1 – The ECD module

The ECD is an optional module for the Autolab PGSTAT. With the ECD module, it is possible to perform measurements at extremely low currents. The ECD module adds two extra current ranges (1 nA and 100 pA) and lowers the current resolution of the instrument by a factor of 100. An internal Sallen-Key filter is available as well, so that noise can be filtered out. An additional offset compensation circuit is present on the module allowing compensation of the DC current, thus enabling current measurements at the highest possible resolution. The ECD does not provide additional electrochemical signals. It simply extends the available current ranges of the PGSTAT.

The ECD module **cannot** be used in galvanostatic mode or in combination with the FRA2 or FRA32M module.

Scope of the tutorial

The aim of this tutorial is to explain how to use the ECD module to perform low current measurements with the Autolab. The use of the offset compensation DAC and the filters on-board the module is illustrated using the Autolab dummy cell.

2 – Hardware setup

In order to use the ECD module, the hardware setup in NOVA must be configured accordingly (see Figure 1).
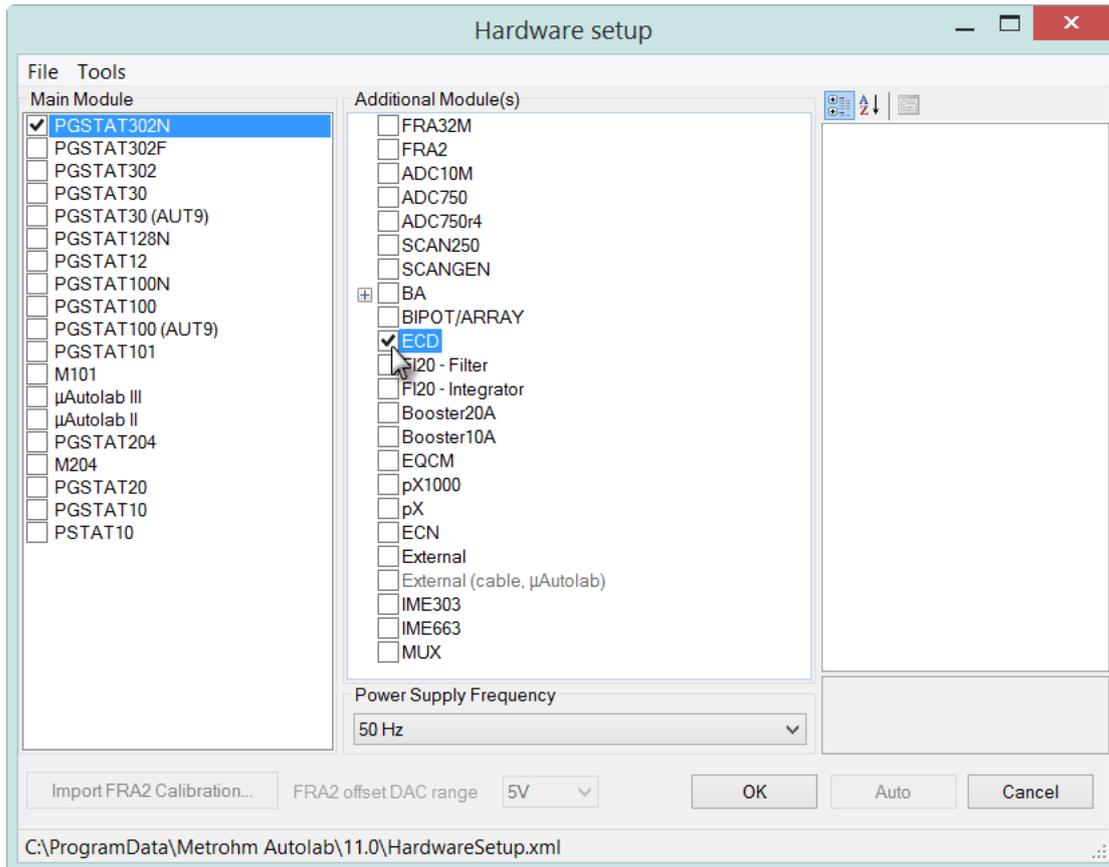
Figure 1 – Selecting the ECD module

> ⚠️ **Warning**
>
> The ECD module and the BIPOT or ARRAY module are both connected to the DAC164 channel #1 (DAC164 channel #1 is labeled DAC164 ←1 on the front panel of the PGSTAT). For this reason, they cannot be used at the same time. This DAC164 channel is also unavailable for controlling external devices, like the Autolab RDE, RRDE and LED Driver, whenever either one of these modules is used.

3 – Using the ECD

To use the ECD module in a procedure, the ECD must be switched on. This can be done manually, by clicking the ECD label on the Autolab display window (see Figure 2). With the ECD on, the available current ranges will change. The current ranges from 1 A to 1 mA will be removed from the display while the 1 nA and the 100 pA current ranges will be added.
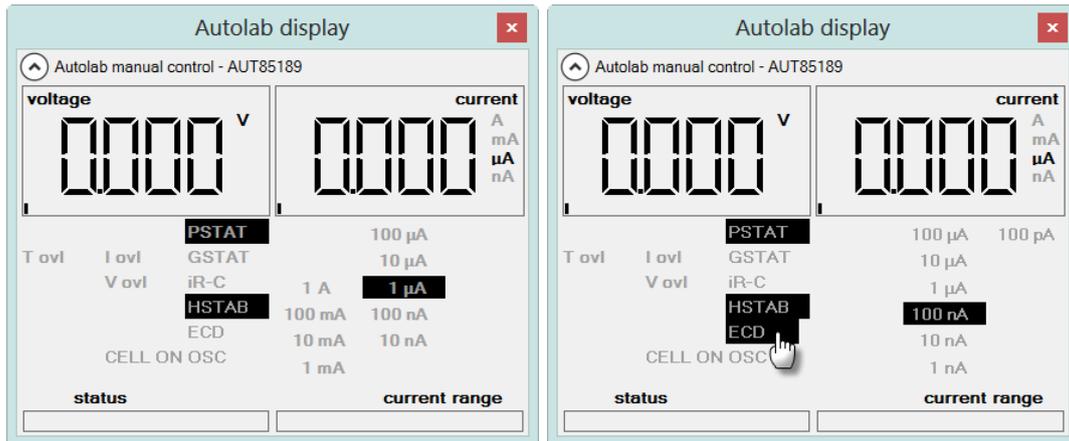
Figure 2 – Switching the ECD mode ON can be done by clicking the ECD label in the Autolab display window (note the difference in available current ranges)

Clicking the ECD label again will switch the ECD off and restore the original configuration of the PGSTAT.

Switching the ECD on or off can also be done during a measurement using the *Autolab control* command. The on/off control of the ECD module is available in the Autolab control window, in the ECD section (see Figure 3).
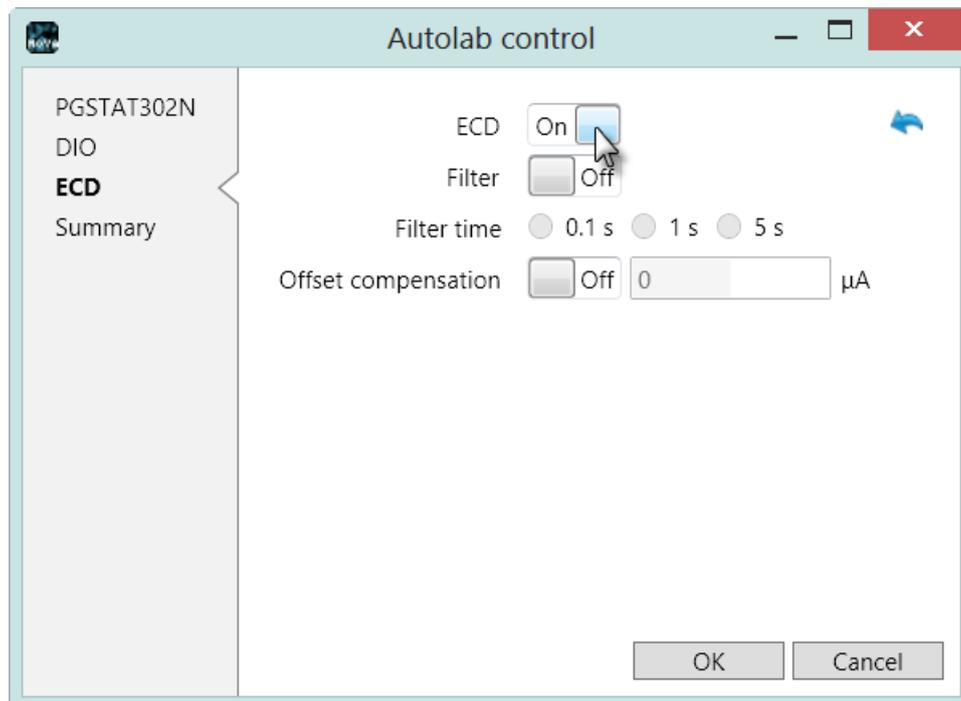

Figure 3 – The Autolab control window can be used to switch the ECD module on or off

The Autolab control window can be used to set other properties of the ECD module, like the Sallen-Key filter time constant and the offset value and resolution (see Figure 3).

The following hardware options are available in the ECD section:

- **ECD (On/Off):** switches the ECD module On or Off.
- **Filter (On/Off):** switches the filter circuit of the ECD module On or Off.
- **Filter time (0.1 s, 1 s, 5 s):** defines the time constant of the Sallen-Key filter. The effect of a filter constant of x s is that x seconds after a potential perturbation has been applied, the current response can be measured correctly. A high time constant results in heavy filtering.
- **Offset compensation (On/Off):** switches the offset compensation circuit of the ECD module On or Off.
- **Current offset (µA):** defines the offset current to use when the offset compensation circuit is active. The offset current is subtracted to current measured by the ECD module. The offset current can be specified between ± 1 µA.

The current offset is generated by a voltage value at the output of the DAC164 channel #3. The offset current can be manually defined using this control. The offset current, i_{offset}, is defined by the DAC voltage (V_{DAC}) multiplied by the offset resolution ($offset_{res}$):

$$i_{offset} = V_{DAC} \cdot offset_{res}$$

The offset resolution and the Set current offset DAC (V) properties are used to control the offset compensation circuit present on the ECD module. The offset resolution is automatically adjusted to the most suitable value.

When this compensation circuit is used, the measurement current, i_{comp} will be given by:

$$i_{comp} = i_{ECD} - i_{offset}$$

> **Note**
>
> The highest value of the offset current is ± 1 µA. The offset current is a convenient tool that allows you to compensate the baseline current during electrochemical detection measurements. With the offset compensation circuit it is possible to adjust the net current close to 0 A, which, in turn, allows for measurements at the highest possible resolution. The actual resolution depends on the value of the compensated current, i_{comp} which defines the maximum gain that can be used during the measurement (gain 1, 10 or 100).

3.1 – Automatic current ranging restrictions

When the ECD module is used in a procedure, the automatic current ranging option can be used like in a regular electrochemical measurement. However, when the ECD module is switched on, the current ranges from 1 A to 1 mA cannot be used.

In practice, this means that the automatic current ranging option can be used, with the ECD module, from 100 µA down to 100 pA (see Figure 4).
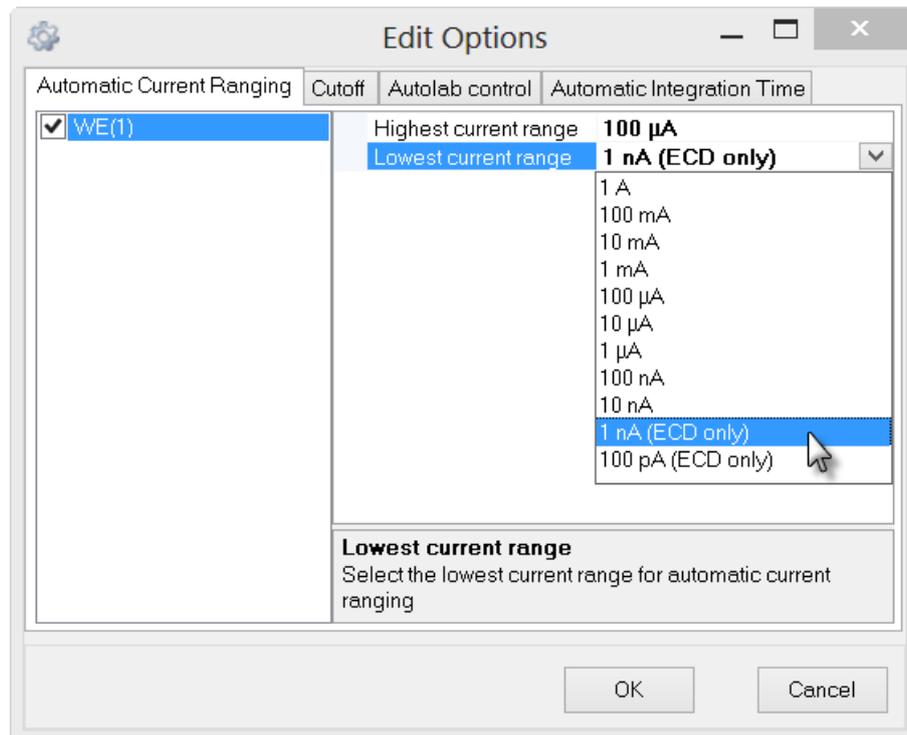

Figure 4 – The automatic current ranging option, with the ECD module is limited between the 100 µA and the 100 pA current range

When the ECD module is used, the current ranges above 100 µA cannot be used. The procedure validation process identifies this as an error situation and displays an **error** message when this situation is encountered (see Figure 5).
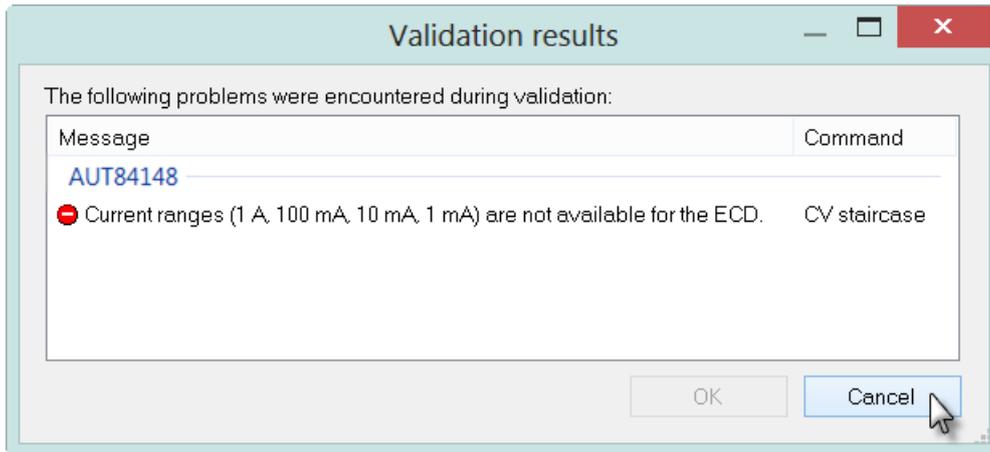
NOVA ECD tutorial

Figure 5 – An error message is displayed when the ECD switched ON and current ranges > 100 µA are selected in the Automatic current ranging option

The Automatic current ranging options need to be adjusted in the options in order to correct this error.

> ⚠️ **Warning**
>
> When the **ECD filter** option module is used during a procedure, the Automatic current ranging option <u>cannot</u> be used. The validation process will display an **error** message whenever this situation is encountered (see Figure 6). This error cannot be ignored and the procedure cannot be started.
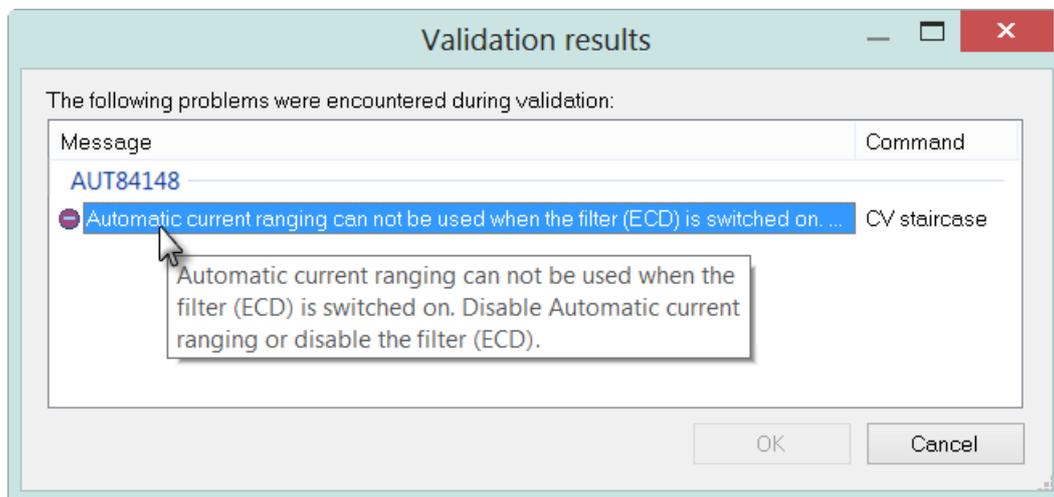

Figure 6 – The ECD filter cannot be used in combination with automatic current ranging

> **Note**
>
> The filter circuit on the ECD module has a limited bandwidth. Depending on the value of the interval time, a warnings can be displayed in the in the procedure validation window, indicating that the selected filter time constant is too slow to measure properly (see Figure 7).
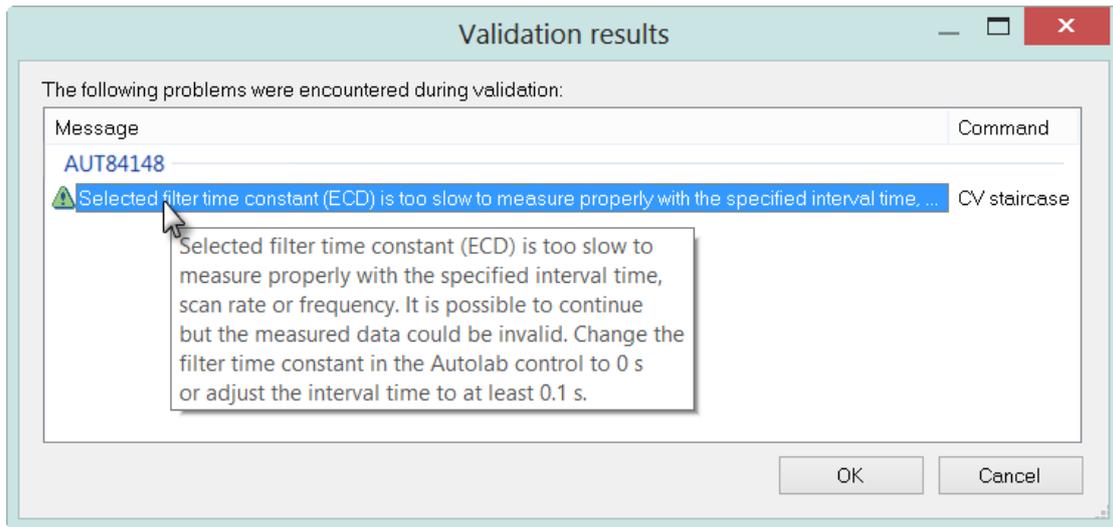

Figure 7 – A warning is displayed in the procedure validation when the selected filter time constant is too slow to measure properly

3.2 – Bandwidth restrictions

The low current ranges provided by the Autolab PGSTAT and the current ranges provided by the ECD module have a limited bandwidth. Depending on the value of the interval time, one or more warnings can be displayed in the in the procedure validation window, indicating that the bandwidth of some of the current ranges used in the experiment are not sufficient (see Figure 8).
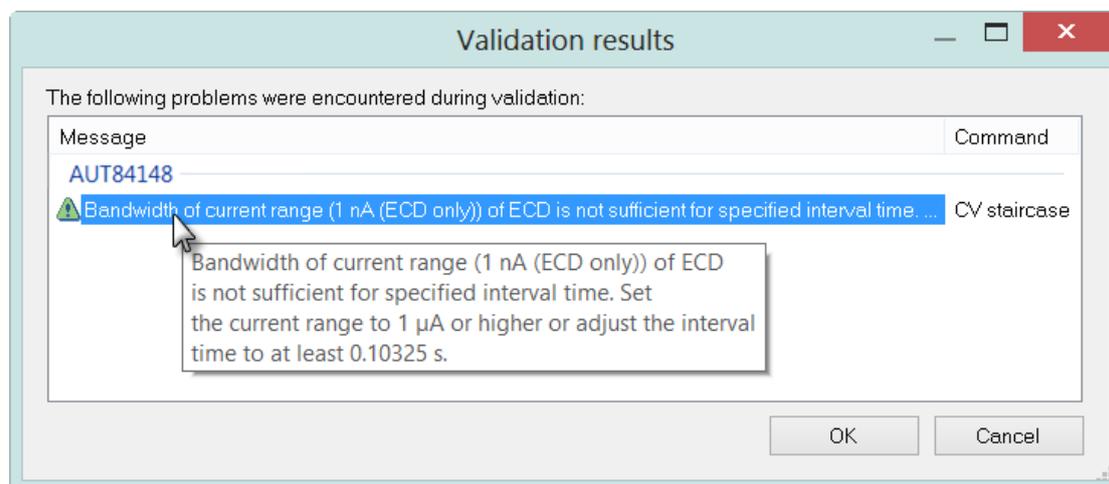

Figure 8 – The bandwidth of the specified current ranges are tested during procedure validation

It is still possible to proceed with the measurement, but there is a possibility that the data will be invalid because of this limitation.

The bandwidth limit of the current ranges is listed in Table 1.

Current range	Bandwidth
100 – 10 µA	2000 Hz
1 µA	1000 Hz
100 nA	250 Hz
10 nA	100 Hz
1 nA	50 Hz
100 pA	10 Hz

Table 1 – Overview of the bandwidth limits of the ECD current ranges

4 – Measurements with the ECD module on the dummy cell

An ECD tutorial folder is located in the **Program Files\Metrohm Autolab\Nova 1.11\Shared Databases\ Tutorials** folder (see Figure 9). Using the database manager, set this folder as the Standard database.
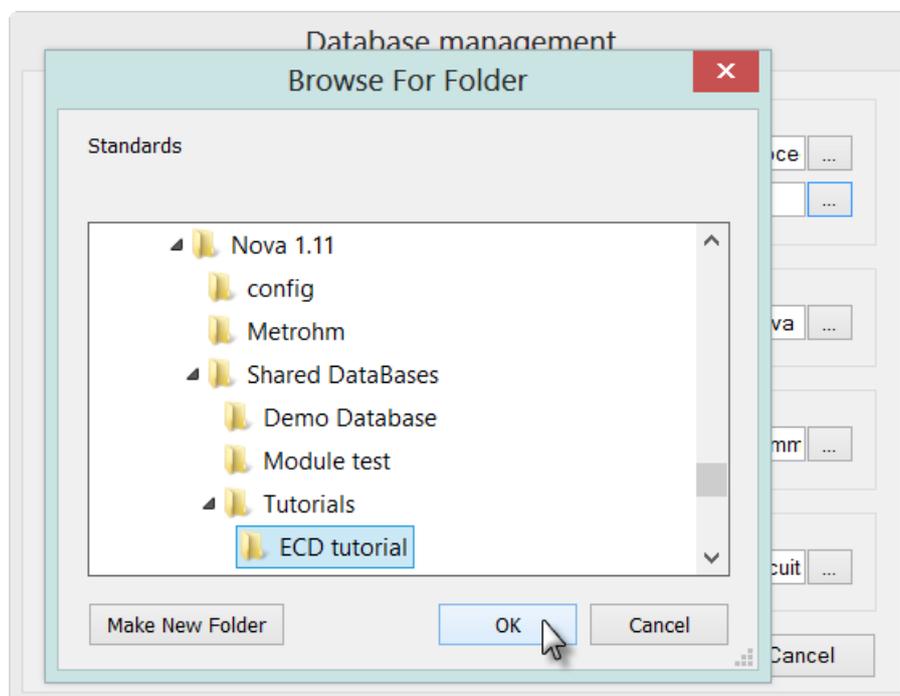

Figure 9 – Loading the ECD tutorial database

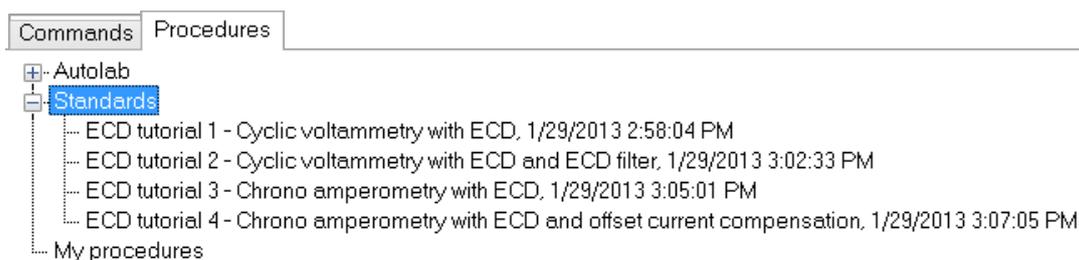The ECD tutorial contains four procedures (see Figure 10).

Figure 10 – Four procedures are provided in the ECD tutorial

4.1 – ECD tutorial 1 – Cyclic voltammetry with ECD module

Load procedure *ECD tutorial 1 – Cyclic voltammetry with ECD module* in the procedure editor. This procedure provides an example of a cyclic voltammetry measurement using the ECD. The ECD module is switched on at the beginning of the procedure, using the *Autolab control* command (see Figure 11).

	Commands	Parameters	Links
	ECD tutorial 1 - Cyclic voltammetry with ECD		
	Remarks	ECD tutorial	...
	End status Autolab		...
	Signal sampler	Time, WE(1).Potential, WE(1).Current	...
	Options	1 Options	...
	Instrument		
	Instrument description		
	Message box		
	Autolab control		...
	WE(1).Mode	Potentiostatic	
	WE(1).Bandwidth	High stability	
	WE(1).Current range	1 µA	
	WE(1).ECD Mode	On	
	Set potential	0.000	
	Set cell	On	...
	Wait time (s)	5	
	Optimize current range	5	
	CV staircase	[0.000, 1.000, -1.000, 0.000, 2, 0.0500000]	
	Set cell	Off	...
	<..>		

Figure 11 – Overview of the ECD tutorial 1 procedure

Connect the cables from the PGSTAT to the Autolab dummy cell as shown in Figure 12 and press the start button to begin the measurement.
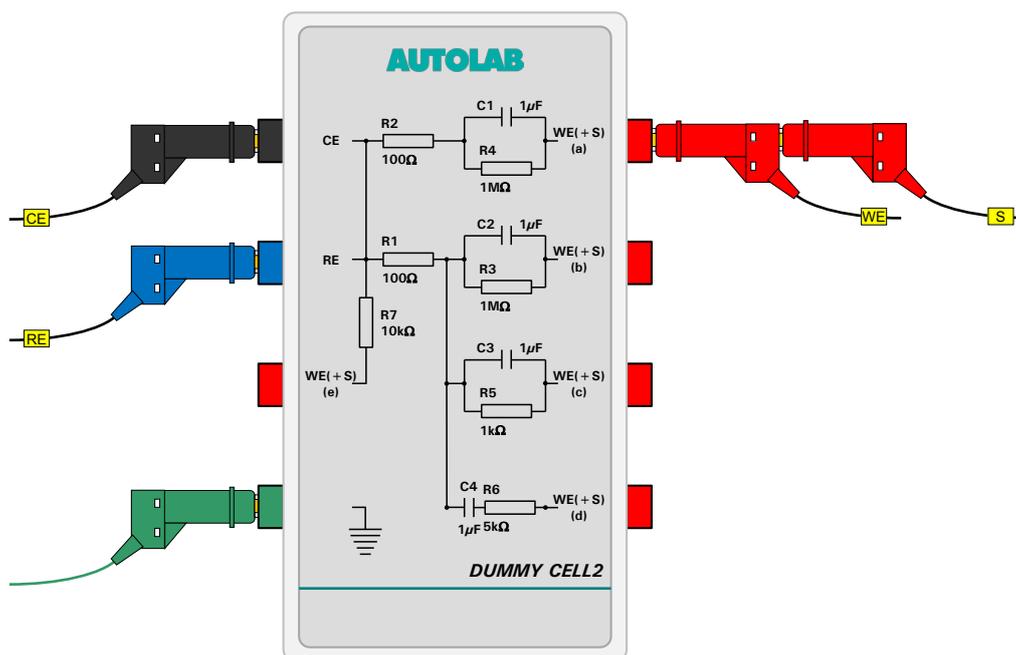

Figure 12 – The connections used for the ECD tutorial procedures

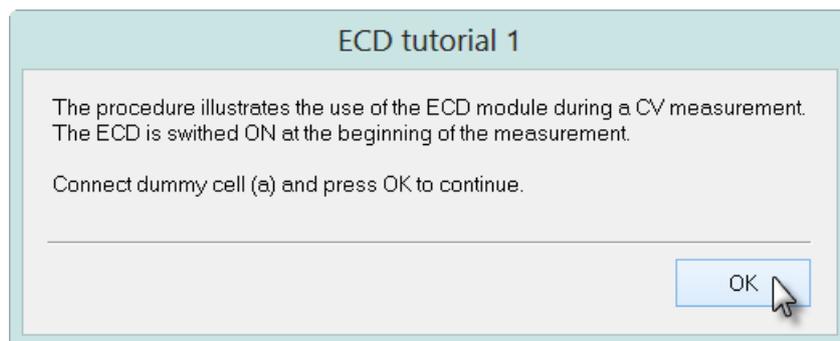Shortly after pressing the Start button, a message will be displayed (see Figure 13).

Figure 13 – The message displayed at the beginning of the measurement

Click the OK button to continue with the measurement. The ECD module is switched on at the beginning of the experiment. During the measurement, the WE(1).Current is plotted versus the potential applied on WE(1), as shown in Figure 14.
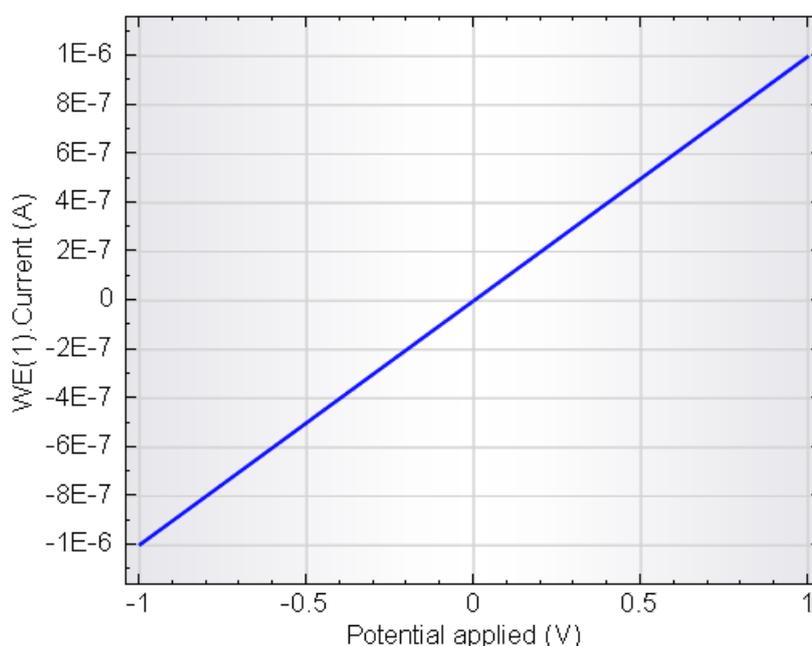

Figure 14 – The data recorded during the ECD tutorial 1 procedure

Since dummy cell (a) is used in this test, the measured current values change between -1 µA and 1 µA as the potential is scanned between -1 V and 1 V.

> **Note**
>
> At the end of the experiment, the ECD module is switched off, through the End status Autolab settings (see Figure 15).
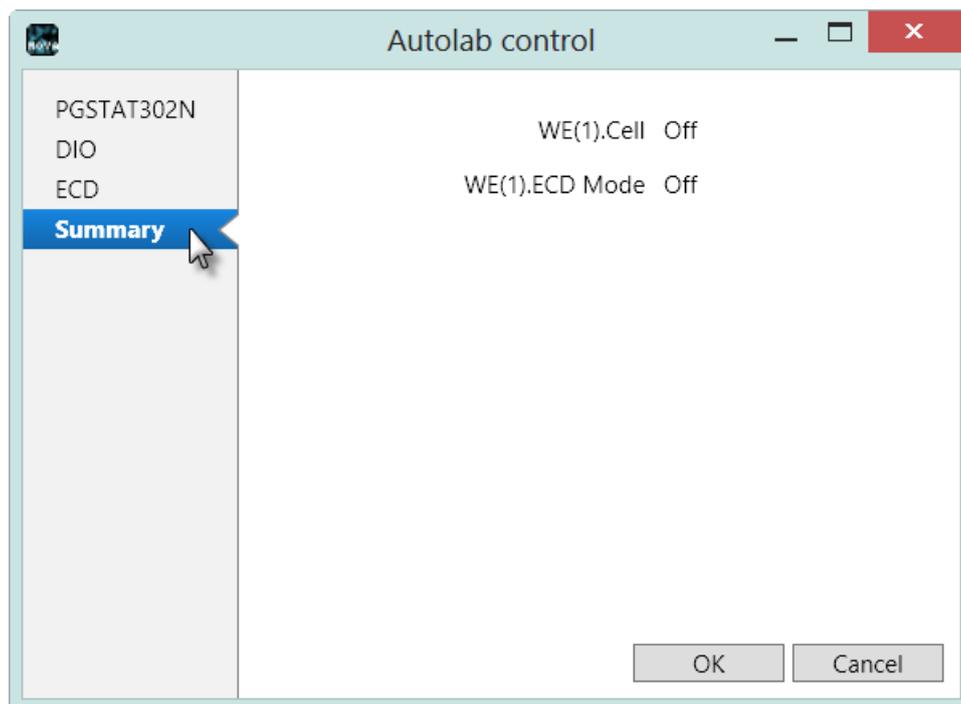
Figure 15 – The End status Autolab used in the ECD tutorial 1 procedure

4.2 – ECD tutorial 2 – Cyclic voltammetry with ECD and ECD filter

Load procedure *ECD tutorial 2 – Cyclic voltammetry with ECD and ECD filter* in the procedure editor. This procedure provides an example of a cyclic voltammetry measurement similar to the tutorial 1 procedure. Additionally, the built-in ECD filter is used during the measurement. The ECD module is switched on at the beginning of the procedure, using the *Autolab control* command. The same command is used to set the filter time-constant of the ECD module to 0.1 s (see Figure 16).

ℹ	**Note**

Because the ECD filter is used in this experiment, automatic current ranging is not possible.

Figure 16 – Overview of the ECD tutorial 2 procedure

Connect the cables from the PGSTAT to the Autolab dummy cell as shown in Figure 12 and press the start button to begin the measurement.

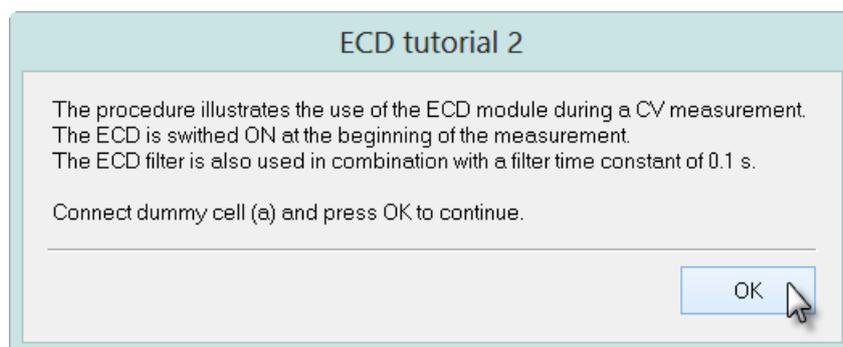Shortly after pressing the Start button, a message will be displayed (see Figure 17).

Figure 17 – The message displayed at the beginning of the measurement

Click the OK button to continue with the measurement. The ECD module and the ECD filter are switched on at the beginning of the experiment. During the measurement, the WE(1).Current is plotted versus the potential applied on WE(1), as shown in Figure 18.
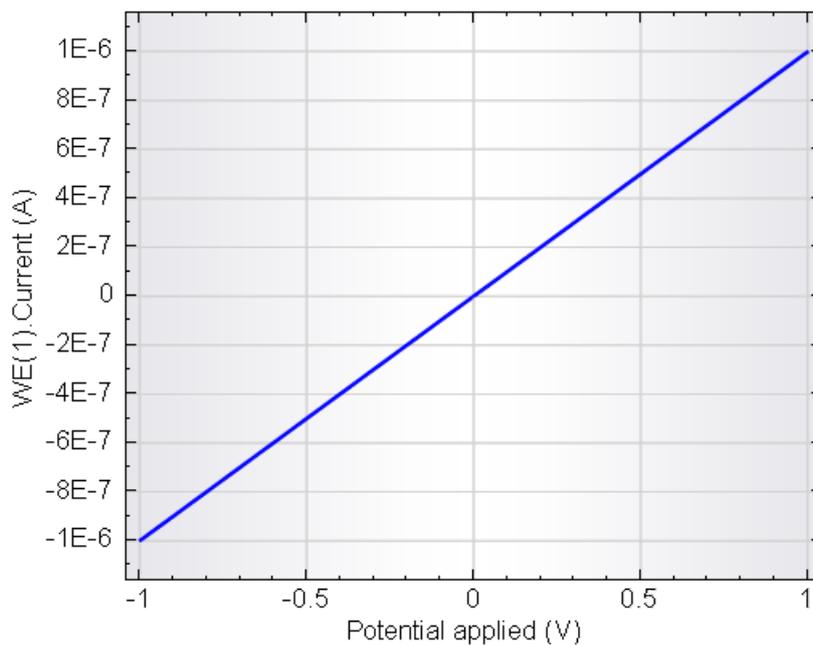
Figure 18 – The data recorded during the ECD tutorial 2 procedure

Since dummy cell (a) is used in this test, the measured current values change between -1 µA and 1 µA as the potential is scanned between -1 V and 1 V.

> **Note**
>
> At the end of the experiment, the ECD module and the ECD filter are switched off, through the End status Autolab settings.

4.3 – ECD tutorial 3 – Chrono amperometry with ECD

Load procedure *ECD tutorial 3 – Chrono amperometry with ECD* in the procedure editor. This procedure performs a potential step from 0 V to 0.5 V. The current is measured before and after the potential step, using the *Record signals (>1 ms)* command. The ECD module is switched on at the beginning of the procedure, using the *Autolab control* command (see Figure 19).

Figure 19 – Overview of the ECD tutorial 3 procedure

Connect the cables from the PGSTAT to the Autolab dummy cell as shown in Figure 12 and press the start button to begin the measurement.

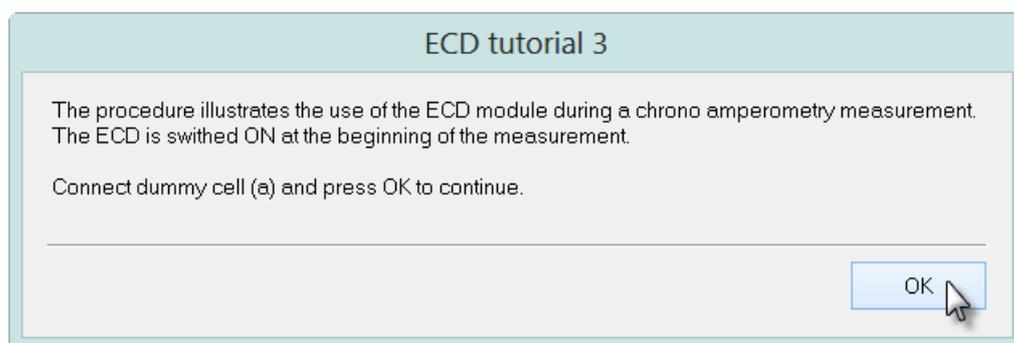Shortly after pressing the Start button, a message will be displayed (see Figure 20).

Figure 20 – The message displayed at the beginning of the measurement

Click the OK button to continue with the measurement. The ECD module is switched on at the beginning of the experiment. During the measurement, the WE(1).Current is plotted versus time, as shown in Figure 21.
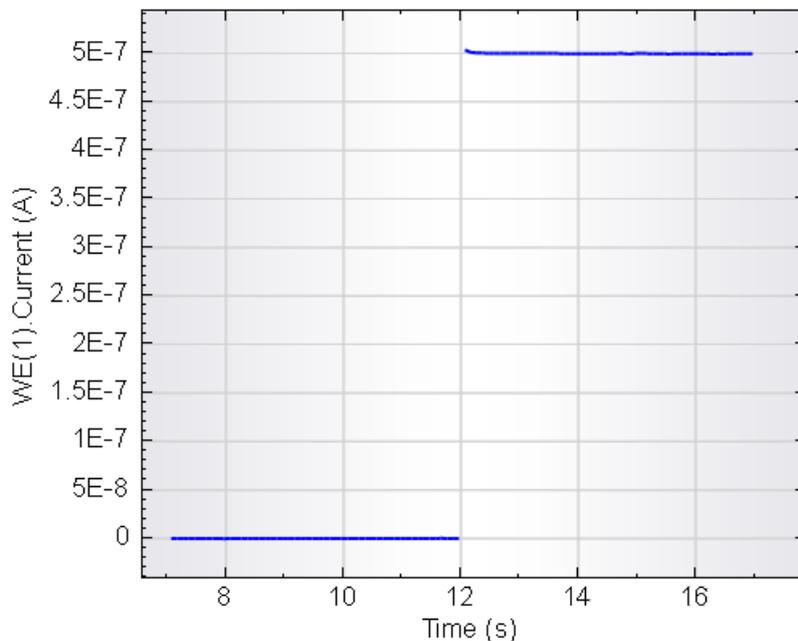
Figure 21 – The data recorded during the ECD tutorial 3 procedure

Since dummy cell (a) is used in this test, the measured current values change from 0 nA and 500 nA as the potential is stepped from 0 V to 0.5 V.

> **Note**
>
> At the end of the experiment, the ECD module is switched off, through the End status Autolab settings.

4.4 – ECD tutorial 4 – Chrono amperometry with ECD and offset current compensation

Load procedure *ECD tutorial 4 – Chrono amperometry with ECD and offset current compensation* in the procedure editor. Similarly to the previous procedure, this experiment performs a potential step from 0 V to 0.5 V. The current is measured before and after the potential step, using the *Record signals (>1 ms)* command. Additionally, the current is sampled again at the end of the second *Record signals (>1 ms)* command, after the ECD offset compensation circuit is switched on, in order to compensate the current measured at 0.5 V. The ECD module is switched on at the beginning of the procedure, using the *Autolab control* command. An additional *Autolab control* command, configured to switch on the offset current compensation circuit, is located after the second *Record signals* command (see Figure 22).

Commands	Parameters	Links
ECD tutorial 4 - Chrono amperometry with ECD and offset current compensation		
Remarks	ECD tutorial	...
End status Autolab		...
Signal sampler	Time, WE(1).Potential, WE(1).Current	...
Options	1 Options	...
Instrument		
Instrument description		
⊞ Message box		
⊟ Autolab control		...
WE(1).Mode	Potentiostatic	
WE(1).Bandwidth	High stability	
WE(1).Current range	1 µA	
WE(1).ECD Mode	On	
⊞ Set potential	0.000	
⊞ Set cell	On	...
⊞ Wait time (s)	5	
Optimize current range	5	
⊞ Record signals (>1 ms)	[5, 0.1]	–
⊞ Set potential	0.500	
⊞ Record signals (>1 ms)	[5, 0.1]	–
⊟ Autolab control		...
ECD(1).Offset resolution	100 nA/V	
ECD(1).Current offset DAC (V)	5	
⊞ Record signals (>1 ms)	[5, 0.1]	–
⊞ Set cell	Off	...
<..>		

Figure 22 – Overview of the ECD tutorial 4 procedure

Figure 23 shows the details of the settings defined on the ECD(1) tab in the second *Autolab control* command used in this tutorial procedure. The *Offset resolution* property is set to 100 nA/V and the *Set Current offset DAC (V)* property is set to 5, resulting in a compensation current of 500 nA.
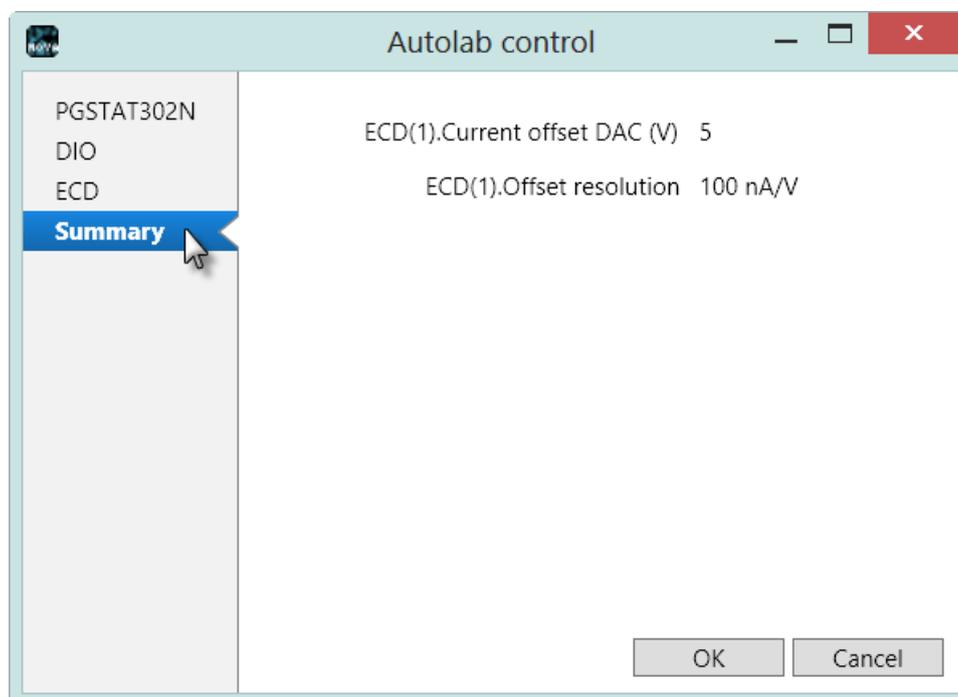
Figure 23 – Details of the ECD settings defined in the second *Autolab control* command

> **i** | **Note**
>
> It is not necessary to switch the cell off when modifying the offset resolution or the current offset value.

Connect the cables from the PGSTAT to the Autolab dummy cell as shown in Figure 12 and press the start button to begin the measurement.

Shortly after pressing the Start button, a message will be displayed (see Figure 24).
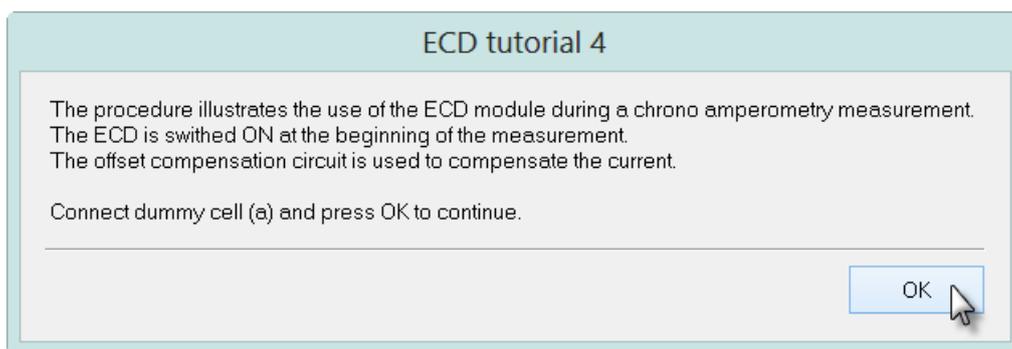

Figure 24 – The message displayed at the beginning of the measurement

Click the OK button to continue with the measurement. The ECD module is switched on at the beginning of the experiment. During the measurement, the WE(1).Current is plotted versus time, as shown in Figure 25. The data plotted in red corresponds to the current measured after the offset current compensation circuit is switched on.
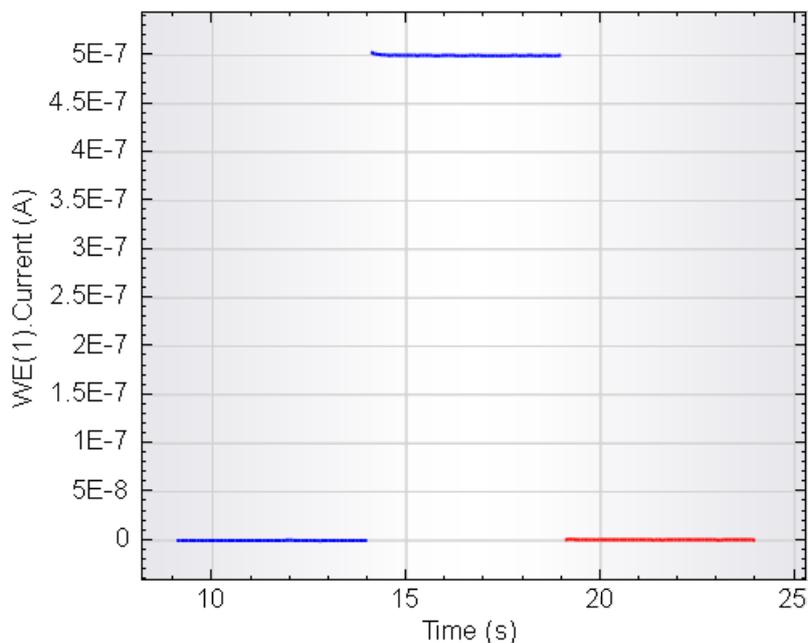
Figure 25 – The data recorded during the ECD tutorial 4 procedure

Since dummy cell (a) is used in this test, the measured current values change from 0 nA and 500 nA as the potential is stepped from 0 V to 0.5 V. At the end of the measurement, the offset current compensation circuit is used to compensate 500 nA (5 V x 100 nA/V). The resulting current is ~ 0 nA and the response of the cell can therefore be measured in a lower current range, which leads to an increase in resolution.

> **Note**
>
> At the end of the experiment, the ECD module and the offset current compensation circuit are switched off, through the End status Autolab settings.

Hardware specifications

The ECD module can be used to extend the current ranges of the Autolab PGSTAT module. The module is compatible with all the PGSTAT instruments.

The ECD module is fitted with an analog third-order Sallen-Key filter as well as an offset compensation circuit driven by the DAC164 of the Autolab. The offset compensation circuit can be used to measure the current differentially with respect to a baseline current in electrochemical detection experiments.

> **Note**
>
> The ECD module cannot be used in galvanostatic mode and cannot be used in combination with the FRA2 or the FRA32M module.

Table 1 provides an overview of some important specifications of the ECD module.

Specification	Value
Current ranges	100 µA to 100 pA, 7 ranges
Current accuracy	± 0.5 % of current range
Current offset	± 2 pA
On board filter	3rd order Sallen-Key
Filter time constants	10 ms, 100 ms and 500 ms
Maximum offset compensation	± 1 µA

Table 2 – Overview of the specifications of the ECD module

> **Warning**
>
> The ECD module cannot be used in combination with the BIPOT or ARRAY module. Remote control of the Autolab RDE, RRDE and LED Driver through the DAC164 module is also not possible when the ECD module is used.