1 – Chrono methods high speed (ADC750 / ADC10M module)

The term *Chrono methods high speed* includes all the measurements of electrochemical signals during a well defined sequence of steps, using the smallest possible interval time.

In NOVA, time resolved measurements are possible using three different measurement strategies:

- Using the *Record signals (Δt> 1 ms)* command: this command can be used at any point in a procedure to record the signals defined in the signal sampler for a specified amount of time and using a well defined interval time. The smallest possible value of the interval time is 1.3 ms. The *Record signals (Δt> 1 ms)* command does not apply a potential or current value. It simply samples the signals defined in the sampler using the specified parameters. The Autolab procedure *Chrono amperometry (Δt> 1 ms)* and *Chrono potentiometry (Δt> 1 ms)* provide good examples of measurements using this type of command. More information on this command can be found in the User manual.
- Using the *Chrono methods* command: this command can be used to perform time resolved measurements with interval times smaller than 1.3 ms. The lowest interval time is roughly 100 µs, and it depends on the type of signals to measure and the number of signals to sample. The measured signals are defined in the signal sampler. More information can be found in the Chrono methods tutorial.
- Using the *Chrono methods high speed* command: this command can be used to perform time resolved measurements at the smallest possible interval time. A dedicated fast sampling ADC module is required for these measurements (ADC750 or ADC10M). This tutorial provides more information on the use of the *Chrono methods high speed* command.

Note: in order to use the *Chrono methods high speed* command, the optional ADC750 or ADC10M must be installed[1].

[1] In the rest of this document, the ADC750 or ADC10M module will be referred to as fast sampling ADC.

Table 1 provides an overview of some of the important features related to the use of the three different commands for time resolved measurements.

Command	Record signals (Δt > 1 ms)	Chrono methods	Chrono methods high speed
Smallest interval time	1.3 ms	~ 100 µs	1.33 µs (ADC750) 0.1 µs (ADC10M)
Setpoint included	No	Yes	Yes
Real time display	Yes	No	No
Signals selection	Sampler	Sampler	Hardware defined (2)
Options support	Yes	No	No
Pause/Stop support	Yes	No	No

Table 1 – Comparison of the commands for time resolved commands

2 – Using the fast sampling ADC module

The fast sampling ADC module (either ADC750 or ADC10M) is a dual channel synchronous Analog-to-Digital converter with a very high sampling rate. This optional module allows recording the electrochemical signals during high speed chrono experiments, with a very small interval time.

ADC750 vs ADC10M

The main difference between the ADC750 and the ADC10M module is the sampling rate. For the first module, the maximum sampling rate is 750 kSamples/s whereas it is 10 MSamples/s for the ADC10M. Both modules are dual channel ADCs. These modules are available for the PGSTAT12, 128N, 30, 302, 302N, 100 and 100N.

2.1 – Hardware setup

In order to use the fast sampling ADC module, the hardware setup must be configured accordingly (see Figure 1).

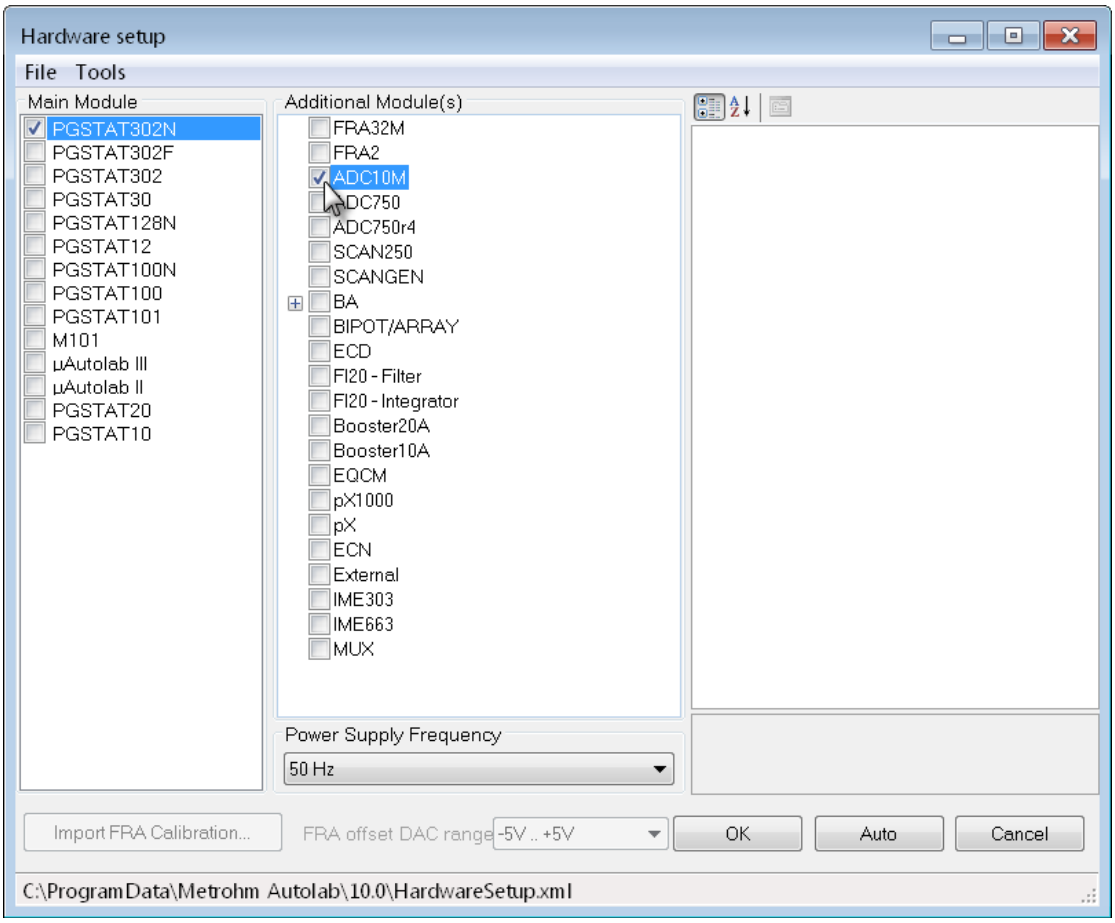

Figure 1 – Selecting the ADC10M module

Note: for ADC750 revision 4.0, please check the ADC750r4 checkbox in the hardware setup. Select the ADC750r4 checkbox if the *High speed adc module(1) not detected*[2] message is shown in the User log after the initialization (see Figure 2).

User log message	Time	Date	Command
High speed adc module(1) not detected	11:37:56 ...	11/19/2010	-
Autolab/USB connected (AUT70530)	11:37:56 ...	11/19/2010	-

Figure 2 – Select the ADC750r4 checkbox when the *High speed adc module(1) not detected* message is shown in the User log after initialization

[2] Both the ADC10M and the ADC750 have an onboard automatic recognition circuit. The revision 4.0 of the ADC750 is not fitted with this circuit and will therefore not be detectable.

2.2 – The fast sampling ADC module

The fast sampling ADC modules are fitted with an on-board memory that can be used to store up to 1 million data points. When the fast sampling ADC module is used in an experiment, each new data point is stored in the on-board memory of the module until the experiment is finished. At the end of the measurement, all the stored data points are transferred to the computer for data analysis.

3 – The chrono methods high speed command

High speed chrono measurements can be performed using the *Chrono methods high speed* command.

The *Chrono methods high speed* command is similar to the *Chrono methods* command. The *Chrono methods high speed* command is designed to apply a user-defined sequence of steps on the electrochemical cell and record the response of the cell, using a high sampling rate. The sequence itself or elements of the sequence can be repeated a number of times without any interruption. When the whole sequence is finished, the data points stored in the high speed ADC module are transferred to the computer.

Note: because the time required to transfer the measured data points from the Autolab to the computer can be a few seconds, it is not possible to display the measured data points in real time in the measurement view. However, the measured data points are displayed at the end of the experiment.

Chrono methods and Chrono methods high speed

The main difference between a chrono measurement using the ADC164 and using a fast sampling ADC is that in the former case, the sampling rate can be changed during the measurement and the sampling can be switched off (please refer to the Chrono methods tutorial for more information). These options are not available with a high speed ADC module, which samples the electrochemical signals at a fixed sampling rate.

Like all the measurement commands, the *Chrono methods high speed*[3] command must be added to a Timed procedure command (see Figure 3).

[3] Available in the Measurement – Chrono methods commands group.

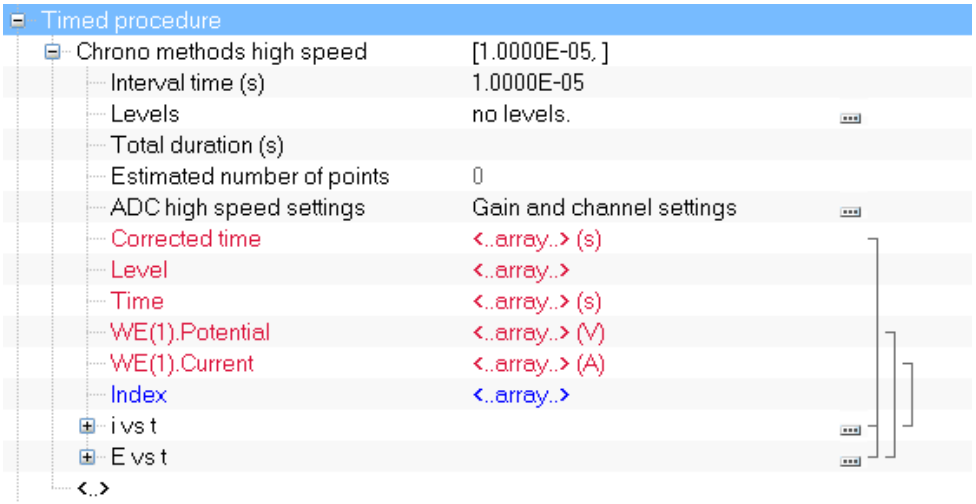

Figure 3 – Placing the *Chrono methods high speed* command into a Timed procedure

Important: the fast sampling ADC module must transfer all the data stored in the on-board memory before it can be used in a new measurement. For this reason, it is not **possible** to perform experiments with several *Chrono methods high speed* commands inside the **same** Timed procedure. It is however possible to perform measurements where each *Chrono methods high speed* command is located inside a dedicated Timed procedure. In between two consecutive Timed procedures, the data stored on the fast sampling ADC module will be transferred to the computer (see Figure 4).

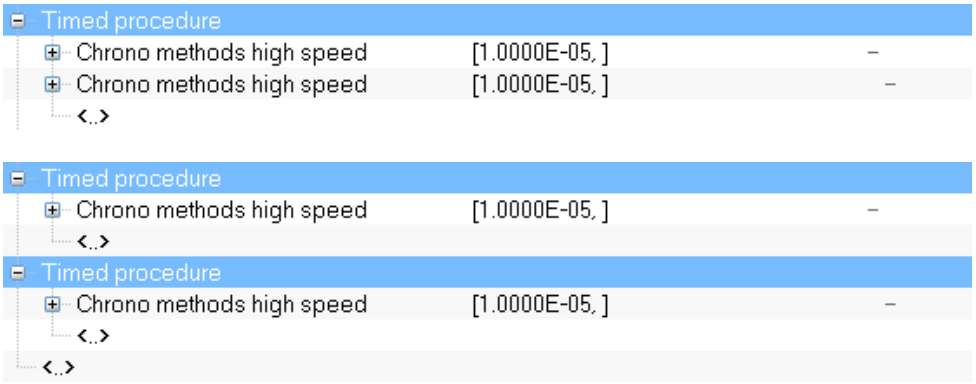

Figure 4 – Example of invalid combination of Timed procedure and *Chrono methods high speed* command (top) and valid combination of Timed procedure and *Chrono methods high speed* command (bottom)

The *Chrono methods high speed* command has the following parameters (see Figure 3):

- **Interval time (s):** defines the interval time, in seconds, for all the steps in the sequence. This interval time is the same for all the steps. The lowest value is defined by the high speed ADC.
- **Levels:** allows you to define the sequence of steps using the Chrono methods high speed editor window.
- **ADC high speed settings:** defines the acquisition settings for the fast sampling ADC (gain values, signals to sample, etc…).

To use the *Chrono methods high speed* command, the sequence of steps must first be defined. To create or edit a sequence of steps, the … button of the Levels parameter must be clicked (see Figure 5).

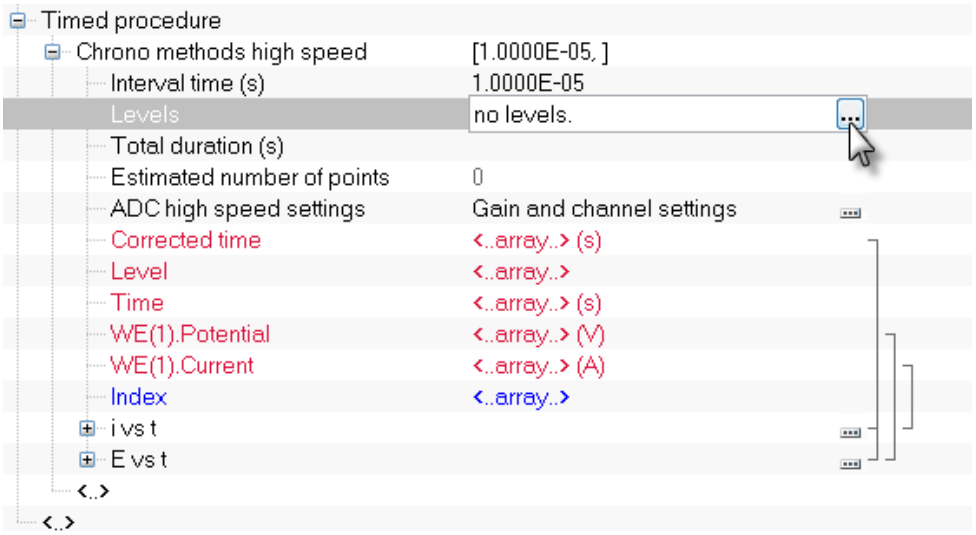

Figure 5 – Opening the Chrono methods high speed editor window

The *Chrono methods high speed* editor window displays three frames (see Figure 6). The frame on the left-hand side contains elements that can be dragged and dropped in the sequence editor in the middle frame. The frame on the right-hand displays the parameters of each element.

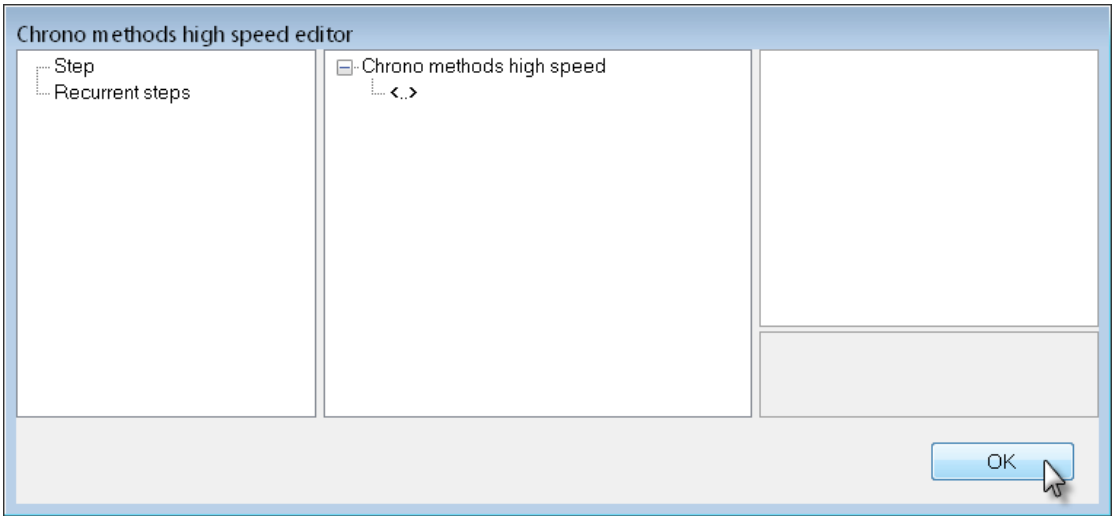

Figure 6 – The Chrono methods high speed editor window

The sequence of steps can be constructed by dragging elements from the list in the left-hand side frame and adding them to the collection sequence.

The following items can be used to construct the required sequence (see Figure 6):

- **Step**: this item creates a step in the sequence. A step is defined by two parameters – the setpoint and the duration. The default values are 0 and 0.001 s.
- **Recurrent steps**: this item creates a new sub-sequence in the main sequence, in which new items can be added. This sub-sequence can be repeated any number of times and the electrochemical response of the cell is sampled during the whole sub-sequence.

To create the required sequence using the Chrono methods high speed editor window drag and drop any item from the list on the left-hand side into the editor frame (see Figure 7).

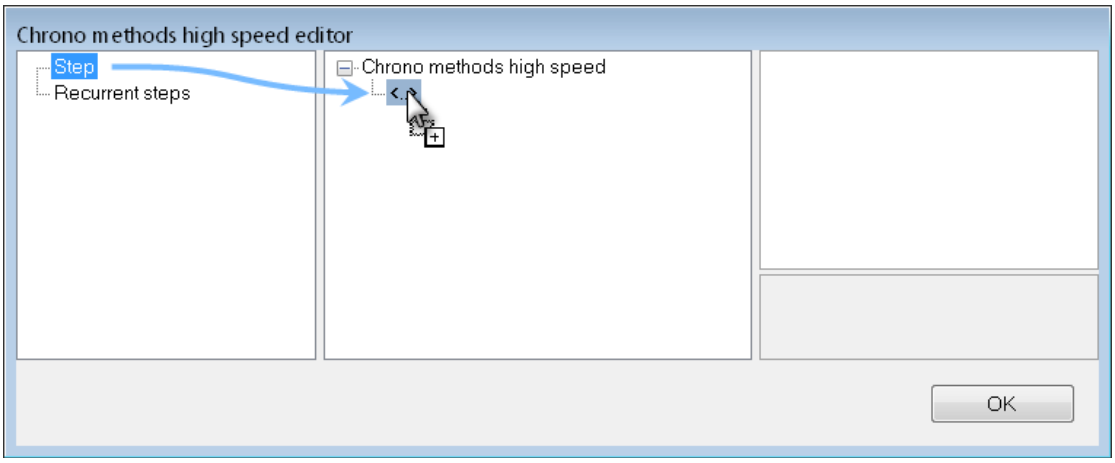

Figure 7 – Dragging and dropping a step item into the sequence editor

Click the step that was added to the sequence to display the parameter details in the frame on the right (see Figure 8).

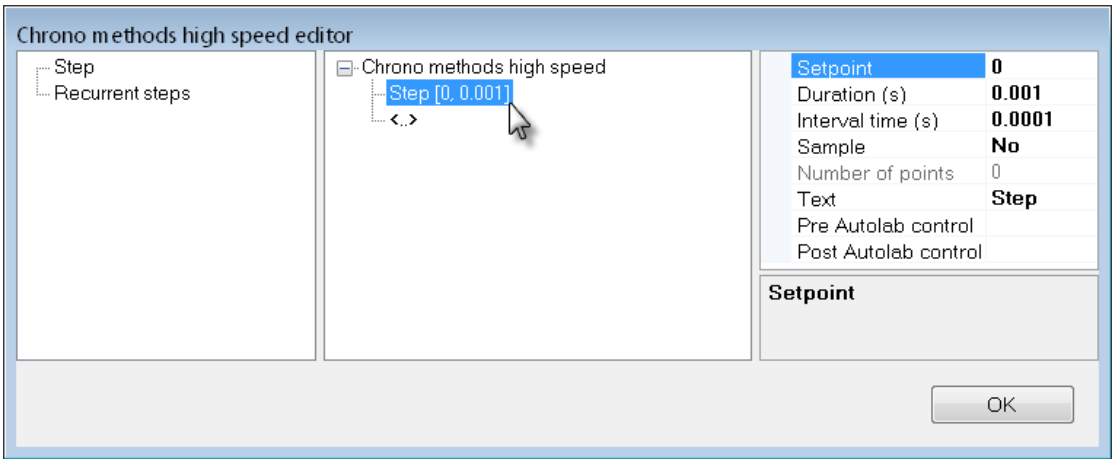

Figure 8 – A detailed view of the Chrono methods high speed editor

Note: the parameters of the step are shown in between brackets in the sequence editor – [0, 0.001].

The step has the following parameters (indicated in black) and properties (indicated in grey):

- Setpoint: 0
- Duration (s): 0.001
- Interval time (s): 0.0001
- Sample: No
- Number of points: 0
- Text: Step

The two additional parameters, *Pre Autolab control* and *Post Autolab control*, are advanced settings that can be used to change the Autolab settings during the sequence. These parameters are available for advanced procedures and their use falls outside of the scope of this tutorial.

Important: the editor window used for the *chrono methods high speed* command is the same as the one used for the *chrono methods* command, which uses the ADC164 to sample the data. Some of the parameters and properties of the chrono methods command are irrelevant for the high speed chrono methods command. The items indicated in red can be ignored, as they are only used in the chrono methods command.

It is possible to change any of the three parameters of the step. Change the duration of the step to 0.005 seconds (see Figure 9). Changing the duration will update the values indicated between brackets.

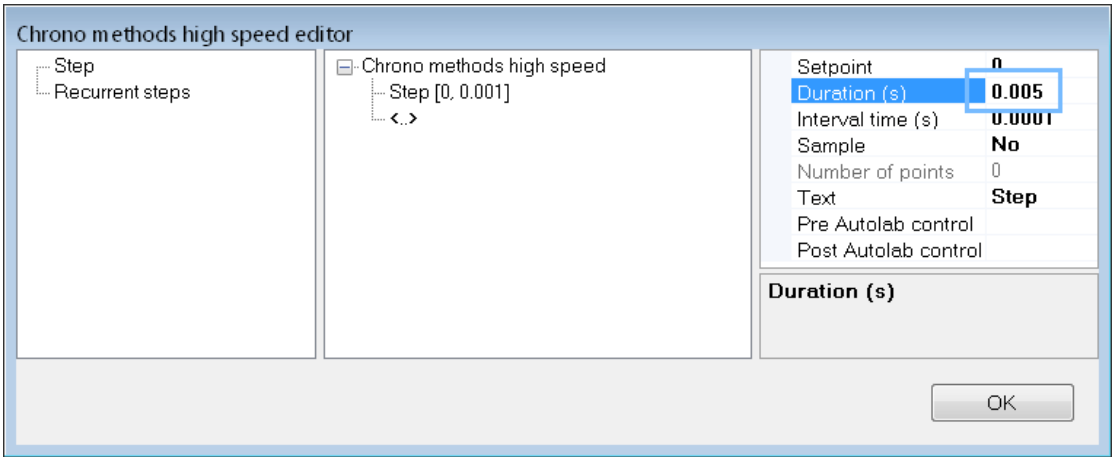

Figure 9 – Changing the duration modifies the values shown in the brackets

Add two more steps to the sequence editor. Just like in the case of first step, the two newly added steps have the default parameters settings (see Figure 10).

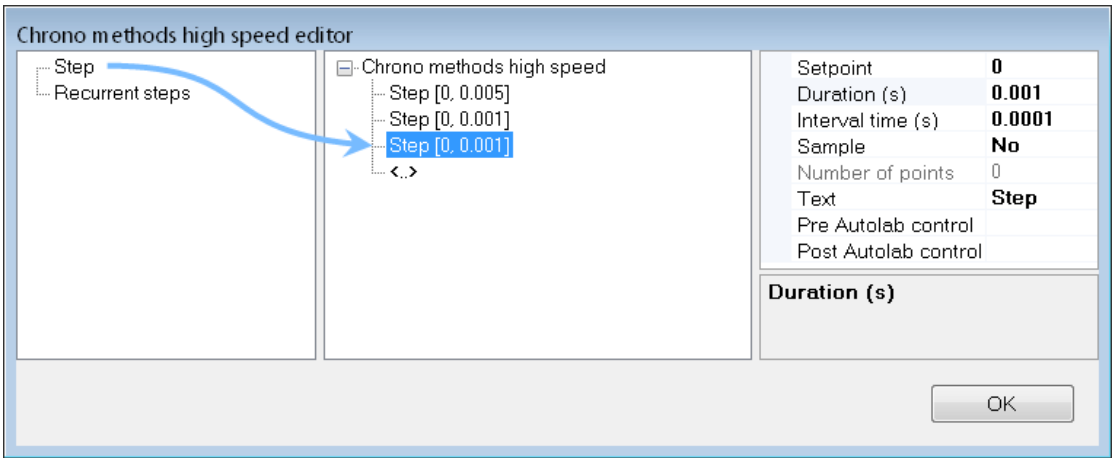

Figure 10 – Adding two more steps to the sequence

The parameters of these steps can be edited individually. Change the setpoint of the second step in the sequence to 0.3 V and the setpoint of the final step to -0.3 V (see Figure 11).

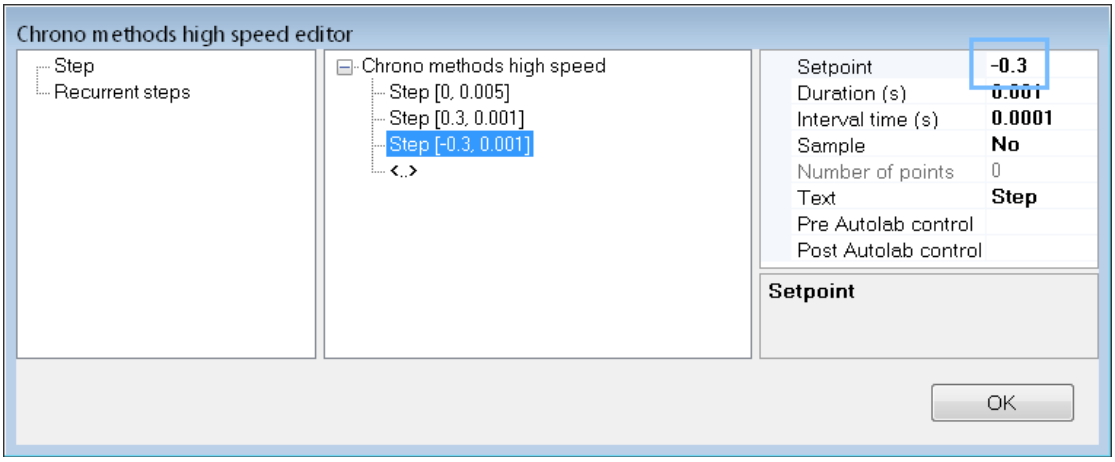

Figure 11 – Changing the setpoint for the steps in the sequence

It is possible to edit the value of the same parameter for multiple items in the sequence. Holding the CTRL key, click the three steps of the sequence. Each step should be highlighted indicating the selected status. Enter a duration of 0.005 seconds in the parameter editor frame. This will change the duration of the three steps to this value (see Figure 12).

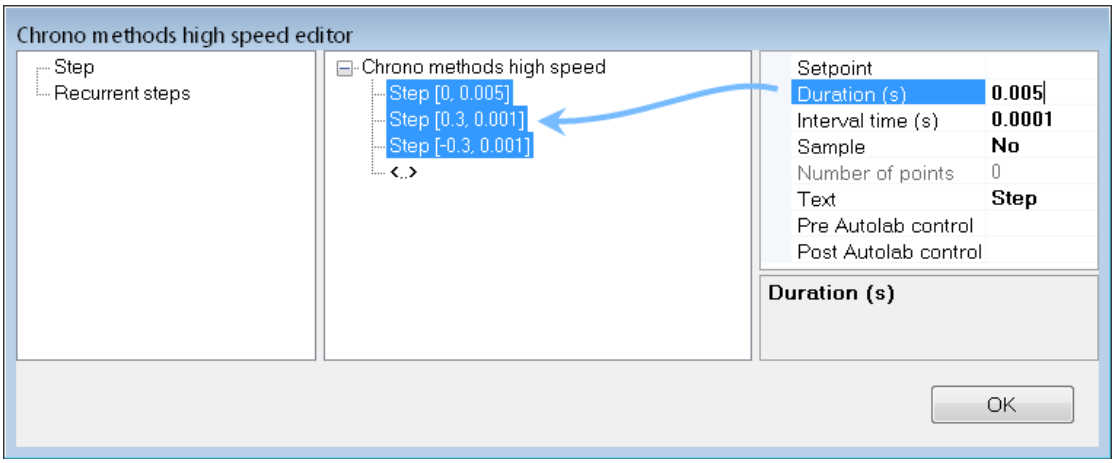

Figure 12 – Selecting multiple items in the sequence

The values between brackets for each step will be updated for the new parameters and the number of points will be calculated:

- Step [0, 0.005]
- Step [0.3, 0.005]
- Step [-0.3, 0.005]

Click the OK button of the Chrono methods high speed editor window to validate the sequence. This will close the window and update the properties of the Chrono methods command in the procedure editor (see Figure 13).

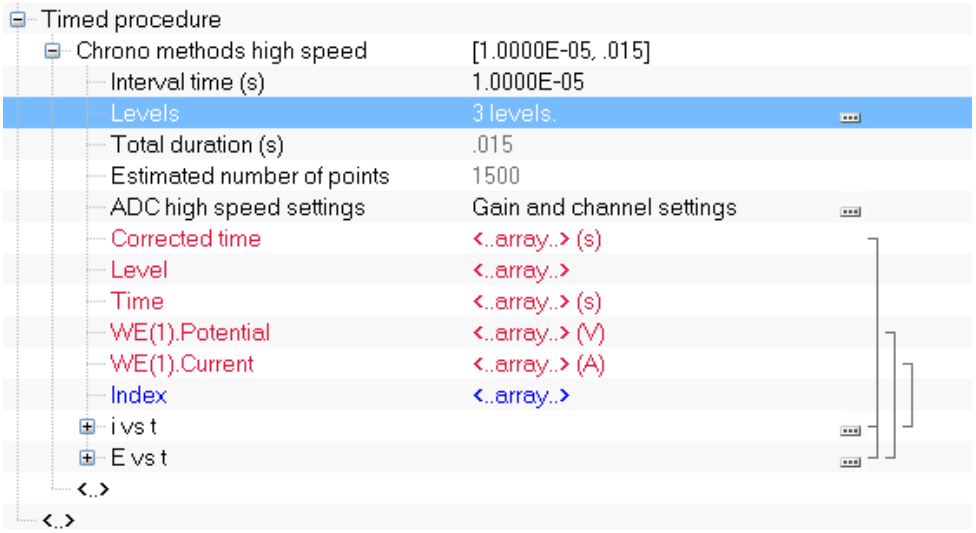

Figure 13 – The updated Chrono methods high speed command

The parameters and properties of the *Chrono methods high speed* command are the following:

- **Interval time (s):** 1.0000E-5
- **Levels:** 3 Commands – the sequence consists of three steps
- **Total duration (s):** 0.015 – each step has a duration of 0.005 seconds
- **Estimated number of points:** 1500 – 500 data points are recorded for each step
- **ADC high speed settings:** defines the acquisition settings for the *Chrono method high speed* command

4 – A measurement using the *Chrono methods high* speed command

A Chrono methods high speed tutorial folder is located in the **Program Files\Metrohm Autolab\Nova 1.8\Shared Databases\Tutorials** folder (see Figure 14). Using the database manager, set this folder as the Standard database.

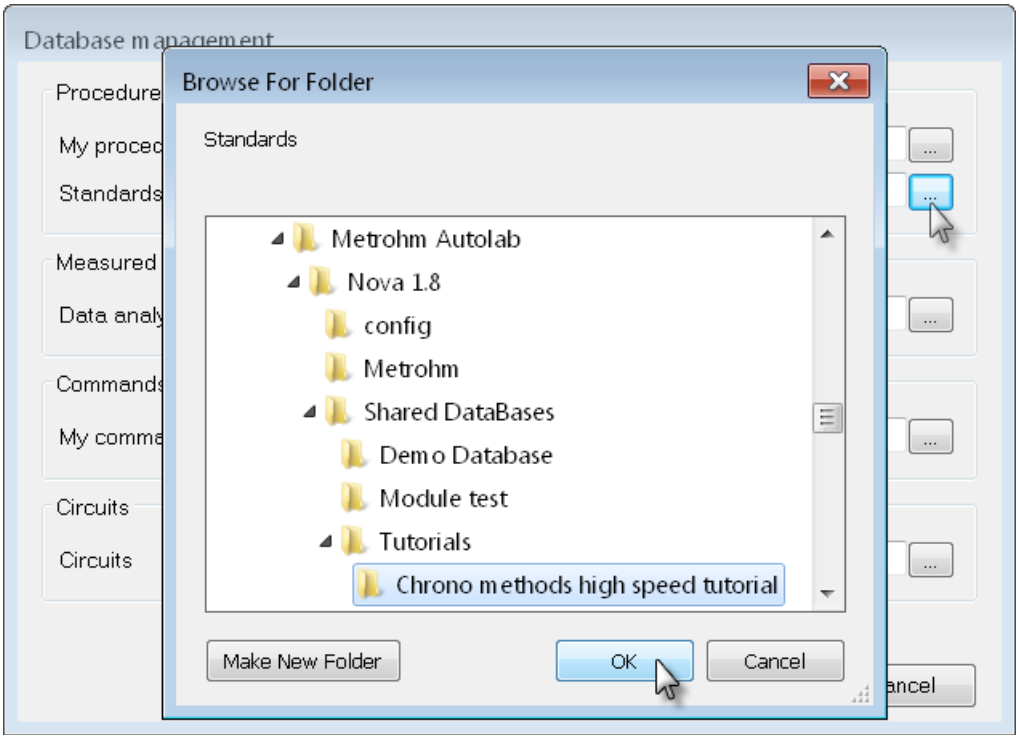

Figure 14 – Loading the Chrono methods high speed tutorial database

Three procedures are included in this tutorial procedure. All the procedures are intended to be used with the standard Autolab dummy cell (see Figure 15).

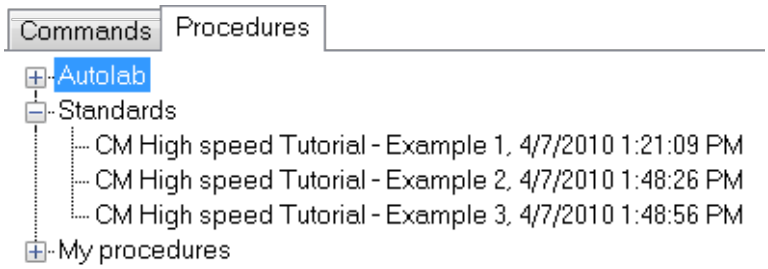

Figure 15 – The three Chrono methods high speed tutorial procedures

4.1 – Chrono methods Tutorial – Example 1

Select the *CM High speed Tutorial – Example 1* procedure from the Standard group. Connect the dummy cell (c) to the instrument and start the measurement.

The procedure will perform a measurement on the dummy cell using the following sequence, using an interval time of 10 µs:

- **Step 1** – setpoint 0 V, duration 0.005 s
- **Step 2** – setpoint 0.3 V, duration 0.005 s
- **Step 3** – setpoint -0.3 V, duration 0.005 s
- **Step 4** – setpoint 0 V, duration 0.005 s

Press the Start button to run the measurement. A message box will be displayed before the measurement starts (see Figure 16).

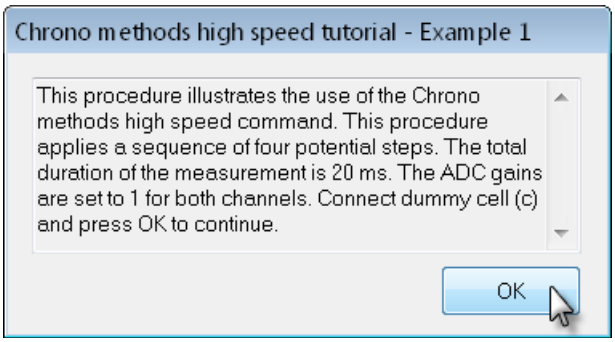

Figure 16 – The message box shown during the example 1 tutorial procedure

When the measurement is finished, the measured data points are displayed in the measurement view (see Figure 17).

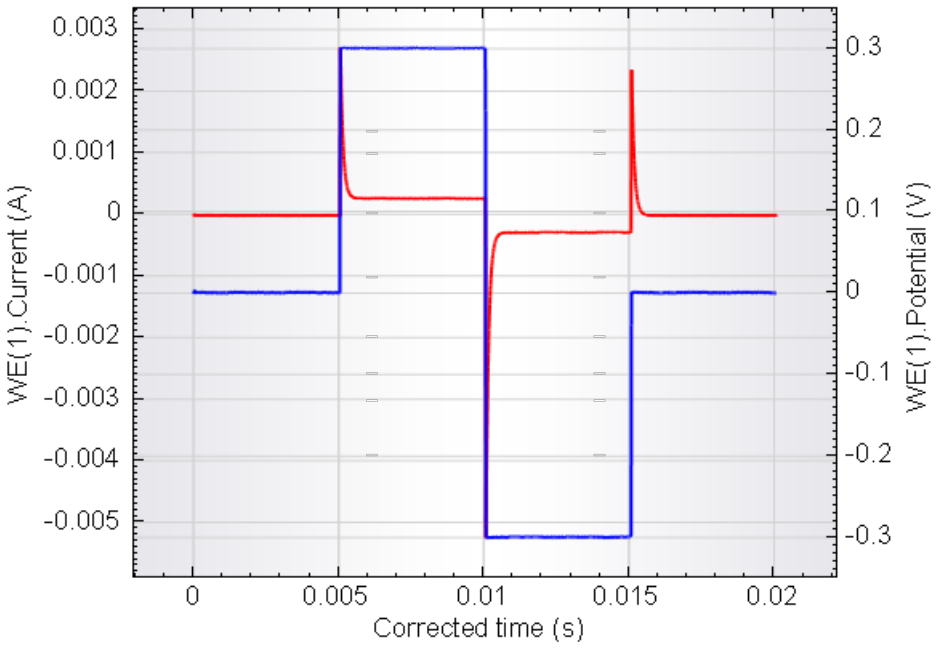

Figure 17 – The potential (blue combi plot) and current (red combi plot) profiles plotted vs Corrected time measured during the tutorial 1 procedure (the data is displayed at the end of the measurement)

As expected, the current of the working electrode, WE(1).Current, goes through three spikes, after each of the potential steps. The data points are measured with an interval time of 10 µs. With the ADC750 module, the interval time can be further decreased to 1.33 µs while with the ADC10M, the smallest possible interval time is 100 ns.

Time vs Corrected time

Like the *Chrono methods* command, the *Chrono methods high speed* command automatically calculates a Corrected time signal after the measurement. This signal is a normalized time scale, relative to the absolute time stamp of the first data point recorded during the measurement. This simplifies overlays using data sets from different experiments, since the absolute timing could be different.

5 – ADC high speed settings

The *Chrono methods high speed command* uses the optional high speed ADC modules to sample two electrochemical signals. Both modules (ADC750 or ADC10M) have specific data acquisition settings that can be edited for the experimental conditions.

To edit the acquisition settings of the high speed ADC module, click on the … button located next the ADC high speed settings in the procedure setup (see Figure 18).

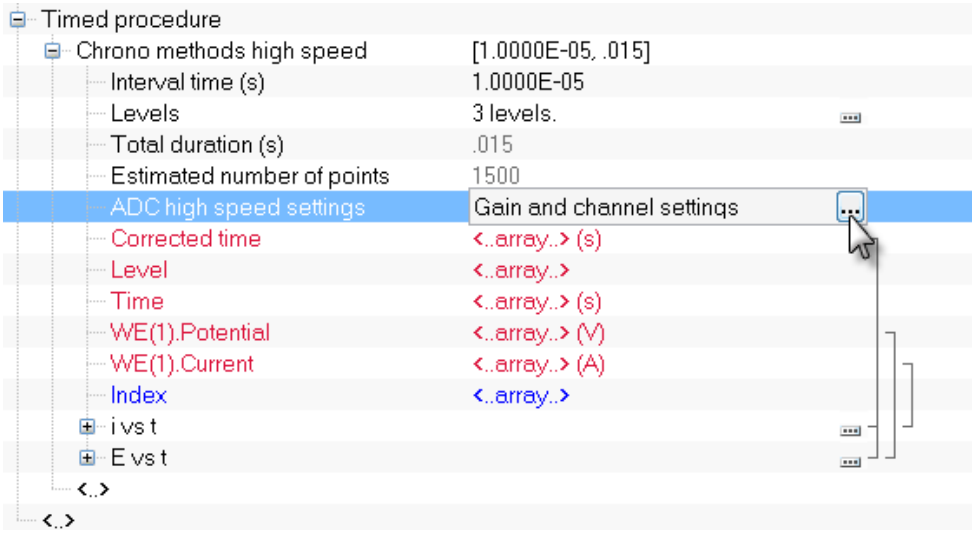

Figure 18 – Click the … button to open the ADC high speed settings

This will open the ADC settings window (see Figure 19).

Note: the ADC10M and the ADC750 modules have different gain settings.

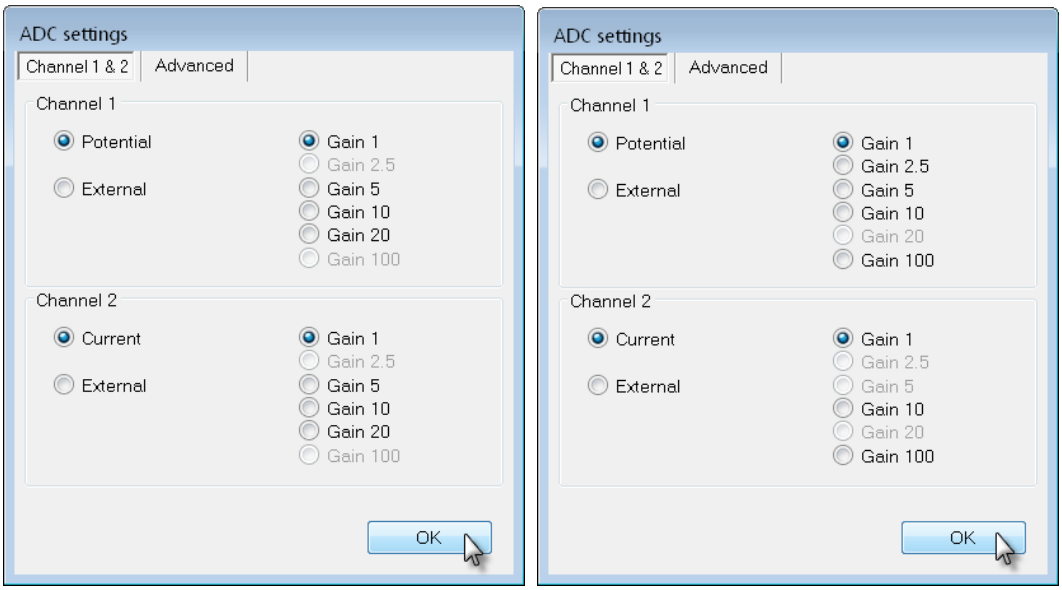

Figure 19 – The high speed ADC module acquisition settings (right – ADC750, left – ADC10M)

Both modules have two ADC channels and each channel can be configured independently. Channel 1 can sample the potential or an external signal, while channel 2 can sample the current or an external signal. The gain settings for each channel can be set using the ADC settings window (see Figure 19).

Note: when external signals are sampled, the external inputs on the front panel of the instrument must be used. These inputs are labelled →1 and →2 (see Figure 20).

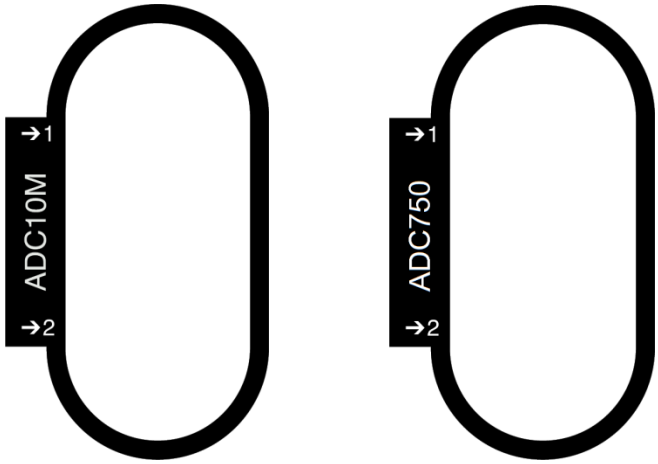

Figure 20 – Module labels for the ADC10M (left) and the ADC750 (right) indicating the locations of the external inputs of the fast sampling ADC module on the front panel of the instrument

5.1 – Chrono methods Tutorial – Example 2

Select the *CM High speed Tutorial – Example 2* procedure from the Standard group. This procedure will perform the same measurement as in Example 1, but using a higher gain setting for ADC channel 1, which is used to measure the WE(1).Potential.

Connect the dummy cell (c) to the instrument and start the measurement.

Press the start button to run the measurement. A message box will be displayed before the measurement starts (see Figure 21).

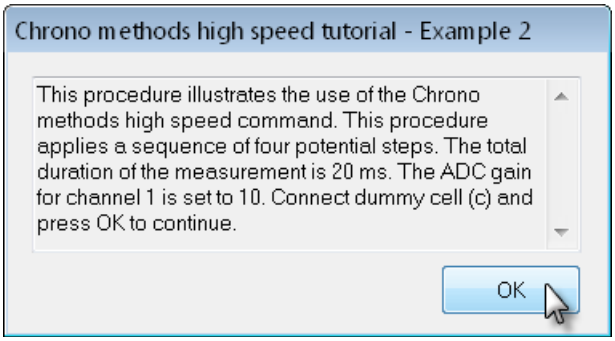

Figure 21 – The message box shown during the example 2 tutorial procedure

When the measurement is finished, the data will be displayed in the measurement view (see Figure 22).

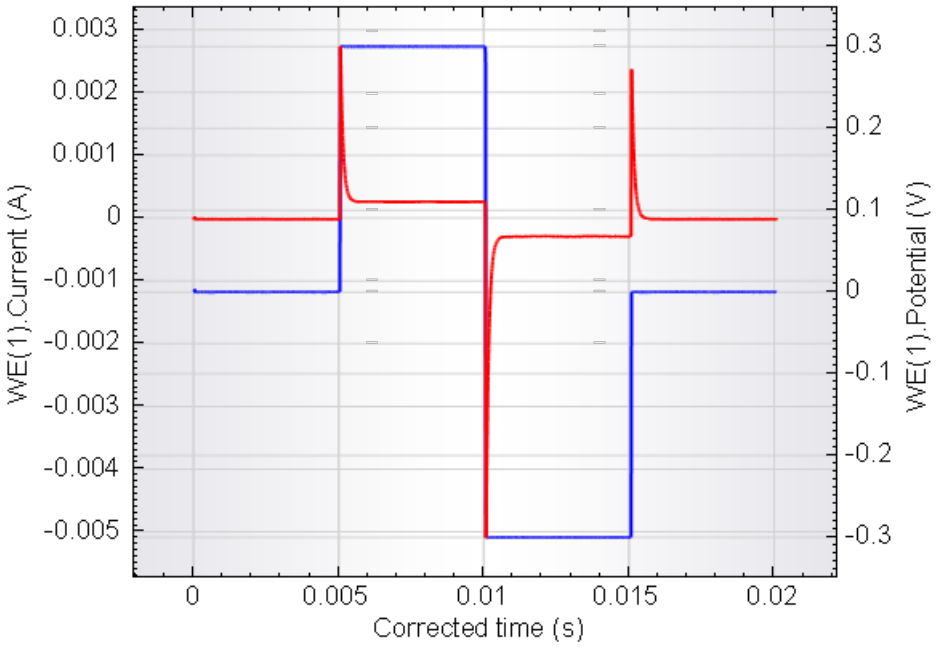

Figure 22 – The potential (blue) and current (red) profiles plotted vs Corrected time measured during the tutorial 2 procedure (the data is displayed at the end of the measurement)

Careful comparison of the WE(1).Potential values measured during the first two tutorial procedures shows how the ADC gain settings can help to improve the signal-to-noise ratio[4]. In the first measurement, the gain setting for channel 1 was set to 1, whereas it was set to 10 for the second measurement. Since the input range of both ADC channels is 0-10 V, setting the gain value to 10 for the WE(1).Potential channel significantly increases the resolution of the signal (see Figure 23).

[4] Switch to the analysis view to compare the measurements.

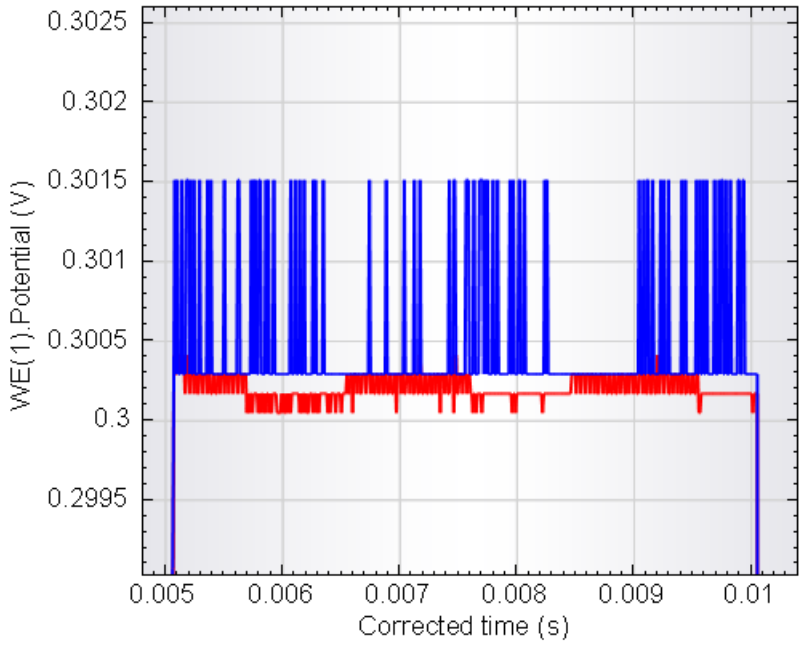

Figure 23 – Comparison of the measured WE(1).Potential signals during the second step of the sequence. Blue curve corresponds to tutorial 1 (gain 1) and red curve corresponds to tutorial 2 (gain 10)

6 – Using the recurrent steps

The *Chrono methods high speed* command offers the possibility of using recurrent steps in the sequence editor.

Inserting recurrent steps in the Chrono methods high speed sequence, creates a sub sequence in which new steps can be added. The steps located in the recurrent steps sequence can be repeated any number of times.

Figure 24 displays the sequence editor window of the previous examples, after the addition of a recurrent steps item.

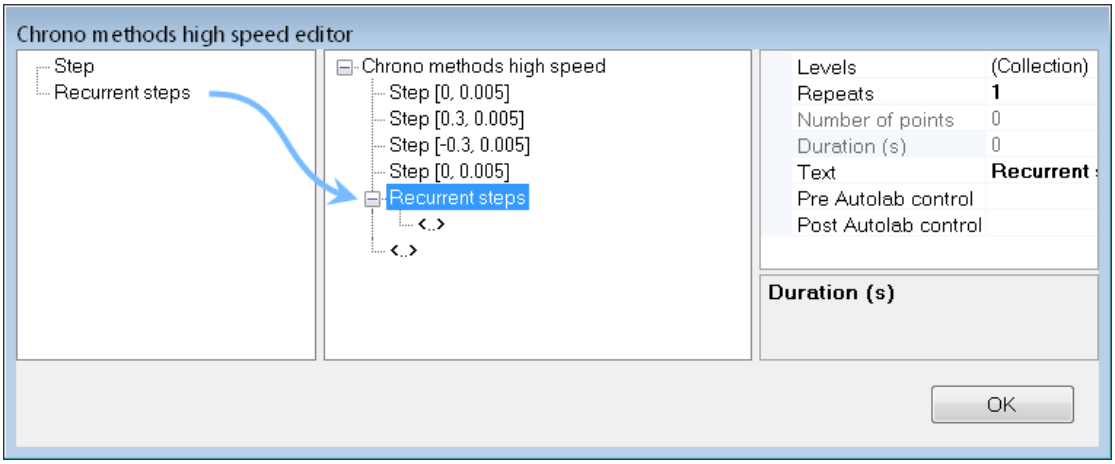

Figure 24 – Inserting a recurrent steps element creates a new sequence in the editor

Any item dragged from the left-hand frame into the measurement collection will be sampled during the measurement, using the interval time of the high speed ADC.

Using the same approach as in the previous examples, add two steps to the measurement collection (see Figure 25). The properties of the sequence will be updated on the right-hand side, indicating the number of items in the sequence and the total duration of the sequence.

Change the setpoint of the first step of the recurrent steps to 0.5 and the setpoint of the second step to -0.5. Change the duration of both steps to 0.001 s (see Figure 25).

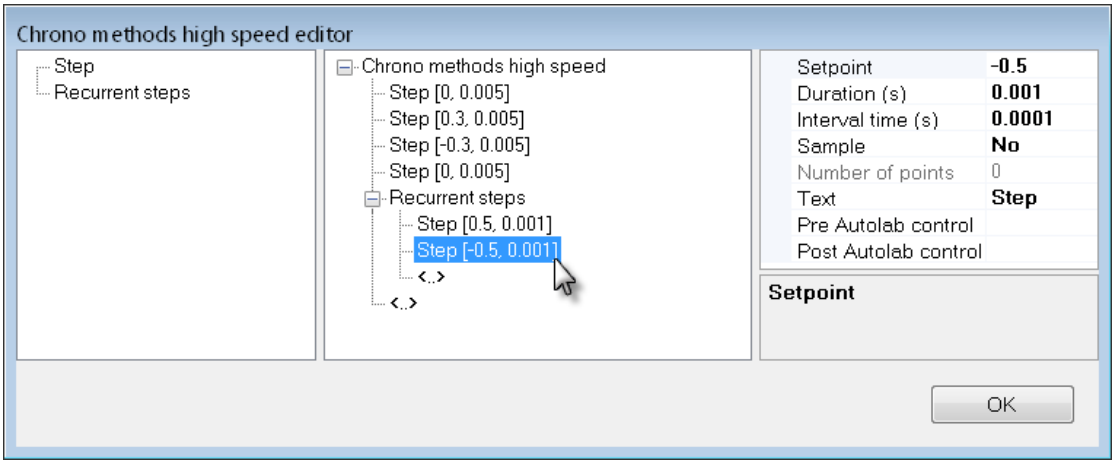

Figure 25 – Adding two steps to the recurrent steps

The recurrent steps sequence can be repeated a number of times in the whole sequence. Click the recurrent steps item in the sequence and set the number of repetitions in the parameters frame (see Figure 26).

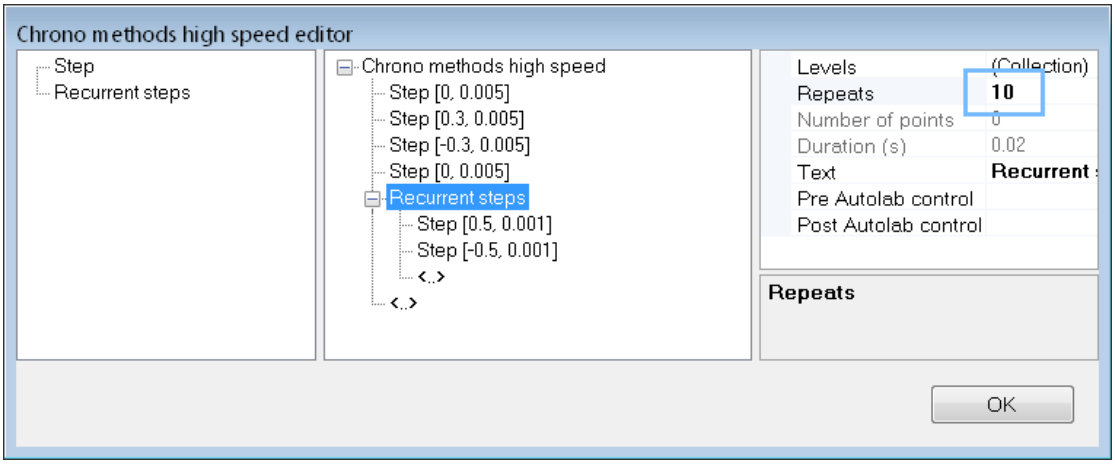

Figure 26 – Setting the number of repetitions to 10 for the whole recurrent steps sequence

Click the OK button to close the sequence editor window. The procedure editor will be updated with the new values (see Figure 27).

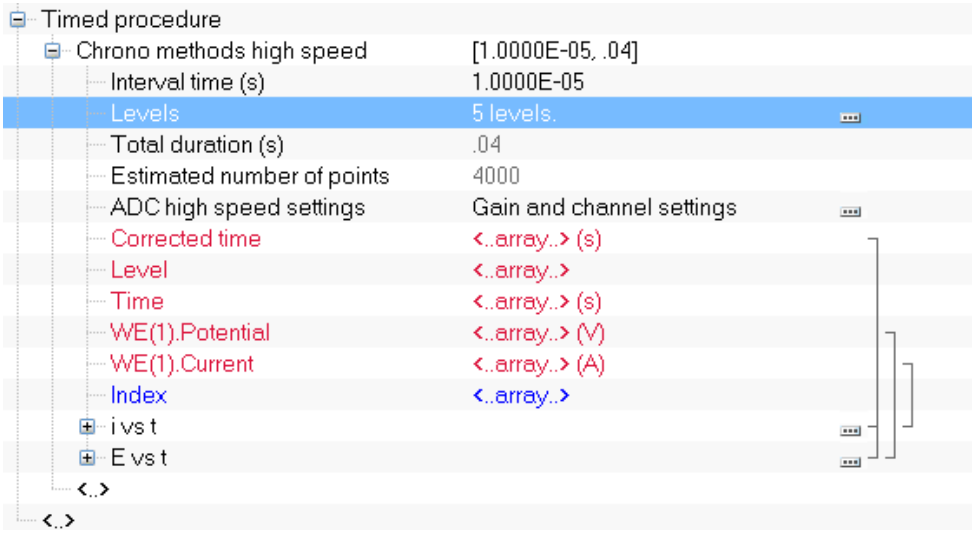

Figure 27 – The updated procedure editor

6.1 – Chrono methods Tutorial – Example 3

Select the *CM High speed Tutorial – Example 3* procedure from the Standard group. This procedure will perform the same measurement as in Example 1, followed by ten repetitions of two additional steps located in a recurrent steps sequence. Gain 10 is used for WE(1).Potential.

Connect the dummy cell (c) to the instrument and start the measurement.

Press the Start button to run the measurement. A message box will be displayed before the measurement starts (see Figure 28).

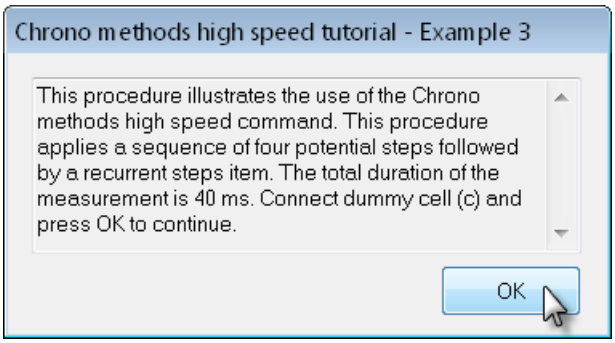

Figure 28 – The message box shown during the example 3 tutorial procedure

After the measurement, a message will be displayed indicating that it is finished. Click OK and switch to the analysis view. Load the data set into the data explorer to analyze the measured data points (see Figure 29).

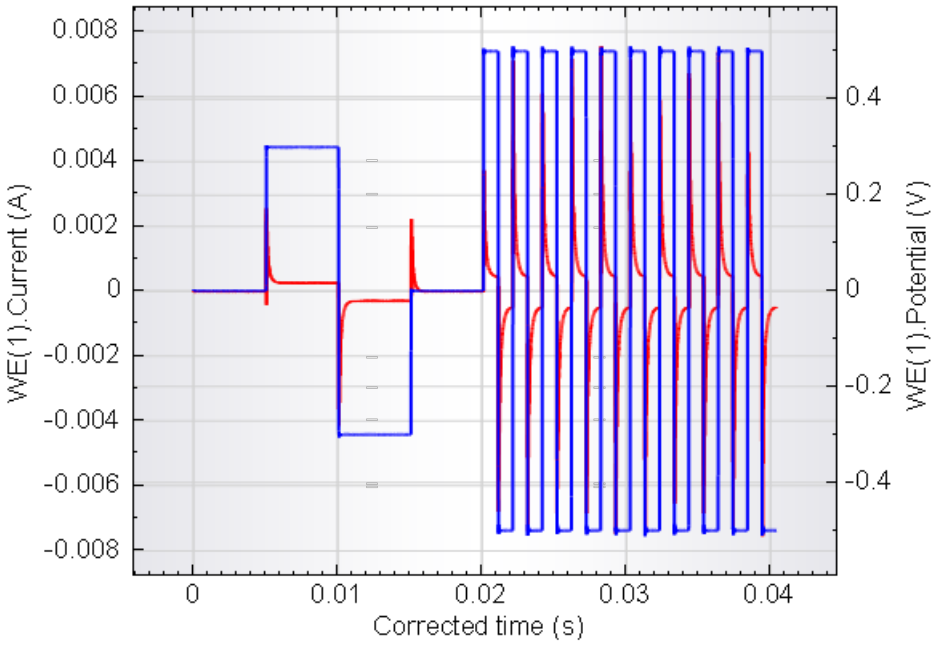

Figure 29 – The potential (blue) and current (red) profiles plotted vs Corrected time measured during the tutorial 3 procedure (the data is displayed at the end of the measurement)

The sequence starts with the four same initial steps of the previous measurements, followed by ten repetitions of two steps, with a duration of 1 ms. The current is displayed as a sequence of spikes after each potential step in the sequence, followed by exponential decays. It is important to note that all the steps are applied without any interruption.

Hardware specifications

The ADC750 and ADC10M modules are dual channel, synchronous, fast sampling A/D converters. Both modules can be installed in all the supported Autolab PGSTAT instruments, except the PGSTAT101 or M101 and the μAutolabII/III.

The ADC750 and ADC10M module can be used for chrono measurements using the smallest possible interval time. These modules can also be used in combination with the linear scan generator modules (SCANGEN or SCAN250).

Table 1 provides an overview of the fast sampling ADC module specifications.

Module	ADC10M	ADC750
Number of channels	2	2
Max. sampling rate	10 MSamples/s	750 kSamples/s
Shortest interval time	100 ns	1.33 μs
ADC resolution	14 bit	12 bit
Max. resolution, E	100 μV (Gain 10)	500 μV (Gain 10)
Max. resolution, i	0.0006 % of C.R. (Gain 10)	0.0025 % of C.R. (Gain 10)
Max. # of points	1.024.000	512.000

Table 2 – Overview of the specifications of the fast sampling ADC modules

Important note: the ADC750 revision 4.0 can only store up to 128.000 points. The specifications of this module are otherwise identical to the specification of the ADC750.