyquist plot of constant phase element.

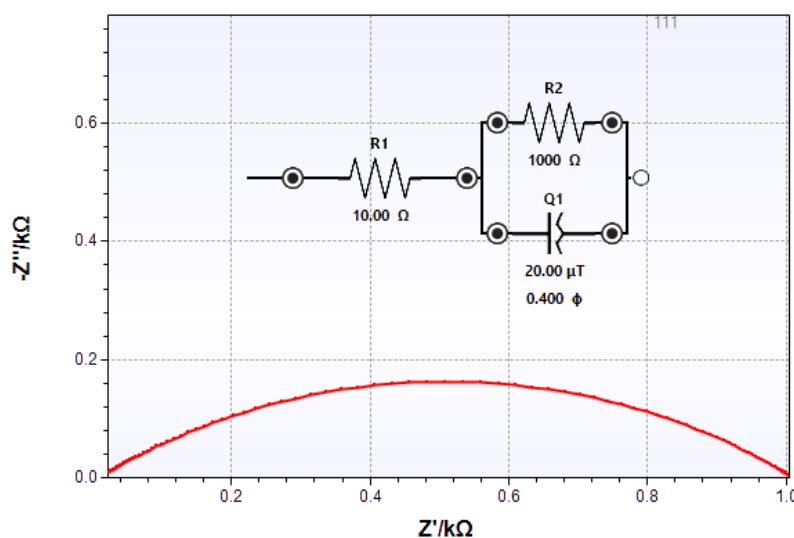


Left: The absolute impedance of a constant phase element with a constant phase exponent of 0.6 ϕ plotted against frequency. *Top right:* Phase shift of a constant phase element over frequency. *Bottom right:* Nyquist plot of constant phase element.

The constant phase element is used instead of a regular capacitor to model the double layer capacitance when an electrode displays a frequency dependent dissipation/dispersion of energy (typical for solid electrodes). When studying a redox reaction without diffusion limitations the dissipation/dispersion of energy presents as a depressed semicircle in the Nyquist, figure below.



Nyquist plot of a redox reaction without diffusion limitations, with a solution resistance of $10\ \Omega$, a charge transfer resistance of $1\ k\Omega$ and a constant phase element that represents the double layer capacitance of an ideally polarizable liquid electrode, i.e. a constant phase element with a phase exponent of $1\ \Phi$ (or a capacitor).



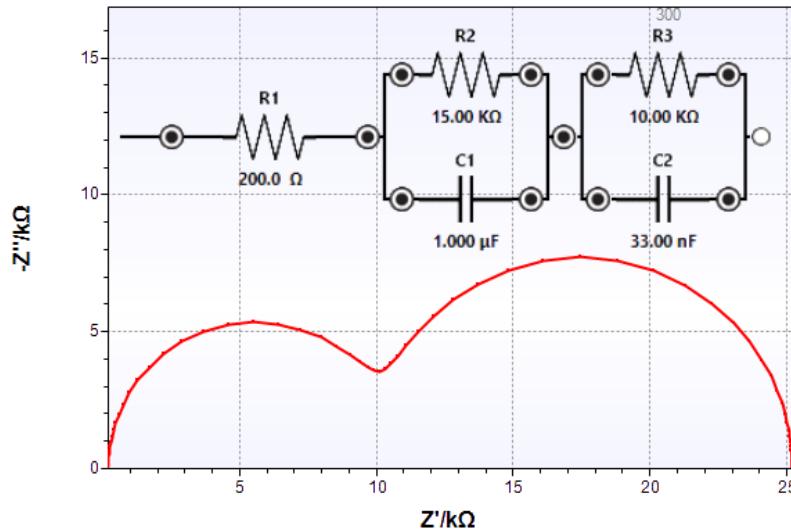
Nyquist plot of a redox reaction without diffusion limitations, with a solution resistance of $10\ \Omega$, a charge transfer resistance of $1\ k\Omega$ and a constant phase element that represents the double layer capacitance of a solid electrode with dispersion/dissipation of energy. Here the semicircle is shifted downwards as a result of the dispersion/dissipation, modelled as a constant phase element with a phase exponent smaller than $1\ \Phi$.

5.8 Fitting Example

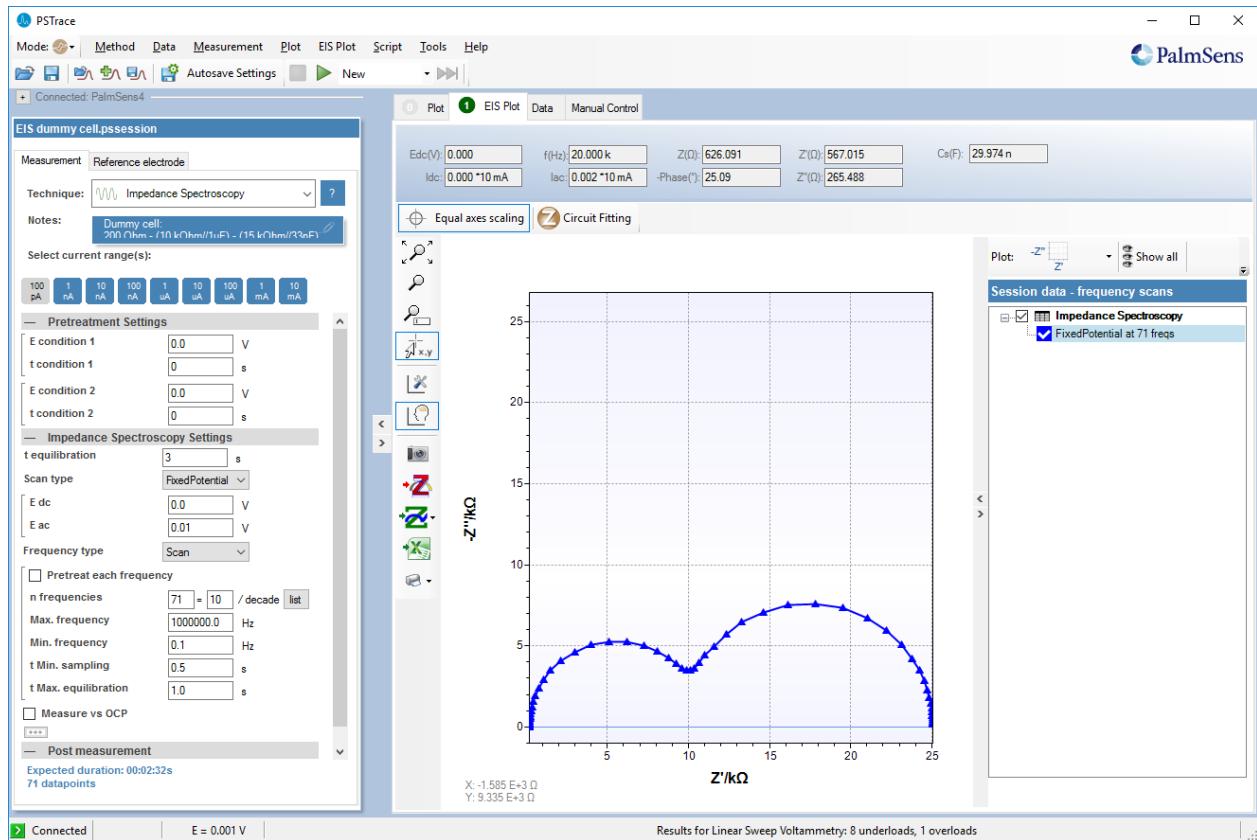
This example demonstrates the fitting an equivalent circuit on a measurement with two distinct time constants (semi-circles). The measurement used in this example was performed on a PalmSens EIS Dummy Cell described in the figure below. The figure

below shows the dummy cell's circuit, the values of its components and a simulated of a Nyquist plot of the dummy cell. Below that is the Nyquist plot of the actual measurement.

The aim of this example is to demonstrate that three similar equivalent circuits can all fit the data accurately. Although the quality of the fit is similar the values of the components differ significantly emphasizing the importance of choosing the right equivalent circuit to interpret a measurement.



Nyquist plot of a simulation of the PalmSens EIS Dummy Cell

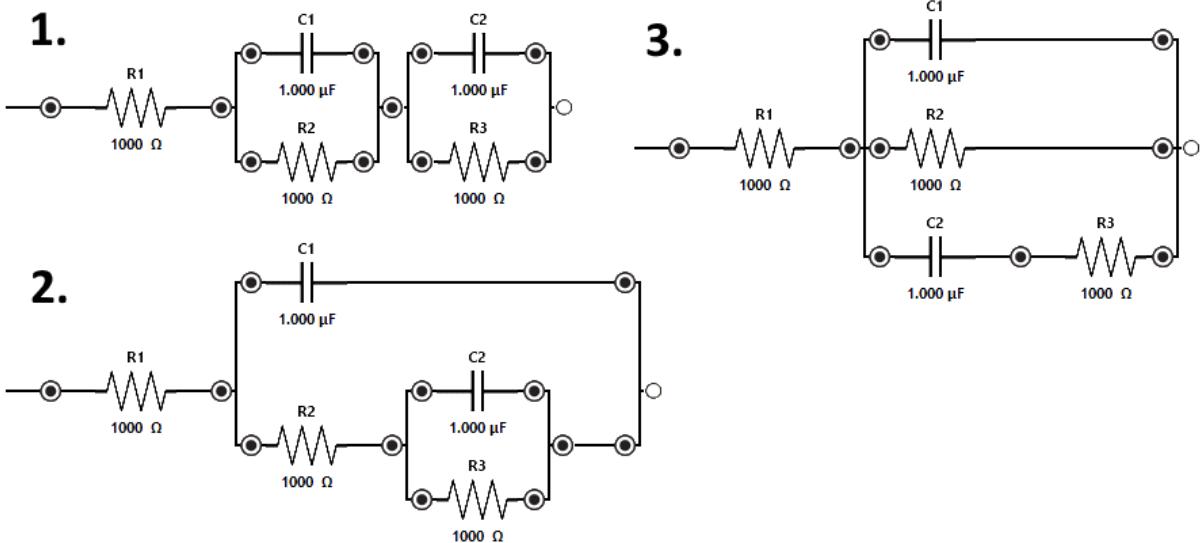


Impedance spectroscopy measurement of the PalmSens EIS Dummy Cell

Designing equivalent circuits

There are two clearly distinct time constants (semi-circles) visible in the Nyquist plot. Time constants can be modelled by placing a capacitor or constant phase element in parallel to a resistance (and optionally a Warburg element). For this example, three different circuits will be used, (1) a circuit with a Voigt structure (the same as the circuit inside the dummy cell), (2) a circuit with a ladder structure and (3) a circuit with a Maxwell structure. Voigt circuits are typically used for modelling the redox process on

an electrode. Ladder circuits can be used when there are one or more adsorbed species. Maxwell circuits have been used to study dielectric phenomena.



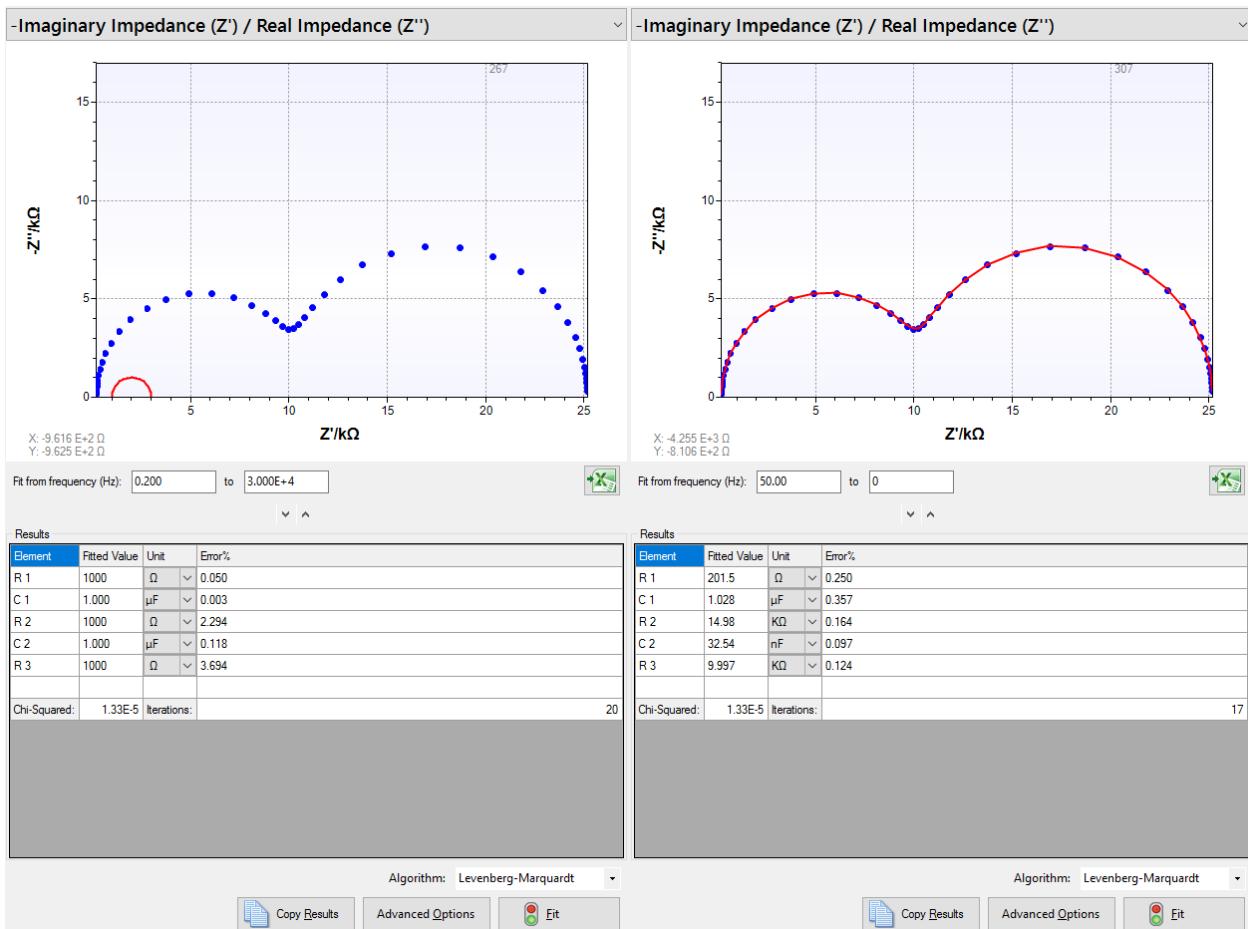
Three different circuits that can model measurements with two time constants. 1: A Voigt circuit (the actual model of the dummy cell). 2: A ladder circuit. 3. A Maxwell circuit.

Fitting the circuits

After the circuit has been built enter the fit mode. Often the default values of the components are sufficiently close to their actual values and the fitting algorithm will fit the circuit correctly. However, in some cases circuit fitting algorithms end up in so called local minima, this inherit to mathematical optimization algorithms. The fitting of the three equivalent circuits on the measurement is demonstrated below. In the fit of the Maxwell circuit some tips are also given on how to avoid getting stuck in local minima.

Voigt

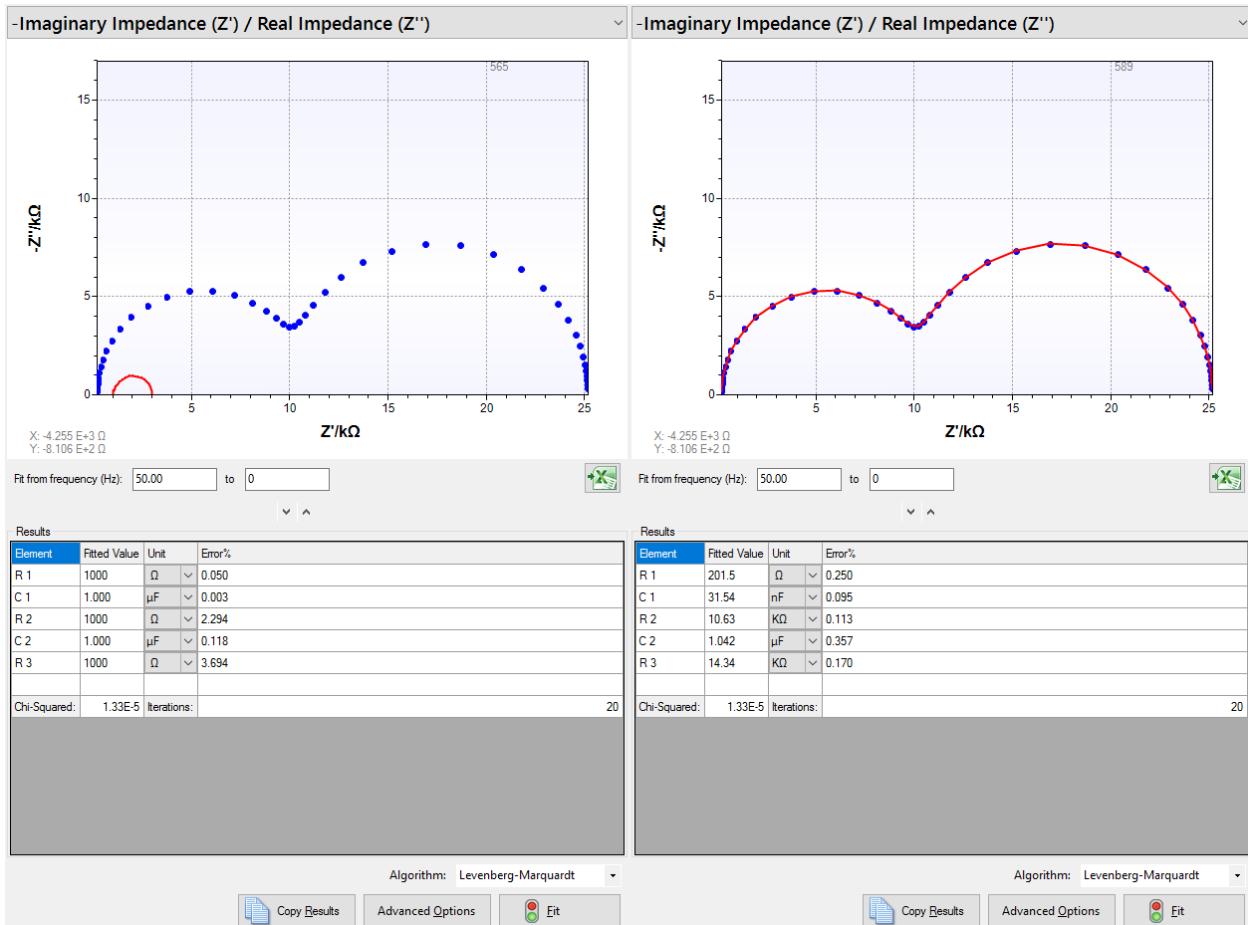
The following image shows the fitting tab with at the top a Nyquist plot of the measurement (blue dots) and a simulation of the Voigt circuit with the circuit editors default values (red line). Clicking on the fit button will fit the equivalent circuit on the measurement. Assuming the measurement was performed correctly this circuit will directly give an accurate fit with the default values of the components.



Fitting of the Voigt circuit. Left: the default values of the components result in the small red semi-circle. Right: After pressing the fit button the circuits semi-circles (time constants) no longer overlap and fit the measurement accurately.

Ladder

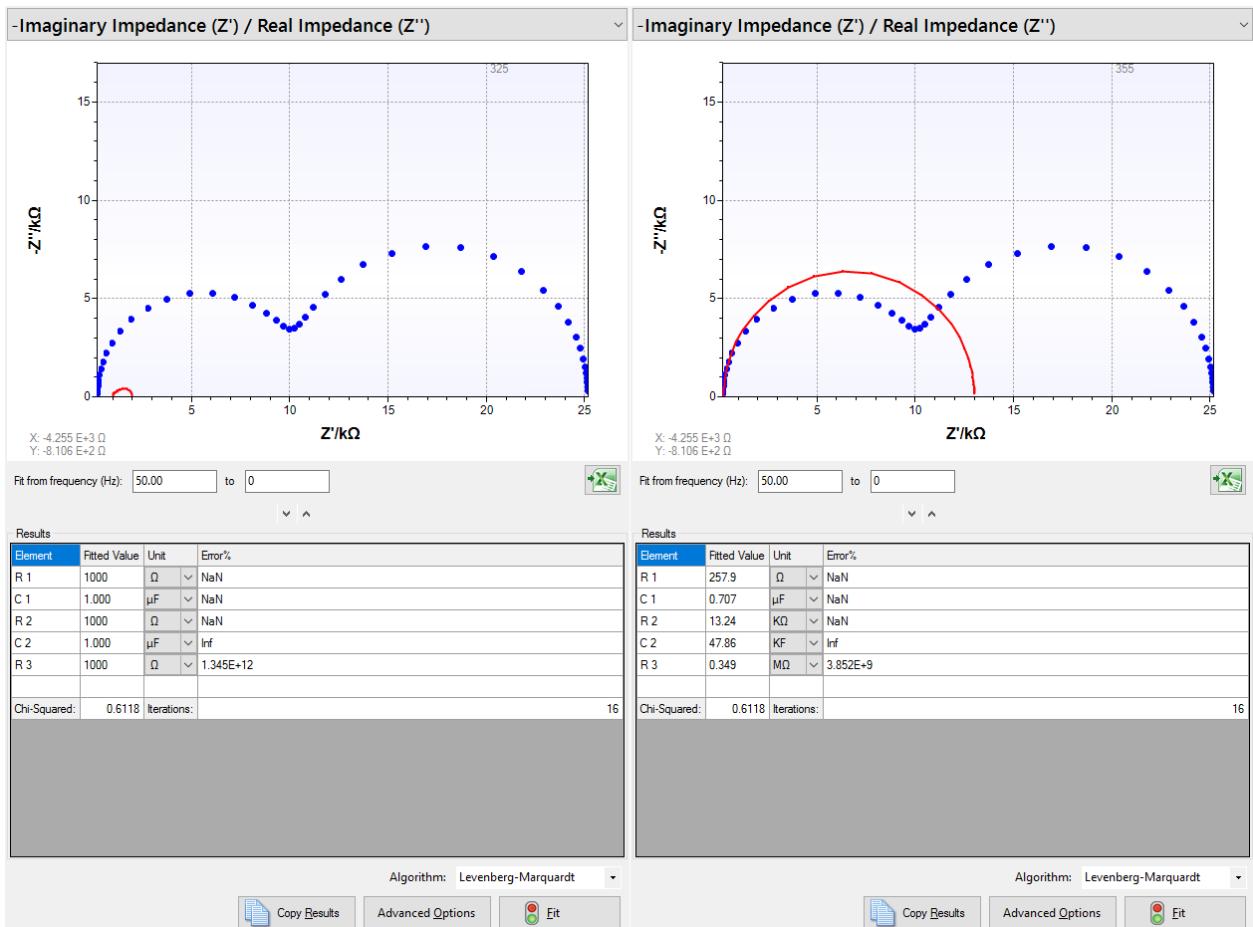
Just as the Voigt circuit the ladder circuit directly fits on the measured data without first getting stuck in a local minimum. The fitted values of the components are even quite close to those of the Voigt model. However, in the Maxwell circuit the resistor R3 is used to obtain the value of the pseudo capacitance and not for modelling the charge transfer resistance.



Fitting of the ladder circuit. Left: the default values of the components result in the small red semi-circle. Right: After pressing the fit button the circuits semi-circles (time constants) no longer overlap and fit the measurement accurately.

Maxwell

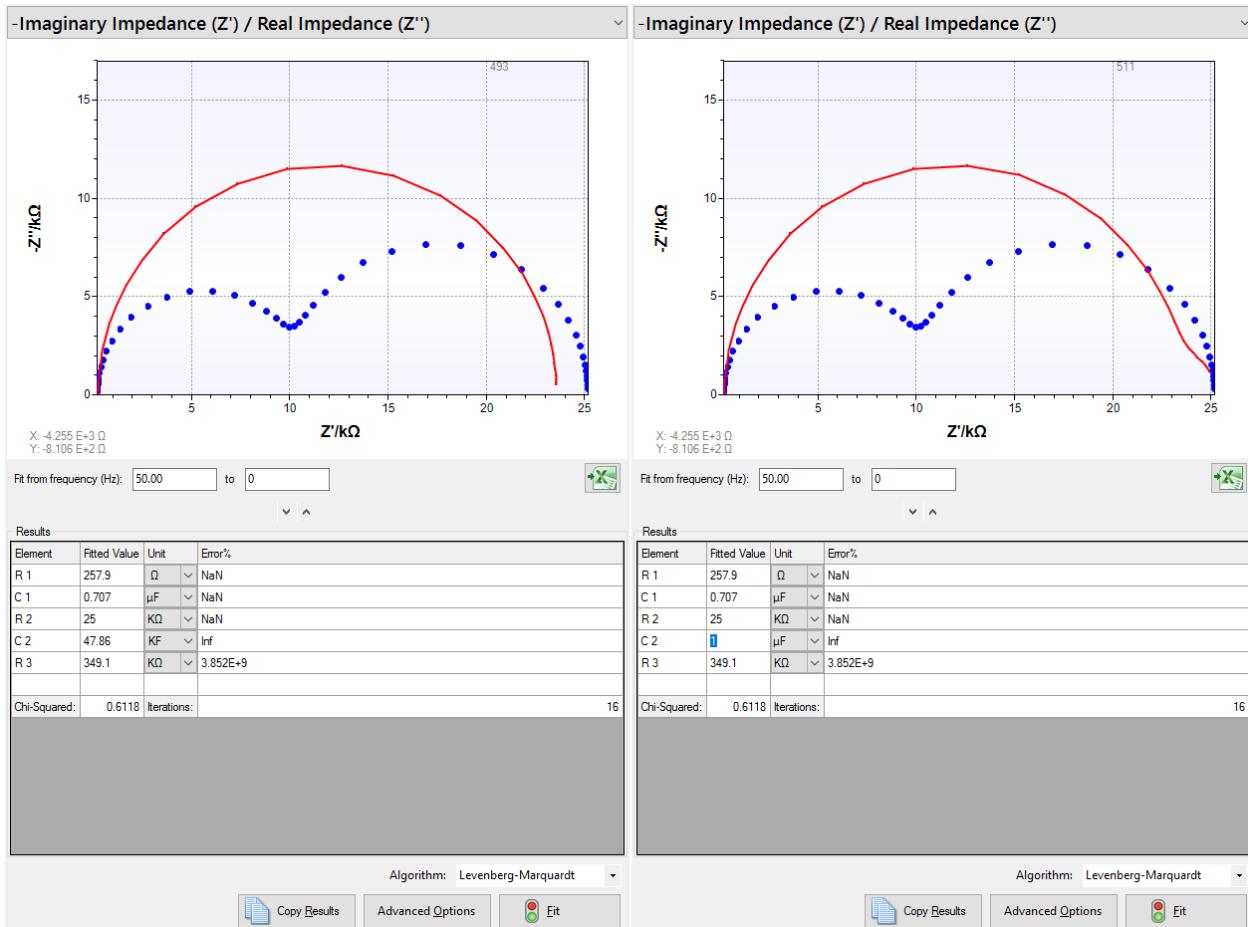
As seen below the Maxwell circuit will not fit directly on the measurement, as it gets stuck in a local minimum. Therefore, it is necessary to refine the initial values of the circuit's components to avoid ending up in this local minimum.



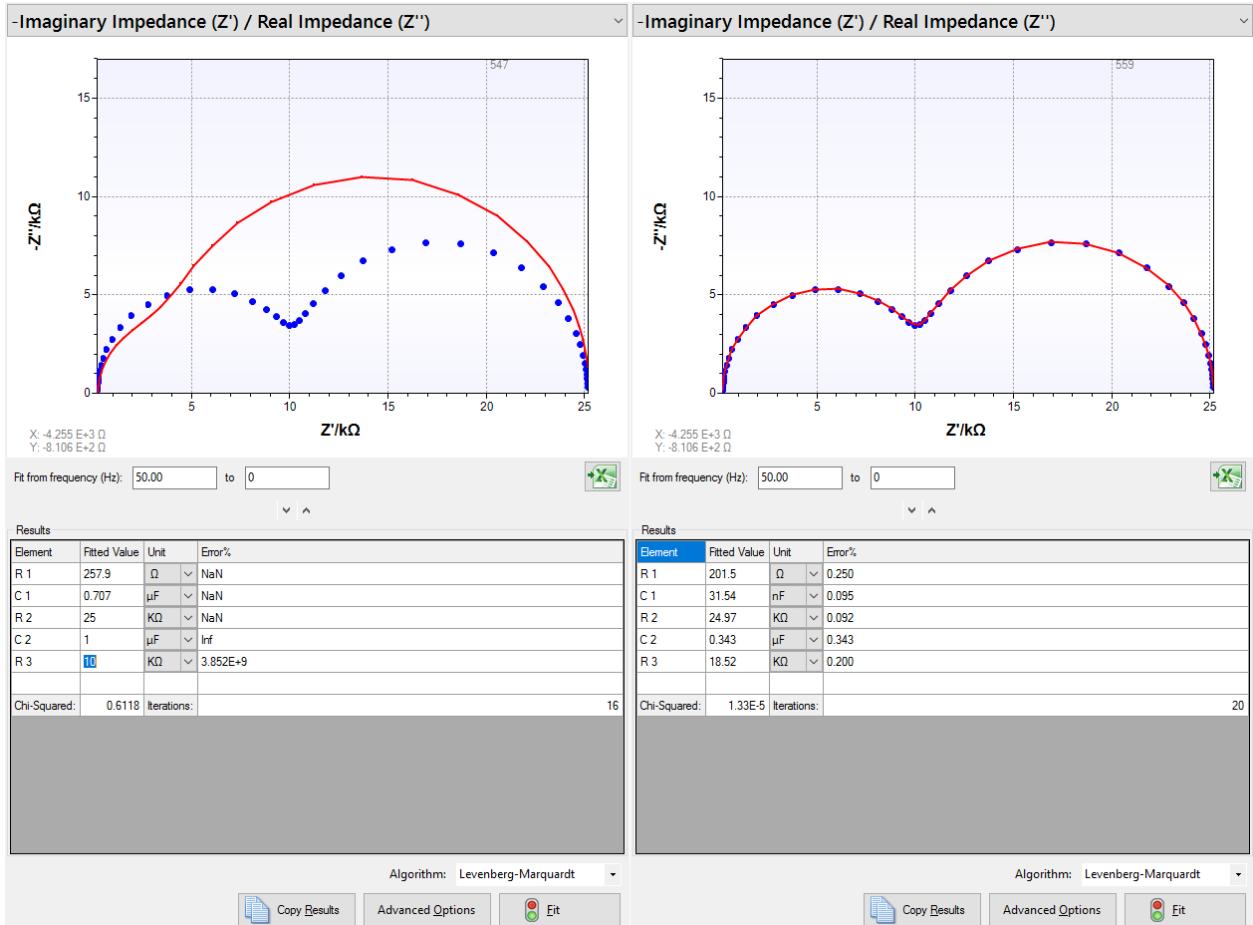
Fitting of the Maxwell circuit. Left: the default values of the components are far from the actual values as the overlapping red semi-circles (time-constants) are much smaller than the ones that were measured. Right: clicking on the fit button will result in the fitting algorithm getting stuck in a local minimum, the model of the semi-circle clearly does not overlap with the measured data also the values several components are unrealistic. Thus values of the components must be adjusted in order to obtain an accurate fit.

A general tip for avoiding local minima is providing a rough initial estimation in which the red semicircle(s) (i.e. the modelled time constants) approaches that of the measurement, preferably set the initial values so that the circuit's semicircles are slightly larger than the measured semi circles.

Based on the Nyquist plot the real component (x-axis) of the impedance is close to 25 k Ω at the lowest frequencies. In the Maxwell circuit resistor R2 is parallel to the second time constant (C2 and R3) and the current will primarily flow through this resistor at low frequencies, thus increasing R2 to 25 k Ω should increase the total size of the overlapping semicircles. Before we will attempt to fit again, we will change the size of the capacitors to decrease the overlap of the resistors. During the last fit the value of C2 got stuck at 48 kF which is unrealistically large, therefore, we will change it back to 1 μF . The value of R3, 349 k Ω , is also too high, so we will set it somewhere between 0 and 25 k Ω (this is where imaginary component (y-axis) of the impedance approaches zero). Then, click on the fit button again and the fit should now be accurate.



Left: the value of resistor R_2 is increased to match the real impedance of the circuit at low frequencies (25 kΩ as seen on the x-axis on the plot above), as a result the semicircle are now almost as wide as the measured semi-circles. Right: The unrealistically high capacitance of C_2 is lowered back to 1 μF , this reduces the overlap of model's the semi-circles.



Left: The very high resistance of R_3 is lowered to $10 \text{ k}\Omega$, a value between 0 and $25 \text{ k}\Omega$ (i.e. the range of the real component of the impedance (x-axis)). This changes how the models semi-circles overlap. *Right:* with the values of the components as specified in the left image the fitting algorithm now finds an accurate fit.

Inspecting the quality of the fit

The results of the fit are displayed in the table after fitting the circuit on the data. The chi-squared test is a general indication of the fit's quality. The lower the chi-squared value, the better is the fit. The square root of the chi-squared statistic gives the average error of the fit. For these fits this is 0.4% which is very good. The individual errors of the components are also given in the table.

Although the quality of the fit is good, the values of the components for the ladder and Maxwell model cannot be interpreted correctly as the specific processes of the cell that these components represent do not comply with the actual measurement, thus it is demonstrated that blindly assuming that your model is an accurate representation, just because it fits, might lead to circuits lacking actual physical meaning.

Voigt			
Element	Fitted Value	Unit	Error%
R 1	201.5	Ω	0.250
C 1	1.028	μF	0.357
R 2	14.98	$\text{k}\Omega$	0.164
C 2	32.54	nF	0.097
R 3	9.997	$\text{k}\Omega$	0.124

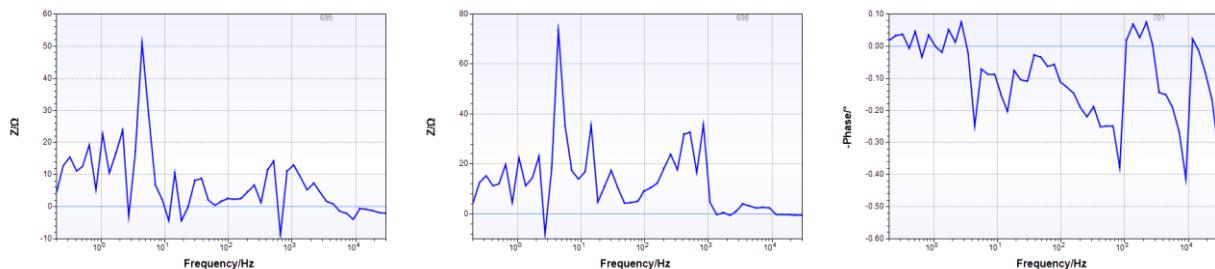
Chi-Squared: 1.33E-5 Iterations: 17

Ladder			
Element	Fitted Value	Unit	Error%
R 1	201.5	Ω	0.250
C 1	31.54	nF	0.095
R 2	10.63	K Ω	0.113
C 2	1.042	μ F	0.357
R 3	14.34	K Ω	0.170
Chi-Squared:	1.33E-5	Iterations:	20

Maxwell			
Element	Fitted Value	Unit	Error%
R 1	201.5	Ω	0.250
C 1	31.54	nF	0.095
R 2	24.97	K Ω	0.092
C 2	0.343	μ F	0.343
R 3	18.52	K Ω	0.200
Chi-Squared:	1.33E-5	Iterations:	10

Fitting results

Visual inspection of the fit's quality is also possible by changing the plot to either the error in the magnitude of the impedance over frequency, the error in the real component of impedance over frequency or the error in phase shift over frequency. These plots represent the difference in magnitude of impedance, real impedance and phase shift between the fit of the equivalent circuit and the measured data. As seen in the figure below there are subtle discrepancies in impedance at the lower frequencies and phase shift at higher frequencies between the equivalent circuit and the measurement.



Error plots displaying the differences in impedance and phase shift between the equivalent circuit and the measurement.

Adjusting the advanced fit options

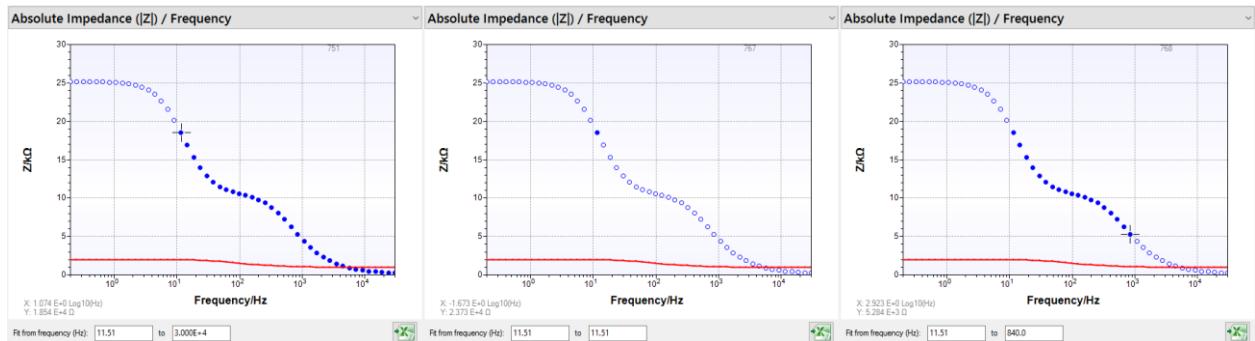
In some cases you may wish to adjust the fitting options in order to obtain the type of fit that you want. In the fit tab of the circuit editor several advanced options can be set, such as selecting a frequency range over which you would like to fit your equivalent circuit and adjustments to the default parameters of the fitting algorithm.

Fitting on a specific frequency range

The frequency over which you desire to fit the circuit can be specified either by clicking in the plot or by entering the values in the corresponding textboxes.

Note: Specifying the frequency range over which to fit the data is only possible when in fit mode. To specify the frequency for a simulation please refer to the help section on simulating a circuit. Specifying the fitting frequency range is only possible in the plots that also show the measured data (i.e. the blue dots).

Specifying fitting frequency with the mouse is done by moving your mouse over the sample from where you would like to start or end your fit, then clicking on that sample (blue dot) twice. Then move your mouse to the data point where you would like to respectively end/start your fit and click on it once. The frequency range selected for fitting is indicated by the solid blue dots.



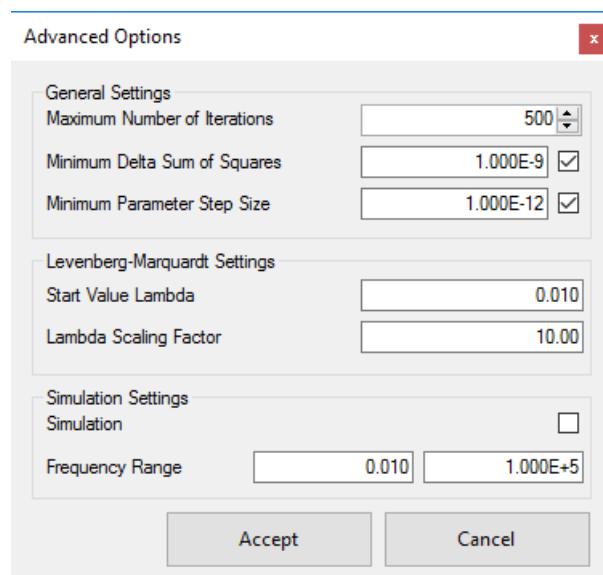
Specifying the frequency range for fitting. Left: First move your mouse to the data point from which you would like to start the fit and click on it. Middle: Click on it again, now it will be the only data point selected (in this case the sample at 11.51 Hz). Right: Then move your mouse to the data point where you would like fitting to end and click on it. The selected frequency range is now indicated by the solid blue dots and the values in the text boxes below the plot.

Excluding outliers

To exclude outliers from a fit hold down the control button on your keyboard and left click on the outlier with your mouse to deselect it. Left clicking on that point again while holding down control will reselect it. While holding down both the control button and the left mouse button it is possible to (de)select all points in the specified area.

5.9 Fitting algorithm

Currently only the Levenberg-Marquardt algorithm is available for finding the minimum complex non-linear sum of squares. Advantages of this algorithm are that it is robust and generally quick at finding a solution. A disadvantage of the Levenberg-Marquardt algorithm is that it was not designed to work with specified minimum and maximum values for components; as a result the algorithm sometimes ends up in local minima with unrealistic values for the components (i.e. extremely large/small or negative values). Local minima are inherent to mathematical optimization algorithms and in some cases a good fit will require changing the default values of the components prior to performing the fit.



Advanced fitting options window

Maximum Iterations

Generally it will not be necessary to increase the maximum number of iterations for fitting. As the Levenberg-Marquardt algorithm usually requires few iterations to achieve a fit. However, when the minimum step size parameters are lowered this could be necessary. When you do not achieve a good fit and see that the number of iterations was 500 in the table of the fit tab increasing the maximum number of iterations may help. Usually it is better to carefully review the design of your circuit and enter more appropriate values for its components before fitting again.

Minimum Step Size

The minimum delta sum of squares and minimum parameter step size are the desired stopping conditions for the fitting algorithm.

The Levenberg-Marquardt algorithm attempts to reduce the sum of squares with each step, the minimum delta sum of squares specifies when further improvements become negligible. This can be lowered to achieve a more precise fit for the value of the components. For this to have an effect you will usually have to lower the minimum parameter step size as well. It is questionable whether lowering the minimum delta sum of squares will improve your fit as generally the accuracy of the fit is limited by the fact

you are fitting a model which is a simplification of the actual ongoing processes in the cell and that will never fit the measurement perfectly.

As the Levenberg-Marquardt algorithm approaches the global minimum (i.e. the desired fit) or a local minimum (i.e. an undesired fit) the differences in the values of the components become smaller each step. Lowering this value is recommended if you expect a component in circuit has a value in the range of 1-10 pico Farad/Henri/Ohm etc.

Lambda

The Levenberg-Marquardt algorithm uses lambda as a damping / scaling parameter. The lambda factor increases/decreases the change in the values of the components for the next step. In the event of a successful step (i.e. the sum of squares decreases) the lambda factor decreases and becomes increasingly smaller as the algorithm approaches a minimum. In the event of an unsuccessful step it becomes larger allowing the algorithm to approach a minimum with less steps.

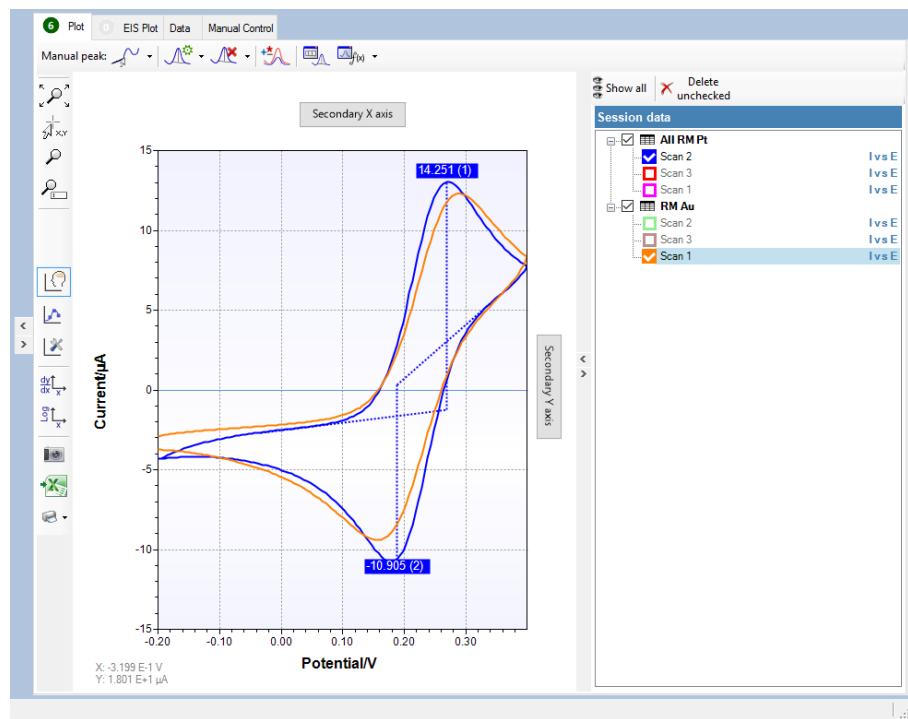
The starting lambda value can be lowered in the case you want to further optimize a fit that was already good or increased to find a minimum in less steps. The same holds for the lambda scaling factor reducing it will increase the amount of iterations required but may be useful if further optimization is required and increasing it could decrease the amount of iterations required to find a minimum or it could make the algorithm unstable.

6 Plot, curves and data

In this chapter all available functions related to measured curves are explained. Since impedance data is presented different from regular curves, please refer to chapter Electrochemical Impedance Spectroscopy for information about working with impedance data.

6.1 Handling curves

There are two Plot tabs in PSTrace; impedance measurement curves (EIS curves) are shown in the ‘EIS Plot’ tab, all other curves are shown in the ‘Plot’ tab.



PSTrace window showing the Plot tab

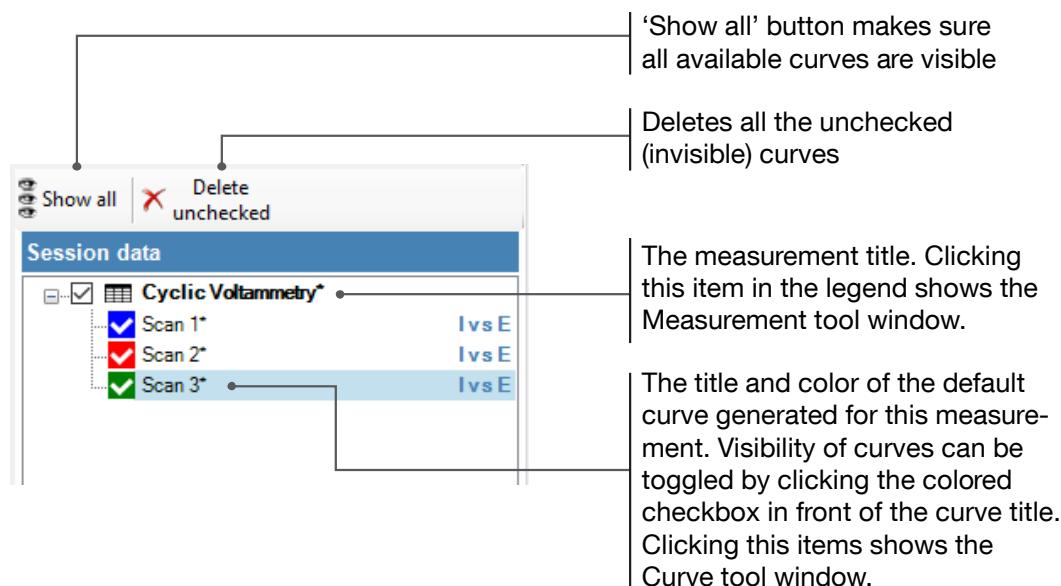
The legend next to the Plot tab shows all available measurements (session data) with corresponding curves.

A ‘Session’ can contain multiple measurements with curves.

See also section Files.

6.2 Session data

When a measurement is started the measurement is added in the Session data list (or legend) next to the plot window and the default curve is added.



The legend showing session data

The curve selected in the curves list determines which curve is active. The active curve is used when saving a single curve, showing data in the Data tab, marking peaks or slopes, etc.

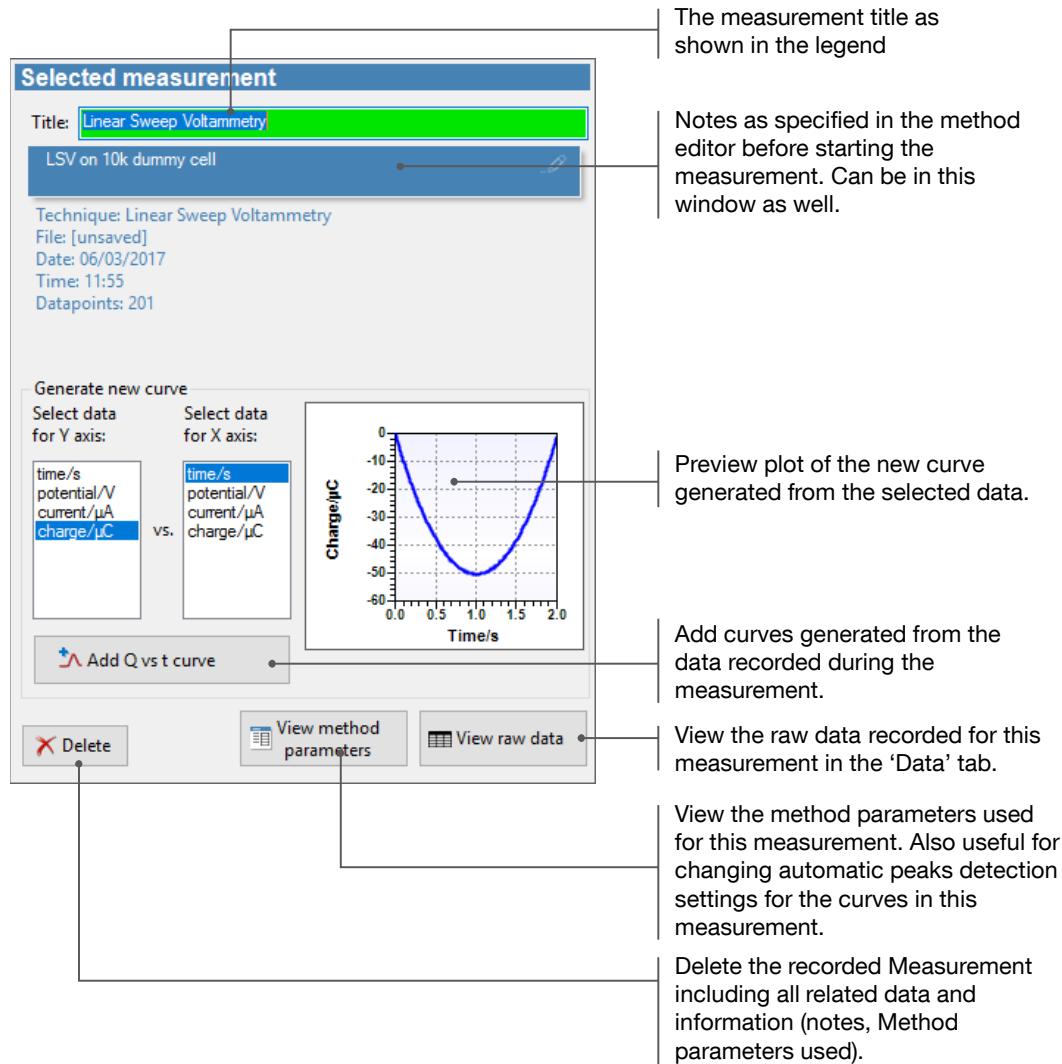
The asterisk (*) next to the titles indicate the measurement or curve is not saved yet. They will disappear when the data is saved to a session file.

When a measurement is selected in the legend, a window appears next to the legend showing all data that was recorded during the measurement together with some other information about the measurement:

Automatic naming of curves

In case of a new measurement, the curve is named 'Curve' by default. In case of a Cyclic Voltammetry measurement the curve receives the name 'Scan n', where n is a sequential number. In case of a multiplexer measurement or measurement using an auxiliary channel, it receives the name of the channel used.

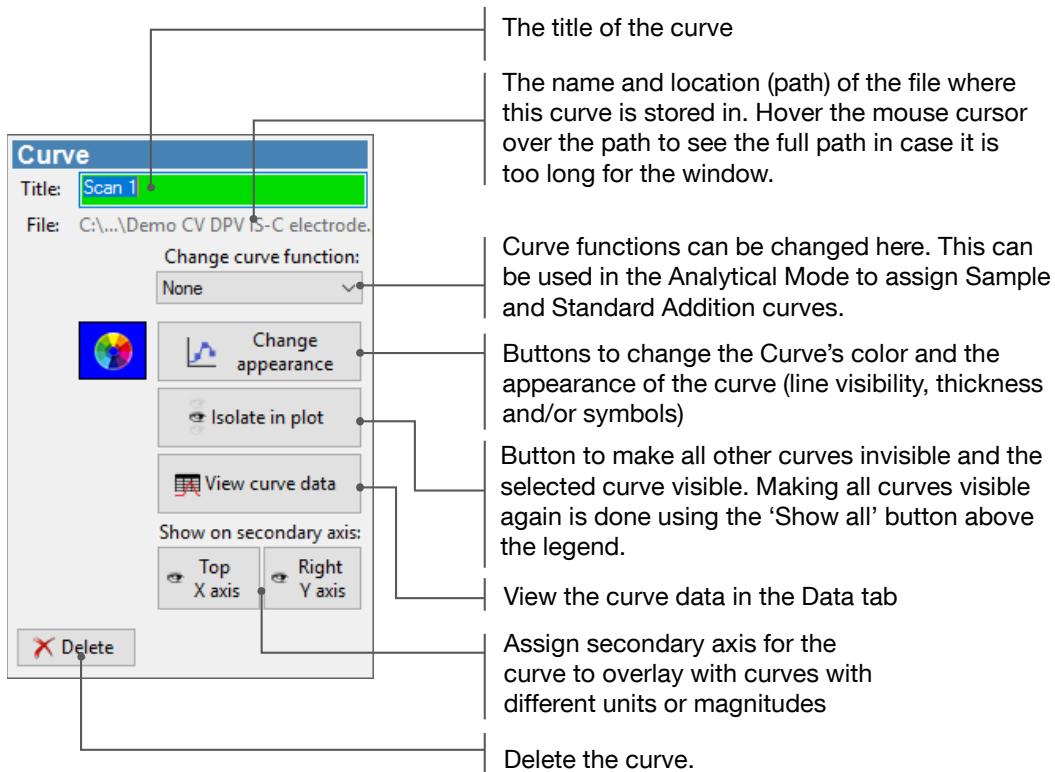
6.2.1 Measurement Tool window



Window with measurement information shown next to the selected measurement in the legend.

Selecting a curve in the legend opens a tool window for this curve.

6.2.2 Curve Tool window



Windows with tools for the selected curve shown next to the legend after selecting a curve

6.3 Plot interactions

Select point



Plot scaling

- Automatic scaling to show all data points
- Use the mouse pointer to drag an area that defines the new scaling boundaries.
- Enter minimum and maximum values for both axis

Clear help lines



Plot behaviour



Toggle smart scaling to automatically round up / down minimum and maximum values for both axes



Toggle grid



Toggle automatic re-scaling during measurement

Other plot options



Plots the derivative of the curve using the centered three-point method



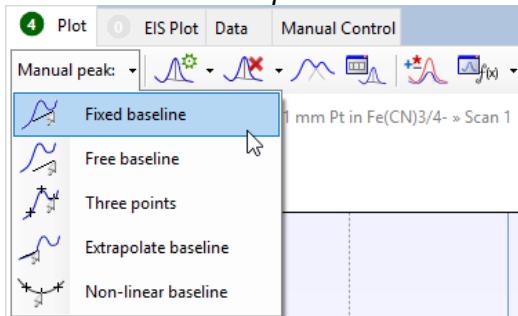
Plots the logarithm (Log_{10}) of the current values.



Shows a print preview and printing options for the plot

6.3.1 Marking peaks manually

The buttons to manual mark peaks in the plot, can be found in the plot toolbar under the button *Manual peak*.

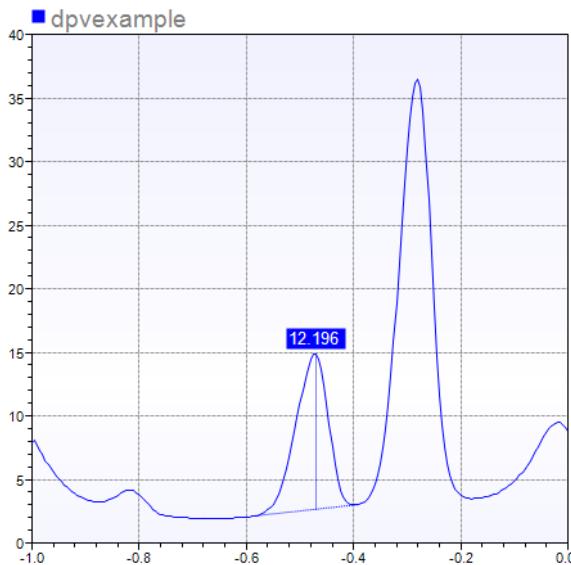


Mark peak manually

Fixed baseline



Draw a baseline fixed on the curve for peak detection.

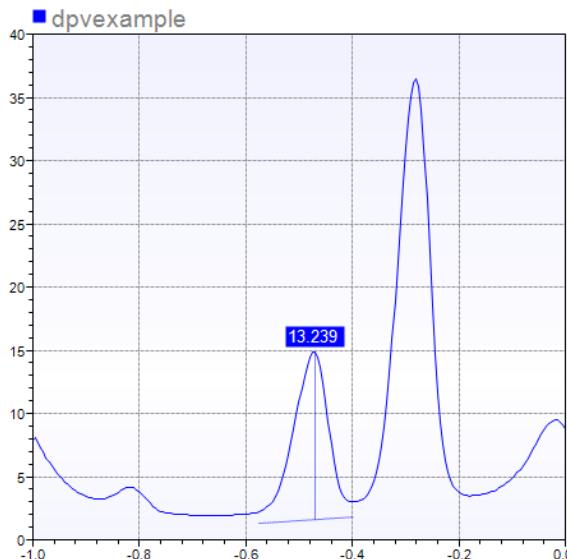


Baseline on curve

Free baseline



The base line is independent from the curve.

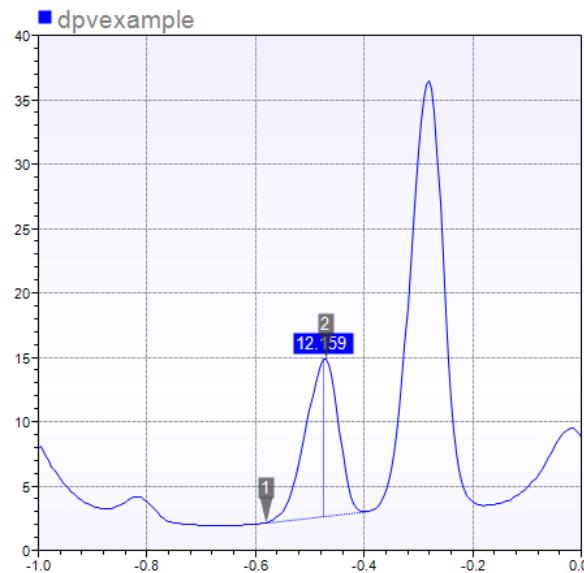


Free baseline

Three points



Three points on the curve determine the left and right of the baseline and top of the peak.

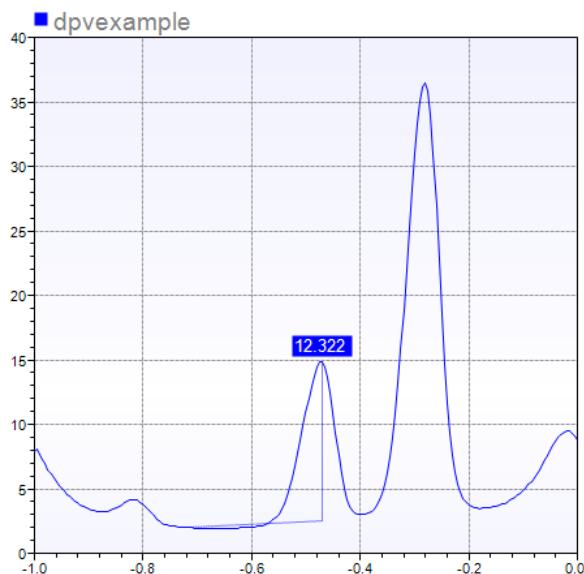


Three points determine baseline and corresponding peak

Extrapolate baseline

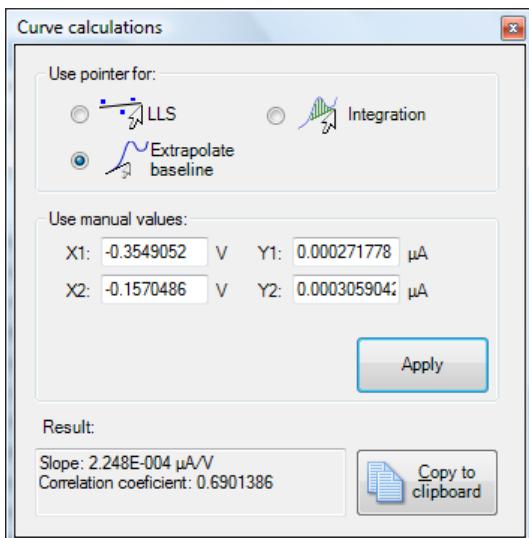


A linear slope (using linear regression) is marked on the curve from which the baseline is extrapolated.



Extrapolate from slope

As soon as the slope for the baseline line has been drawn, the Curve calculations window is shown:



Calculations window showing the properties of the slope

The values shown in the window can be changed manually and applied again on the curve.

Non-linear baseline

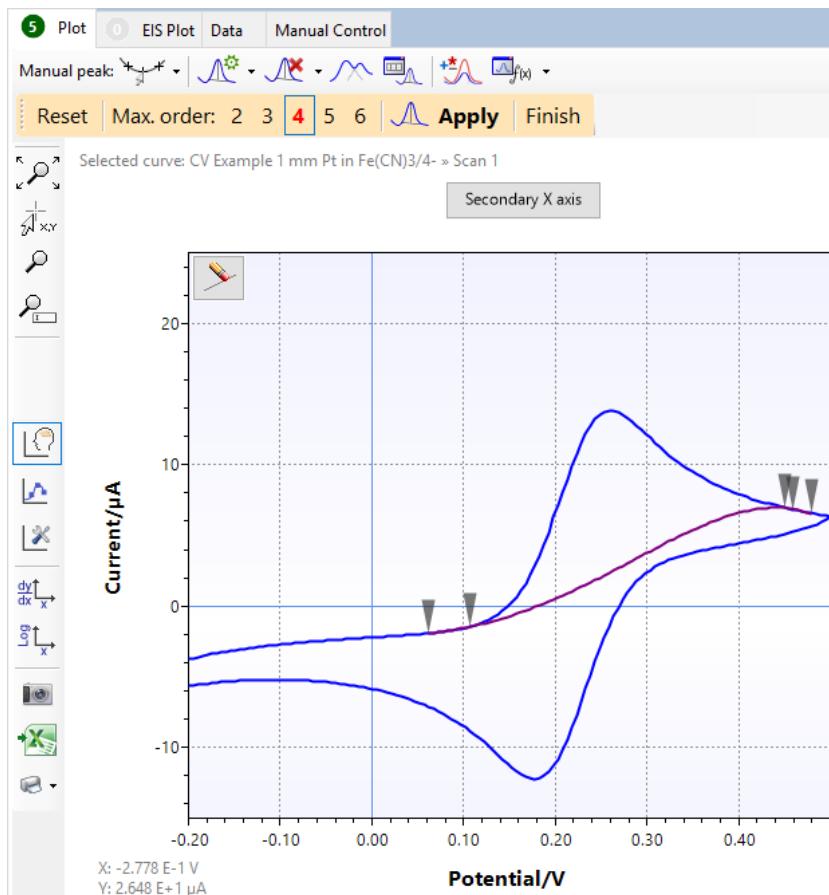
A polynomial with a specified order is fitted through the selected points on the curve.

The following buttons are shown during selection:

Reset | Max. order: 2 **3** 4 5 6 | **Apply** | Finish

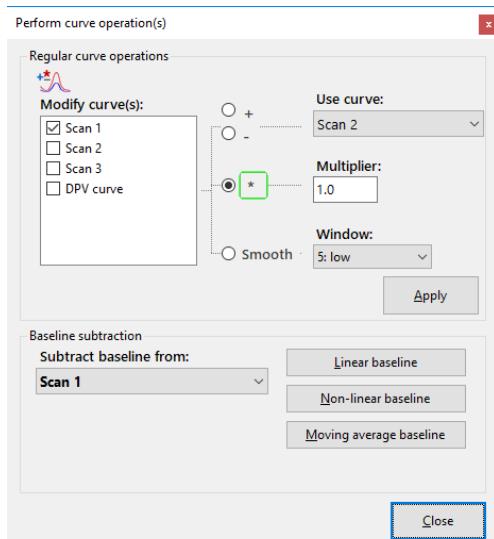
The selected ‘Max. order’ defines the maximum (n) order applied for the polynomial:
 $a_0 + a_1x + a_2x^2 + \dots + a_nx^n$,

The number in red represents the current order n applied. When a polynomial is set, the button ‘Apply’ shows a preview of the peak using the polynomial as baseline. Each time the polynomial is changed; the ‘Apply’ button should be clicked in order to mark a new peak using the changed polynomial as baseline. The ‘Close’ button should be clicked when a satisfactory peak is found.



Marking a peak in a CV curve

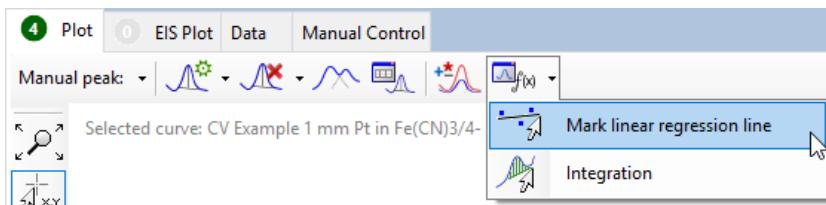
The baselines can also be used for subtraction. This can be done in the Curve Operations Window (see [Toolbars](#) on page 158).



Curve operations window

6.3.2 Other calculations on the curve

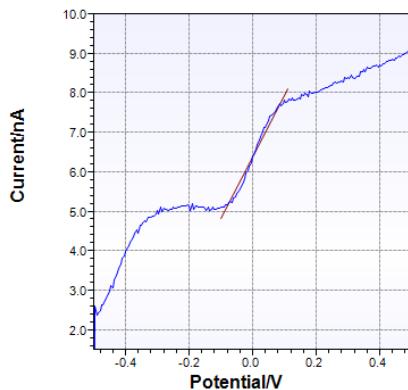
The buttons for integration and marking a linear regression line can be found under the *Curve operations* button.



Calculations on the curve

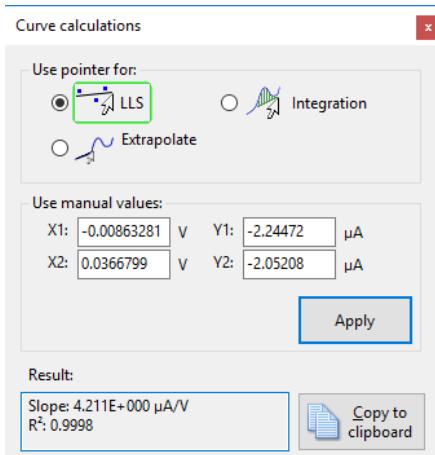
Linear regression

- Mark begin and end on curve for linear regression using linear least squares (LLS).



Calculation of a slope using LLS.

As soon as the line has been drawn, the Curve calculations window with the results is shown:



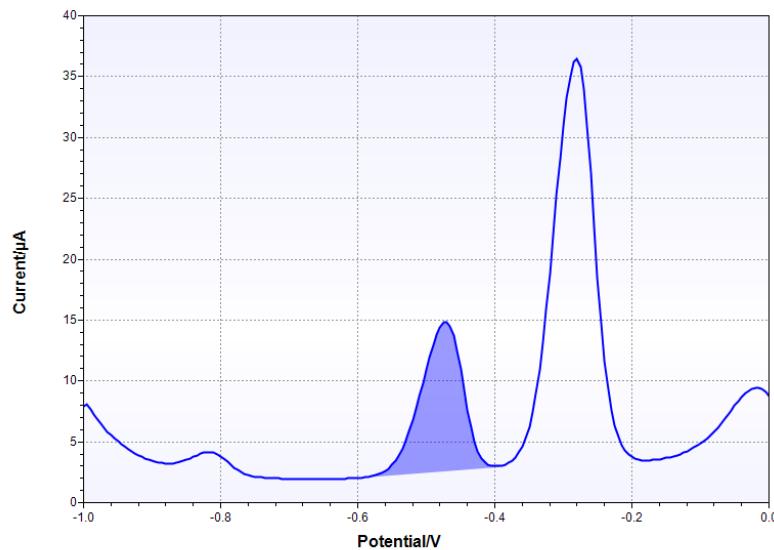
Calculations window showing the properties of the slope

The values shown in the window can be changed manually and applied again on the curve.

Integration

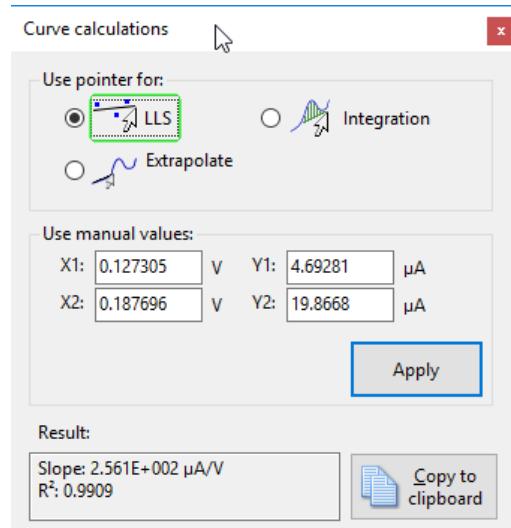


Draw a baseline for integration on curve.



Result of drawing a baseline for integration

The integration result is shown in the Curve calculations window:



Calculations window showing the integration results in two different units

The values shown in the window can be changed manually and applied again for integration of part of the curve.

6.4 Toolbars



Detect peaks



Find peaks

The settings in the Peaks tab are used for peak finding.

Results are shown in the Peaks Data window.

Note: This button is replaced by the 'Find levels' button if the last measurement was versus time. This can be reversed in the Peaks tab.

Remove peaks



Remove all peaks, or remove the peaks of a specific curve.

Find levels



Available if measured as a function of time and *Current Level* is checked in the Peaks tab.

The settings in the Peaks tab are used for the level finding.

Results are shown in the Peaks Data window.

Remove levels

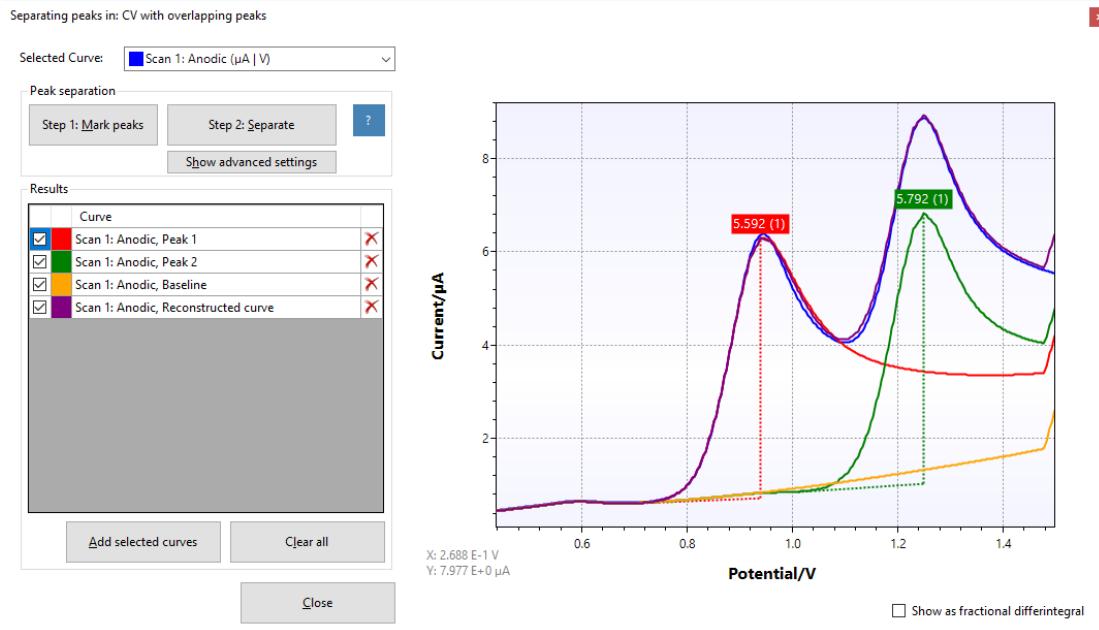


Remove all levels, or remove the levels of a specific curve.

Windows



Overlapping peaks separation window



Window showing separation of overlapping peaks in a CV measurement.

The [overlapping peaks separation window](#) on page 167 allows for the separation of two or more overlapping peaks. This tool window is only accessible for LSV and CV measurements.



Toggle peaks or levels data window

Peaks Data - CV Example 1 mm Pt in Fe(CN)3/4-								
Select measurement: CV Example 1 mm Pt in Fe(CN)3/4- Refresh								
	Peak	Potential/V	Height/µA	Area/µAV	Width/V	Y Offset/µA	Max slope/µA/V	Min slope/µA/V
Scan 1	1	0.25824	14.6157	NaN	NaN	-0.79995	184.756	-90.5291
	2	0.18270	-13.9135	NaN	NaN	1.75285	184.756	-60.4771
Scan 2	1	0.25824	14.5110	NaN	NaN	-1.10917	187.548	-90.6857
	2	0.18270	-14.0160	NaN	NaN	1.77239	187.548	-60.4301
Scan 3	1	0.25824	14.5311	NaN	NaN	-1.17888	187.776	-90.9182
	2	0.18270	-14.0557	NaN	NaN	1.82123	187.776	-61.8893

Automatic peak detection settings

Minimum peak/level width: V

Minimum peak/level height: µA

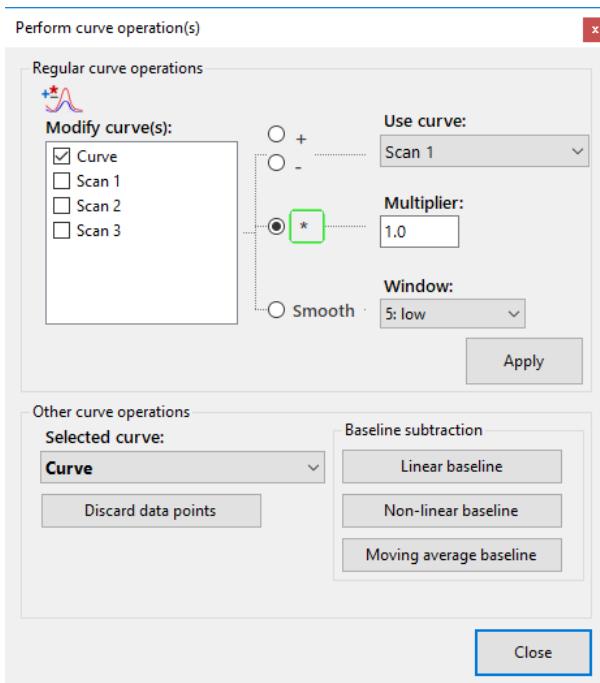
Window showing peak or level data

The table shows the values for the peak potential, peak height, peak area, peak width at half height, the value at the baseline as well as the maximum values for the ascending and descending slopes and the sum of both values. These results can be

copied to the clipboard. The measurement's automatic peak detection parameters can be adjusted and the automatic peak detection can be performed again. Additionally, there is an option to separate overlapping peaks in cyclic and linear sweep voltammetry measurements.



Show Curve operations window



Curve operations window

- Select one or multiple curves to apply operations on.
- Choose the mode of operation.
- Click 'Apply' to perform the operation.

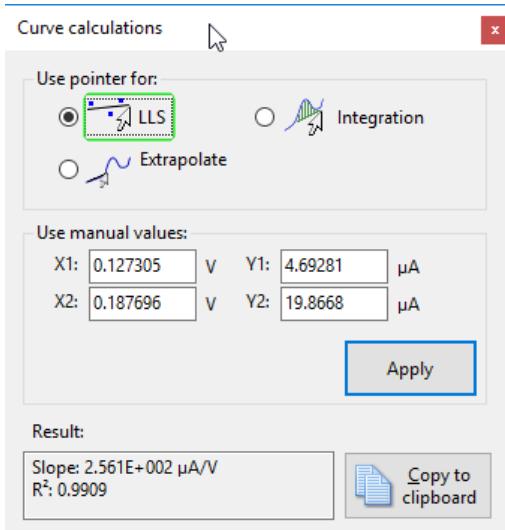
Except for 'Smooth', new curves will be generated based on the selected operation.

For the Baseline subtraction buttons, see sections

[Linear baseline subtraction](#) on page 161, [Non-linear baseline subtraction](#) on page 162 and Moving average baseline



Toggle Curve calculations window



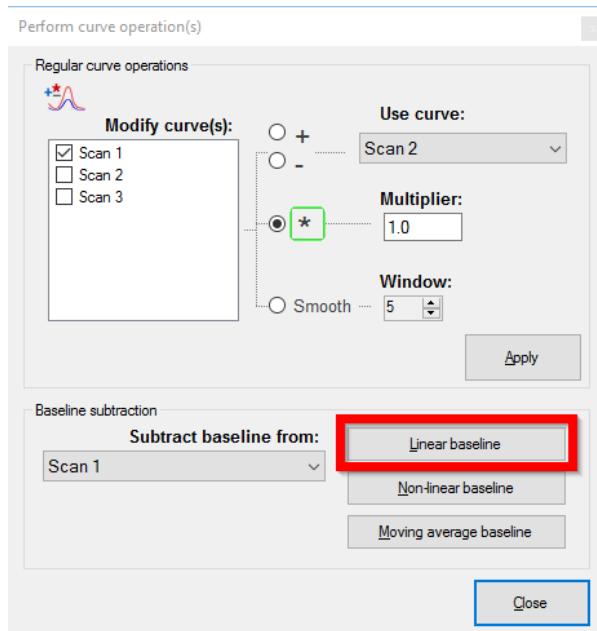
Curve calculations window

The values obtained by using the pointer are shown in the ‘Use manual values:’ frame so they can be fine-tuned and re-applied. These values are saved when PSTrace is closed.

Using the button ‘Copy to clipboard’ the results can be pasted (usually using Ctrl+V) as plain text into any other program.

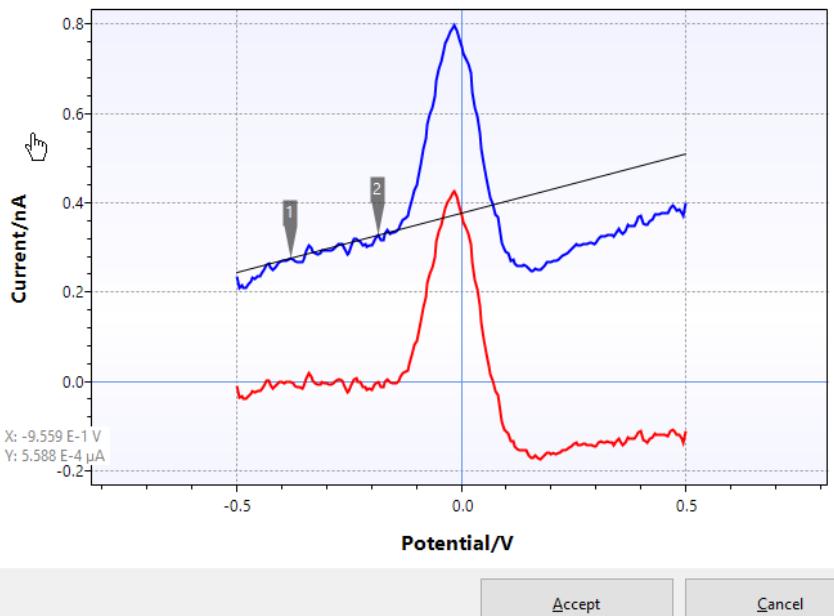
6.5 Linear baseline subtraction

In order to do a linear baseline subtraction, click on the 'Subtract linear baseline' button in the Curve Operations window. This is opened using the  in the plot toolbar. Or in the menu ‘Peaks’ → ‘Curve operations’.



Clicking on this button will open a new window with a plot of the selected curve. Set two markers on the curve. As soon as the second marker is set, a preview is shown. A third click on the plot will remove the preview, reset the markers and place a first one again. If the preview seems satisfactory, click Accept.

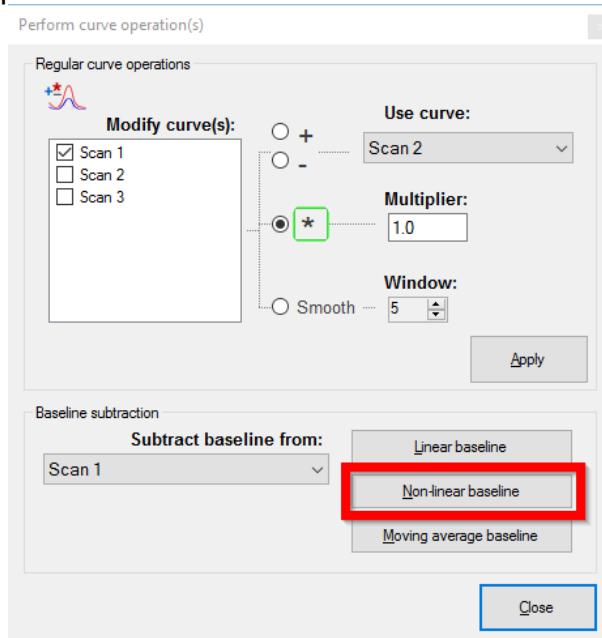
Click Accept to add the corrected curve to the current session or click again to adjust the linear baseline



Plot showing a preview of a linear baseline subtraction

6.6 Non-linear baseline subtraction

In order to do a non-linear baseline subtraction, click on the 'Subtract non-linear baseline' button in the Curve Operations window. This is opened using the  in the plot toolbar.



The non-linear baseline button in the Curve Operations window

The following buttons are shown during selection:

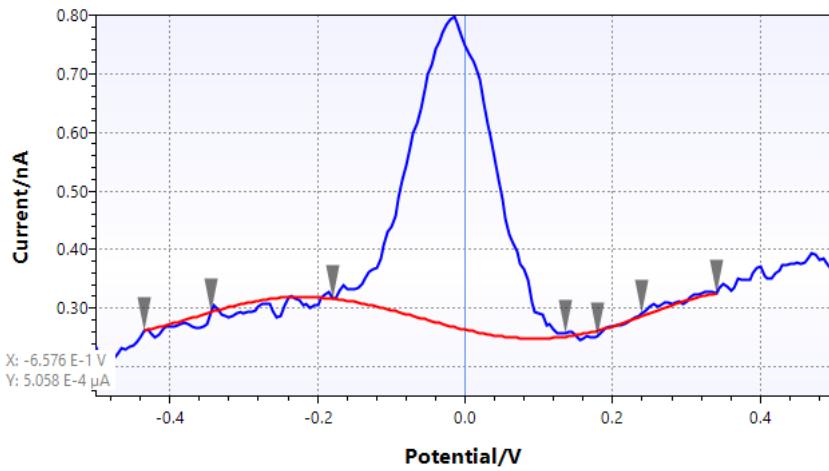


The selected 'Max. order' defines the maximum (n) order applied for the polynomial:
 $a_0 + a_1x + a_2x^2 + \dots + a_nx^n$,

A polynomial with a specified order is fitted through the selected points on the curve. A polynomial requires a minimum of n+1 markers. So a 3rd order polynomial requires three markers.

The number in red represents the current order n applied. When a polynomial is set, the button 'Apply' shows a preview of subtracted curve using the polynomial as baseline. Each time the polynomial is changed; the 'Apply' button should be clicked in order update the preview. The 'Accept' button should be clicked when the preview is satisfactory.

Order applied: 5, to generate the polynomial press Apply

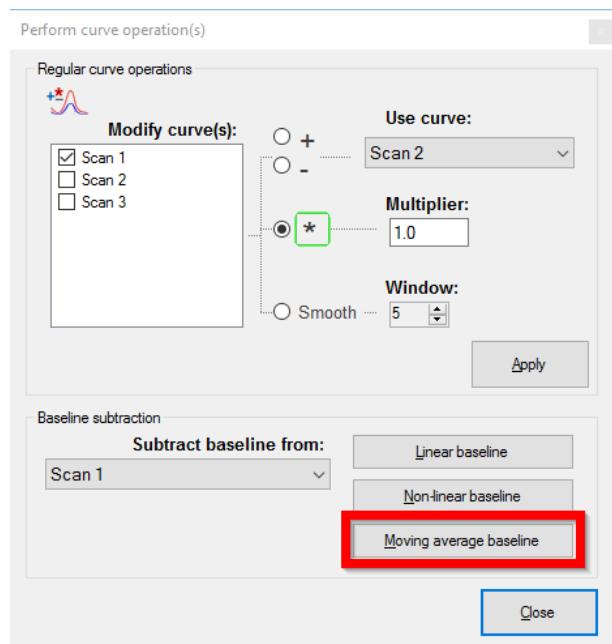


Setting markers on a DPV curve

6.7 Moving average baseline subtraction

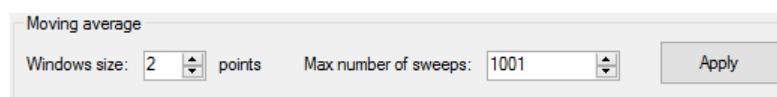
In order to do a moving average baseline subtraction, click on the 'Moving average baseline' button in the Curve Operations window. This is opened using the  in the plot toolbar.

Note: Moving average baseline subtraction is not applicable on Cyclic Voltammograms.



The Moving average baseline button in the Curve Operations window

By clicking on the Moving average baseline button, a preview window opens. In this window the window size and maximum number of sweeps can be adjusted to obtain the desired result. The grey line represents a preview of the baseline correction, it is updated instantly after changing the window size and maximum number of sweeps.



Moving average baseline settings

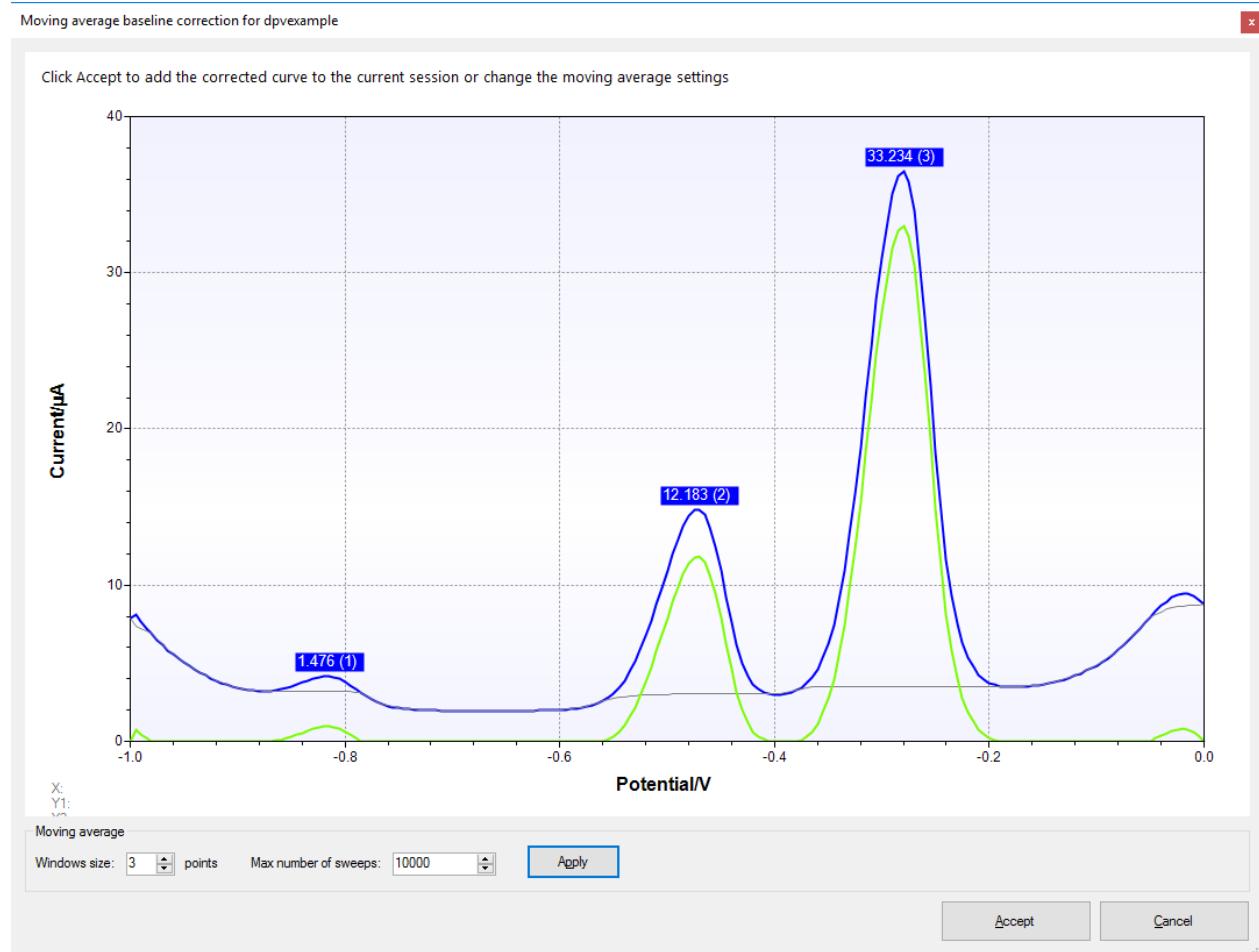
When performing a moving average baseline correction, it is recommended to change the window size first.

Increasing the window size will increase the number of data points that are used to determine the new value of the data points with the moving average correction. The ideal window size depends on the number of data points in your measurement and the

width of the peaks. A window size that is too large will result in unwanted rounding errors.

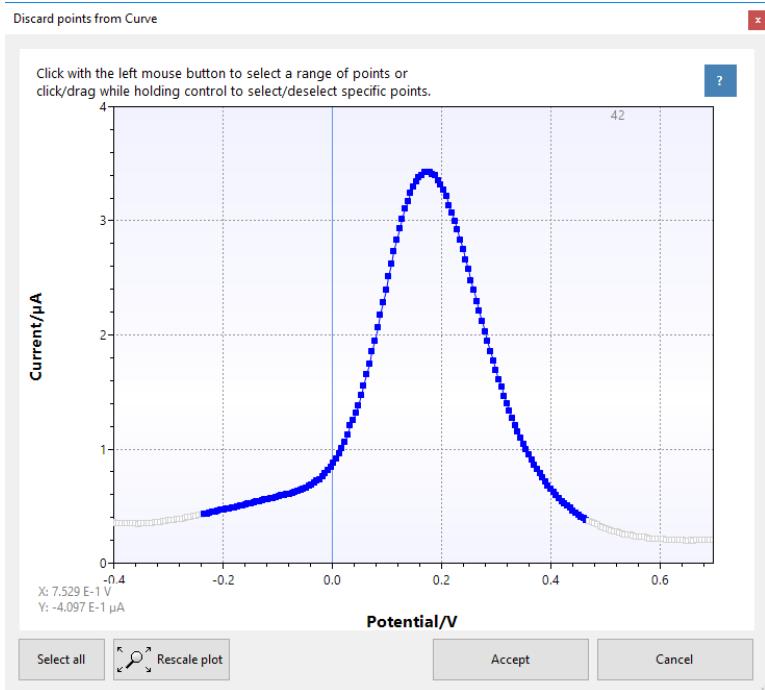
When the desired result cannot be obtained by increasing the window size the maximum number of sweeps (i.e. the iterations of the moving average correction applied to the curve) can be increased to achieve the desired effect.

To apply the moving average baseline correction, click on apply and clicking on accept will add the curve to the session manager.

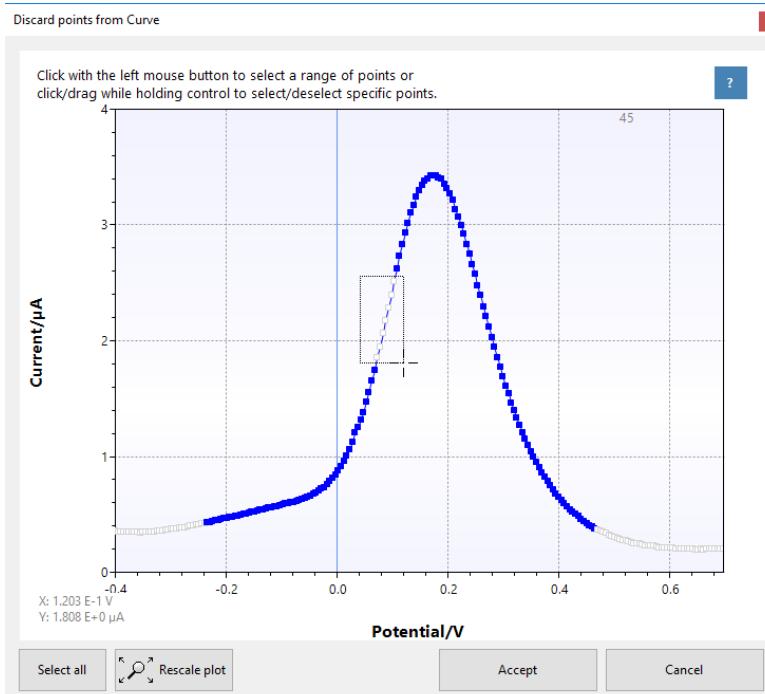


6.8 Discarding data points

Using this option, it is possible to create a new curve from a specific selection of a curve. Specifying the selection of the curve to keep with the mouse by moving your mouse over the sample from where you would like to start or end your selection, then clicking on that sample (blue dot) twice. Then move your mouse to the data point where you would like to respectively end/start your selection and click on it once. The selected range for the new curve is indicated by the solid markers.



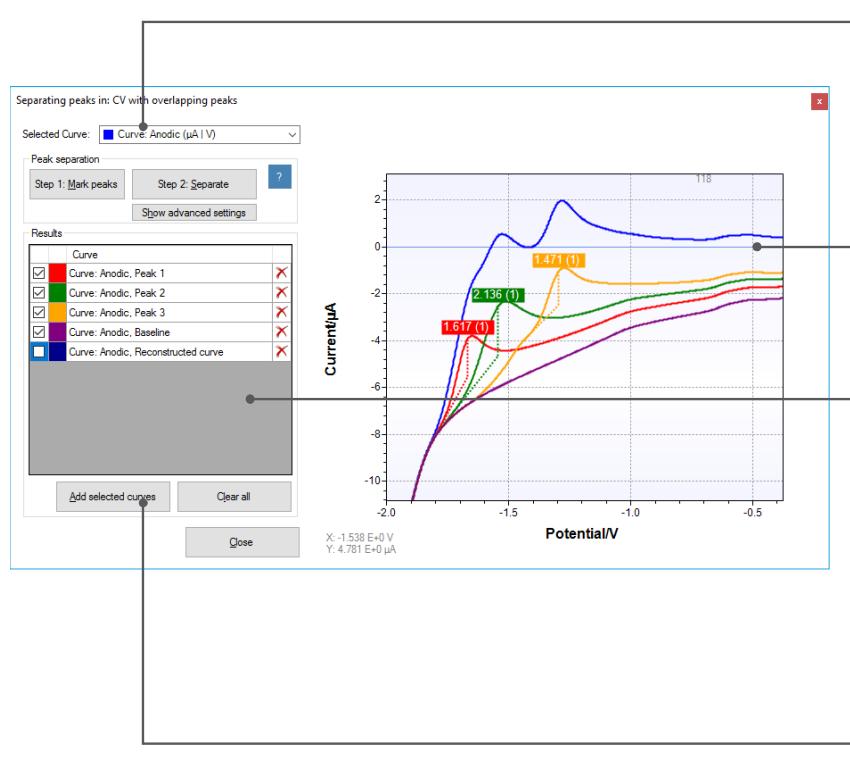
Alternatively, it single points can be (de)selected by holding down the control button on your keyboard and left clicking on the outlier with your mouse. Left clicking on that point again while holding down control will reselect it. While holding down both the control button and the left mouse button it is possible to (de)select all points in the specified area.



Click accept to add the new curve based on the selection to the current session.

6.9 Separating overlapping peaks

Overlapping peaks in a cyclic or linear sweep voltammetry measurement can be separated using the peak separation window. The peak separation window can be opened from the toolbar above the plot . Peak separation works best for reversible peaks, the amount of overlap and number of overlapping peaks determine how well the peaks can be separated from each other (separating peaks is not guaranteed to work properly in all cases).



Dropdown list from which you can select the anodic or cathodic parts of the curves in the measurement.

Table and plot containing the results of the peak separation.

The blue curve is the original curve (highlighted in the top left).

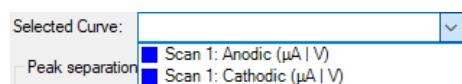
The red, green and yellow curves are the separated peaks.

The purple curve is the baseline and the dark blue curve is a reconstruction of the original curve using the three separated curves.

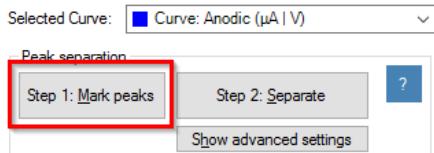
Adds the resulting curves to the main window.

6.9.1 Separating peaks

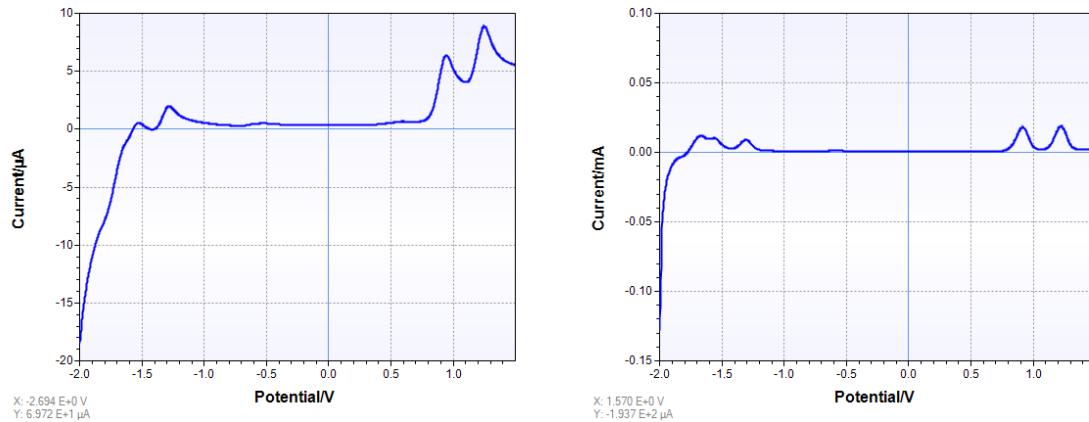
Select the measurement that contains the curve that you would like to separate in the [legend of the Plot tab](#) on page 148 in the main window. Then the peaks or levels data window  should be opened and the  separate overlapping peaks button clicked. Select the anodic or cathodic curve that you would like to separate peaks in from the dropdown menu in the top left corner of the peak separation window.



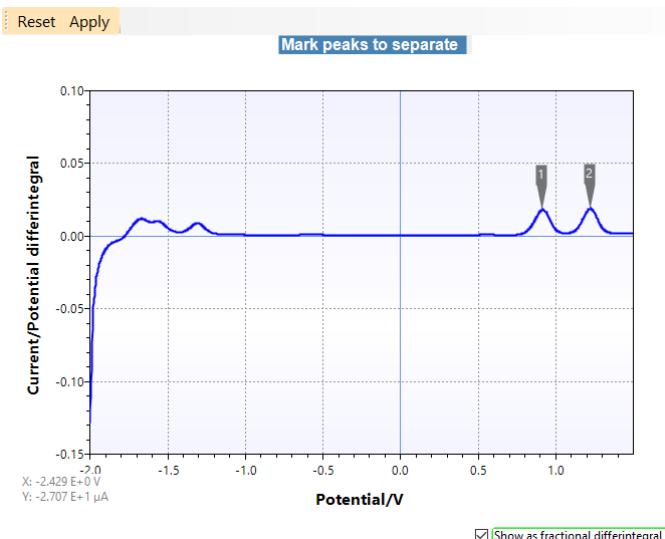
Before you can separate the overlapping peaks, they should be marked in the plot to the right. Click on mark peaks, this will change the view in the plot to the different integral view. The peaks are still at approximately the same potential, however, in this view they are more distinct.



First step: Mark peaks to separate

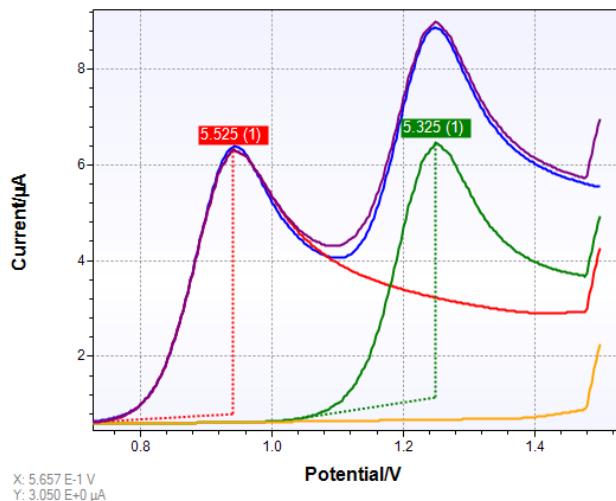


Once you selected the peaks you want to separate click on apply. **Tip: you can zoom in by scrolling the mouse and pan using the right mouse button.** Selecting peaks that do not overlap will not work and selecting more than three peaks takes much longer to compute.



Marking the peaks in a curve

Once the peaks have been marked they can be separated by clicking on the respective button. This will change the plot back to the regular view and display the results.



Results of the peak separation. Blue curve: original curve. Red and green curves: curves of the peaks that were separated. Yellow curve: baseline curve (both peaks removed). Purple curve: sum of the separated curves.

The results are also shown in the table on the left. This table can be used to hide/show and show the peaks corresponding curves, select curves to add to your measurement and to delete curves (by clicking on the red cross).

Results		
	Curve	
<input checked="" type="checkbox"/>	Scan 1: Anodic, Peak 1	
<input checked="" type="checkbox"/>	Scan 1: Anodic, Peak 2	
<input checked="" type="checkbox"/>	Scan 1: Anodic, Baseline	
<input checked="" type="checkbox"/>	Scan 1: Anodic, Reconstructed curve	

Add selected curves Clear all

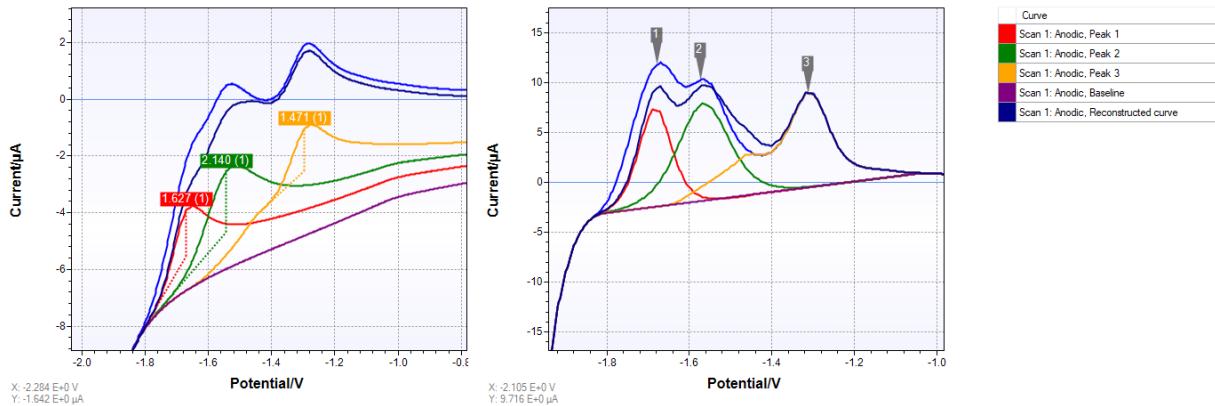
The results can be added to your measurement in the main Session manager (the legend in the main window showing all available session data) using the add button below the table. The clear button removes all the results from the table and the plot.

6.9.2 Advanced settings

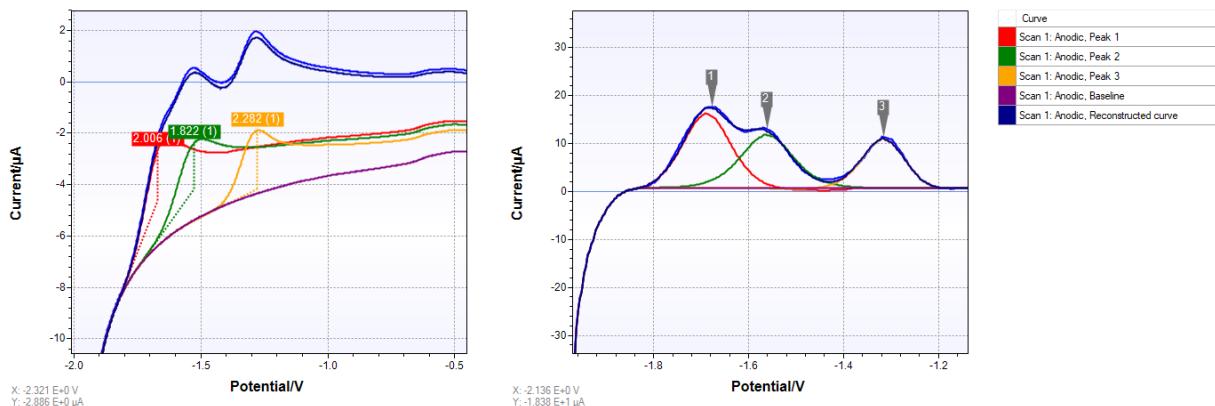
In some cases, the separation of the peaks can be improved by adjusting the default settings in the advanced settings.

Advanced peak separation settings	
Fractional derivative order (Value from -2.0 to 2.0, default 0.5)	<input type="text" value="0.5"/>
Moving average filter window size (No filtering at 0)	<input type="text" value="2"/>
Peak model	Reversible

The order of the differintegral is specified in the fractional derivative order text box. By default the 0.5 semi-derivative is used to separate the peaks from each other. The peaks are best separated when they do not or barely overlap in the differintegral view and when the beginning and end of the peaks are on the same level / the baseline is not slanted.



Results of the peak separation with the default settings. Notice that the baseline (purple curve) is slanted in the differintegral view (right), this often leads to sub optimal results (the purple curve deviates from the original blue curve).



Increasing the order of the fractional derivative to 0.61 improves the separation of the peaks significantly.

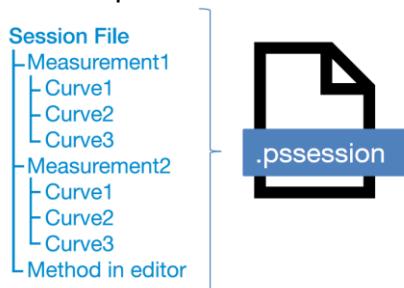
The show as differintegral check box toggles between the regular and differintegral view. Toggling back to the differintegral view is useful when optimizing the separation of the peaks.

The window size of the moving average filter is used to prevent noise from interfering with the peak separation. The separation works best with smooth curves, however there is a trade-off between large and small window sizes. Large window sizes can result in an underestimation of the peak height and small window sizes can result in errors when separating the peaks.

Finally, depending on the type of reaction switching between the reversible and irreversible peak model can improve the peak separation. The reversible peak model works best with peaks that are symmetrical in the differintegral view and the irreversible peak model works best with asymmetrical peaks (peaks where the second half is steeper).

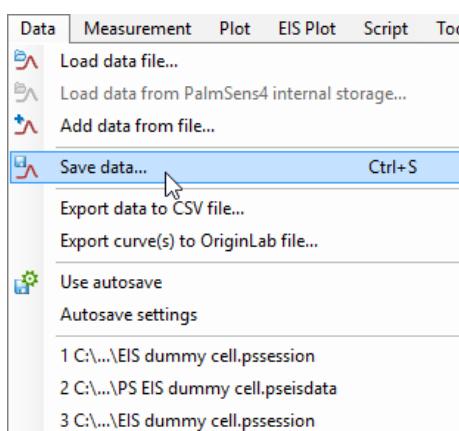
6.10 Saving data

All measurements and curves that are present in the Plot and EIS Plot tabs and the method present in the Method Editor can be saved to a single ‘.pssession’ file.

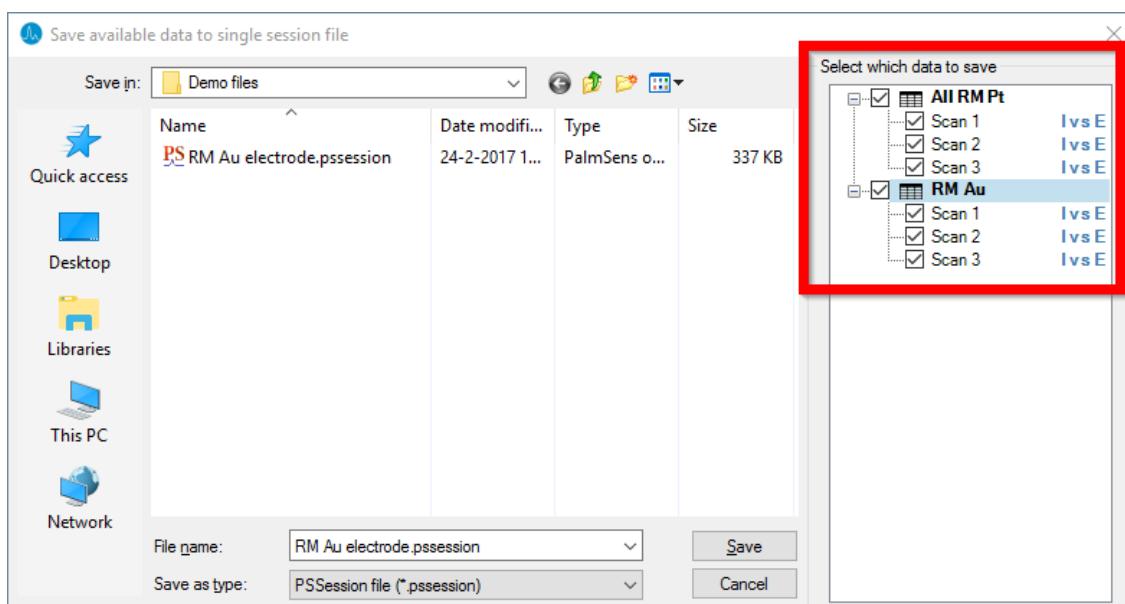


A PSSession (.pssession) file contains basically all the data available at a given moment.

Data is saved via the menu: ‘Data’ → ‘Save data...’



Data menu



Save Data dialog for saving to a PSSession file

In the tree at the right side of the Save Data dialog window data can be selected that will be included in the PSSession file.

CSV

Files can also be exported to a CSV (Comma Separated Values) format. This is a common file format supported by many applications like Excel, OpenOffice Calc and Origin.

OriginLab

Files can be exported to a native .OPJ file for use in Origin.

See also section Files

6.10.1 Legacy curve files

Since the release of PSTrace v5 and MultiTrace v4, the following file formats can no longer be used for saving data:

.pss, .pst, .mux, .psd and .pseisdata.

The new .pssession file format has replaced the need for keeping these different formats.

All these old file formats can still be loaded in PSTrace v5 and MultiTrace v4.

See also section Files

6.11 Exporting curves

PSTrace allows curves to be exported to third party software with a single click.



Export options shown in the Plot menu

Excel

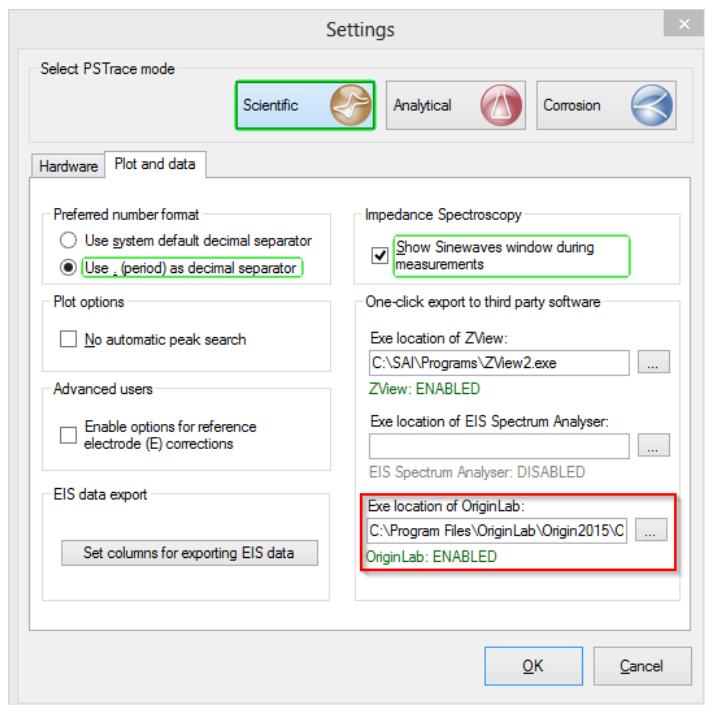
If Excel version 2007 or newer is installed an 'Open in Excel' menu item is added to the Plot menu and a extra button is added at the left hand side of the Plot. Clicking the menu item or the button will open an Excel window and automatically export the data of all visible curves to the spreadsheet. A graph will be generated or all exported data. The template for the graph can be found in the installation folder of PSTrace.

Origin

If Origin is installed an 'Open in Origin' menu item is added to the Plot menu and an extra button is added at the left-hand side of the Plot. Clicking the menu item or the

button will open an Origin window and automatically export the data of all visible curves to a separate book and graphs will be generated for each exported curve.

If the button is not showing and Origin is installed, open the General settings window in the menu (Tools → General settings...) and check in the ‘Plot and data’ tab if the location for Origin is properly set.



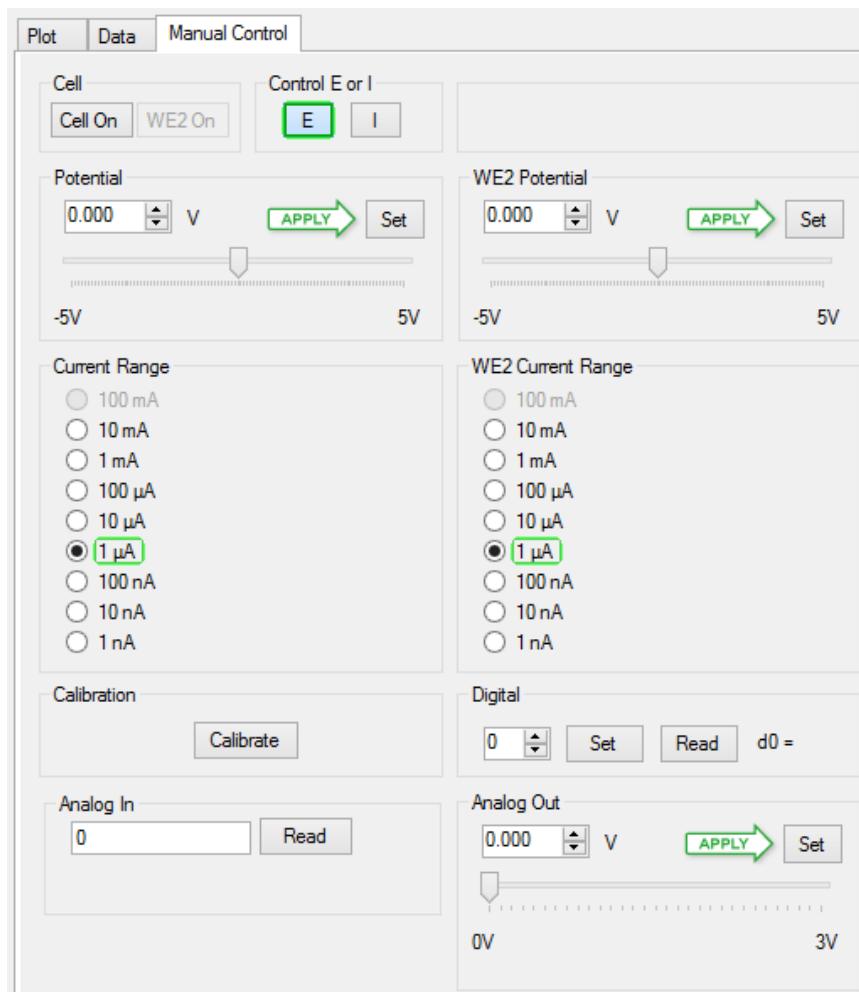
Location for Origin specified in the Settings window.

7 Manual Control

The Manual Control tab can be used to control PalmSens or EmStat directly.

7.1 Manual Control tab

The Manual Control tab shows the following options to control PalmSens or EmStat directly.



Manual Control tab

Cell On is used to connect the sensor to PalmSens. If the cell is off only the potential is measured. If the BiPot module is present, WE2 can also be switched on or off. Please refer to the paragraph ‘Noise’ in the chapter ‘Measuring’.

Control E or I is used to set the mode of PalmSens. Selecting E is to set the potential and to read the current response, i.e. the instrument is used as a potentiostat. Selecting I will allow to control the current and to read the potential, i.e. the instrument is set as galvanostat.
In short: Potentiostat (E) or Galvanostat (I).

Potential or Current allows to set either one of these depending on the set mode with ‘Control E or I’. The scrollbar and textbox are used to specify the potential or the current.

Current Range specifies the sensitivity of the measurement of the current. The resolution of the measurement is equal to 0.001 of the current range. Measurements are optimal if their value is between 0.1 and 1.8 of the applied current range.

Multiplexer Channel is enabled if the use of a multiplexer is enabled in the Settings window. In this frame the channel which is used for control and measurement can be selected.

The **WE2 Potential** and **WE2 Current Range** frames are visible if BiPot is enabled in the Configuration window.

The **Calibrate** button is used to calibrate PalmSens or EmStat. This can be done when the measured potential differs more than 0.3% +/- 0.003 V from the specified potential (when the cell is switched on in E control mode!).

Checking **Stirrer On** sets the digital ports d0 to high and d1 to low (and vice versa) of the auxiliary port of PalmSens or the I/O pins on the EmStat board.

Analog In reads the voltage applied on miniDIN pin 7 or the corresponding pin on the EmStat board.

Analog Out set a specific potential between 0 and 4.095 V to pin 8 of the miniDIN port or the corresponding pin on the EmStat board.

In case the ‘Speed control’ for the stirrer is enabled, Analog Out controls the stirrer speed.

Use battery power only is visible when a PalmSens3 is connected. This forces the PalmSens3 to work on the battery when connected to a PC with a USB cable. This may reduce noise.

8 Analytical mode



The analytical extension of program PSTrace for Voltammetric Analysis provides the possibility to do quantitative analysis by means of:

- Standard addition
- Using a calibration curve

8.1 Supported techniques

The supported electrochemical techniques for voltammetric analysis are shown in the Technique list:

- Linear Sweep voltammetry
- Differential Pulse voltammetry
- Square Wave voltammetry
- Chronopotentiometric Stripping

PSDummyCell_LSV.psmethod

Measurement		Peaks
Technique:	<input style="width: 150px; height: 25px; border: 1px solid #ccc; border-radius: 5px; padding: 2px 10px; margin-bottom: 5px;" type="button" value="Linear Sweep Voltammetry"/> ?	
Notes:	<input style="width: 150px; height: 25px; border: 1px solid #ccc; border-radius: 5px; padding: 2px 10px; margin-bottom: 5px;" type="text" value="Analytical techniques"/> <input style="width: 25px; height: 25px; border: 1px solid #ccc; border-radius: 5px; background-color: #e0f2f1; margin-bottom: 5px;" type="button" value="Edit"/>	
Select current:	<input style="width: 50px; height: 25px; border: 1px solid #ccc; border-radius: 5px; padding: 2px 10px; margin-right: 10px;" type="button" value="100 pA"/> <input style="width: 50px; height: 25px; border: 1px solid #ccc; border-radius: 5px; padding: 2px 10px; margin-right: 10px;" type="button" value="1 nA"/> <input style="width: 50px; height: 25px; border: 1px solid #ccc; border-radius: 5px; padding: 2px 10px;" type="button" value="100 mA"/>	

List showing available techniques

The other available techniques for PalmSens or EmStat are not listed when PSTrace is set in Analytical mode.

8.2 Setting up parameters

When the program is set to ‘Analytical mode’ in the Settings window or the top left of the main window, new tabs called ‘Analysis’ and ‘Analytical result’ are shown. The ‘Analysis’ tab in the method editor is used to enter analysis parameters beforehand for a series of measurements. The ‘Analytical result’ tab is used to show the standard addition or calibration curve(s) and the calculated peak heights as well as the obtained concentration, in this tab the analysis parameters of existing measurements can also be edited. The parameters of the standard solution as well as the analyte(s) or component(s) to be determined can be defined in the ‘Analysis settings’ group in the top left of the tab. The program allows measurement of up to four analytes using up to four standard solutions.

PSTrace allows subtraction of a separately measured blank voltammogram. This blank voltammogram can be measured before the other curves or can be loaded as data file.

Analysis parameters can be entered before a measurement in the ‘Analysis’ tab of the method editor or edited for existing measurements in the ‘Analysis settings’ group of the ‘Analytical result’ tab.

The screenshot shows two side-by-side windows of the PSTrace software. The left window is the 'Analysis' tab in the method editor, and the right window is the 'Analysis settings' group in the Analytical result tab.

Analysis tab (Method Editor):

- Determination:** Standard addition (radio button selected).
- Concentration unit:** mg/l (dropdown menu).
- Added volumes in µl:** (radio button selected).
- Table:**

	Analyte	Analyte	Analyte	Analyte
► Id	Cu	Pb	Cd	Zn
Sol nr.	1	1	1000	1000
Conc	10	10	10	10
St. 1	10	10	10	10
St. 2	10	10	10	10
St. 3	10	10	10	10
St. 4	10	10	10	10
- Volumes:**
 - Sample volume (ml): 10.0
 - Cell volume (ml): 10.0
- Peak Settings:**
 - Use value: height (radio button selected).
 - Table:

	E peak	Auto	E left	E right
► Cu	-0.05	<input checked="" type="checkbox"/>	0	0
Pb	-0.4	<input checked="" type="checkbox"/>	0	0
Cd	-0.6	<input checked="" type="checkbox"/>	0	0
Zn	-1	<input checked="" type="checkbox"/>	0	0
 - Auto peak search window around E peak (V): 0.1
 - For minimum peak width and height: see tab 'Peaks'

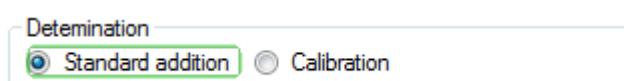
Analysis settings (Analytical result tab):

- Determination:** Calibration (radio button selected).
- Concentration unit:** ppm (dropdown menu).
- Concentration in cell:** (radio button selected).
- Table:**

	Analyte	Analyte	Analyte	Analyte
► Id	Cu	Pb	Cd	
St. 1	25	100	100	10
St. 2	125	300	300	10
St. 3	100	100	10	10
St. 4	10	10	10	10
- Peak Settings:**
 - Use value: height (radio button selected).
 - Table:

	E peak	Auto	E left	E right
► Cu	-0.3	<input checked="" type="checkbox"/>	9999	9999
Pb	-0.6	<input checked="" type="checkbox"/>	9999	9999
Cd	-0.8	<input checked="" type="checkbox"/>	9999	9999
		<input type="checkbox"/>		
 - Auto peak search window around E peak (V): 0.15
 - For minimum peak width and height settings see menu: Plot » Peaks » Peak Data

Analysis tab in method editor and the analysis settings group in the Analytical result tab.



The mode of the determination is either **Standard addition** or **Calibration**. The content of the table is either **Added volumes** or **Concentration in the cell**.

Analyses

Concentration unit: ppm

Added volumes in μl Concentration in cell

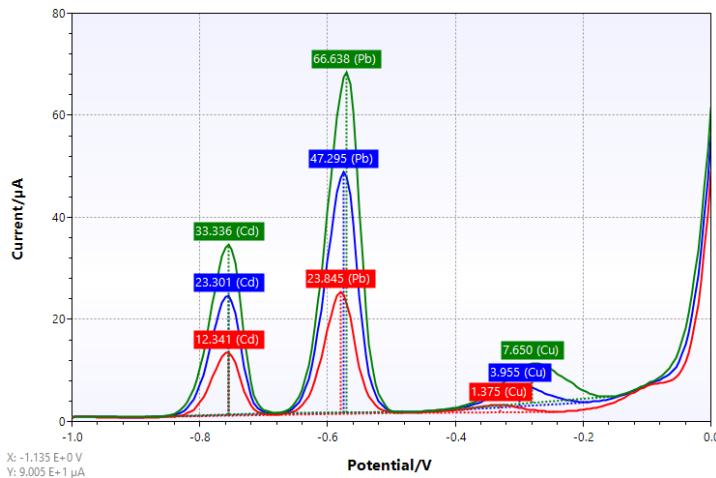
	Analyte 1	Analyte 2	Analyte 3	Analyte 4
► Id	Cu	Pb	Cd	
Sol nr.	1	2	3	4
Conc	10	10	10	10000
St. 1	50	50	10	10
St. 2	50	50	10	10
St. 3	100	100	10	10
St. 4	10	10	10	10

Volumes added for each analyte

The concentration unit has to be selected from the given list. Please note that the selection of the concentration unit does not influence the calculations of the concentration from the curves. So changing the unit does not change the numerical results, but the unit of the result.

The column **Id** is used to specify which analyte(s) or component(s) has to be determined, e.g. Cd, Pb, Cu, antibiotics, pesticides. If an Id field is empty, the column is marked in grey and the specified values are not used.

The Id's of the peaks are also given in the voltammetric plots in the peak values.



Peaks found for each Id showing in the Plot tab

Specifying added volumes

If the **Table content** is **Added volume in μl** then the fields **St. n** of the table contains the added volumes of standard solutions in μl for up to 4 additions. In the conc line the concentration given in the specified concentration unit of each analyte in the standard solution must be set. In case more than 1 analyte is measured, a standard solution may

contain 1 or more analytes, if they have the same concentration. If an analyte is added from another solution or has another concentration than the previous, a new **Solution number (Sol nr.)** has to be specified.

So if for example only 1 analyte is determined, the Sol nr. can be 1. In case 4 analytes are determined and four different standard solutions are used, the Sol. nr values can be different so for instance 1, 2, 3 and 4. If a standard solution contains more than 1 analyte, the next row is automatically set to the first value.

Specifying concentrations in cell

If concentration in cell was chosen in the Analytes section, the absolute concentration of analyte in the cell according to the specified unit needs to be put into the table assuming that the original sample contained no analyte.

The cell volume is used to correct peak heights or peak areas for dilution effects due to addition of standard solutions. So the cell volume is the total volume in which the measurement is performed, which can for instance be the sample + separate base electrolyte. If the cell is filled with sample solution only then the cell volume and sample volume are equal. This dilution factor due to the standard additions is shown in the 'Analytical result' window.

Peak settings

Three different peak features can be used for determination:

- Peak height
- Peak area
- And the sum of the peak's slopes

Peak settings				
	E peak	Auto	E left	E right
► Cu	-0.3	<input checked="" type="checkbox"/>	0	0
Pb	-0.6	<input checked="" type="checkbox"/>	0	0
Cd	-0.8	<input checked="" type="checkbox"/>	0	0
		<input type="checkbox"/>		

Auto peak search window around E peak (V):

Peak locations for each analyte with options for manual baselines

The column 'E peak' gives the expected peak potential. If a peak is found in the peak window E peak +/- Peak window, it will be assigned to the given Id.

If a manual baseline should be used for the specific analyte, E left and E right can be specified by entering values in the corresponding cells. As soon as the values are entered the peaks will be updated in the plot window. It is also possible to draw a

baseline manually using the manual peak options in the Plot toolbar (see section **Marking peaks manually**)

The ‘Auto peak search window’ determines the maximum width of the peak. The peak for each analyte will be searched in E peak +/- Peak window.

If a peak is not assigned, the peak potential is wrong, or the peak window is too narrow; change the peak parameters in the Peaks tab on the left and click the **Mark peaks** button to apply the new peak parameters.



Mark peaks button

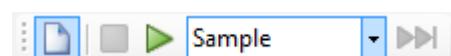
The sample volume is needed in order to calculate the concentration of the analyte(s) in the sample. The program first calculates the concentration of the analyte(s) in the cell. These values are shown in the tables of **Analytical result** under **cCell**. The value of the concentration in the sample is simply found by multiplying **cCell** by the factor ‘Cell volume / Sample volume’. Thus the sample volume cannot exceed the cell volume. Please note that in case the addition of the standard solutions have a negligible effect on the cell volume, the final cell volume is not relevant.

	cSample ppm	cCell ppm	CorC	Slope
► Cu	1.867E-1	1.697E-2	0.9886	7.023E+1
Pb	5.544E-1	5.040E-2	0.9976	4.853E+2
Cd	1.152E-1	1.047E-2	0.9996	1.190E+3

Table showing results of each analyte

8.3 Running a measurement

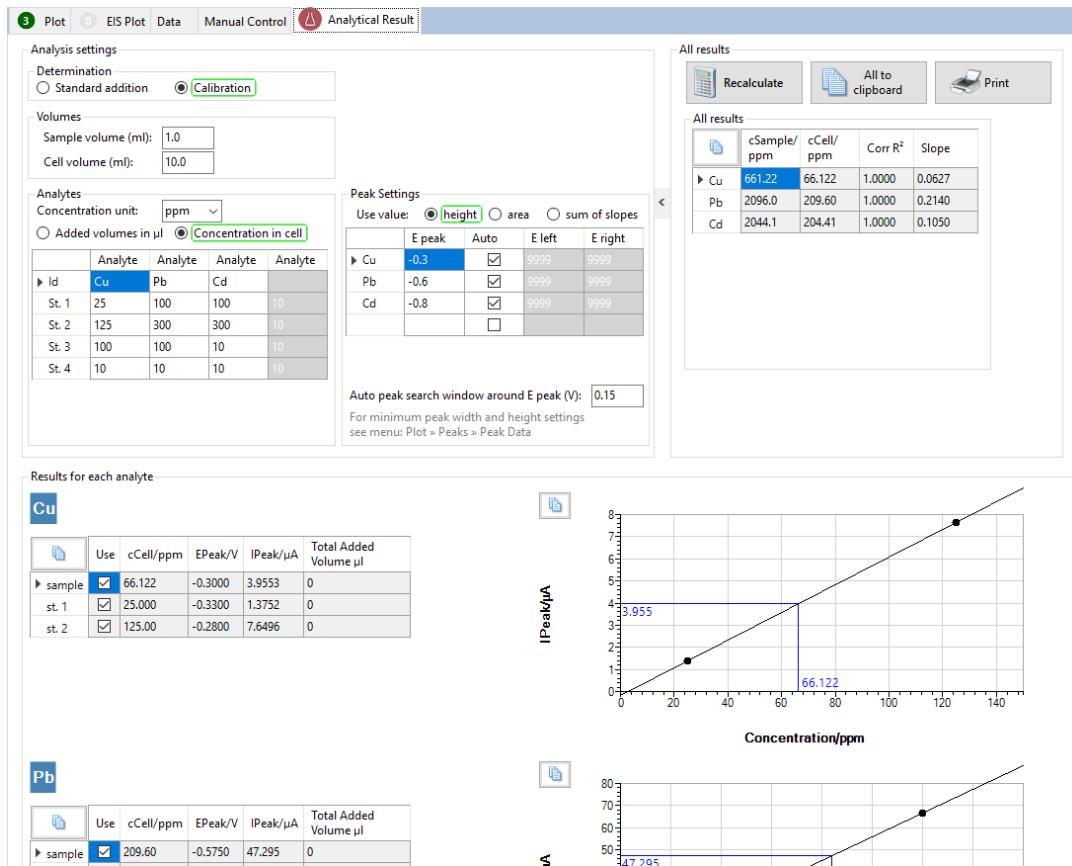
Before starting a new determination, click the **New** button in the toolbar, or select ‘**New analysis**’ in the Analysis menu.



Analysis measurement toolbar

For a determination, a ‘Sample’ and at least one ‘Standard’ curve is required. The type of curve measured after pressing the green ‘Start’ button is shown as selected item in the list next to this button. If blank correction is required, the ‘Blank’ solution also has to be measured or the blank curve has to be loaded from file. After a blank curve has been measured, it can be saved as blank file by using ‘Save blank’ in the Analysis menu.

The ‘Plot’ tab shows the voltammograms and the ‘Analytical results’ tab gives the calibration or standard additions plots. Please note that the correlation coefficient for linear least squares lines are given. Also the slope of the calibration or standard addition curves are shown. This value of the slope is an important value for the sensitivity of the electrode or sensor.



Analytical Result tab

Standard addition measurement

A determination by means of standard addition requires at least two curves: sample and one standard addition. As soon as both curves are available, the analytical results can be obtained in the window ‘Analytical result’. It is advised to use at least two additions in order to check the linearity of the curve. The standard additions have to be done before a standard curve is measured.

Measurement by using a calibration curve

The calibration curve is measured or loaded before a sample is measured. If only one standard is measured, the calibration curve is calculated with $c=0$ and $I_{peak}=0$ as second point.

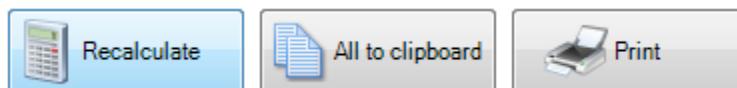
After the sample has been measured, the calibration plot will show lines from which the concentration is obtained.

Using Blank subtraction

See chapter Using Blank subtraction.

8.4 Result analysis

After measurements of the curves, parameters in the Analysis window can be changed if required. New calculations of the analytical results are shown after pressing the button **Recalculate**.



Recalculate button

It is possible correct for a blank curve and also to undo blank correction afterwards by using the ‘Use blank’ box.

Results of measurements can be stored by using the ‘Analysis’ menu. Results can be printed with the **Print button** in the ‘Analysis Result’ window or copied to another program (e.g. Excel) by using the button **All to clipboard**.

If a point in the calibration or standard addition curve has to be neglected, the corresponding checkbox in the ‘Results for each analyte’ window can be used.

	Use	cCell/ppm	EPeak/V	IPeak/µA	Total Added Volume µl	Dilution factor
sample	<input checked="" type="checkbox"/>	1.940E+1	-0.33	1.395E+0	0	1
st. 1	<input type="checkbox"/>	OK E+1	-0.3	3.948E+0	0	1
st. 2	<input checked="" type="checkbox"/>	1.000E+2	-0.28	7.622E+0	0	1

Uncheck to remove this value from the linear plot

8.4.1 Standard Addition

The Standard Addition Method is performed in the sample’s matrix and the influences of other species on the sensitivity are already taken into account. A known volume of the sample and a known volume of the supporting electrolyte are added to the cell. The measurement is performed. A fixed volume of standard solution with a known

concentration is added. The measurement is repeated. These two steps are repeated until a sufficient amount of standard additions have been measured. From these values a linear regression is calculated. The zero point of this function is the analyte's concentration in the cell.

To create the points for the linear regression, the concentration of the artificially added analyte in the cell $cCell$ must be known after each addition of standard. For the measurement of the sample no standard was added, so the value is 0. For the other measurements $cCell$ is calculated as follows:

$$cCell = \frac{\text{Total Added Volume in } \mu\text{L} * \text{Conc}}{\text{Cell Volume} + \text{Total Added Volume in } \mu\text{L}}$$

Conc is the concentration of the standard solution.

After the IPeak is plotted versus $cCell$ the slope of the linear regression is calculated with the general equation:

$$\text{Slope} = \frac{\sum(x - \bar{x})(y - \bar{y})}{\sum(x - \bar{x})^2}$$

The IPeak values are y and \bar{y} is the average of all known y values. The $cCell$ values are x and \bar{x} is the average of all known x . The intersection of the linear regression is:

$$\text{Intersection} = \bar{y} - \text{Slope} * \bar{x}$$

With these two parameters you can calculate the null of the curve. The concentration of $cCellSample$ is the null * (-1). This means:

$$cCellSample = \frac{\text{Intersection}}{\text{Slope}}$$

For the concentration of the Analyte in the Sample $cSample$, the dilution by the supporting electrolyte needs to be considered:

$$cSample = \frac{cCellSample * \text{Cell volume}}{\text{Sample volume}}$$

8.5 Example data files

The program comes with two example files. These files are stored in the default PS Data folder:

“My Documents\PSData\Analytical mode examples”.

You can load these in PSTrace using the menu ‘Data → ‘Load data file...’

The file “Standard Addition Example.psession” shows a determination of some heavy metal ions in a nickel galvanic bath. This determination is based on standard. The measurement was done by adding 1 ml sample to a base electrolyte with a final cell volume of 10 ml and using 3 different standard solutions.

The file “Calibration Example.psession” shows a determination by using a calibration curve. In this file the table ‘Analysis’ contains the concentration values of the analytes in the cell.

9 Corrosion mode

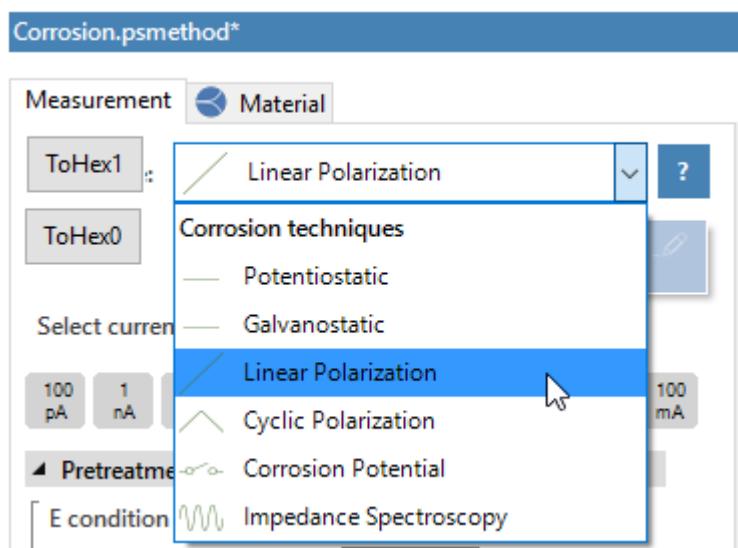


The corrosion extension of program PSTrace provides the possibility to do specific types of corrosion measurement and analysis of obtained curves.

9.1 Supported techniques

The available techniques in the Corrosion mode are:

- Potentiostatic (apply constant potential)
- Galvanostatic (apply constant current)
- Linear Polarization (potential sweep)
- Cyclic Polarization (bi-directional potential sweep)
- Corrosion Potential (open circuit potential)
- Impedance Spectroscopy



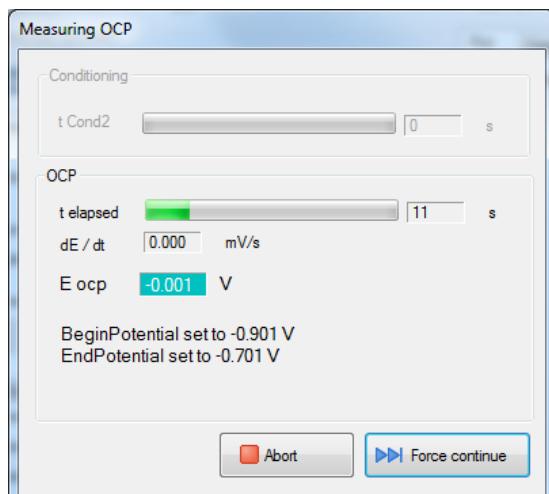
List showing available techniques

The other standard available techniques for PalmSens or EmStat are not listed when PSTrace is set in the Corrosion mode.

9.2 Running a measurement

The sequence of a measurement is:

1. If $t_{Cond1} > 0$ s then E_{cond1} is applied for t_{Cond1} s.
2. If $t_{Cond1} > 0$ s then E_{cond2} is applied for t_{Cond2} s.
3. The cell is switched off if the measurement of E_{oc} or OCP is required.
4. Now the value of E_{oc} is continuously measured until either ‘Max. OCP time’ is reached OR until the stability criterion is met OR the button ‘Force continue’ is pressed.
5. Now the cell is switched on at the value of E or E_{begin} for ‘ t_{eq} ’ s, after which the actual measurement starts.



Waiting for the OCP to meet the stability criterion.

Measure versus OCP

Corrosion measurements can be done by specifying the potential scan with respect to the Open Circuit Potential OCP or with absolute values versus the reference electrode. In case one or more potentials are specified with respect to the OCP, the open circuit potential has to be determined before the actual measurement is done. This OCP measurement requires a variable time, which is determined by the drift of the open circuit potential and the maximum time to measure the OCP value. The OCP value is set as soon as the drift is lower than the specified value for the ‘Stability criterion’ or when the ‘t Max. OCP’ has elapsed.

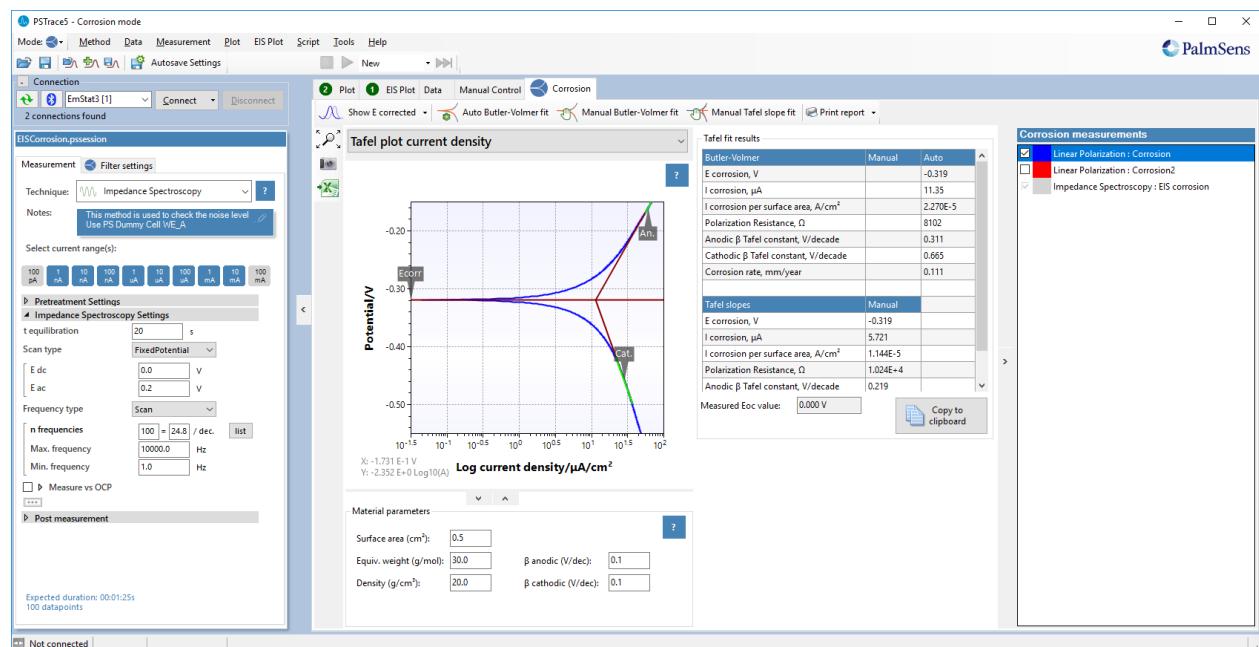
<input checked="" type="checkbox"/> Measure vs OCP		
<input checked="" type="checkbox"/> E begin versus OCP		
<input checked="" type="checkbox"/> E end versus OCP		
t Max. OCP	1.0	s
Stability criterion	0.1	mV/s

OCP parameters

It is possible to condition the electrode or the corrosion sample before this OCP is obtained. For this purpose two potentials can be applied: ‘E cond1’, during a period of ‘t cond1’ and ‘E cond2’ during a period of ‘t cond2’. In case the value of ‘t cond’ is set to 0 s, the corresponding conditioning potential is not applied. So if both values for ‘t cond’ are 0, the electrode is not conditioned at all.

9.3 Result analysis

The Corrosion tab in the plot window is used for analysis of linear polarization and electrochemical impedance spectroscopy measurements. The supported measurements are shown in the legend on the right and the material settings of the selected measurement are shown on the left.



9.3.1 Setting up material parameters

The material parameters required for analysis can be entered before the measurement in the Method Editor or after the measurement in the “Corrosion” tab.

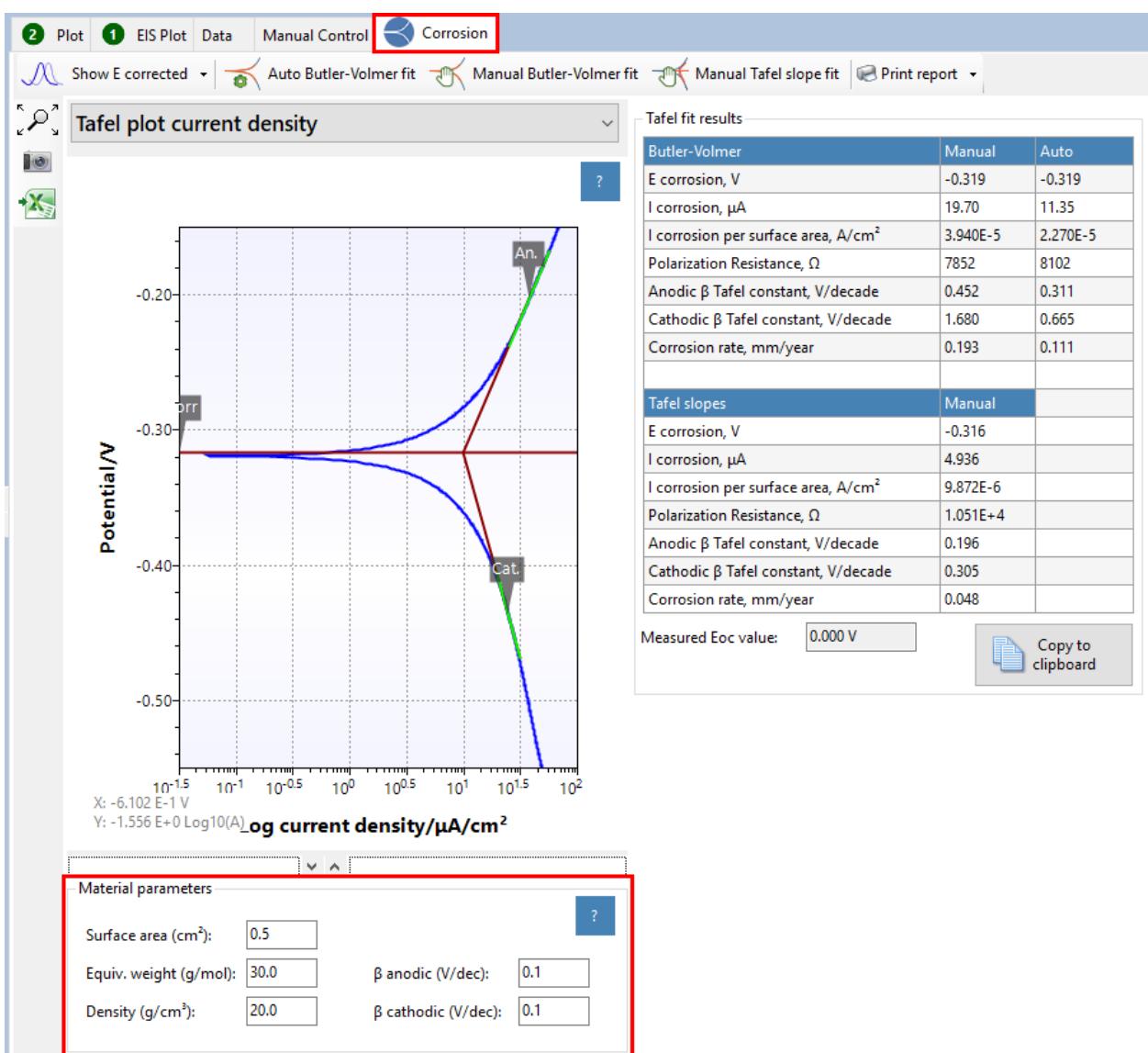
Measurement **Material**

Surface area (cm ²):	0.001
Equiv. Weight (g/mol):	0.0
Density (g/cm ³):	0.1
β anodic (V/dec):	0.1
β cathodic (V/dec):	0.0
Data smoothing (Savitzky-Golay):	0: spike rejection

Tab with Material properties in the Method Editor

The values set in the Material tab of the Method Editor are copied to the tab for Corrosion analysis when a measurement is started.

In the Corrosion tab, the material parameter input fields are beneath the plot.



The material parameters are required to determine the corrosion rate. Linear polarization measurements require surface area, equivalent weight and density and

impedance measurements also require the anodic and cathodic Tafel slopes, β_{anodic} and $\beta_{cathodic}$.

- Surface area is the area of the sample in cm².
- Equivalent weight is the equivalent mass of one mole of the sample material in g/mol.
- Density is the density of the sample material in g/cm³.
- β_{anodic} and $\beta_{cathodic}$ are the Tafel slope parameters for the sample material, these can be determined from a linear polarization measurement or from literature.

9.3.2 Linear polarization

Linear polarization is typically used to study the corrosion response of metallic coatings. The following analysis techniques are supported for the estimation of the corrosion rate based on linear polarization measurements:

- Auto Butler-Volmer fit: Fitting the Butler-Volmer model over an automatically detected range.
- Manual Butler-Volmer fit: Fitting the Butler-Volmer model over a manually selected range.
- Manual Tafel slope fit: Fitting Tafel slopes in the linear regions of the anodic and cathodic slopes.

Note: To achieve an accurate estimation of the corrosion rate it is recommended to use a measurement with at least one linear Tafel slope that ranges over one decade in current density. Additionally, the distance between the Tafel slope and the corrosion potential should at least be 50 mV.

The results of these analysis techniques are presented in the Tafel fit results table.

Tafel fit results		
	Manual	Auto
Butler-Volmer		
E corrosion, V	-0.319	-0.319
I corrosion, μA	13.17	13.99
I corrosion per surface area, A/cm^2	2.635E-5	2.797E-5
Polarization Resistance, Ω	7926	7891
Anodic β Tafel constant, V/decade	0.347	0.358
Cathodic β Tafel constant, V/decade	0.784	0.879
Corrosion rate, mm/year	0.129	0.137
Tafel slopes	Manual	
E corrosion, V	-0.312	
I corrosion, μA	5.874	
I corrosion per surface area, A/cm^2	1.175E-5	
Polarization Resistance, Ω	1.006E+4	
Anodic β Tafel constant, V/decade	0.212	
Cathodic β Tafel constant, V/decade	0.380	
Corrosion rate, mm/year	0.058	

Measured Eoc value:

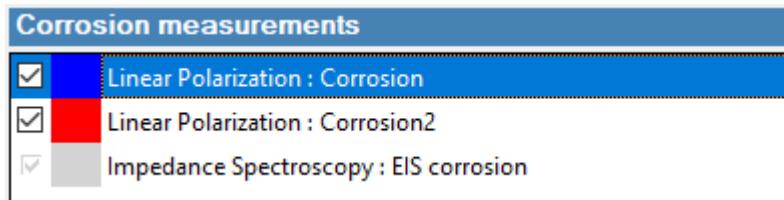


- The corrosion potential (E corrosion) is the potential at which the anodic and cathodic reaction rates are equal. The measured current approaches zero at the corrosion potential, because all the electrons released by the dissolving of the metal are consumed by reduction reactions. For the Butler-Volmer techniques the corrosion potential is determined as the potential where the log the measured current is the smallest. In the Tafel slope method the corrosion potential is the potential where the anodic and cathodic Tafel slopes intersect.
- The corrosion current (I corrosion) is a measure of the rate of corrosion, measuring it directly is not possible. The corrosion current can be estimated the current at which the Tafel slopes intersect or by fitting the Butler-Volmer equation on a linear polarization measurement.

- $$I = I_{corrosion} \left(e^{\left(\frac{2.303(E - E_{corrosion})}{\beta_{anodic}} \right)} - e^{\left(\frac{-2.303(E - E_{corrosion})}{\beta_{cathodic}} \right)} \right)$$
- β_{anodic} and $\beta_{cathodic}$ are the Tafel slopes, these represent the change in Volts per decade of current in the Tafel plot.
- When plotting current over potential a linear slope is equals resistance (i.e. $R=U/I$). The slope close to the corrosion potential is approximately linear, this is referred to as the polarization resistance. The polarization resistance is inversely proportional to the corrosion current, assuming that the Tafel slopes are constants (Stern-Geary equation).
- $$I_{corrosion} = \frac{\beta_{anodic} \cdot \beta_{cathodic}}{R_{polarization}(\beta_{anodic} + \beta_{cathodic})}$$
- The corrosion rate in mm/year can be calculated according to the standard practice described in the ASTM Standard G 102. To calculate this an estimation of corrosion current is needed as well as the following [material parameters](#) on page 189: equivalent weight (EW) in g/mol, the density (d) in grams/cm³, and the sample area (A) in cm² of the study sample. Combined with a constant (K) defined by the ASTM (3272 mm/(amp*cm*year)) this information is used to determine the corrosion rate in mm/year.
- $$\text{Corrosion Rate} = \frac{I_{corrosion} \cdot K \cdot EW}{d \cdot A}$$

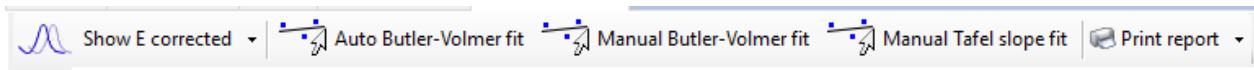
Selecting a curve for corrosion analysis

On the right-hand side of the screen is a legend which contains all compatible corrosion measurements. To perform a Butler-Volmer or Tafel slope fit select a Linear Polarization measurement from the legend. The checkbox in front of the measurements indicate whether they are also visible in the plot window.



Performing an automatic Butler-Volmer fit

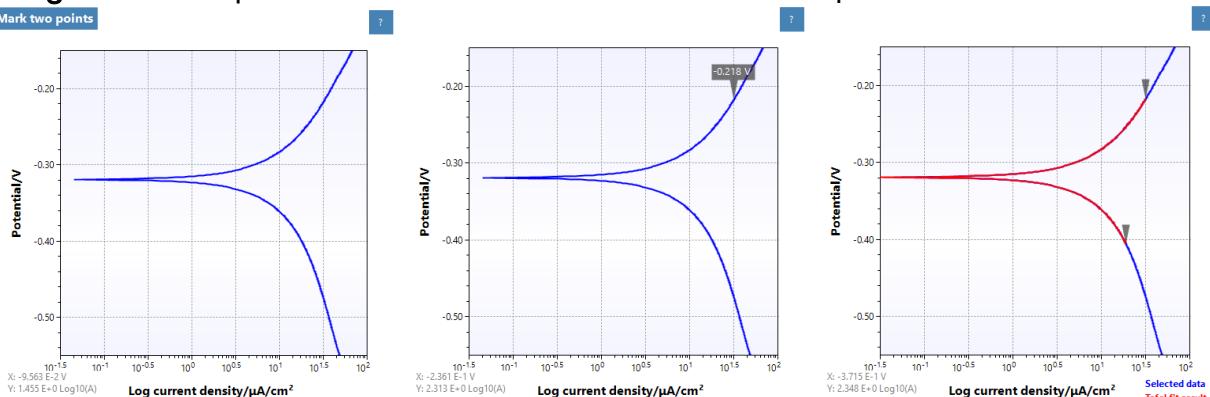
The auto Butler-Volmer fit is automatically applied after selecting a Linear Polarization curve from the legend and after changing the value of one of the material parameters. Alternatively, clicking on the Auto Butler-Volmer fit button in the toolbar above the plot also applies the fit.



Performing a manual Butler-Volmer fit

By selecting the Manual Butler-Volmer fit from the toolbar above the plot the range for the Butler-Volmer can be set manually.

Usage: click two points on the curve to mark start and end point

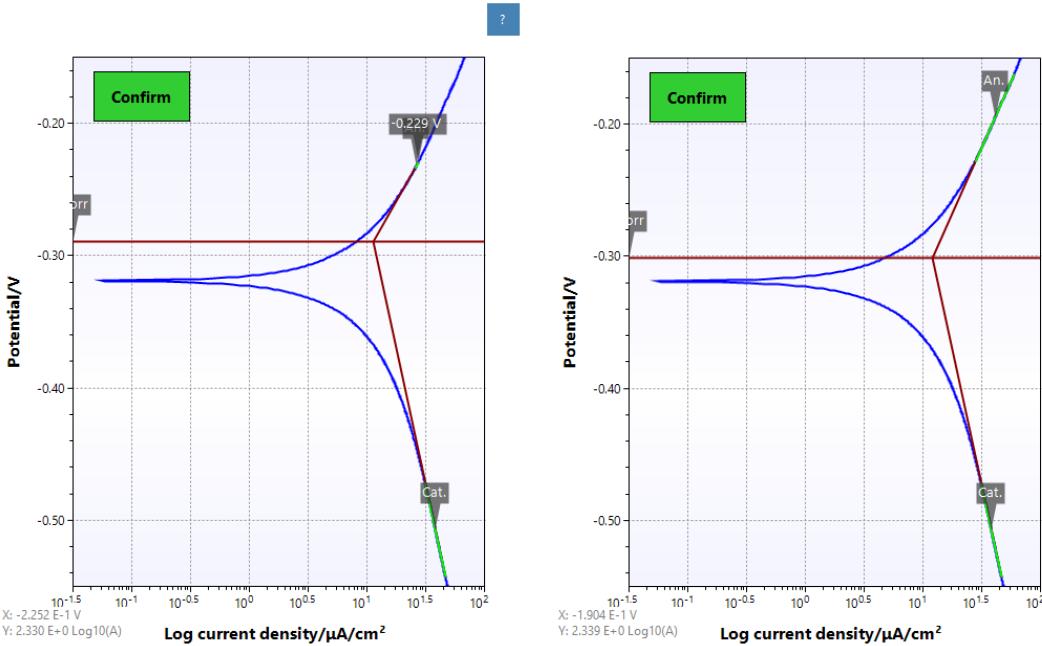


Marking two points for a logarithmic fit

Performing a Tafel slope fit

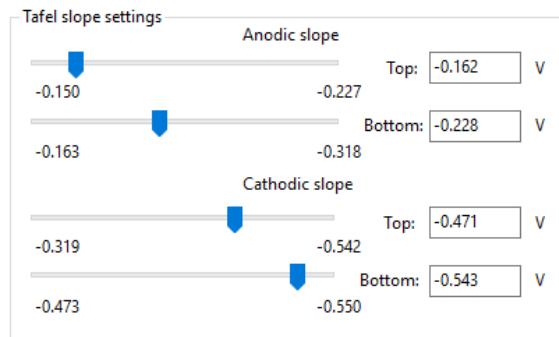
To perform a Tafel slope fit click on the Manual Tafel slope fit button in the toolbar above the plot. The Tafel slopes (Evan's diagram) are drawn in the plot, they are either fit automatically or loaded from the previous fit. The ranges of the slopes can be adjusted in two ways. The range can be specified by clicking twice on a linear section of either the anodic or cathodic part of the corrosion measurement.

Usage: mark two points for the anodic slope line and/or two points for the cathodic slope line. After selecting two points a green line is drawn representing the Tafel slope.



Setting the anodic and cathodic slope lines for Tafel plot analysis.

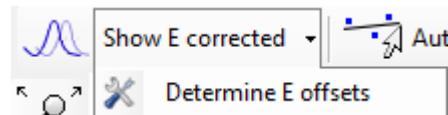
Alternatively, the ranges of the slopes can be adjusted using the Tafel slope settings. Either by adjusting the ranges of the slopes using sliders or by entering the potential ranges in the text boxes.



To confirm the fit of the Tafel slopes click on Confirm in the top left corner of the plot.

Correcting for the potential of the reference electrode

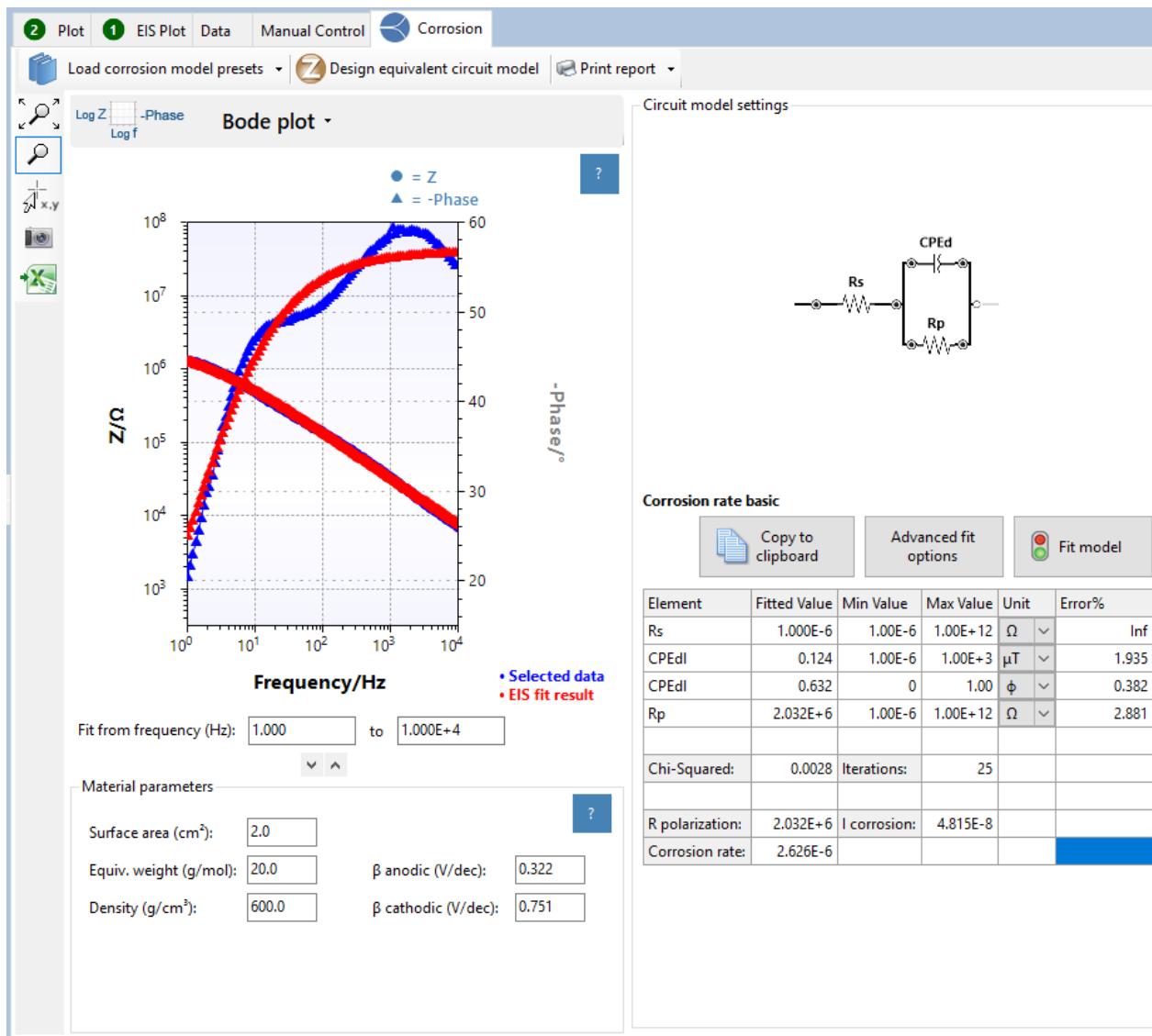
In the corrosion mode it is possible to apply a reference electrode correction to the measured potential. Click on the downward arrow of the Show E corrected button in the toolbar above the plot and select Determine E offsets.



From this menu you can select a correction for the potential of the reference electrode.

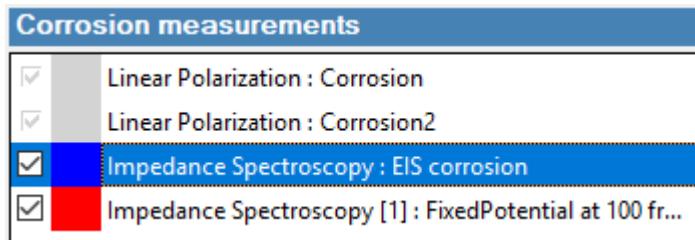
9.3.3 Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) can be used to study corrosion and the effects of a wide range of coatings. For example, anodized coatings (anodized aluminium), conversion coatings (Chromate conversion coating), or organic coatings (paint). The corrosion rate and the pitting/disbanding of coatings are studied by fitting equivalent circuit models on the EIS measurement.



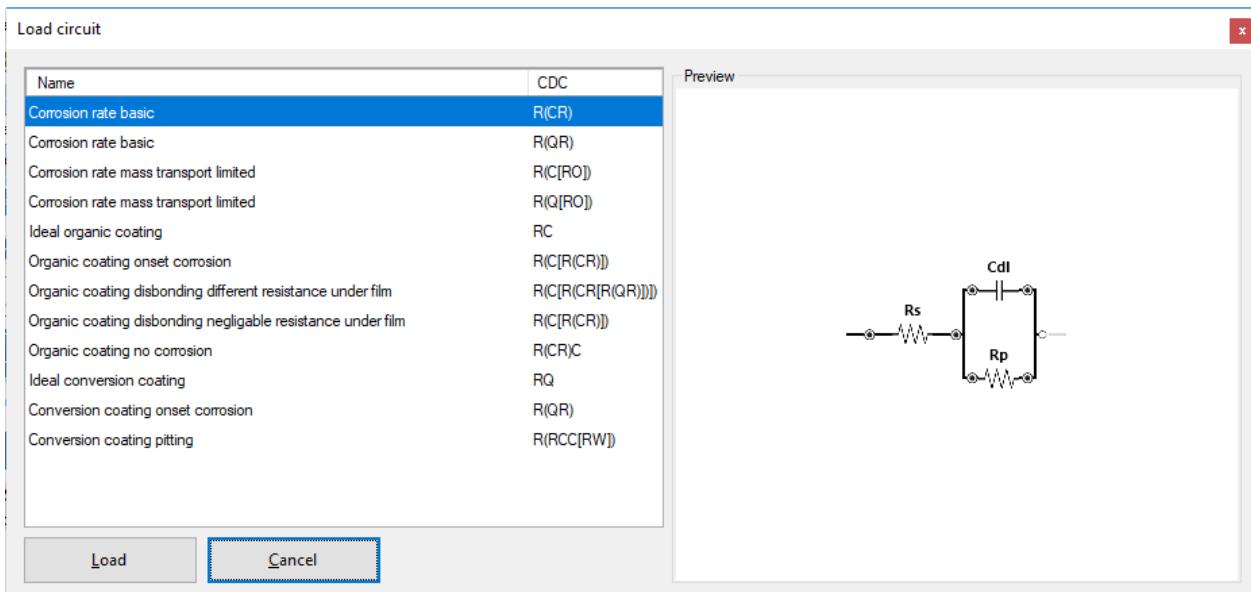
Selecting a curve for corrosion analysis

On the right-hand side of the screen is a legend which contains all compatible corrosion measurements. To perform an equivalent circuit fit select a EIS measurement from the legend. The checkbox in front of the other EIS measurements indicate whether they are also visible in the plot window.

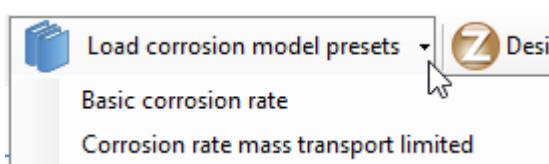


Selecting an equivalent circuit

To change the selected equivalent circuit either click on the Load corrosion model presets button above the plot window to open the circuit library or click on the downward arrow of the button to quickly select a circuit.



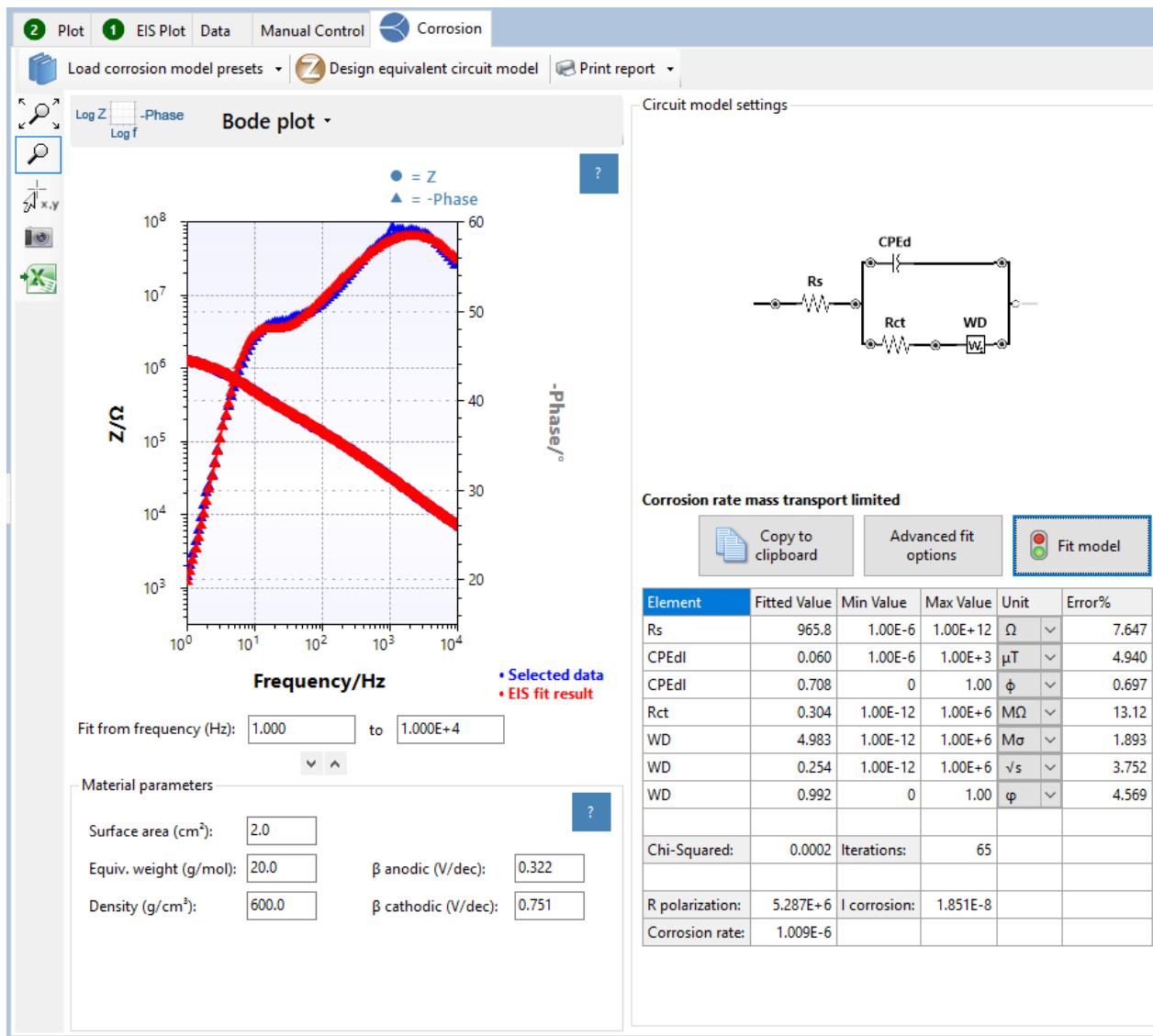
Corrosion circuit library.



Corrosion circuits quick access.

Loading a circuit from the circuit library or the quick select menu will update the circuit model settings. A graphical representation of the selected equivalent circuit is displayed, below the image is a table with circuits corresponding parameters. When selecting one of the four corrosion rate circuits the corrosion parameters are added to the table: polarization resistance (R polarization in Ohm (Ω)), corrosion current (I corrosion in Ampere (A)) and corrosion rate in mm/year.

Note: for the corrosion parameters to be calculated all material parameter values must be greater than 0. See also section [Setting up material parameters](#) on page 189.

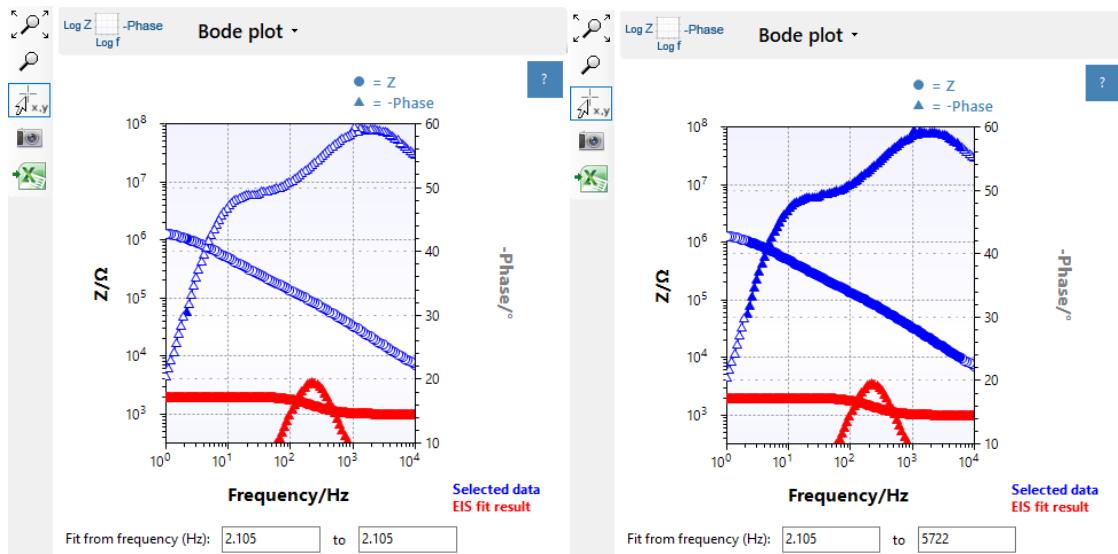


Fitting the equivalent circuit

Before fitting a circuit, the frequency range on which to perform the fit can be selected. By default, a fit is performed over the entire measurement. To select a frequency either enter the desired range in frequency range text boxes below the plot.

Fit from frequency (Hz): to

Alternatively, it is possible to specify the frequency range in the plot by selecting the “Select fit range” mouse pointer button from the toolbar left to the plot and clicking in the plot.



Selecting the fit frequency range. Double click on a point in the plot. Then select the point to where the fit should be performed.

To fit the model on the measurement, click on the “Fit model” button. The result of the fit is stored in your measurement, but to store the fit result it is necessary to save your measurement. Simple circuits with few components will often fit directly, but more complex circuits will require fine tuning of the circuit parameters before a good fit is obtained. To fine tune the model, you can either use your prior knowledge of the cell or you can estimate certain parameter values from the Bode and Nyquist plots. For more information on circuit fitting please refer to the help section on circuit fitting.

9.4 Exporting results

There are three ways to export the results from your Tafel or circuit fit:

1. Copying the results to the clipboard.

Butler-Volmer		Manual	Auto
E corrosion, V		-0.319	-0.319
I corrosion, μA		16.23	11.35
I corrosion per surface area, A/cm^2		3.246E-5	2.270E-5
Polarization Resistance, Ω		7902	8102
Anodic β Tafel constant, V/decade		0.403	0.311
Cathodic β Tafel constant, V/decade		1.103	0.665
Corrosion rate, mm/year		0.159	0.111

Tafel slopes		Manual
E corrosion, V		-0.317
I corrosion, μA		6.627
I corrosion per surface area, A/cm^2		1.325E-5
Polarization Resistance, Ω		9854
Anodic β Tafel constant, V/decade		0.236
Cathodic β Tafel constant, V/decade		0.416
Corrosion rate, mm/year		0.065

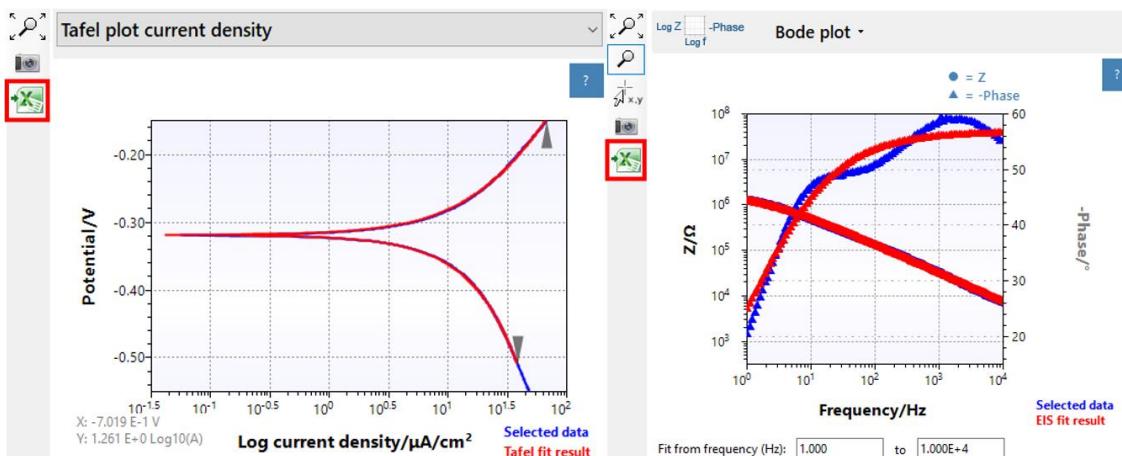
Measured Eoc value: 0.000 V

Copy to clipboard

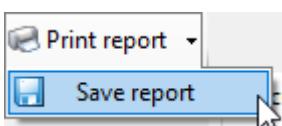
Element	Fitted Value	Min Value	Max Value	Unit	Error%	
Rs	965.9	1.00E-6	1.00E+12	Ω	v	7.645
CPEdl	0.060	1.00E-6	1.00E+3	μT	v	4.940
CPEdl	0.708	0	1.00	ϕ	v	0.696
Rct	0.304	1.00E-12	1.00E+6	$M\Omega$	v	13.13
WD	4.983	1.00E-12	1.00E+6	$M\sigma$	v	1.893
WD	0.254	1.00E-12	1.00E+6	$\sqrt{\text{s}}$	v	3.751
WD	0.992	0	1.00	φ	v	4.573
Chi-Squared:	0.0002	Iterations:	27			
R polarization:	5.287E+6	I corrosion:	1.709E-8			
Corrosion rate:	4.149E-8					

Left: Copying Tafel fit results to clipboard. Right: Copying circuit fit results to clipboard.

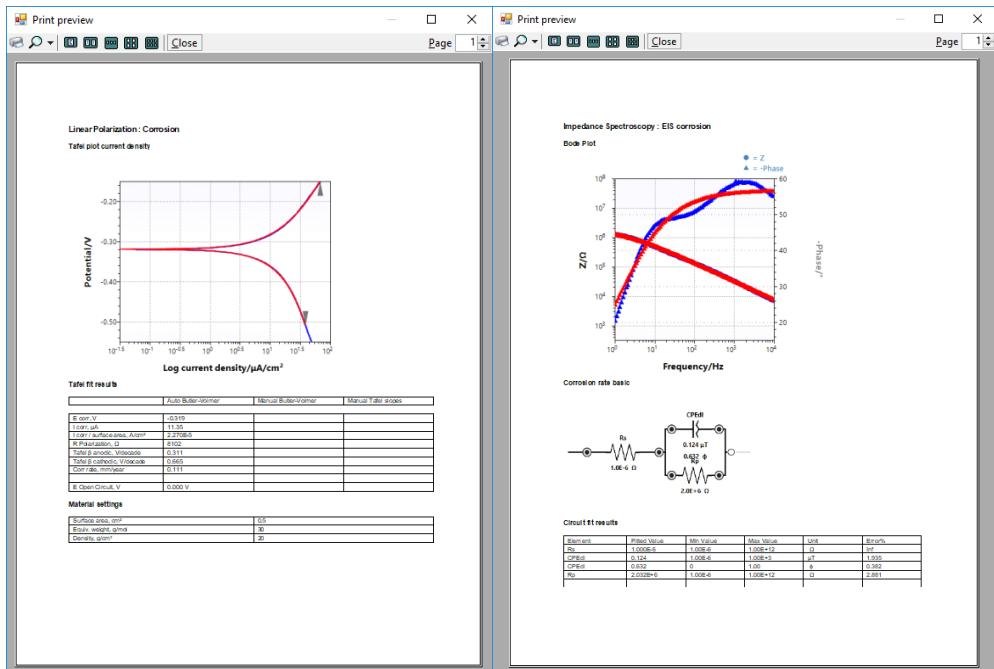
2. Exporting a Tafel plot or a circuit fit curve to Excel (Bode or Nyquist) by pressing the export to Excel button on the left-hand side of the plot.



3. Printing/saving a report as a .rtf file by clicking on the print report button or selecting the save report button in the toolbar above the plot.



Print and save report buttons.



Left: Tafel fit report. Right: Circuit fit report.

9.5 Example data files

The program comes with an example file stored in the default PS Data folder: “My Documents\PSData\Corrosion mode examples\Corrosion.pssession”. You can load this file in PSTrace using the menu ‘Data → ‘Load data file...’

10 Files

PSTrace uses a number of different file formats. This chapter describes which file types are used by PSTrace.

10.1 File types

PSTrace creates a number of different files in ASCII format.

The files are default stored in the folder:

My Documents\PSData

The following files are currently supported by PSTrace and Multitrace

Method	.psmethod
Raw measurement data, curves and methods	.pssession
Script	.psscript
MultiTrace project file	.psproject

Obsolete file formats

The following list of file formats has become obsolete. They can still be loaded in latest versions of PSTrace, but no longer be saved in the particular format.

Method (old style)	.pms (scans) or pmt (vs time)
Curve	.pss (scans) or .pst (vs time)
EISdata	.pseisdata
Multiple curves	.mux
Analysis curves	.pds
Info	.rtf

Method files

Methods can be saved separately or are automatically saved with a curve.

Curve files (obsolete)

If a curve (.pss, .pst) is saved or multiple curves (.mux, .pds) are saved, a method file with the same name and corresponding extension is always saved. This method file also contains the last plot view window used (zoom).

The curve file contains measured data of potential and current or time and current.

EIS data files (obsolete)

Electrochemical Impedance Spectroscopy data is saved in an .pseisdata file. These files are plain text and contain values for frequency, current range, Z, phase, ldc and lac.

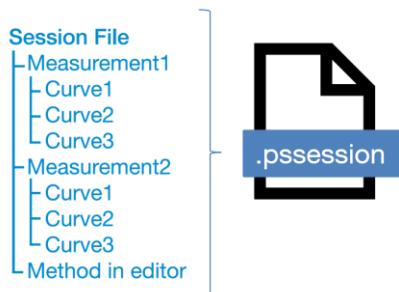
RTF files (obsolete)

PSTrace offers the option to save extra information with a method file. This information is stored in an .rtf file and allows text formatting copy/pasted from Word for example. The file itself can also be edited in Word or any other word processor supporting the RTF format.

This feature has been abandoned from PSTrace 5.0.

Session files

Session files can contain all the data available at any time in a PSTrace session. All available measurements, corresponding curves and method, including the active method in the method editor can be stored to a single .pssession file format.



PSScript files

The .PSScript files are plain ASCII files containing a script that can be loaded and run in the Script window of PSTrace. (See section Scripting)

10.2 Loading and saving data

Methods and measurements can be loaded and stored from and to a hard-drive or other storage solution.

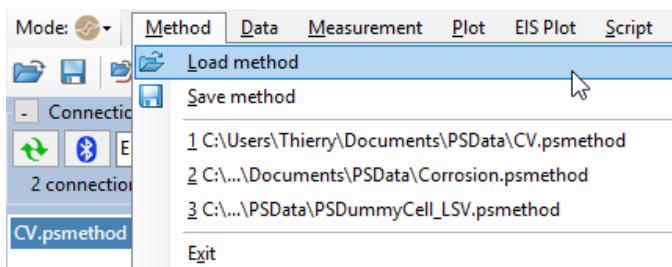
Loading methods

There are three ways to load a method (.psmethod) file:

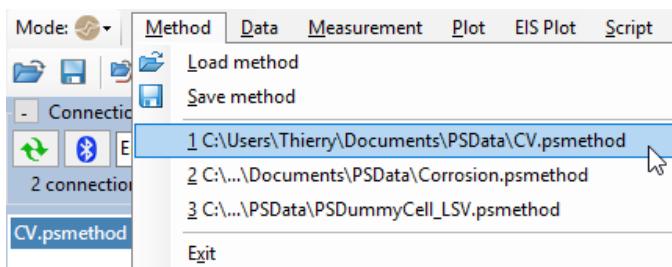
1. Selecting the load method file button from the toolbar;



2. Selecting load method from the method menu;



3. Selecting a recently loaded method from the recent methods list;



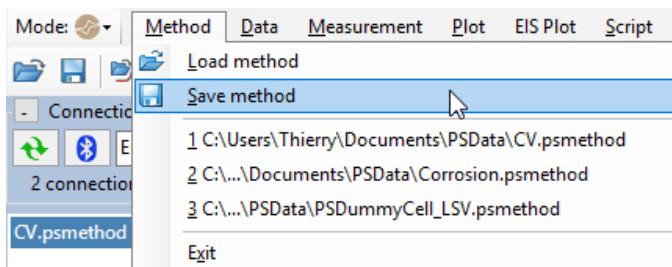
Saving methods

Methods can be saved as psmethod files by:

1. Selecting the save method file button from the toolbar;



2. Selecting save method from the method menu;



Loading measurements

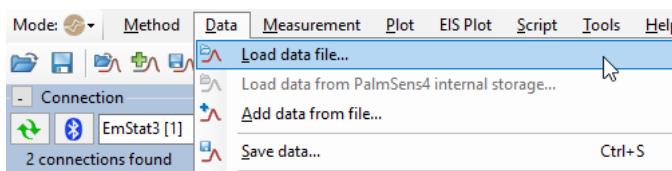
Measurements and sessions can be loaded or added to your current session, i.e. loading a pssession/pss/pst/pseisdata/mux/pds file will replace all other data in your current session.

There are three ways to load measurements:

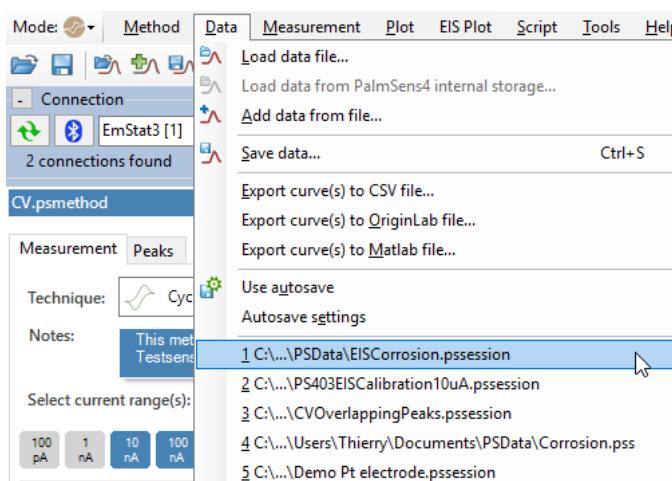
1. Selecting the load data button from the toolbar;



2. Selecting load data file from the data menu;



3. Selecting a recently loaded data file from the recent data list;

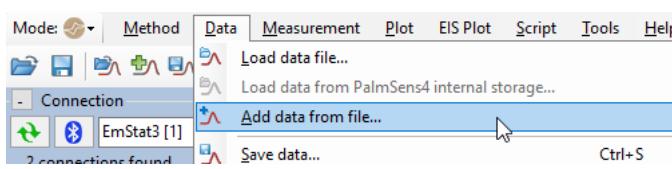


Data files can be added to your current session by:

1. Selecting the add curve button from the toolbar;



2. Selecting load data file from the data menu;



Saving measurements

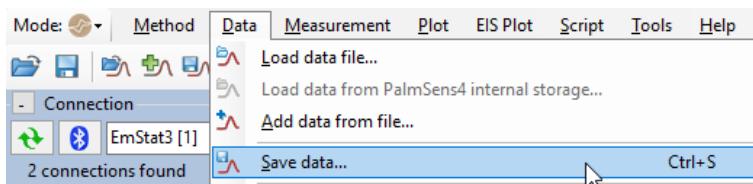
The measurements in your current session can be saved in a psession file. In the save dialog you can specify the measurements and curves that should be stored in the psession file. The save dialog can be opened by:

1. Pressing control + s on the keyboard;

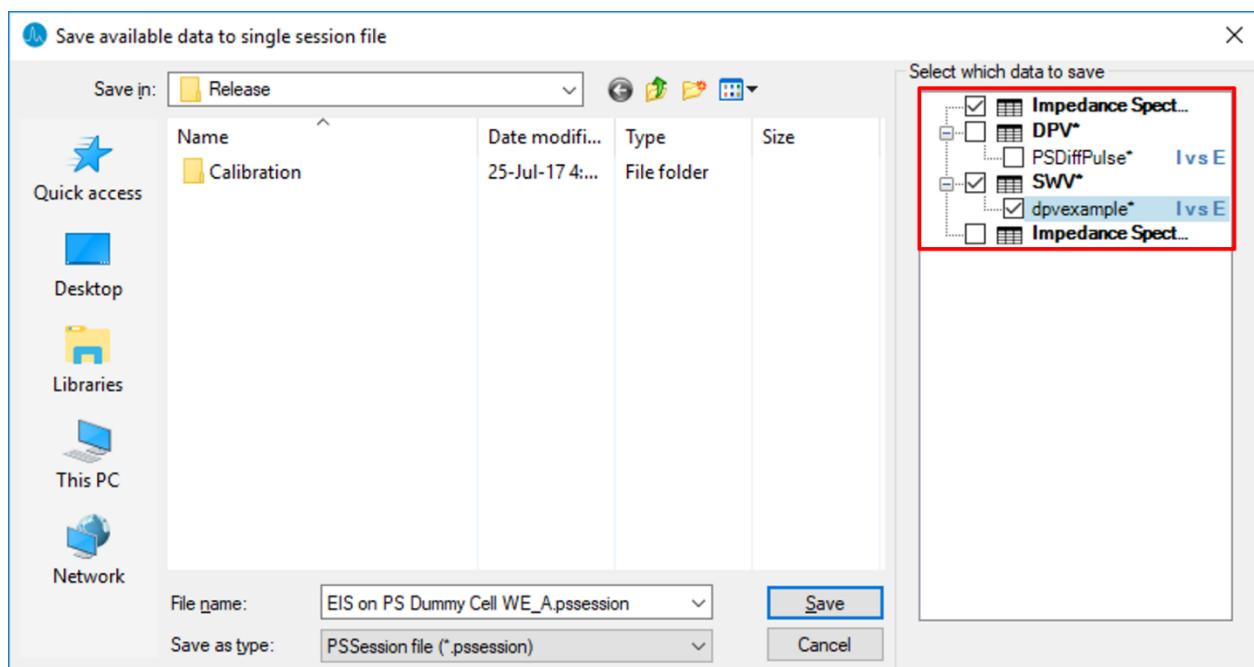
2. Selecting the save data button from the toolbar;



3. Selecting save data from the data menu;

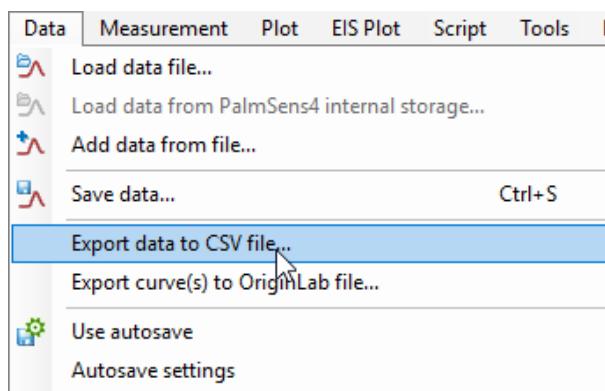


On the right-hand side of the save dialog you can (un)check the data that you would like to save, only checked measurements/curves are saved.



10.3 Exporting data to other file formats

Measured data can be exported to different file formats. The export options are available in the ‘Curve’ menu.



Curve menu showing export options

CSV

The **CSV** (Comma Separated Values) is a popular format in plain ASCII, supported by many applications like Excel, OpenOffice Calc and Origin. To change the values exported for EIS data, open the ‘Settings’ window (menu: ‘Tools’ → ‘General settings...’) and click the ‘Plot and data’ tab. Then click the button:

Set columns for exporting EIS data

Origin

Origin from OriginLab is scientific graphing and data analysis software widely used at universities.

See for more information: <http://www.originlab.com/>

To change the values exported for EIS data, open the ‘Settings’ window (menu: ‘Tools’ → ‘General settings...’) and click the ‘Plot and data’ tab. Then click the button:

Set columns for exporting EIS data

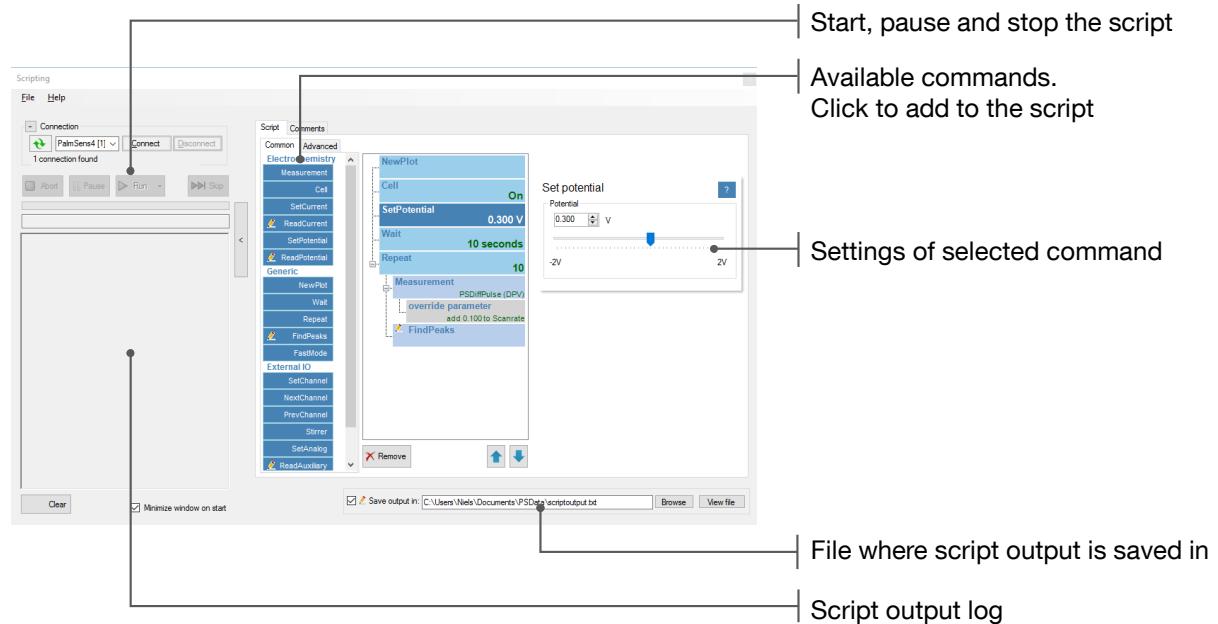
Origin does not need to be installed on the PC to export curves to the Origin format.

11 Scripting

Using the scripting functionality in PSTrace a list of commands can be executed automatically.

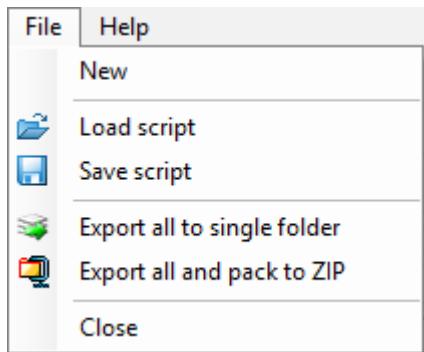
In the default data folder (normally ‘My Documents\PSData’) a script file is available as example.

11.1 Features



Scripting main window

11.1.1 File menu



New

Clears the script.

Load script

Loads a saved script.

Save script

Saves a script to a specific location. All the file references to method or curve files in the script will be made relative to the location of the script file. For example, if the script file is in location:

C:\directory A\script.psscript

and the script refers to files in location

C:\directory A\ directory B\

the file references in the script file will be for example

directory B\file1.psmethod
directory B\file2.psmethod

and not

C:\directory A\directory B\file1.psmethod
C:\directory A\directory B\file2.psmethod

So if the directory A including script and sub-directory is copied to another location or PC, the references will still be intact.

Export all to single folder

Copies all files that are referred to and the actual script file to the folder chosen to save the new script file into. So if a script file is at location:

C:\directory A\script.psscript

and file references in the script are for example to:

C:\directory B\file1.psmethod

C:\directory C\file2.psmethod

All files will be copied to a single folder and all file references will be changed to this folder. This allows you to save all relevant files to a single location for back-up purposes.

Export all and pack to ZIP

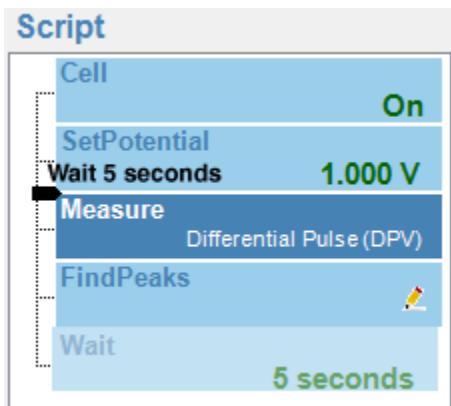
This function does the same as 'Export all to single folder' as described above, but instead of targeting a folder all files are saved to a single ZIP file.

11.1.2 Composing a script

The script contains of a sequence of commands which is run from the top down. Add commands using the list of available commands shown at the left of the script.

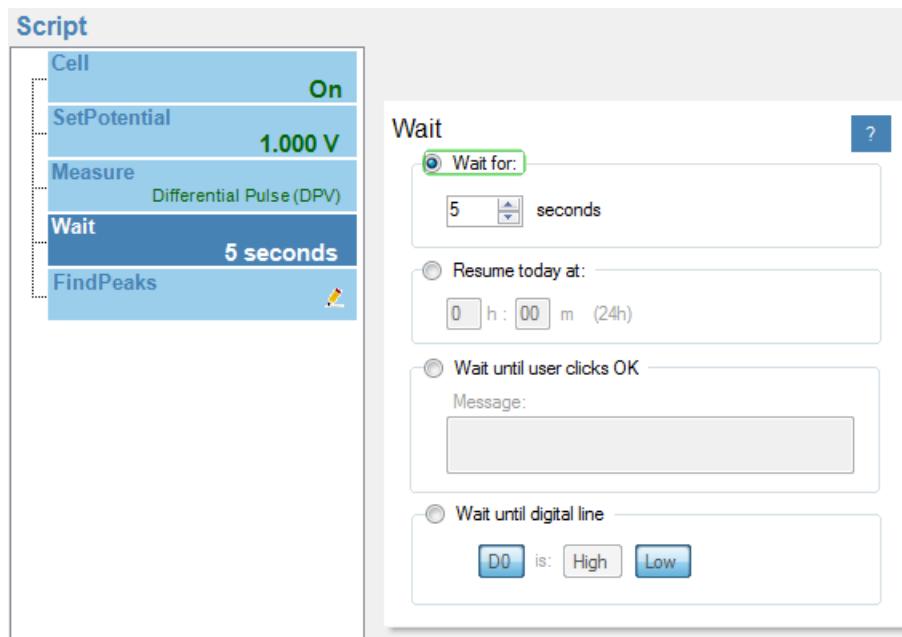
The order of the commands in the script can easily be changed by dragging and dropping them. Click and hold on the text of a command and drag the command to a location where you want. The black arrow shows where the command will be dropped:

In the picture below the Wait command is dragged above the Measure command:



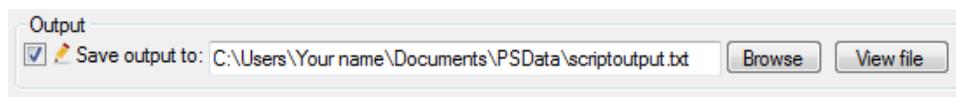
11.1.3 Changing parameters

The parameters for each command can be changed in the panel at the right side of the script. This panel shows the settings for the selected command. Click the ? button to get help for the selected command.



11.1.4 Using the output file

The output file can be specified by typing in the textbox or using the Browse button.

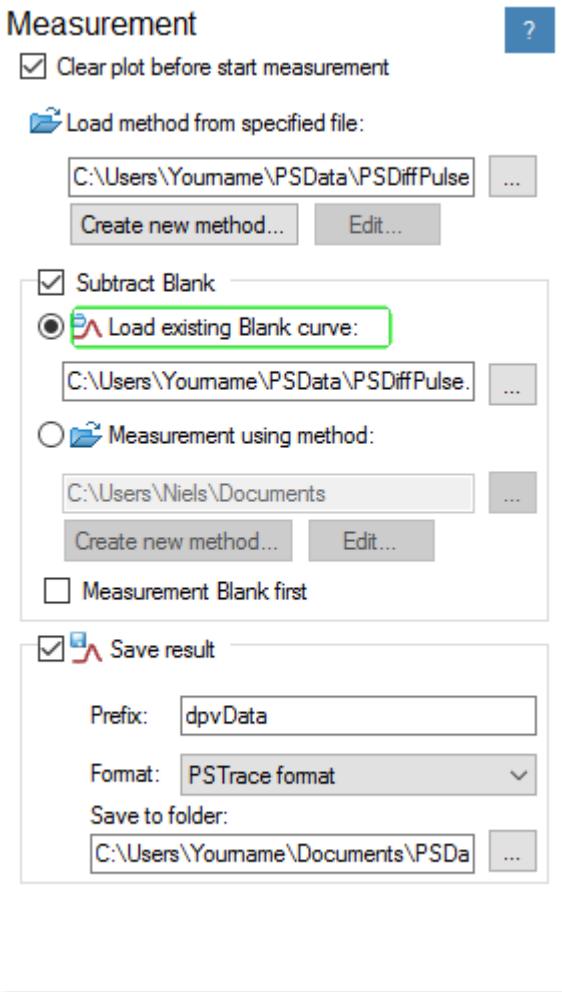


If one of the following commands is used in the script and the output checkbox is checked, the corresponding results are appended to the text file provided.

- ReadCurrent
- ReadPotential
- FindPeaks
- ReadAnalog
- ReadDigitalIO

The file can be read using any text editor like Notepad, or they can be loaded in Excel. The columns are separated using tabs.

11.2 Measure command



Clear plot before start measurement

If checked; the plot and legend will be cleared before the measurement is started. In case a Blank is measured first or afterwards, both the Blank and the actual measurement curve will be displayed in the plot.

Load method from specified file:

The specified method will be loaded for this measurement. A new method can be created and saved instantly using the 'Create new method...' button. The 'Edit...' button allows to make changes in the method file and save (overwrite) these changes to the specified file.

Subtract Blank

If subtract blank is checked a Blank curve will be subtracted from the measured curve. This curve can be an existing curve (**Load existing Blank curve**) or can be measured (**Measure using method**).

If **Measure Blank first** is checked, the method for the blank will be loaded first and used for measurement, then the actual measurement will be done. As soon as the latter is finished, the Blank will be subtracted from the measured curve.

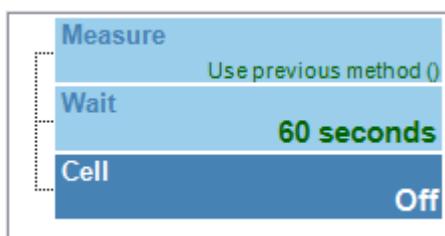
Save result

When checked, the measured curve (or curves in case a Blank was used) will be saved using the prefix, followed by a number. This number automatically increments if multiple curves are saved with the same prefix. If curves are not saved from within the Script, all curves in the PSTrace plot can be saved manually to a single session file (.pssession) using the 'Data' menu as well.

Cell on after measurement

In case a method is used with the setting 'Cell on after measurement' together with 'cell off after n seconds', the latter setting is ignored in the script so the cell can be turned off after a specific period in the script.

To keep the cell on after a measurement for a period, you should use the 'Wait' command in combination with the 'Cell' command.



11.3 Fast Mode command

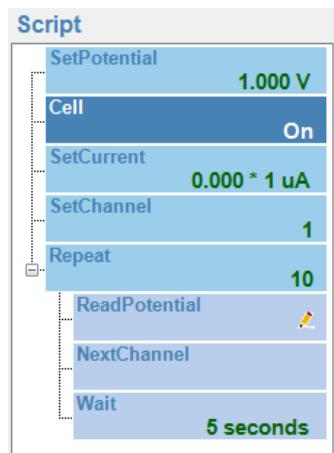
When a PalmSens or EmStat is idle, it normally sends an idle status package with voltage, current and auxiliary readings every second. If an instrument receives a command while measuring the values for the idle status package it will not be able to process the received command immediately. Setting FastMode on disables the idle packages being sent every second. This way the response time of the instrument is always optimal.

11.4 Cell command

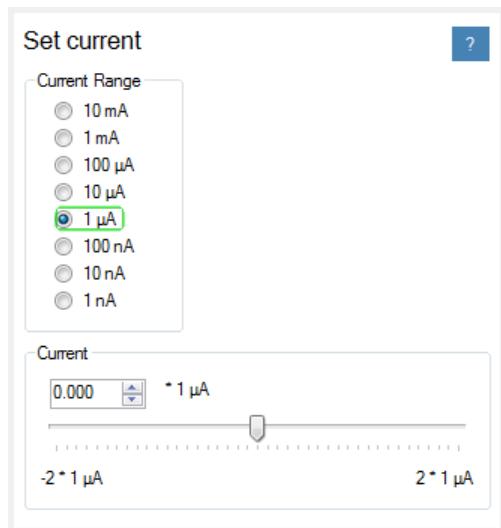


Turns the cell on or off.

Example:

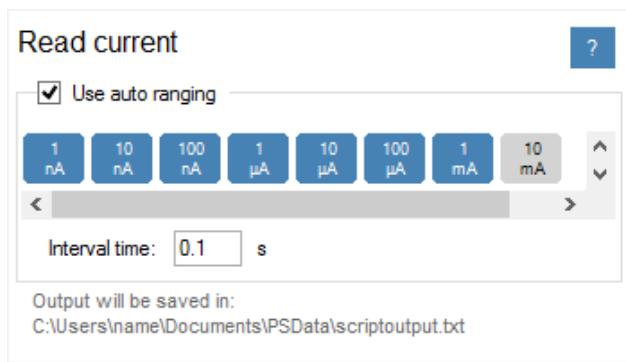


11.5 Set current command



Set current sets the connected device in galvanostatic mode and applies a current at the specified current range. This command is not supported by the EmStat series.

11.6 Read current command



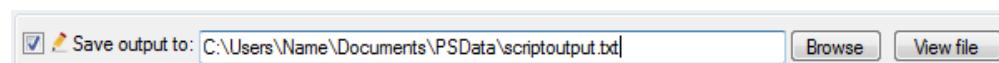
The read current command should be used when the cell is on. It reads the current and stores the value in the text file specified at the bottom of the script window.

Auto ranging

If the ‘Use auto ranging’ checkbox is used, the current range will be evaluated at each interval time and changed if necessary. If the correct current range has been found or the minimum or maximum range is set, the current will be read.

The first current range to evaluate is the highest current range.

If ‘Use auto ranging’ is not used the Read current command will leave the current range unchanged. The current range can be changed in the script using the ‘Current range’ command. See next section.



Output

If there is no column in the text file yet, it will add the line with columns first and then the line with values. The same columns are used for potentials.

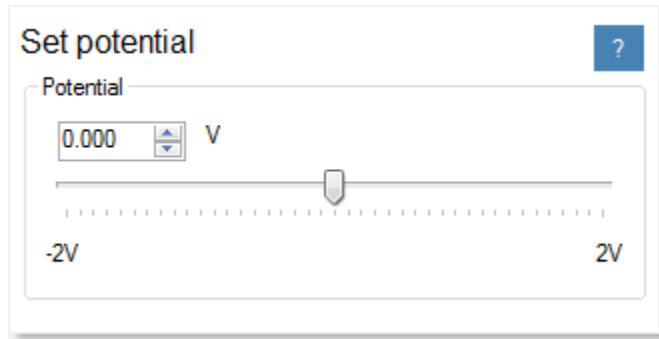
The values are all separated by a TAB, and can be imported in Excel.

Example output:

Script output 12/07/2012 - 17:42:43:

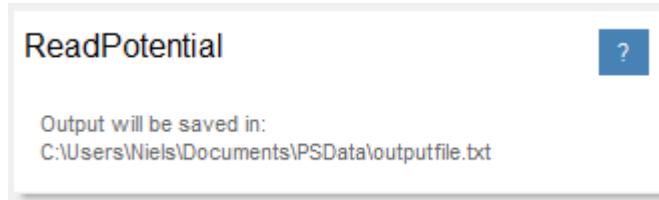
Time	Potential in V	Current in uA
12/07/2012 17:42:45		-3.313E-5
12/07/2012 17:42:46		-7.501E-6
12/07/2012 17:42:47		5.250E-5
12/07/2012 17:42:48		-4.250E-5

11.7 Set potential command



The set potential command sets the connected device in potentiostatic mode and sets the potential to the given value. The cell state (on or off) is not changed.

11.8 Read potential command



The read potential command outputs the Potential to the output file.

Output

If there is no column in the text file yet, it will add the line with columns first and then the line with values. The same columns are used for currents.

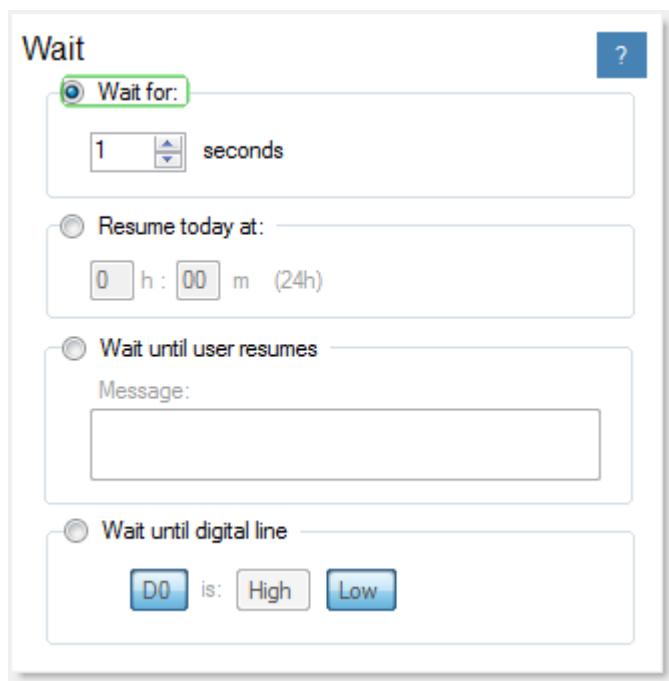
The values are all separated by a TAB, and can be imported in Excel.

Example output:

Script output 12/07/2012 - 17:45:59:

Time	Potential in V	Current in uA
12/07/2012 17:46:01	-1.501	
12/07/2012 17:46:02	-1.401	
12/07/2012 17:46:03	-1.299	
12/07/2012 17:46:04	-1.200	
12/07/2012 17:46:05	-1.098	

11.9 Wait command



The Wait command interrupts the script for a specified period or until an event occurs.

Wait for:

The script continues after the specified amount of seconds.

Resume today at:

The script continues at the specified time of day (this can go on for multiple days)

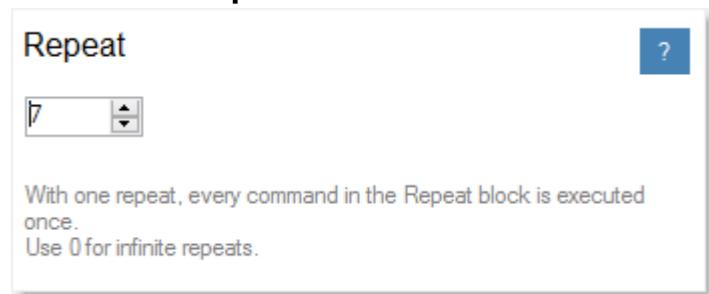
Wait until user resumes:

The script shows the message in the script result box (see Features) and waits until the user clicks the active Pause button to resume.

Wait until digital line:

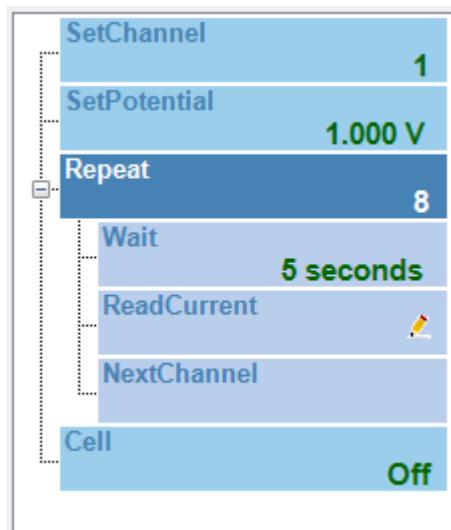
The script waits until the External IO line D0 is set high or low. This feature can be used to let an external device determine if the script can continue.

11.10 Repeat command



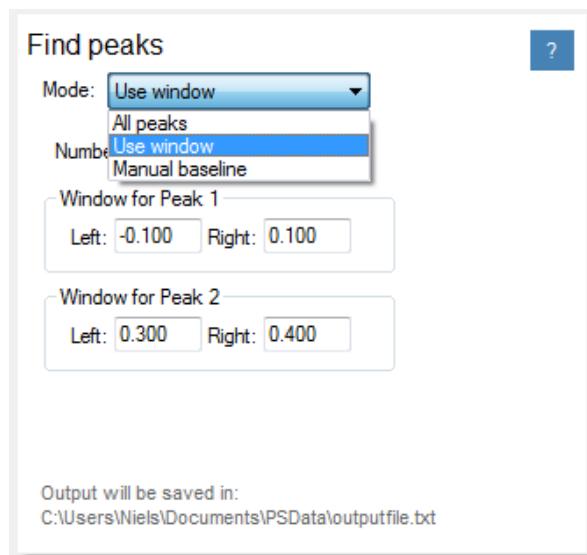
Using the repeat command, a set of commands can be repeated. The commands to repeat should be attached to the Repeat instruction in the list.
Use a value of 0 for infinite repeats.

Example:



The Repeat instruction itself cannot contain any repeats.

11.11 FindPeaks command



The FindPeaks command performs a peak search over the last measured curve available. This instruction is therefore logically preceded by the Measure command. The peaks found are written to the output file specified.

All peaks:

All peaks are searched using the parameters as specified in the most recent method file loaded.

Use window:

The number of peaks has to be specified and for each peak the left and right of the search window has to be provided.

Manual baseline:

The provided left and right values for each peak are used as left and right of the peak baseline, therefore forcing the finding of a peak.

Output

If there are no columns set yet in the output file, a line with columns will be added first. All values are separated by a TAB and can be imported to Excel.

Script output 12/07/2012 - 16:36:02:

Curve	Peak#	Date	Time	Potential/V	Height/µA	Area/µAV	Width/V	Y Offset/µA	Sum/µA/V
Curve	1	12/07/2012	16:36:23	0.0280	-1.2007E-3	-6.6505E-5	0.080	6.5409E-3	1.5656E-1

11.12 SetChannel command



This command sets the channel of a CH8 or MUX multiplexer.

11.13 NextChannel command

Sets the CH8 or MUX multiplexer to the next channel. If the maximum available channel is exceeded, the first channel will be set.

11.14 PrevChannel command

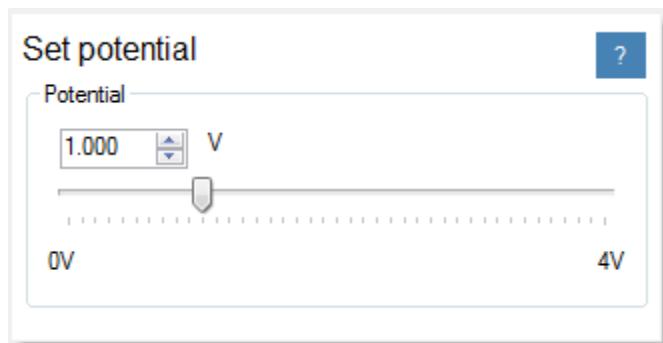
Sets the CH8 or MUX multiplexer one channel lower. If the first channel is exceeded, the last channel will be set.

11.15 Stirrer command



Sets the stirrer on or off.

11.16 SetAnalog command



This command sets a potential on the Analog output of the connected device. This is pin 8 of the miniDIN port in case of a PalmSens. The output range depends on the connected instrument.

See Auxiliary port pin-outs.

11.17 ReadAuxiliary command

Reads the value for the auxiliary input port of the connected device and appends the result to the output file. The input range depends on the instrument connected and/or the auxiliary input type connected.

See for the ranges and location of the auxiliary pins: Auxiliary port pin-outs

See for setting the type of auxiliary input: Configuring PSTrace

Output example for a Pt1000 temperature sensor:

Script output 18/08/2014 - 10:00:32:

18/08/2014 10:00:32	Aux. In:	T = 29.276 °C
18/08/2014 10:01:32	Aux. In:	T = 30.275 °C
18/08/2014 10:02:32	Aux. In:	T = 30.388 °C
18/08/2014 10:03:32	Aux. In:	T = 30.497 °C
18/08/2014 10:04:32	Aux. In:	T = 30.613 °C

11.18 SetDigitalIO command



Set the digital IO ports of the connected device. Selected and highlighted buttons stand for a 1 otherwise 0, so in the example above the digital lines set are: 0101
The digital IO pins are pins 3 to 6 on the PalmSens miniDIN port. See Auxiliary port pin-outs.

11.19 ReadDigitalIO command

Reads the digital input states of the 3 or 4 digital lines of the connected device and appends the result to the output file.

Output example:

Script output 12/07/2012 - 18:15:56:

12/07/2012 18:15:56	Digital lines: 0 0 0 0
12/07/2012 18:15:57	Digital lines: 0 0 0 1
12/07/2012 18:15:58	Digital lines: 0 0 1 0

11.20 Override parameter command

The Override parameter command is always attached to a Measure command. The value provided can either be 'Fixed' or an 'Added value'.



Advanced tab

The command can be found under the 'advanced' tab. This command is helpful, if you want to repeat the same methods in one experiment several times with different parameters each time.

Parameter:

The method parameter to override.

Fixed:

In case the potential is 'Fixed' the parameter of the method used with the Measure command is overridden with the value given in 'Set potential'.

Added value:

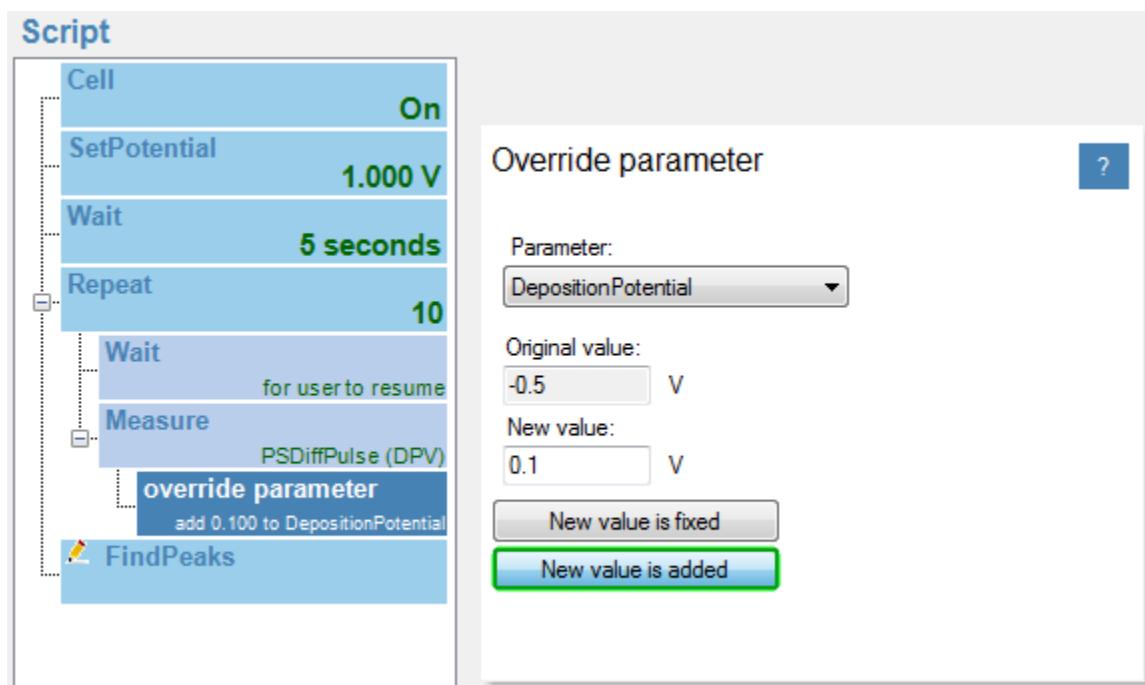
In case 'Added value' is selected, the original parameter value from the method is added with the value given in 'New value'. In case the measure command is used within a Repeat block as shown in the example below, this means that the result of the previous iteration will be used for each new value.

If the resulting value is not valid, because it exceeds the parameter limits, the script will continue using the last valid value.

Using the override parameter for Pseudo Polarography

The override parameter can be used to change the deposition potential for each iteration in a repeat loop. In the example below the deposition potential (E dep) is read as 1.000 V in the method provided for the Measure command. The Override parameter

command is attached to the Measure command. The Override parameter command adds 0.1 V with each iteration to the deposition potential. This results in a deposition potential in the first iteration of 1.100 V, in the second of 1.200 V, etc.



11.21 Run a script from the command line

Running PSTrace from the command line provides the following options:

> pstrace.exe ["path to .psscript file"] [-q] [-d#] [-h]

If a script file is specified, PSTrace will do the following automatically at startup:

- Connect to the first known device (PalmSens or EmStat) found.
- If -d# is used it will connect to the device on position # as shown in the devicelist. So -d1 will connect to the first device in the list, -d2 to the second, etc. (If -h is used in combination if -d#, PSTrace and the script window will remain invisible to the user.)
- Open the script window.
- Load the specified script file.
- Start the script.
- If -q is provided then PSTrace will be closed when the script has finished.

PLEASE NOTE TO USE QUOTES AROUND THE FILE PATH.

Example

The following two lines could be included in a batch file (.BAT) or run from an external application to automate a measurement sequence:

```
cd "C:\Program Files (x86)\PalmSens BV\PSTrace 5.0"  
pstrace.exe "C:\Users\John\Documents\PSData\script.psscript" -q
```


12 CH8 Multiplexer



The multiplexer CH8 is used with PalmSens2 if a sensor-array is used. This instrument is no longer sold since 2012. If you own a MUX8 which is similar to the CH8, please refer to chapter MUX8 multiplexer.

CH8 is connected to the sensor connector of PalmSens. The miniDIN cable has to be connected to the connector at the left-hand side of the instrument. This miniDIN cable is used to power the multiplexer and to control the channel-selection.

12.1 Sensor configurations

The multiplexer can be used in different modes. Each mode is set by a number of jumpers. On the board of the instrument there are seven jumpers marked by J1 ... J7.

Possible sensor configurations are:

- 1 Sensorarrays with (up to) eight working, reference and counter electrodes
- 2 Sensorarrays with eight working and eight combined reference/counter electrodes
- 3 Sensorarrays with eight working electrodes sharing a reference and a counter electrode
- 4 Sensorarrays with eight working electrodes sharing a combined reference/counter electrode

In all configurations the sensors can be multiplexed, leaving the not-selected sensors at open circuit.

Sensor configurations 2, 3 and 4 have the possibility to leave not-selected sensors or cells at open circuit or to apply the same potential to all sensors or cells.

Jumpers:

- J1: Is placed when the sensor has a combined reference and counter electrode. This jumper therefore connects RE to CE.
- J2: If the sensor array has more than one working electrode, but one counter and/or reference electrode, this jumper is placed. CE from PalmSens is connected directly to pin 1 and pin 19 of the 36-pin connector
- J3: If the sensor array has more than one working electrode, but one counter and/or reference, this jumper is placed. RE from PalmSens is connected directly to pin 7 and pin 25 of the 36-pin connector
- J4: This jumper is placed if CE has to be multiplexed. This is the case when each of the sensors has its own counter electrode.
- J5: This jumper is placed if RE has to be multiplexed. This is the case when each of the sensors has its own reference electrode.
- J6: Is placed if all unselected working electrodes or sensors have to remain polarized at the potential as set by PalmSens. If this jumper is not placed only the selected channel is polarized.
In case CE and RE are multiplexed as in **Conf 1**, so when J4 and J5 are placed, this jumper is not relevant, since only the selected channel's WE, CE and RE are polarized.
- J7: For future use. Is left open normally.

Possible configurations:

- **Conf. 1:** Sensor array with up to eight working, eight reference and eight counter electrodes:
 - o Jumpers placed are: J4 and J5
The potential is only applied to the selected channel. All channels NOT selected are at open circuit. (See remark below *)
- **Conf. 2a:** Sensor array with up to eight working and eight combined reference/counter electrodes:
 - o Jumpers placed are: J4, J5 and J1
Note: all leads CE1-8 and RE1-8 are connected together and this combined lead is connected to all eight combined reference/ counter electrodes.
The potential is only applied to the selected channel. All channels NOT selected are at open circuit. (See remark below *)

When J6 is also placed, the potential is applied to all working electrodes continuously.

- **Conf. 2b:** Sensor array with up to eight working and eight combined reference/counter electrodes:
 - o Jumpers placed are: J2, J3 and J1

Note: the combined reference/counter electrodes are connected to the leads CE Direct and/or RE Direct

When J6 is also placed, the potential is applied to all working electrodes continuously.

- **Conf. 3:** Sensor array with up to eight working electrodes all sharing one reference and one counter electrode:
 - o Jumpers placed are: J2 and J3

Note: the reference and counter electrodes are connected to RE Direct and CE Direct respectively.
- **Conf. 4:** Sensor array with up to eight working electrodes all sharing one combined reference/counter electrode:
 - o Jumpers placed are: J2, J3 and J1

Note: the reference/counter electrode is connected to RE Direct and/or CE Direct.

When J6 is also placed, the potential is applied to all working electrodes continuously.

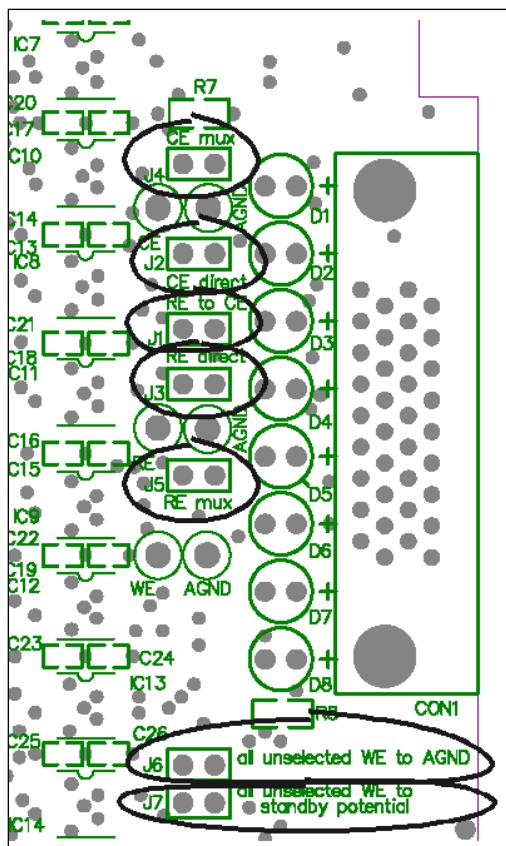
*** IMPORTANT REMARK**

It is not possible to apply a potential simultaneously to more than one sensor or cell each with three electrodes. This requires a multipotentiostat, one potentiostat for each channel. This is however possible with two electrode sensors or cells, so when combined counter and reference electrodes are applied.

12.2 Changing the configuration

In order to change the configuration, follow the next steps:

- be aware of static electricity and use an anti-static wrist band if possible or connect yourself to safety ground and work on a anti-static bench mat
- disconnect CH8 from PalmSens
- remove the black caps from the screw holes (if present) using a needle or something similar (be careful)
- remove the four screws
- remove the two screws of the high density connector (if present)
- remove the upper part of the housing by levering it with a small screwdriver from the side
- remove the PCB from the housing
- configure the instrument by means of the jumpers
- place the PCB back in the housing
- fasten the screws of the high density connector(if present)
- fasten the four screws of the side panels



Location of the jumpers.

12.3 Pin layout

The pins of the high density Centronics connector on the CH8 module are:

Pin 1	CE when J2 is placed.	Pin 19	CE when J2 is placed.
Pin 2	CE channel 1	Pin 20	CE channel 2
Pin 3	CE channel 3	Pin 21	CE channel 4
Pin 4	CE channel 5	Pin 22	CE channel 6
Pin 5	CE channel 7	Pin 23	CE channel 8
Pin 6	Ground	Pin 24	Ground
Pin 7	RE when J3 is placed.	Pin 25	RE when J3 is placed.
Pin 8	RE channel 1	Pin 26	RE channel 2
Pin 9	RE channel 3	Pin 27	RE channel 4
Pin 10	RE channel 5	Pin 28	RE channel 6
Pin 11	RE channel 7	Pin 29	RE channel 8
Pin 12	Ground	Pin 30	Ground
Pin 13	Ground	Pin 31	Ground
Pin 14	WE channel 1	Pin 32	WE channel 2
Pin 15	WE channel 3	Pin 33	WE channel 4
Pin 16	WE channel 5	Pin 34	WE channel 6
Pin 17	WE channel 7	Pin 35	WE channel 8
Pin 18	Ground	Pin 36	Ground

Location of the pins:

Pin1	right upper	Pin 19	right lower
Pin 18	left upper	Pin 36	left lower

12.4 CH8 cable lay out

Pin assignment of the CH8 high density plug of the cable:

1 upper left	18 upper right
19 lower left	36 lower right

12.4.1 Belkin cable (dark grey) Colour codes

Brown	1	CE Direct
Brown black	19	CE Direct

Red	2	CE1
Red black	20	CE2

Orange	3	CE3
Orange black	21	CE4

Yellow	4	CE5
yellow black	22	CE6

Green	5	CE7
Green black	23	CE8

Blue	6	GND
Blue black	24	GND

Purple	7	RE Direct
Purple black	25	RE Direct

White	8	RE1
White black	26	RE2

Pink	9	RE3
Pink black	27	RE4

Pink brown	10	RE5
Grey brown	28	RE6

Brown white	11	RE7
Red white	29	RE8

Orange white	12	GND
Yellow white	30	GND

Green white	13	GND
Blue white	31	GND
Grey red	14	WE1
Brown red	32	WE2
Orange brown	15	WE3
Green brown	33	WE4
Red brown	16	WE5
Yellow brown	34	WE6
Blue brown	17	WE7
Purple brown	35	WE8
Purple white	18	GND
Grey white	36	GND

12.4.2 CH8 cable COPARTNER E119932-U Version 2 Colour codes

Yellow	1	CE Direct
Yellow black	19	CE Direct
Red	2	CE1
Red black	20	CE2
		CE2
Brown	3	CE3
Brown white	21	CE4
Light blue	4	CE5
Light blue black	22	CE6
Blue green	5	CE7
Blue yellow	23	CE8
Green	6	GND
Green black	24	GND
Blue	7	RE Direct
Blue white	25	RE Direct
White	8	RE1
White black	27	RE2

Pink	9	RE3
Pink black	27	RE4
Purple	10	RE5
Purple white	28	RE6
Grey	11	RE7
Grey black	29	RE8
Orange	12	GND
Orange black	30	GND
Pink white	13	GND
Pink yellow	31	GND
Grey green	14	WE1
Grey yellow	32	WE2
White yellow	15	WE3
White green	33	WE4
Green brown	16	WE5
Green blue	34	WE6
Light blue dark blue	17	WE7
Light blue red	35	WE8
N/a	18	not connected
N/a	36	not connected

12.4.3 Specifications

Number of channels	8
On resistance	WE and RE channels: 85 ohm typical CE channel 900 ohm typical
Leakage current	10 pA typical at 25 °C 100 pA typical at 25 °C
Charge injection	-0.5 pC typical

13 MUX8 and MUX16 multiplexers



Both EmStat (except EmStat3+) and PalmSens can be used with a MUX8 or MUX16 multiplexer.

MUX 8 and MUX16 are used to switch electrodes to the EmStat or PalmSens potentiostat.

Please note that a potentiostat with a multiplexer is not a multipotentiostat.

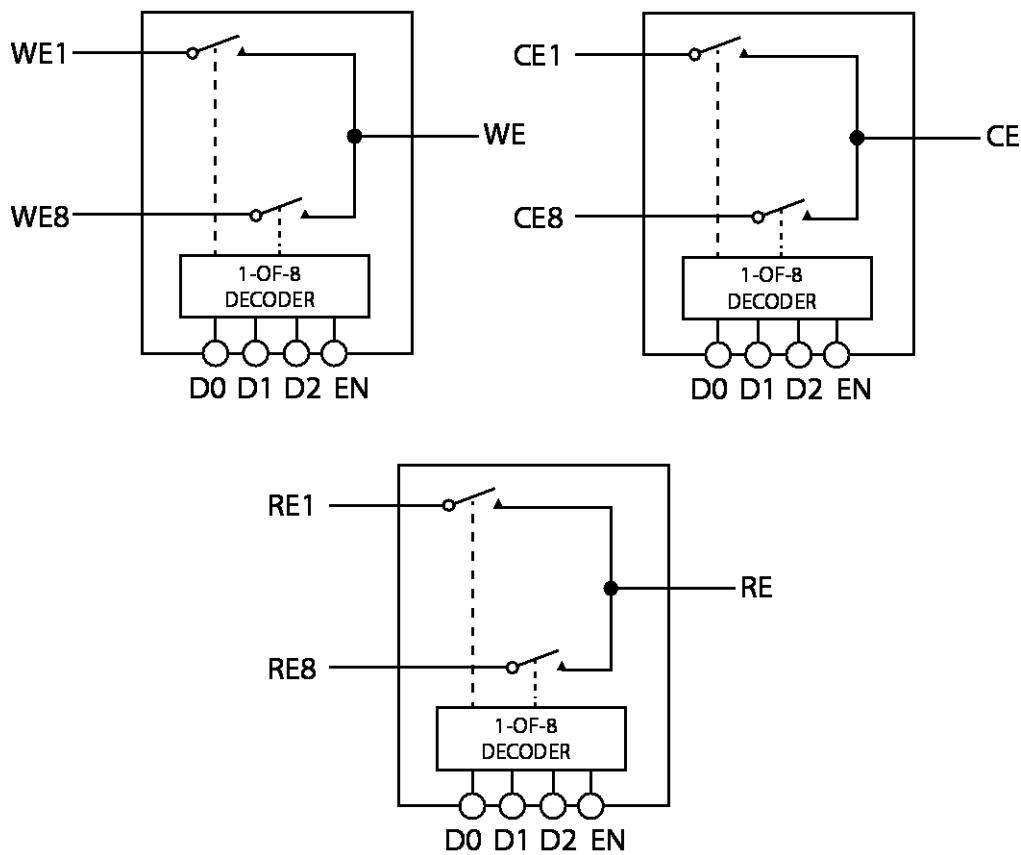
The EmStat with multiplexer come as a combination in one housing. This product is called EmStatMUX.

For the PalmSens and EmStat Blue the multiplexers come optional in a separate housing.

13.1 MUX8 multiplexer

The MUX8 multiplexer is used with 2- or 3- electrode sensors or cells up to 8 channels.

13.1.1 Functional diagram



13.1.2 Specifications

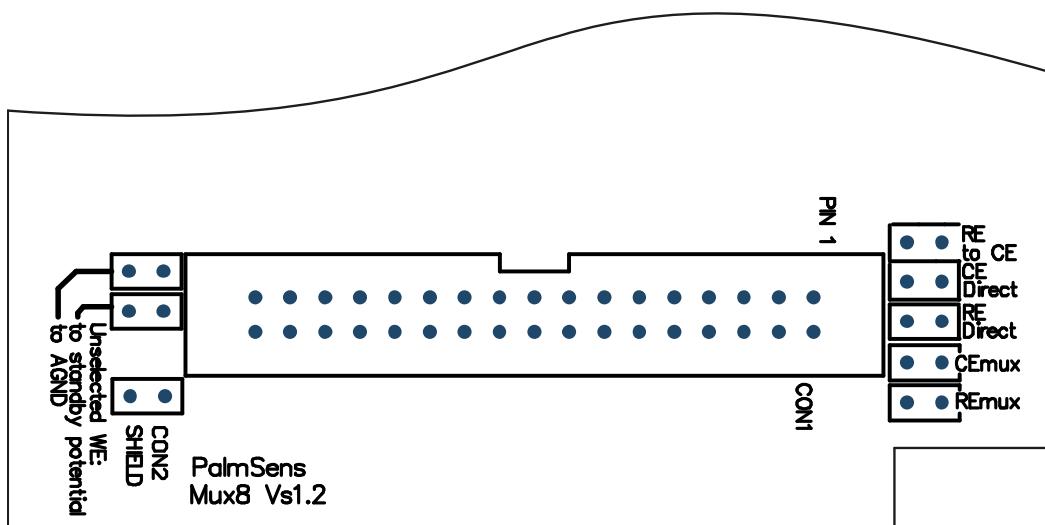
- | | |
|----------------------|--|
| - number of channels | 2-8 |
| - multiplexer use: | <ul style="list-style-type: none"> - Sensorarrays with up to eight working, reference and counter electrodes - Sensorarrays with up to eight working and eight combined reference/counter electrodes - Sensorarrays with up to eight working electrodes all sharing the same reference and the same counter electrode - Sensorarrays with eight working electrodes all sharing the same combined reference/counter electrode |
| On resistance | WE, CE and RE channels: 2 ohm typical (see note) |
| Leakage current | 10 pA typical at 25 °C (see note) |
| Charge injection | 20 pC typical (see note) |
| Connections: | Shielded flat cable, with stripped end leads or by means of the MUX8 Terminal Block (in shielded housing) |
| | <ul style="list-style-type: none"> - eight WE's - eight CE's |

- eight RE's
- one CE used when all WE's share one counter electrode
- one RE used when all WE's share one reference electrode
- analog ground for shielding

Dimensions of PCB
76 x 74 mm

13.1.3 Sensor configurations

The multiplexer can be used in different modes. Each mode is set by a number of jumpers.



Possible sensor configurations are:

- 5 Sensorarrays with (up to) eight working, reference and counter electrodes
- 6 Sensorarrays with eight working and eight combined reference/counter electrodes
- 7 Sensorarrays with eight working electrodes sharing a reference and a counter electrode
- 8 Sensorarrays with eight working electrodes sharing a combined reference/counter electrode

In all configurations the sensors can be multiplexed, leaving the not-selected sensors or cells at open circuit.

Sensor configurations 2, 3 and 4 have the possibility to leave not-selected sensors or cells at open circuit or to apply the same potential to all sensors or cells.

Jumpers:**J1: RE to CE**

Is placed when the sensor has a combined reference and counter electrode. This jumper therefore connects RE to CE.

J2: CE Direct

If the sensor array has more than one working electrode, but one counter and/or reference electrode, this jumper is placed. CE from PalmSens is connected directly to pin 1 and pin 2 of CON1

J3: RE Direct

If the sensor array has more than one working electrode, but one counter and/or reference, this jumper is placed. RE from PalmSens is connected directly to pin 13 and 14 of CON1

J4: CE Mux

This jumper is placed if CE has to be multiplexed. This is the case when each of the sensors has its own counter electrode using pin3 to 10.

J5: RE Mux

This jumper is placed if RE has to be multiplexed. This is the case when each of the sensors has its own reference electrode using pin 15 to 22

J6: Unselected WE to AGND:

Is placed if all unselected working electrodes or sensors have to remain polarized at the potential as set by PalmSens or EmStat. If this jumper is not placed only the selected channel is polarized.

In case CE and RE are multiplexed as in **Conf 1**, so when J4 and J5 are placed, this jumper is not relevant since only the selected channel's WE, CE and RE are polarized.

J7: Unselected WE to standby potential

Is always left open.

Jumper settings for the available configurations:

- **Conf. 1:** Sensor array with up to eight working, eight reference and eight counter electrodes:
 - o Jumpers to be placed are: J4 and J5
The potential is only applied to the selected channel. All channels NOT selected are at open circuit. (See remark below *)
- **Conf. 2a:** Sensor array with up to eight working and eight combined reference/counter electrodes:
 - o Jumpers to be placed are: J1, J4 and J5
Note: all leads CE1-8 and RE1-8 are connected together and this combined lead is connected to all eight combined reference/ counter electrodes.
The potential is only applied to the selected channel. All channels NOT selected are at open circuit. (See remark below *)

When J6 is also placed, the potential is applied to all working electrodes continuously.

- **Conf. 2b:** Sensor array with up to eight working and eight combined reference/counter electrodes:
 - o Jumpers placed are: J1, J2 and J3

Note: the combined reference/counter electrodes are connected to the leads CE Direct and/or RE Direct

When J6 is also placed, the potential is applied to all working electrodes continuously.
- **Conf. 3:** Sensor array with up to eight working electrodes all sharing one reference and one counter electrode:
 - o Jumpers placed are: J2 and J3

Note: the reference and counter electrodes are connected to RE Direct and CE Direct respectively.

When J6 is also placed, the potential is applied to all working electrodes continuously.
- **Conf. 4:** Sensor array with up to eight working electrodes all sharing one combined reference/counter electrode:
 - o Jumpers placed are: J1, J2 and J3

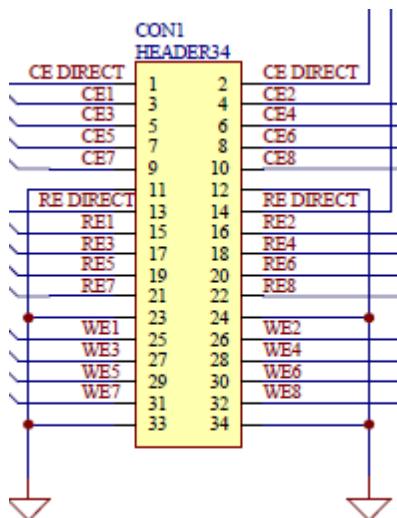
Note: the reference/counter electrode is connected to RE Direct and/or CE Direct.

When J6 is also placed, the potential is applied to all working electrodes continuously.

* IMPORTANT REMARK

It is not possible to apply a potential simultaneously to more than one sensor or cell each with three electrodes. This requires a multipotentiostat, one potentiostat for each channel. This is however possible with two electrode sensors or cells, so when combined counter and reference electrodes are applied.

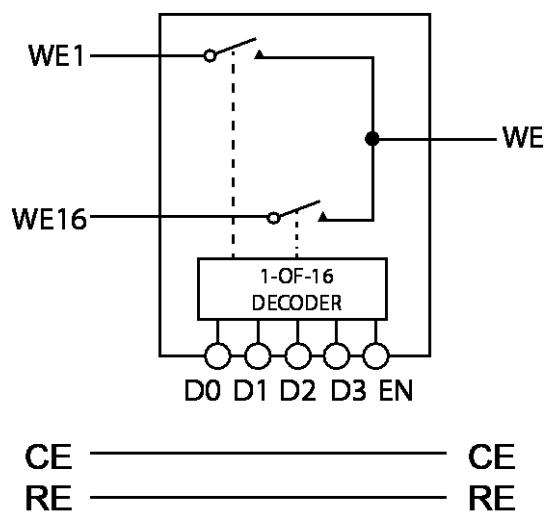
13.1.4 Electrode connections



13.2 MUX16 multiplexer

The MUX16 multiplexer is used with 2 electrode sensors or cells up to 16 channels. It can have a shared counter and reference electrode, or each working electrode with each its own combined reference/counter electrode.

13.2.1 Functional diagram



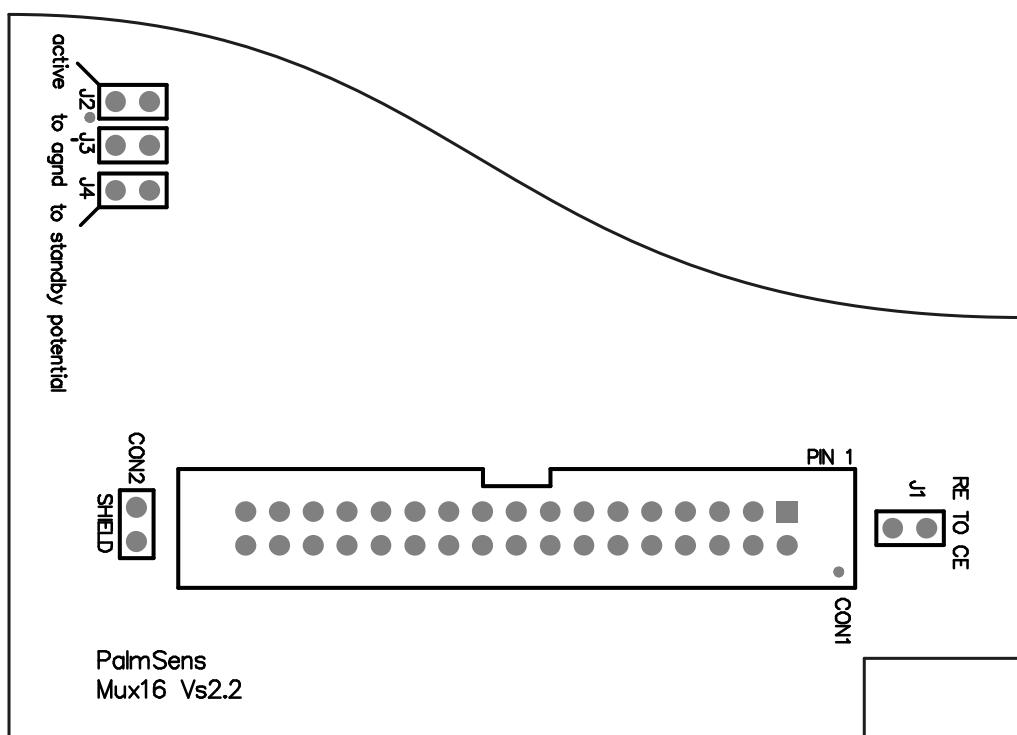
13.2.2 Specifications

Number of channels	2-16
Multiplexer use:	<ul style="list-style-type: none"> - Sensorarrays with up to 16 working electrodes all sharing the same counter and same reference electrode - Sensorarrays with up to 16 eight working and the same combined reference/counter electrode - Sensorarrays with up to 16 working electrodes, each with its own combined reference/counter electrode
On resistance	WE channels: 2 ohm typical (see note)
Leakage current	10 pA typical at 25 °C (see note)
Charge injection	20 pC typical (see note)
Connections:	<p>Shielded flat cable, with stripped end leads or by means of the MUX16 Terminal Block (in shielded housing)</p> <ul style="list-style-type: none"> - 16 WE's - CE - RE - RE and CE can be connected together and in this case connected to up to 16 combined CE/RE electrode

Dimensions of PCB 76 x 74 mm
 - analog ground for shielding

Note: for very low current applications, the PCB can be populated with components with lower leakage (10 pA typical) and lower charge injection (1 pC) properties. These components can be used for measurements with currents always below approx. 100 uA.

13.2.3 Sensor configurations



Possible sensor configurations are:

- 1 Sensorarrays with up to 16 working and 16 combined reference/counter electrodes
- 2 Sensorarrays with up to 16 working electrodes all sharing a reference and a counter electrode
- 3 Sensorarrays with up to 16 working electrodes sharing a combined reference/counter electrode

So the sensor configuration with 16 WE's all having their own reference and separate counter electrode is NOT applicable with the MUX16 multiplexer.

In these configurations the sensors or electrodes can be multiplexed, leaving the not-selected sensors at open circuit when jumper J3 is not placed.

J3 is placed when the potential has to be applied to all working electrodes simultaneously

Jumpers:

J1: RE to CE

Connects the CE and RE leads when placed. Place J1 when only a combined CE and RE is applied. An alternative is to leave J1 open and always connect both the CE and RE leads to your RE/CE electrode

J2: active

Jumper is always placed.

J3: (unselected WE) to AGND

Keeps all WE's at applied potential when placed. If not placed only the selected WE has an applied potential leaving not-selected WE's at open circuit.

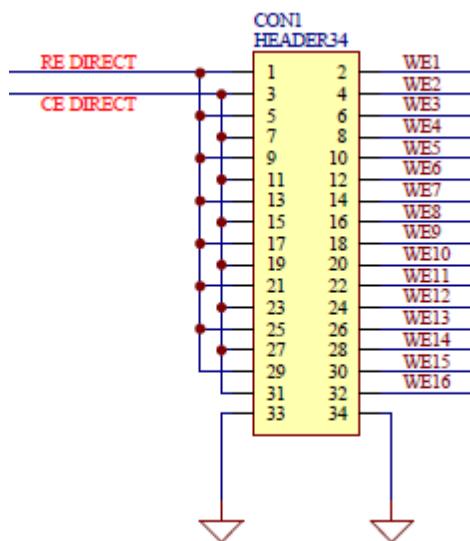
J4: (unselected WE) to standby potential

Is always left open

Jumper settings for the available configurations:

- **Conf. 1:** Sensor array with up to 16 working and 16 combined reference/counter electrodes:
 - o Jumpers to be placed: J1 and J2
When J3 is also placed, the potential is applied to all working electrodes continuously.
Use pin 1, 3, 5 to 31 to connect all combined RE/CE electrodes.
- **Conf. 2:** Sensor array with up to 16 working electrodes all sharing one reference and one counter electrode:
 - o Jumper to be placed: J2
When J3 is also placed, the potential is applied to all working electrodes continuously.
Use pin 1, 5, 9, 13, 17, 21, 25 or 29 to connect RE
Use pin 3, 7, 11, 15, 18, 23, 27 or 31 to connect CE
- **Conf. 3:** Sensor array with up to 16 working electrodes all sharing one combined reference/counter electrode:
 - o Jumpers placed are: J1 and J2
When J3 is also placed, the potential is applied to all working electrodes continuously.
Use pin 1, 3, 5..... to 31 to connect RE/CE

13.2.4 Electrodes connections



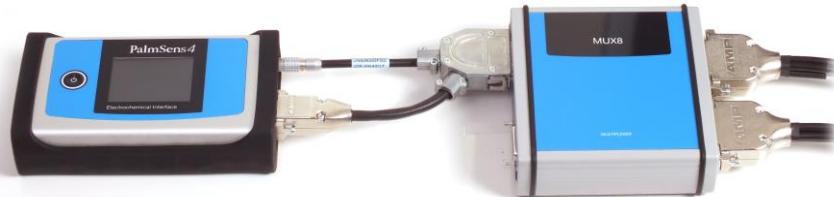
* IMPORTANT REMARK

It is not possible to apply a potential simultaneously to more than one sensor or cell each with three electrodes. This requires a multipotentiostat, one potentiostat for each channel. This is however possible with two electrode sensors or cells, so when combined counter and reference electrodes are applied.

14 MUX8-R2 multiplexer

The MUX8-R2 multiplexer can be used to expand a PalmSens3, PalmSens4 or EmStat Blue potentiostat. Or the MUX8-R2 can have an integrated EmStat3 or EmStat3+ potentiostat.

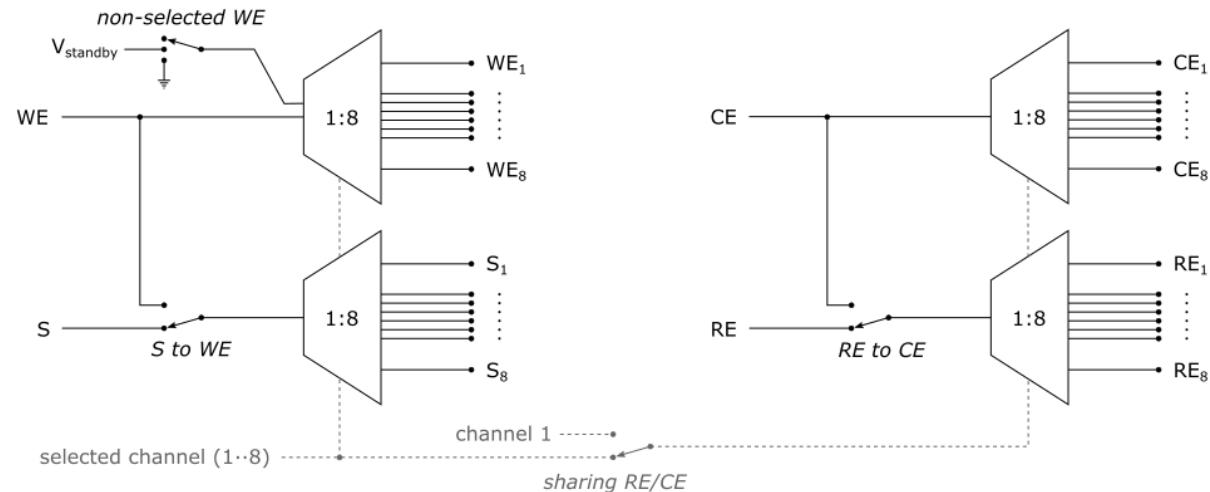
The multiplexer allows to increase productivity by automatically switching between multiple electrochemical cells each with their own WE, RE and CE electrodes.



PalmSens4 connected to MUX8-R2 multiplexer

The MUX8-R2 multiplexer is designed for up to 8 channels with 2- or 3- electrode sensors or cells.

14.1 MUX8-R2 Functional Diagram



14.2 Specifications

MUX8 multiplexer

▪ number of channels	8 (up to 128 channels when daisy chained)
▪ multiplexer	switches 8 x (WE, S, RE and CE)
▪ on resistance for WE	1.5 ohm typical
▪ charge injection on WE	20 pC typical
▪ leakage current	< 20 pA (5 pA typical) at 25 °C
▪ switching time	2 ms
▪ compliance voltage	±10 V

Limitations for Electrochemical Impedance Spectroscopy (EIS)

- **max. frequency**
 - 100 kHz when switching WE/S, RE and CE
 - 1 MHz when switching WE/S and RE+CE combined (2 electrodes configuration)

14.3 Configurations

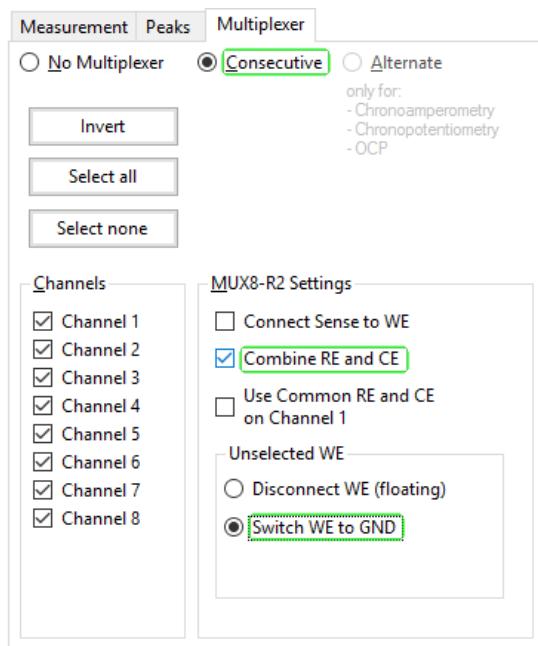
The multiplexer can be used with different electrode or sensor configurations:

- 1 Eight separate cells or sensors each with a working/sense, reference and counter electrode
- 2 Eight separate cells or sensors each with a working/sense and combined reference and counter electrode
- 3 Cell or sensor array with eight working/sense electrodes sharing one reference and one counter electrode
- 4 Cell or sensor array with eight working/sense electrodes sharing one combined reference/counter electrode

In all configurations the cells can be multiplexed, leaving the non-selected working electrodes either at open circuit (individually floating) or at Ground potential.

In configurations 3 and 4, the unselected channels can be switched to Ground which means they will maintain their potential when they are not connected (since the active WE is always at Ground potential).

Another option for configuration 3 and 4 is to have the unselected channels at a different potential which can be an offset of -1.5 to 1.5 V from the applied potential on the active WE.

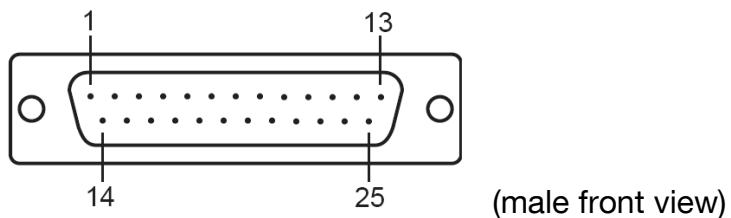


The MUX8-R2 multiplexer settings can be changed in the Multiplexer tab.

14.4 Connections

Connector	Function
Input	Y-cable connects to both potentiostat sensor connector and (digital) AUX
AUX	Can be used to measure auxiliary input like temperature or pH, and to switch external hardware using two digital control lines that can be set in PStree
Link	Connects to Input of next multiplexer, for daisy-chaining multiple multiplexers.
USB-C	For providing extra power in case more than 2 multiplexers are connected to a single instrument.
Channel 1-4	Connects to sensor cables 1-4
Channel 5-8	Connects to sensor cables 5-8

14.5 MUX8-R2 Pin-outs

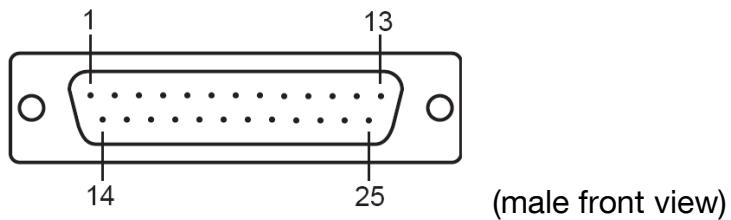


Channel 1-4

Pin	Function
1	CE4
2	RE4
3	RE_SHIELD4
4	CE3
5	RE3
6	RE_SHIELD3
7	CE2
8	RE2
9	RE_SHIELD2
10	CE1

Pin	Function
11	RE1
12	RE_SHIELD1
13	NC
14	WE4
15	AGND
16	SENSE4
17	WE3
18	AGND
19	SENSE3
20	WE2

Pin	Function
21	AGND
22	SENSE2
23	WE1
24	AGND
25	SENSE1



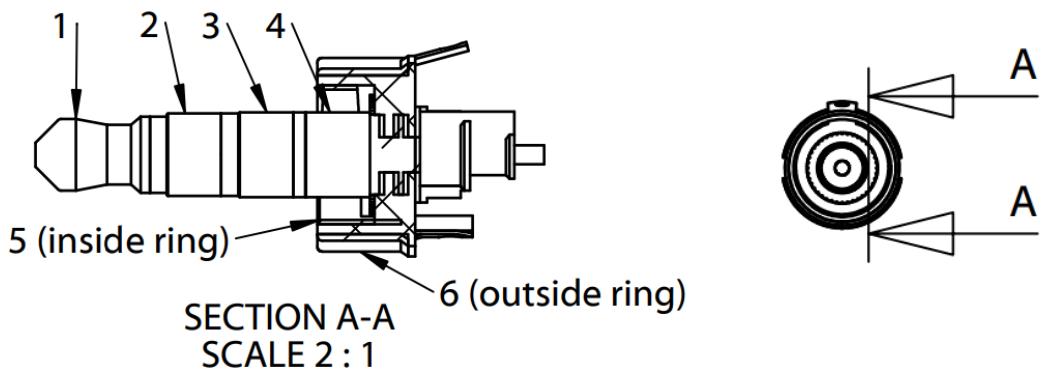
Channel 5-8

Pin	Function
1	CE8
2	RE8
3	RE_SHIELD8
4	CE7
5	RE7
6	RE_SHIELD7
7	CE6
8	RE6
9	RE_SHIELD6
10	CE5

Pin	Function
11	RE5
12	RE_SHIELD5
13	NC
14	WE8
15	AGND
16	SENSE8
17	WE7
18	AGND
19	SENSE7
20	WE6

Pin	Function
21	AGND
22	SENSE6
23	WE5
24	AGND
25	SENSE5

AUX port:



Ring	Lead colour	Function
1	Red	NC
2	Black	D0 (digital I/O)
3	Yellow	Analog Input
4	White	D1 (digital I/O)
5	Green	GND
6	Blue	5V

14.6 Stacking

Each multiplexer has a Link connector which can be used to daisy chain to another MUX8-R2 multiplexer, expanding the number of channels. A maximum of 16 multiplexers can be connected in a daisy chain, giving a maximum of 128 channels. The PSTrace software detects automatically how many multiplexers are daisy chained and shows the available number of channels in the user interface.



The MUX8-R2 has magnetic feet and magnets at the top for easy stacking

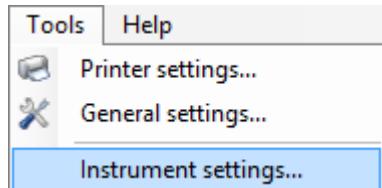
15 PalmSens or EmStat firmware update

The firmware which runs on PalmSens or EmStat might need to be updated when a new version of PSTrace is installed. PSTrace will prompt a message and take care of the firmware update if this is necessary.

15.1 Firmware update

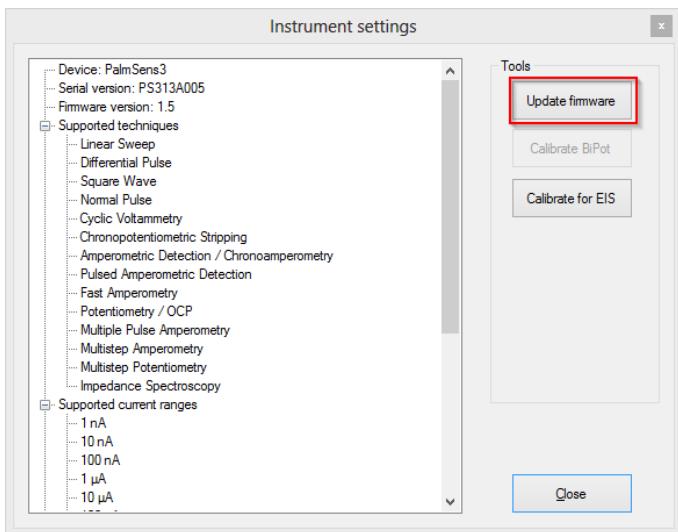
If a specific version of the firmware should be downloaded the firmware can be updated using the firmware update window found in PSTrace via the menu ‘Tools’ → ‘Instrument settings’...

Normally this should not be necessary because PSTrace will prompt a message and take care of the firmware update if this is necessary.



Instrument settings menu

The ‘Update firmware’ button is found at the right top of the window:



Instrument settings window

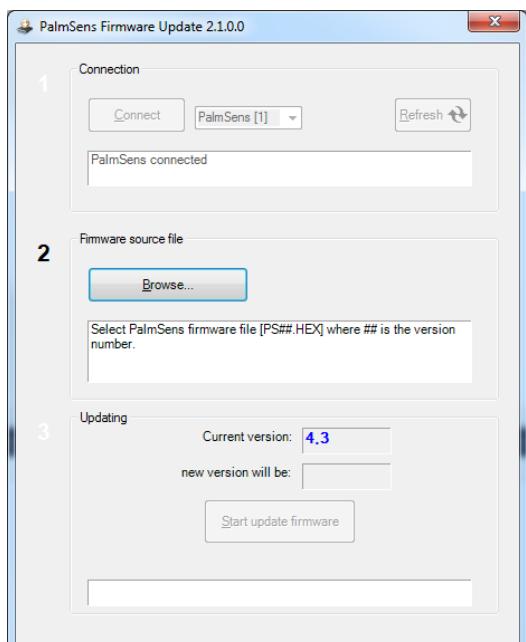
1. If not already connected; connect the instrument to the PC and in case of a PalmSens1 or PalmSens2; to the ac-adapter and the PC.

IMPORTANT:

It is essential that the instrument is not switched off during the process of updating the firmware.

In case of a PalmSens1 or PalmSens2:

Be sure that the batteries are full or that PalmSens is connected to the ac-adapter.

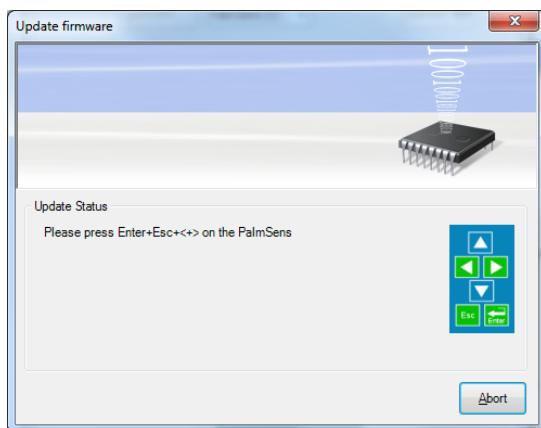


1. Now click the 'Browse...' button and select the appropriate HEX file.

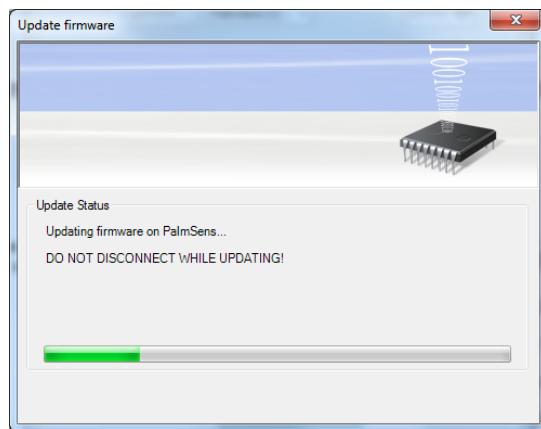
2. Now press the ‘Start update firmware’ button.

In case of a PalmSens1 or PalmSens2 only:

3. The window now tells you to press the four keys ‘Enter + Esc + < + >’ simultaneously.
DO THIS ONLY ONCE! The updating process will start immediately after pressing the four keys.



4. If the instrument is in download mode, the status bar of the firmware update is shown. If this screen does not appear, the program can be closed and started again.



5. After completing the update, the program will show “UPDATE COMPLETE”.

16 PalmSens instrument specifications



PalmSens is a hand-held battery powered instrument for use with electrochemical sensors or electrochemical cells. The instrument contains a microprocessor and a low noise and low-current potentiostat/galvanostat which controls the potential or current applied to the sensor and measures the current or potential response. The PalmSens3 and PalmSens4 can also optionally be equipped with FRA for impedance spectroscopy.

16.1 Description

In general, the PalmSens instruments are used with electrochemical sensors or electrochemical cells with three electrodes: working electrode, reference electrode and auxiliary or counter electrode. In the so-called two-electrode configuration the counter and reference electrodes can be combined to a single electrode. In that case the counter and reference connectors are tied together.

The instrument can be extended with a bipotentiostat module (BiPot) or with a multiplexer for use with up to eight or sixteen sensors or electrochemical cells.

16.2 PalmSens1 and 2 specifications



PalmSens model 1 and 2

Potentiostat (controlled potential mode)

- dc-potential range ± 2.000 V
- compliance voltage ± 8.0 V
- dc-potential resolution 1 mV
- dc-offset error 2 mV
- accuracy ≤ 0.2 %
- ac-potential amplitude 1 mV to 250 mV
- current ranges 1 nA to 10 mA (8 ranges)
- maximum current ± 10 mA
- current resolution 0.1 % of current range
- 1 pA on lowest current range
- accuracy ≤ 0.2 % of current range at 100 nA to 1 mA
 ≤ 0.5 % at 10 nA and ≤ 1 % at 1 nA
 all with additional 0.2 % offset error

Galvanostat (controlled current mode)

- current ranges 1 μ A to 1 mA
- dc-current range -2 to + 2 times selected current range
- dc-current resolution 0.1 % of selected current range
- dc-offset error ≤ 0.2 %
- current accuracy ≤ 0.4 %
- maximum output voltage ± 8 V

General

- electrometer amplifier input > 100 Gohm // 4 pF
- rise time approx. 50 μ s
- Keypad $\blacktriangle \blacktriangleright \blacktriangledown \blacktriangleleft$ ENTER ESC and Power (7 keys)
- Display 4 lines of 16 characters with backlight

▪ Dimensions	155 mm x 85 mm x 35 mm
▪ Temperature range	0° C to + 40° C
▪ Weight	0.43 kg
▪ Power	2 AA cells NiMH 2500 mAh for > 8 hours operation. Battery charger included (6 V- 1500 mA)
▪ Interfacing	Serial RS232 Default serial mode: 57600 baud, 8 bits data, no parity, 1 stopbit.
▪ External I/O	Analog: 1 input and 1 output channel (0 V - 4.096 V) Digital: 1 input and 4 output lines

16.3 BiPot specifications for PalmSens1 and PalmSens2

The table below shows the specifications of the optional Bipotentiostat module for PalmSens1 and PalmSens2.

General

▪ dc-potential range	± 2.000 V
▪ dc-potential resolution	1 mV
▪ dc-offset error	3 mV
▪ accuracy	≤ 0.3 %
▪ current ranges	1 nA to 10 mA (8 ranges)
▪ maximum measured current	± 10 mA
▪ current resolution	0.1 % of current range 1 pA on lowest current range
▪ accuracy	≤ 0.3 % of current range at 1 µA to 100 µA ≤ 0.5 % at 100 nA and ≤ 1 % at 10 and 1 nA all with additional 0.2 % offset error
▪ connection	Use requires a cable with additionally a (yellow) connector for WE2

16.4 PalmSens3 specifications



PalmSens 3

Potentiostat (controlled potential mode)

- dc-potential range ± 5.000 V
- compliance voltage ± 8.0 V
- dc-potential resolution 0.15 mV
- applied potential accuracy ≤ 0.2 %
with max. 2 mV offset error
- current ranges 100 pA to 10 mA (9 ranges)
- maximum measured current ± 30 mA (typical)
- current resolution 0.01 % of current range
 ≤ 1 % of current range at 1 nA (≤ 5 % at 100 pA)
 ≤ 0.5 % at 10 nA
 ≤ 0.2 % at 100 nA to 1 mA
 ≤ 0.5 % at 10 mA
all with max. 0.2 % offset error
- max. acquisition rate 200 000 data points/s

Galvanostat (controlled current mode)

- current ranges 1 μ A to 10 mA
- dc-current range ± 3.000 times selected current range
- dc-current resolution 0.01 % of selected current range
- max. dc-offset error ≤ 0.2 %
- current accuracy (deviation) ≤ 0.4 %
- maximum output voltage ± 8 V

Impedance measurements

- frequency range 100 μ Hz to 50 kHz
- ac- amplitude range 1 mV to 0.25 V (rms)

General

- **electrometer amplifier input** > 100 Gohm // 4 pF
- **rise time** programmable from min. 0.5 µs

Other

- **keypad** run, skip, abort, backlight and power
- **housing** aluminium: 155 mm x 85 mm x 35 mm
- **weight** 430 g
- **temperature range** 0° C to + 40° C
- **power supply** USB or internal Li-ion battery
- **battery time** >9 hours idle time with Bluetooth extension
- **communication** USB

Auxiliary port (D-Sub 15)

- **external I/O** analog: 1 input and 1 output channel (0 V - 3 V)
digital: 1 input and 4 output lines (3.3V)

16.5 BiPot specifications for PalmSens3

The table below shows the specifications of the optional Bipotentiostat module for PalmSens3.

General

- **dc-potential range** ± 5.000 V
- **dc-potential resolution** 0.15 mV
- **dc-offset error** 3 mV
- **accuracy** ≤ 0.3 %
- **current ranges** 1 nA to 10 mA (8 ranges)
- **maximum measured current** ± 10 mA
- **current resolution** 0.01 % of current range
0.1 pA on lowest current range
- **accuracy** ≤ 0.3 % of current range at 1 µA to 100 µA
≤ 0.5 % at 100 nA and ≤ 1 % at 10 and 1 nA
all with additional 0.2 % offset error
- **connection** Use requires a cable with additionally a (yellow) connector for WE2

16.6 PalmSens4 specifications



PalmSens4

General

- dc-potential range ± 10 V (or ± 5 V)
- compliance voltage ± 10 V
- maximum current ± 30 mA (typical)
- max. acquisition rate 150000 data points/s

Potentiostat (controlled potential mode)

- applied dc-potential resolution 75 μ V
- applied potential accuracy $\leq 0.1\%$ ± 1 mV offset
- current ranges 100 pA to 10 mA (9 ranges)
- current accuracy ≤ 0.1 % at FSR¹
- measured current resolution 0.006 % of current range (5 fA on 100 pA range)

Potentiostat (controlled potential mode)

- current ranges 1 nA to 10 mA (8 ranges)
- applied dc-current range ± 6 times applied current range
- applied dc-current resolution 0.005 % of applied current range
- measured dc-potential resolution 75 μ V at ± 10 V
7.5 μ V at ± 1 V
0.75 μ V at ± 0.1 V

FRA / EIS (impedance measurements)

- frequency range 10 μ Hz to 1 MHz (or 10 μ Hz to 100 kHz)
- ac-amplitude range 1 mV to 0.25 V rms, or 0.6 V p-p

Electrometer

- electrometer amplifier input > 1 T Ω // 10 pF
- bandwidth 1 MHz

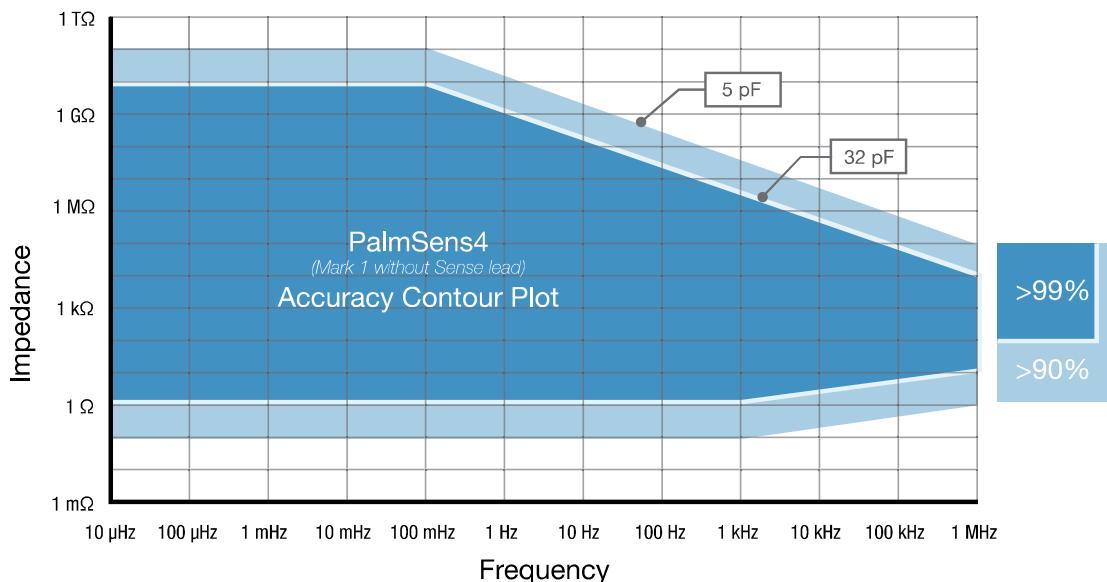
¹ FSR = at full scale range

Other

- **housing** aluminium with rubber sleeve: 15.7 x 9.7 x 3.5 cm³
- **weight** 500 g
- **temperature range** 0 °C to + 50 °C
- **power supply** USB or internal LiPo battery
- **communication** USB and Bluetooth
- **battery time** > 16 hours idle time
> 4 hours with cell on at max. current
Extendible by means of power bank
- **internal storage space** 4 GB
4 GB
or +/- 400000 measurements incl. method info
(assuming 200 data points per measurement)

Auxiliary port (D-Sub 15)

- **analog input** ± 10 V, 18 bit
- **analog output** 0-10 V, 12 bit (1 kOhm output impedance)
- **4 digital outputs** 0-3.3 V
- **1 digital input** 0-3.3 V (5 V tolerant)
- **I-out and E-out** raw output of current and potential
E-out ± 10 V (1 kOhm output impedance)
I-out ± 6 V (1 kOhm output impedance)
- **power** 5 V output (max. 150 mA)

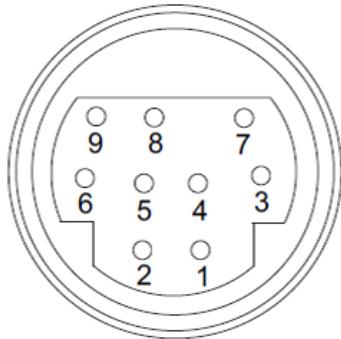
EIS contour accuracy plot:**Note**

The accuracy contour plot was determined under lab conditions and should be used for reference purposes. Please note that the true limits of an impedance measurement are influenced by all components in the system, e.g. cables, the environment, and the cell.

16.7 Auxiliary port pin-outs

PalmSens2 AUX port pin-out

Front view of female port:



pin 1	Vadapter (6 V- 1.5 A) for serial numbers PS0201 to PS04200 and d3 digital output for PS04201 and higher
pin 2	analog ground
pin 3	d0 digital output (maximum current 5 mA source or sink)
pin 4	d1 digital output (maximum current 5 mA source or sink)
pin 5	d2 digital output (maximum current 5 mA source or sink)
pin 6	d0 digital input
pin 7	auxiliary analog input
pin 8	auxiliary analog output (advised resistive load > 10 kohm)
pin 9	5 V digital power line (maximum current 100 mA)
shield	digital ground

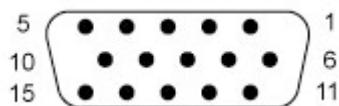
Maximum ratings:

Digital input and output lines: -0.3 V to 5.3 V

Analog input and output lines: -0.3 V to 5.3 V

PalmSens3 AUX port pin-out

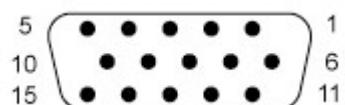
Front view of female port:



- | | |
|---------------|---|
| pin 1 | d0 digital output (5V) |
| pin 2 | d3 digital output (5V) |
| pin 3 | auxiliary analog input
(>0.5 Mohm input impedance) |
| pin 4 | Rx (TTL default, or RS232 see pin 12) |
| pin 5 | Tx (TTL default, or RS232 see pin 12) |
| pin 6 | d1 digital output (5V) |
| pin 7 | d0 digital input (5V) |
| pin 8 | I out (V in current range) |
| pin 9 | 5 V digital power line
(max. 50mA) |
| pin 10 | digital ground |
| pin 11 | d2 digital output (5V) |
| pin 12 | Connect to pin 10 (DGND) for
RS232 comm on pin 4 and pin 5 |
| pin 13 | E out (-5 to +5V) |
| pin 14 | analog ground |
| pin 15 | DAC out (0-3V) |
| shield | digital ground |

PalmSens4 AUX port pin-out

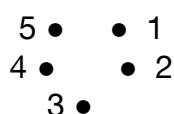
Front view of female port:



pin 1	d0 digital output (3.3V)
pin 2	d3 digital output (3.3V)
pin 3	auxiliary analog input -10 to +10 V, 18 bit, >0.5 MΩ input impedance
pin 4	RESERVED
pin 5	RESERVED
pin 6	d1 digital output (3.3V)
pin 7	d0 digital input (3.3V)
pin 8	I out (V in current range)
pin 9	5V digital power line (max. 300mA)
pin 10	digital ground
pin 11	d2 digital output (3.3V)
pin 12	Connect to pin 10 (DGND) for TTL 3.3V comm on pin 4 and pin 5
pin 13	E out (-5 to +5V)
pin 14	analog ground
pin 15	analog out (0 to 10 V at 12 bit)
shield	digital ground

16.8 Sensor connector pin-outs**PalmSens1 and PalmSens2 sensor connector pin-out**

Front view of male plug:



Solder side of male plug:

1 • • 5
2 • • 4
3 •

1. WE: red connector is working electrode
2. AGND: green connector is ground
3. Not connected in default plug or WE2 if BiPot is present
4. CE: black connector or counter electrode
5. RE: blue connector or reference electrode

PalmSens3 sensor connector pin-out

Front view of male plug:

4 • • 1
3 • • 2

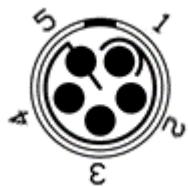
Solder side of male plug:

1 • • 4
2 • • 3

1. RE: blue connector or reference electrode
 2. CE: black connector or counter electrode
 3. Not connected in default plug or WE2 if BiPot is present
 4. WE: red connector is working electrode
- [shield] AGND: green connector is ground

PalmSens4 sensor connector pin-out

Front view of male plug:



Solder side of male plug:



1. RE: blue connector or reference electrode
 2. RE Shield
 3. CE: black connector or counter electrode
 4. Not connected in default plug or WE2 if BiPot is present
 5. WE: red connector is working electrode
- [shield] AGND: green connector is ground

IMPORTANT:

The shield of the cable must make contact with the metal case of the sensors connector.

16.9 Battery maintenance

In case the battery capacity decreases it is advised to switch on PalmSens and wait until it switches off automatically. After charging the batteries, their capacity might be restored again.

Warning: Do not charge the batteries when the ambient temperature is below 0 °C or above 40 °C. Charging is done most efficiently in the range of 10 °C to 30 °C.

Do not store the instrument with batteries in places where the ambient temperature is below 0 °C or above 40 °C.

Do not connect the charger with reversed polarity.

Detailed instructions for battery replacement are available from PalmSens BV: send a message to info@palmsens.com

Note: the batterypack must be obtained from PalmSens BV.

Ordering codes:

- PS2BATT (for PalmSens1 or 2, old models)
- PS3BATT for PalmSens3
- PS4BATT for PalmSens4

17 EmStat instruments specifications



The EmStat, EmStat2, EmStat3 and EmStat3+ (embedded potentiostat) are the smallest, commercially available computer controlled potentiostats. The EmStat3 Blue and EmStat3+ Blue models allow to connect via Bluetooth, have an integrated battery, an additional auxiliary port and connector for a wide collection of screen printed electrodes (SPE).

17.1 Description

EmStat1 has six current ranges from 1 nA to 100 uA full scale, with a minimum resolution of 1 pA. EmStat2 and EmStat3 have additionally two current ranges of 1 mA and 10 mA. EmStat3+ has current ranges from 1 nA up to 100 mA.

The potentiostat is normally controlled by means of a USB cable.

Multiple channels

The instruments (except EmStat3+) can be delivered with a 8- or 16-channel multiplexer integrated in a single housing as EmStatMUX. They can also be configured as MultiEmStat where a single instrument contains 4, 8 or 12 individual EmStat units..

17.2 EmStat and EmStat2 specifications

General

- dc-potential range ± 2.000 V
- compliance voltage ± 4.5 V
- maximum output current ± 20 mA

Potentiostat (controlled potential mode)

- dc-potential resolution 1 mV
- applied dc-potential accuracy ≤ 0.2 %
- max. dc-offset error 2 mV
- current ranges 1 nA to 100 μ A (6 ranges)
1 nA to 10 mA (8 ranges) for EmStat2
- current resolution 0.1 % of current range
1 pA on lowest current range
- current accuracy ≤ 0.3 % of current range at 1 μ A to 100 μ A
 ≤ 0.5 % at 100 nA and ≤ 1 % at 10 and 1 nA
all with additional 0.2 % offset error

Electrometer

- electrometer amplifier input > 100 Gohm // 4 pF
- rise time approx. 200 μ s

Other

- dimensions EmStat: 6.2 cm x 4.6 cm x (1.7 to 2.8 cm)
EmStat2: 6.2 cm x 4.8 cm x (1.7 to 2.6 cm)
- power 5 V / 60 mA from USB connector (or ac-adapter ¹)
- interfacing USB (or RS-232 ¹)
- external I/O options ¹ analog: 1 input and 1 output channel (both 0 V - 4.096 V)
digital: 4 input and/or output lines
- options 8 or 16 channel multiplexer
- sensor connection shielded cable with circular connector (PalmSens compatible)
or specific connector ¹

¹ Means that a modification is required.

17.3 EmStat3 and EmStat3+ specifications

Main differences between EmStat and EmStat Blue models

	EmStat3 and 3+	EmStat3 and 3+ blue
		
Size (cm)	6.7 x 5.0 x 2.8	10.0 x 6.0 x 3.4
Weight	85 g	250 g
Battery	no	yes
Communication	USB	USB + Bluetooth
Auxiliary port	no	yes
Sensor connector	LEMO	LEMO + SPE ²

	EmStat3	EmStat3+
dc-potential range	± 3.000 V	± 4.000 V
compliance voltage	± 5 V	± 8 V
applied dc-potential resolution	0.1 mV	0.125 mV
applied potential accuracy	≤ 0.2 % with max. 2 mV offset error	≤ 0.3 % with max. 3 mV offset error
current ranges	1 nA to 10 mA (8 ranges)	1 nA to 100 mA (9 ranges)
maximum measured current	± 20 mA typical and ± 15 mA minimum	± 100 mA typical

² The SPE connector allows for direct insertion of the most popular types of Screen Printed Electrodes.

EmStat 3 and 3+ Potentiostat (controlled potential mode)

- **current resolution** 0.1 % of current range
1 pA on lowest current range
- **current accuracy** ≤ 1 % of current range at 1 nA
≤ 0.5 % at 10 nA
≤ 0.2 % at 100 nA to 100 uA
≤ 0.5 % at 1 mA, 10 mA and 100 mA
all with additional 0.2 % offset error

Electrometer / other

- **electrometer amplifier input** > 100 Gohm // 4 pF
- **rise time** approx. 200 µs
- **sensor connection** shielded cable with circular connector for WE, RE, CE and Sense (100 mA for ES3+ only)

EmStat 3 and 3+ regular model

- **housing** anodized aluminium: 6.7 cm x 5.0 cm x (1.9 to 2.8 cm)
- **weight** 85 g
- **power supply** 5 V, min. 130 mA (ES3) or 500 mA (ES3+) via USB
- **communication** USB
- **auxiliary port present** no

EmStat 3 and 3+ Blue model

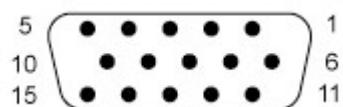
- **housing** anodized aluminium: 100 mm x 60 mm x (27 to 34 mm)
- **weight** 85 g
- **power supply** USB or internal Li-Po battery
5 V, min. 130 mA (ES3) or 500 mA (ES3+)
- **battery time** > 8 hours with cell off
> 6 hours with continuous cell on at 1uA current
full charge takes approx. 3 hours
- **communication** USB or Bluetooth
- **auxiliary port present** yes
- **external I/O options** analog: 1 input and 1 output channel
(both 0 V - 4.096 V)
digital: 1 input, 4 output lines
(maximum rating: -0.3 V to 5.3 V)

The EmStat3 and EmStat3+ Blue have an auxiliary port to control external accessories. The instrument is also available as OEM device for integration in instruments for specific electrochemical sensors or other applications.

17.4 EmStat Blue auxiliary port pin-out

EmStat3 or 3+ Blue

Front view of female port:



D-Sub15	Description	EmStat PCB pin (CON-PIN)
pin 1	d0 digital output (5V)	1-4
pin 2	d3 digital output (5V)	1-1
pin 3	auxiliary analog input (0 – 4.095 V)	2-9
pin 4	Rx (TTL comm)	2-2
pin 5	Tx (TTL comm)	2-1
pin 6	d1 digital output (5V)	1-3
pin 7	d0 digital input (5V)	1-4
pin 8	RESERVED	-
pin 9	5 V digital power line (max. 50mA)	2-12
pin 10	digital ground	2-11
pin 11	d2 digital output (5V)	1-2
pin 12	RESERVED	-
pin 13	RESERVED	-
pin 14	analog ground	1-9
pin 15	DAC out (0-3V)	2-10
shield	digital ground	-

17.5 Sensor connector pin-outs

EmStat1 and EmStat2

Front view of male plug:

U	
5 •	• 1
4 •	• 2
3 •	

Solder side of male plug:

U	
1 •	• 5
2 •	• 4
3 •	

1. WE: red connector is working electrode
2. AGND: green connector is ground
3. Other (optional) use.
4. CE: black connector or counter electrode
5. RE: blue connector or reference electrode

EmStat3(Blue) and EmStat3+(Blue)

Front view of male plug:

U	
1 •	• 4
2 •	• 3

Solder side of male plug:

U	
4 •	• 1
3 •	• 2

1. RE: blue connector or reference electrode
2. CE: black connector or counter electrode
3. S: Sense connector for working electrode on EmStat3+ or other (optional) use on EmStat3
4. WE: red connector is working electrode

Metal casing AGND: green connector is ground

18 Multi-channel instruments specifications

The EmStat-4WE, MultiEmStat3, MultiEmstat3+ and MultiPalmSens4 are instruments with multiple potentiostat modules for running multiple measurements in parallel.

18.1 MultiPalmSens4 specifications

The MultiPalmSens4 is a flexible multi-channel potentiostat, galvanostat and impedance analyser. Each channel consists of a single PalmSens4 potentiostat unit which can be extended with BiPot- or IR-drop compensation-module.

See [PalmSens4 specifications](#) on page 260 for potentiostat and AUX specifications.

MultiPalmSens4 specifications

▪ housing	15 x 25 x 25 cm ³
▪ weight	+/- 4 kg
▪ temperature range	0 °C to + 50 °C
▪ power supply	external 12 V AC/DC adapter
▪ communication	USB (type A)
▪ internal storage space	8 GB per channel or +/- 800000 measurements incl. method info (assuming 200 data points per measurement)

18.2 MultiEmStat3 / 3+ specifications

The MultiEmStat is a multi-channel potentiostat with 4, 8 or 12 independent EmStat3 or EmStat3+ modules, each with its own WE, RE and CE.

See [EmSat3 and 3+ specifications](#) on page 271 for potentiostat.

Specifications of MultiEmStat3 / 3+ with 4 channels

▪ housing	115 mm x 85 mm x 35 mm
▪ weight	+/- 260 g
▪ temperature range	0 °C to + 50 °C
▪ power supply	external 5 V AC/DC adapter
▪ communication	USB (type A)

Specifications of MultiEmStat3 / 3+ with 8 or 12 channels

▪ housing	120 mm x 210 mm x 75 mm
▪ weight	+/- 2 kg
▪ temperature range	0 °C to + 50 °C
▪ power supply	external 12 V AC/DC adapter
▪ communication	USB (type A)

18.3 EmStat-4WE specifications

EmStat4WE is a polypotentiostat with 4 working electrodes, that makes parallel measuring of multiple electrodes in one electrochemical cell possible. With this polypotentiostat one electrochemical cell can be equipped with 1, 2, 3 or 4 working electrodes and all of these will be measured parallel.

The additional WE's can each individually be used in two different modes:

1. The potential of the additional WE has a constant dc-potential offset with respect to WE1, i.e. it is following the potential change of WE1.
2. The potential of the additional WE has an independent fixed dc-potential.

Each potentiostat has eight current ranges: 1 nA to 10 mA with a resolution of 1 pA at the lowest current range and can automatically select the optimal current range.



A cell can be setup with one reference and one counter electrode or one combined reference and counter electrode.

The EmStat3-4WE consist of a standard EmStat3 potentiostat and additionally three polypotentiostat (bipotentiostat-like) modules. The instrument is used for electrochemical systems with 1, 2, 3, or 4 working electrodes (WE1 - 4) all sharing the same counter (CE) and reference electrodes (RE) or combined CE/RE. The embedded software of the EmStat3 instruments provides all relevant methods for electrochemical sensors.

All techniques supported by EmStat3 are available for the EmStat3 4WE.

EmStat3 4WE	Main potentiostat	Polypotentiostat modules
dc-potential range	± 3.000 V	± 3.000 V
compliance voltage	± 5 V	± 5 V
dc-potential resolution	0.1 mV	0.1 mV
max. dc-offset error	2 mV	3 mV
potential accuracy	0.2 %	0.2 %
current ranges	1 nA to 10 mA (8 ranges)	1 nA to 10 mA (8 ranges)
maximum current	± 20 mA typical and ± 15 mA minimum for the sum of WE1, W2, W3 and W4	
current resolution	0.1% of current range, 1 pA at lowest current range	
electrometer amplifier	> 100 GOhm // 4 pF	> 100 GOhm // 4 pF
input		
rise time	approx. 100 μ s	approx. 100 μ s

Housing:

dimensions	12 cm x 8.5 cm x 3.5 cm
weight	250 g
power	5 V external power supply
interfacing	USB

19 Troubleshooting

In this section solutions to known issues are described.

19.1 Test procedure for PalmSens and EmStat.

PalmSens as well EmStat can be tested by using the test sensor supplied with the instrument.

If PalmSens or EmStat seem to function and PSTrace recognizes the instrument, perform the tests as described in chapter ‘First measurements’.

It is also possible to test the instrument by means of a fixed resistor with a value of for instance 1 Mohm. The WE lead is connected to one side and both RE and CE to the other side of the resistor. Any of the electrochemical techniques can be applied. The current response obtained with a resistor with value R is equal to the applied potential or potential pulse divided by the value of R. So if a potential of 0.5 V is applied on a resistor of 1 Mohm, the obtained current should be $0.5 \text{ V} / 1 \text{ Mohm} = 0.5 \mu\text{A}$.

Contact PalmSens BV if the problems are found: info@palmsens.com and report the problems as detailed as possible.

19.2 Replacement of PalmSens1 or PalmSens2 battery

IMPORTANT:

This section does not apply to the PalmSens3 or PalmSens4!
A PalmSens1 or PalmSens2 has a green LCD.



Necessary tools:

- Size 14 spanner
- Phillips or TORX T-10 screwdriver
- Flat screwdriver
- Pointy tool

Step 1



Untighten the bolt very carefully with the spanner, without scratching the surface of the housing.

Screw it off using your fingers.

Step 2

If present remove the two protective caps using the pointy tool by sticking it between the cap and housing and levering it out.

Step 3

Remove the sensor side of the housing.

Step 4

Pull out the battery connector using the tongs.

Replace the battery and connect it to the printed circuit board.

Step 5 Closing the housing

1. Place the ring back over the sensor connector and screw the sensor side of the housing back on.

IMPORTANT:

Do not use too much force while screwing, this may cause the screw to slip or break!

2. Place the nut back onto the sensor connector and screw it using your fingers as fixed as you can. Then tighten the nut by turning it one quarter more using the spanner. Tightening it too much will damage the housing.
3. If available put the protective caps in place.
4. New batteries may be empty, so first connect PalmSens to the ac-adapter and charge the batteries completely.

19.3 Restoring PalmSens3 in case of freeze

IMPORTANT:

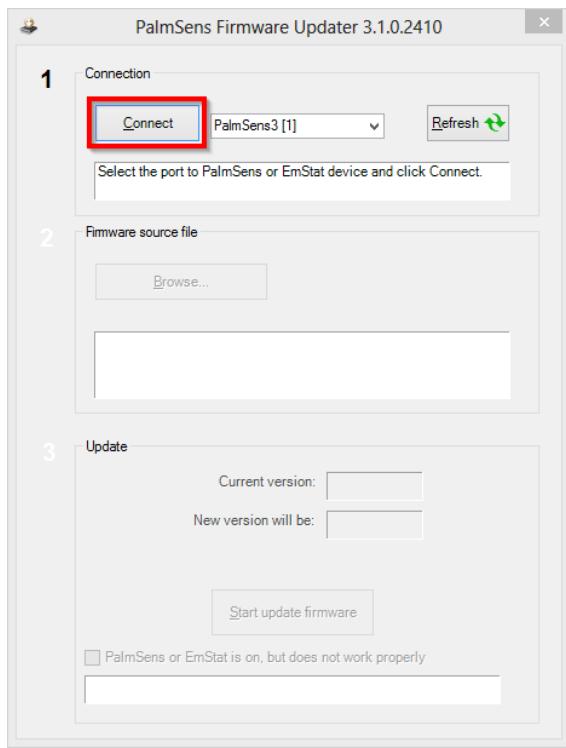
Please use this procedure only if your PalmSens3 shows a blue screen without characters when turning on:



Follow these steps to restore your PalmSens3:

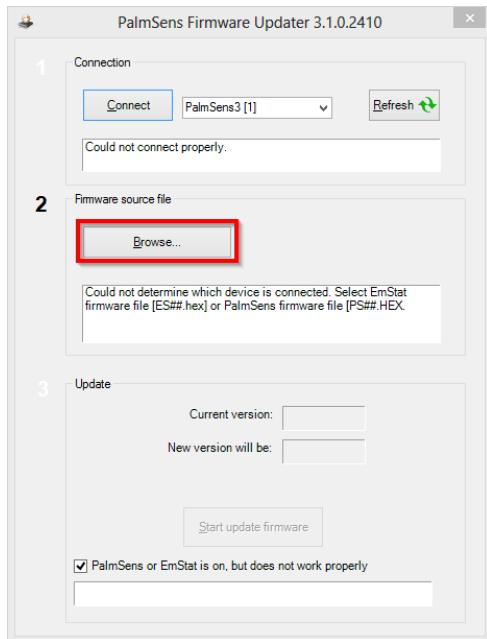
1. Open the Update Firmware program from the Start Menu:
Start → All Programs → PalmSens → PSTrace → Update Firmware
2. Make sure the USB cable is connected and PalmSens3 shows in the list next to the 'Connect' button.

3. Click the ‘Connect’ button:



4. The program will say “Could not connect properly.” Ignore this.

5. Click the ‘Browse’ button.

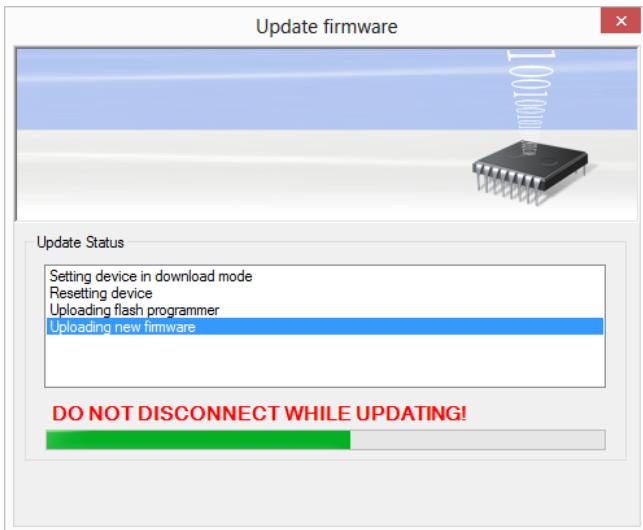


6. Select a .HEX file with the signature PalmSens3_firmware_v##.hex. Where ## is the version number.

7. Click the button ‘Start update firmware’.

Start update firmware

8. The firmware will be restored:



Normally it takes only a few minutes to download new firmware to the PalmSens3.
If the update procedure does not start or something is still wrong
contact PalmSens BV by e-mail: info@palmsens.com

19.4 EIS Calibration

Follow the instructions of this section only if your PalmSens3 has EIS capabilities.

After the PalmSens3 has been restored it is advised to run the EIS calibration procedure.

To do this open PSTrace. Then go to menu: Tools → Instrument settings... and click the “Calibrate for EIS” button.

Follow the instructions on the screen.

A normal calibration procedure takes about 5 minutes.

Appendix A – CE Certificate



DECLARATION OF CONFORMITY

We: PalmSens BV
Randhoeve 221
3995 GA Houten
The Netherlands

Certify that the products

PalmSens, EmStat, EmStat Blue, MultiEmStat and MultiPalmSens
are in conformity with EC Standard: EN 61326-1:2013
(Electrical equipment for measurement control and laboratory use),
referring to the following norms:

Emissions:

CISPR 11

Immunity:

IEC 61000-4-2
IEC 61000-4-3
IEC 61000-4-4
IEC 61000-4-5
IEC 61000-4-6
IEC 61000-4-11

Houten, May 2018

A handwritten signature in black ink, appearing to read 'C.J. van Velzen'.

C.J. van Velzen, director

PalmSens BV, Houten, The Netherlands, will not accept any liability for damages caused directly or indirectly by connecting this instrument to devices which do not meet the relevant safety standards. PalmSens is designed as an instrument for use with electrochemical sensors. PalmSens cannot, under any circumstance, be held responsible for the outcome or interpretation of data measured with PalmSens instruments.

20 Index

.pssession 171, 201
 / 151, 162
 ac-voltammogram 102
 Allow AC coupled measurements > 200 Hz 97
 Amplitude 51
 Analog In 175
 Analog Out 175
 Analytical mode 178
 Auto peak search window 178
 auto ranging 29
 autosave 31
 Autosave settings window 31
 Auxiliary port (PalmSens) 262
 auxiliay input 10
 backlight 3, 4
 battery 3
 battery (maintanance) 267
 BiPot 10, 37
 Blank 39
 blank curve 31
 Bluetooth 14
 Calibrate 175
 calibration curve 177, 181
 capacitor 125
 CDC circuit editor 112
 Cell On 175
 Cell volume 178
 chi-squared 134
 Chronopotentiometric Stripping 64
 circuit components 112
 circuit editor 112
 Circuit menu 119
 Clear help lines 150
 command line 222
 constant phase element 125
 Control E or I 175

Corrosion 189
 Corrosion current 191
 Corrosion potential 191
 Corrosion rate 191
 CSV 171, 206
 Current Level or Peaks 33
 current range 29, 97, 175
 Curve calculations 151, 156
 Curve calculations window 156, 158
 Curve operations window 158
 Cycles 76, 77, 79
 Data tab 148
 decimal separator 12
 differintegral 167
 Disable use of High Stability mode 97
 double layer capacitance 125
 Dummy Cell 19
 dynamic potential window 91
 E ac 56, 97
 E begin 44, 48, 51, 53, 56, 79, 97
 E cond1 188
 E cond2 188
 E dc 66, 68, 71, 79, 97
 E end 44, 48, 51, 53, 56, 64, 79, 97
 E equilibration 71
 E level [n] 76, 79
 E peak 178
 E pulse 48, 68
 E start 59, 62
 E step 44, 48, 51, 53, 56, 59, 62, 79, 97
 E vertex1 59, 62
 E vertex2 59, 62
 E1(measure) 72
 E2 72
 E3 72
 Edit Mode 111
 EIS Plot tab 147
 EIS Spectrum Analyzer 104
 Enable options for E corrections 12
 equivalent circuits 109, 195
 Excel 172
 Export 208
 Exporting curves 172
 Extrapolate baseline 151
 fast mode 4
 fit 109
 Fit Mode 111
 Fixed baseline 151

FRA	255
fractional derivative order.....	169
Free baseline.....	151
Frequency	51, 56, 97
Frequency type	97
Gerischer element	125
grid150	
High Speed mode	91
I applied	73, 79
I level [n]	77
impedance	93
inductor	125
Integration	156
ladder	134
Levels.....	33, 76, 77, 79
Linear polarization.....	187, 191, 195
Linear regression.....	156
Linear Sweep Voltammetry	44, 191
low battery	3
PalmSens2	3
Low Speed mode	91
Mains Frequency.....	10
Manual Control.....	175
manual mark peaks.....	151
max stability filter	97
Max. frequency	97
Maxwell	134
Measure vs OCP	97
Measurement tab	97
Measurement time	64
Min. frequency	97
miniDIN	3
Minimum Peak Height.....	33
Minimum Peak Width	33
mode	9, 68
Multiplexer Channel	175
Multiplexer tab	34
n averaged scans	62
n equil. scans	62
n frequencies.....	97
noise level	41
Non-linear baseline	151
Notes.....	27, 97
Number of scans	59, 62
OCP	188
Open Circuit Potential	188
Open Circuit Potential (OCP).....	87
Origin.....	106, 172
Overlapping peaks	167
overload	25
Override parameter	221
Oxidation or Reduction	33
peak separation window	167
Peak window.....	178
Peaks	33, 158
Plot scaling	150
Plot tab	147
Polarization resistance	191
Potential or Current.....	175
Pretreat each scan	97
printing	150
Pseudo Polarography	221
Readings	25
real E step	27
Recalculate	183
requirements	1
resistor	125
Sample volume	178
Scaling	150
Scan rate.....	44, 48, 53, 56, 59, 62, 79
Scan type	97
scripting	207
Select point	150
Sensitivity mode	97
sequence	86
Settings	8
simulate	109
smart scaling	150
Smooth Window	33
Solution number	178
solution resistance	125
Standard addition	177, 181
status	25
status bar	25
stirrer	10
Stirrer On	175
stirrer speed	175
Stripping chronopotentiometry	64
Stripping Current	64
t [n]76, 77, 79	
t cond1	188
t cond2	188
t interval ...66, 68, 71, 73, 75, 76, 77, 79,	97
t pulse	48, 53, 68
t run.....	66, 68, 71, 72, 73, 75, 79, 97

- t. Max equilibration..... 97
- t. Min. sampling..... 97
- t1 72
- t2 72
- t3 72
- Tafel slopes..... 191
- techniques list 27
- TestSensor 19
- Three points 151
- underload 25
- Use battery power only 175
- Voigt 134
- Voltage overload 25
- Voltammetric Analysis 177
- voltammetric measurement..... 86
- Warburg element..... 125
- warning message (method) 27
- WE2 Current Range 175
- WE2 Potential..... 175
- ZIP 208