

NOVA

EQCM Tutorial



1 – The Electrochemical Quartz Crystal Microbalance (EQCM)

The EQCM is an optional module for the Autolab PGSTAT and Multi Autolab. The EQCM module provides the means to perform Electrochemical Quartz Crystal Microbalance measurements. The EQCM module measures a mass change per unit area by measuring the change in resonant frequency of a quartz crystal.

Quartz crystals belong to a group of materials displaying the so-called piezoelectric effect. When a properly cut crystal (AT-cut) is exposed to an AC current, the crystal starts to oscillate at its resonant frequency and a standing shear wave is generated.

In first approximation, the resonant frequency depends on the thickness of the crystal. As mass is deposited on the surface of the crystal, the thickness increases; consequently the frequency of oscillation decreases from the initial value. With some simplifying assumptions, this frequency change can be quantified and correlated precisely to the mass change using Sauerbrey's equation:

$$\Delta f = -\frac{2f_0^2}{A\sqrt{\rho_q\mu_q}} \cdot \Delta m$$

Where Δf is the change in frequency, in Hz, f_0 is the nominal resonant frequency of the crystal (6 MHz), Δm is the change in mass, in g/cm², A is the area of the crystal in cm², ρ_q is the density of quartz, in g/cm³ and μ_q is the shear modulus of quartz, in g/cm·s².

For a 6 MHz crystal, the same equation can be reduced to:

$$-\Delta f = \Delta m \cdot C_f$$

Where C_f is 0.0815 Hz/ng/cm².

More information about the EQCM module can be found in the EQCM user manual.

2 – Hardware setup

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

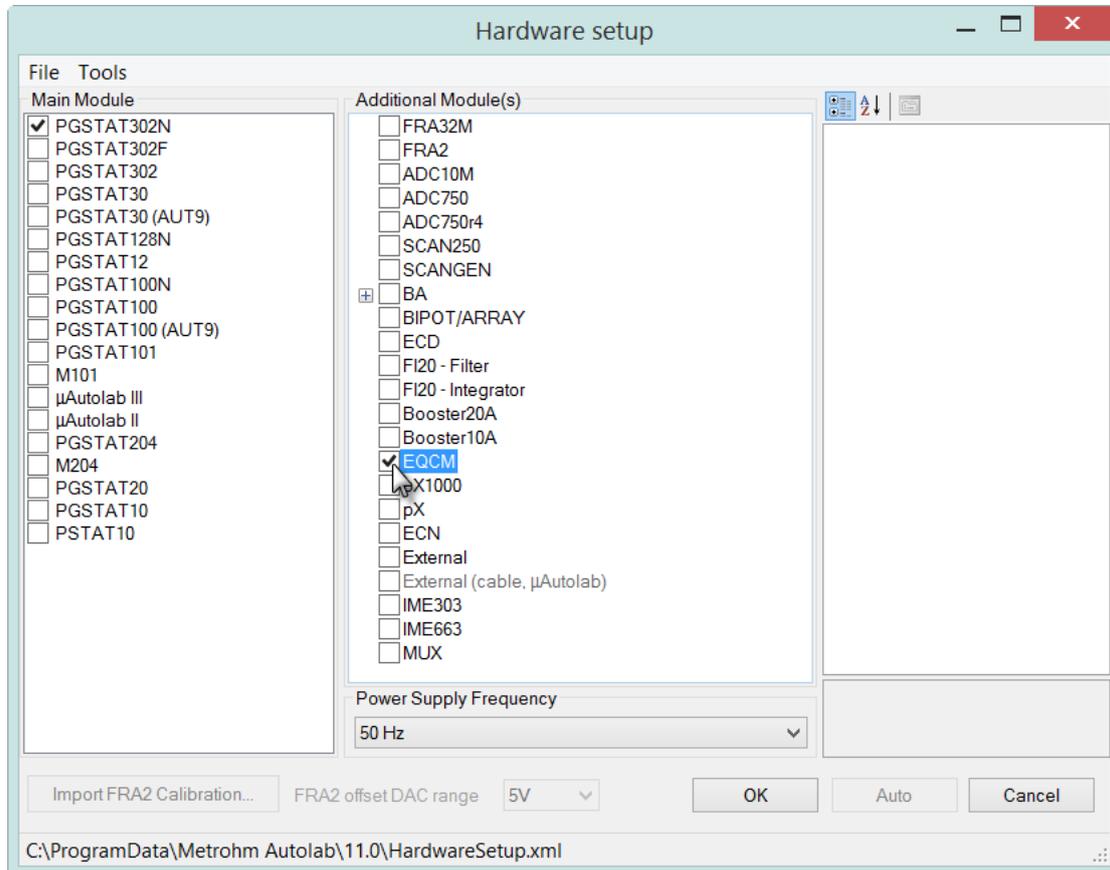


Figure 1 – Selecting the EQCM module

3 – Measuring the EQCM signals

Regardless of the type of crystal connected to the EQCM oscillator, a total of three electrochemical signals can be selected in the Sampler (see Figure 2):

- EQCM(1).Temperature
- EQCM(1).Driving force
- EQCM(1). Δ Frequency

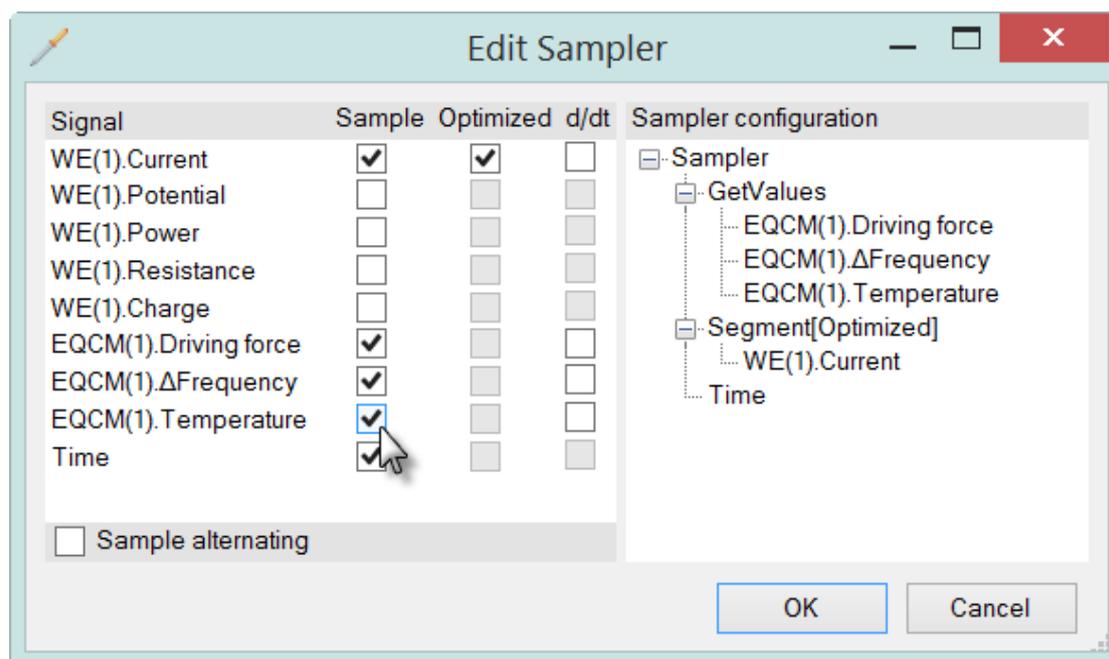


Figure 2 – The signals provided by the EQCM are available in the sampler

The temperature signal is measured by the sensor located at the bottom of the EQCM cell. This signal is provided in °C. The driving force signal corresponds to a voltage value between 0 V and 2.5 V. This value represents the amount of energy required to sustain the oscillation of the crystal. When the loading of the crystal increases, the driving force also increases. In air, the typical driving force is close to 0 V. In water, the driving force is about 0.85 V. The Δ Frequency signal corresponds to the relative change in oscillation frequency of the quartz crystal. This variation is expressed with respect to an arbitrary, user-defined reference frequency (zero Hz).



Note

The electrochemical signals provided by the EQCM are not sampled through the ADC164 module. These signals are directly provided by the EQCM module. This means that these signals cannot be sampled in 'optimized mode'.



Warning

The highest possible sampling rate of the EQCM module is 50 samples/s (20 ms interval time). If measurements with shorter interval times are performed, the last values of the EQCM signals will be recorded multiple times until new samples are obtained for these signals.

4 – Using the EQCM

Before the signals from the EQCM module can be sampled in a procedure, the EQCM module must be switched ON. The ON/OFF control of the oscillator is available in the Autolab control command, on the EQCM tab (see Figure 3).

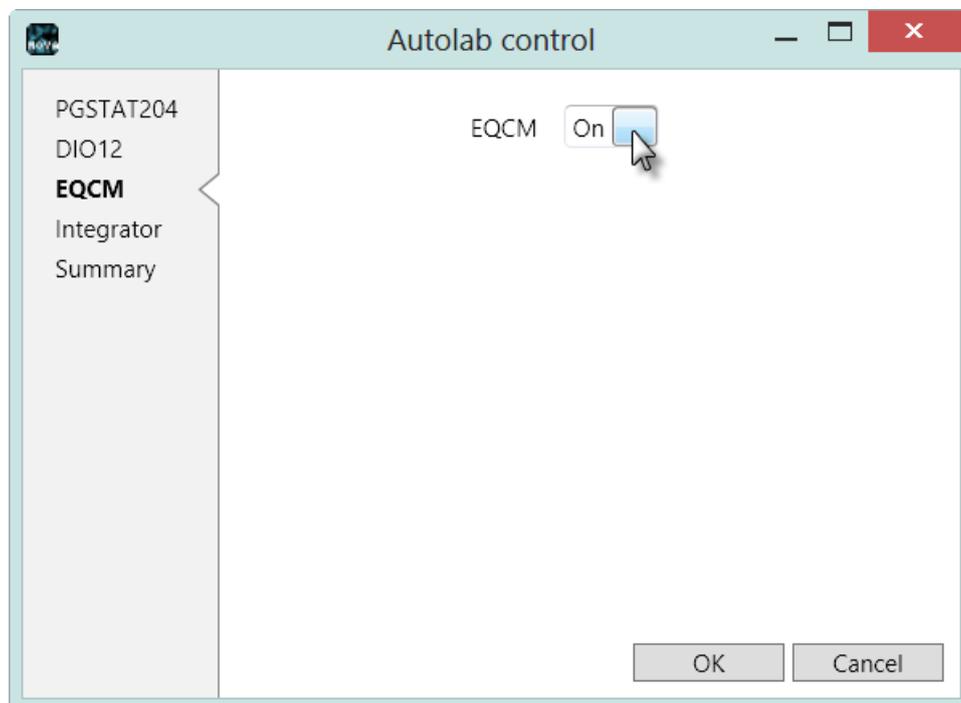


Figure 3 – The Autolab control window can be used to switch the EQCM module ON or OFF

Once the EQCM has been switched on, the electrochemical signals provided by the EQCM module can be sampled, using any available measurement command (except measurement commands using the FRA2/FRA32M module or the fast-sampling ADC module¹).

¹ ADC750 or ADC10M.

5 – Zeroing the Δ Frequency

It is common practice to measure the relative frequency change with respect to a control situation. In order to do this, the user has to control the potential relative to the reference electrode or control the current flowing through the working electrode coated on the quartz crystal with the Autolab potentiostat/galvanostat and set the frequency change to 0 Hz. All consequent frequency changes will then be measured with respect to the defined control situation. A dedicated command, *Reset EQCM Δ Frequency*, is available for this purpose.

This command is located in the Measurement – General group of commands (see Figure 4).

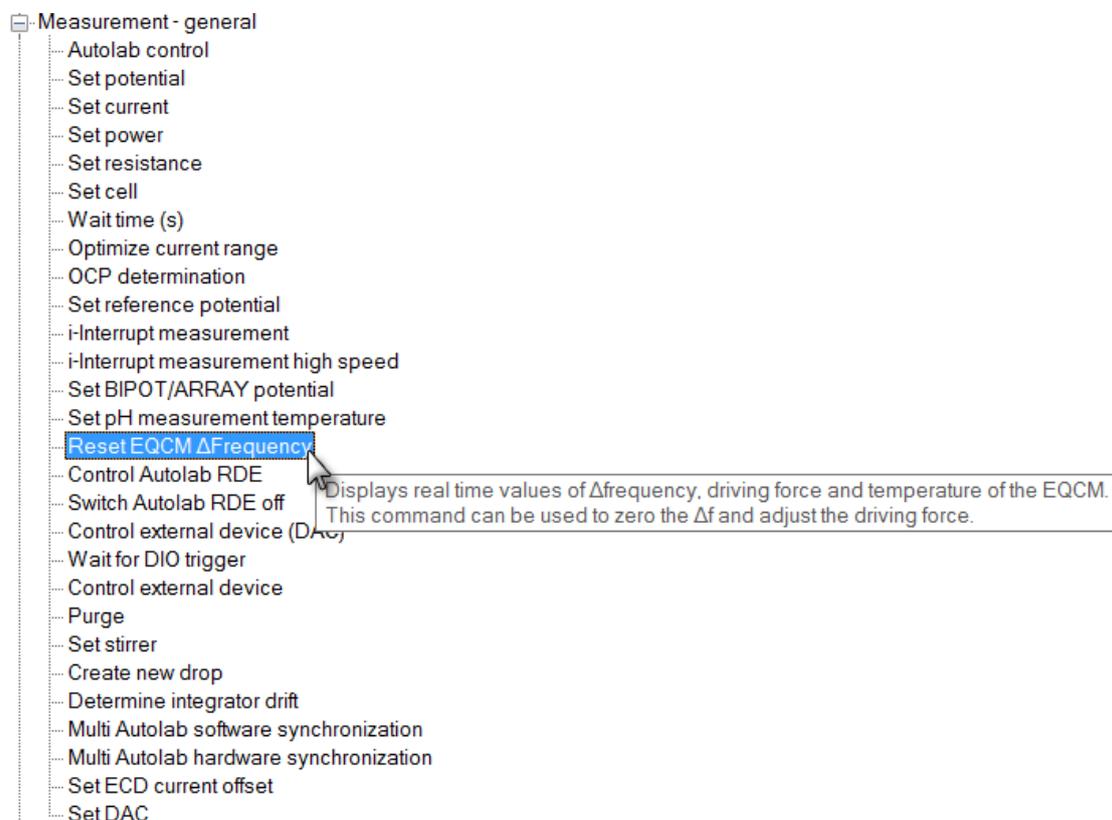


Figure 4 – The *Reset EQCM Δ Frequency* command can be found in the Measurement – General group



Note

The *Reset EQCM Δ Frequency* command is an intermediate command and will not be visible if the Basic profile is active. Please adjust the Profile scheme accordingly.

This command can be added anywhere in a procedure. Whenever the *Reset EQCM Δ Frequency* command is used, a window allowing fine tuning of the EQCM driving force and zeroing of the Δ Frequency value will be displayed (see Figure 5).

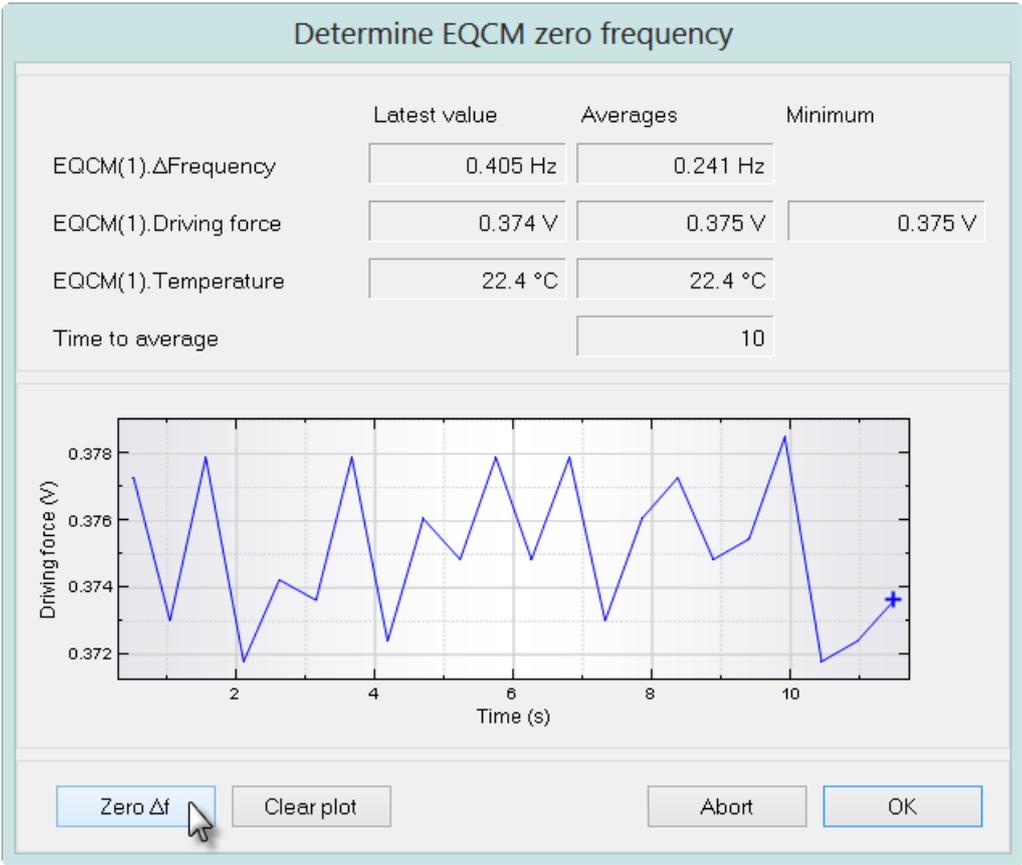


Figure 5 – The Determine EQCM zero frequency window

The Determine EQCM zero frequency window contains three sections:

The *topmost* section, shown in Figure 6, displays real time information on the measured signals provided by the EQCM:

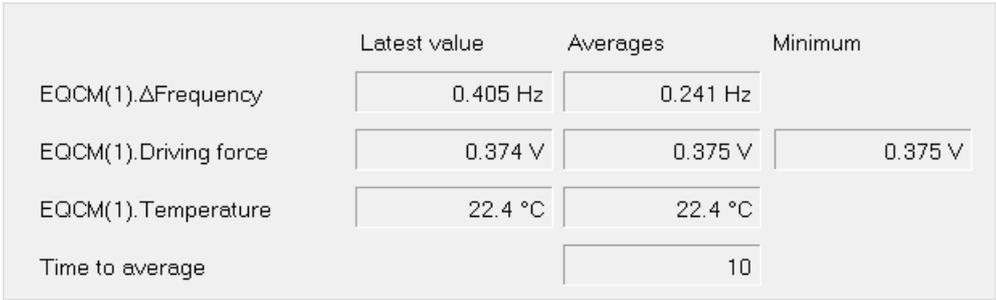


Figure 6 – The topmost section of the Determine EQCM zero frequency window displays the measured values in real time

- **EQCM(1). Δ Frequency (Latest value, Averages):** these fields show the latest and averaged Δ Frequency values measured by the EQCM, respectively. The average is obtained from a moving average over the last ten values.
- **EQCM(1).Driving force (Latest, Averages, Minimum):** these fields show the latest, the averaged and the minimum value of the driving force, respectively. The driving force is a measure of the sustainability of the oscillation. The average value is obtained from a moving average over the last ten values. The measurable range of driving force is between 0 V and 2.5 V. The minimum field shows the absolute minimum value recorded.
- **EQCM(1).Temperature (Latest, Averages):** these fields show the latest and averaged temperature values measured by the EQCM, respectively. The average is obtained from a moving average over the last ten values.
- **Time to average:** this field indicates the number of values used in the moving average determination (hardcoded to 10).

The *middle* section, shown in Figure 7, displays the recorded values of the driving force plotted versus time.

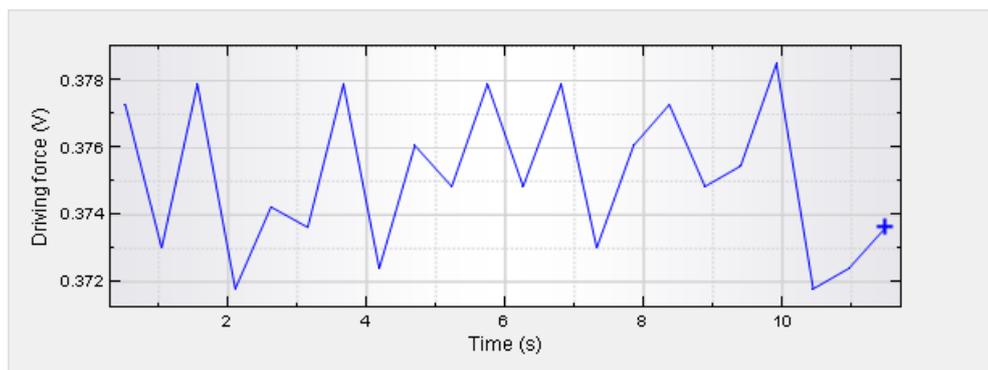


Figure 7 – The middle section of the Determine EQCM zero frequency window displays the measured driving force plotted versus time

The *bottom* section, shown in Figure 8, displays a series of buttons that can be used to control the behavior of the Determine EQCM zero frequency:

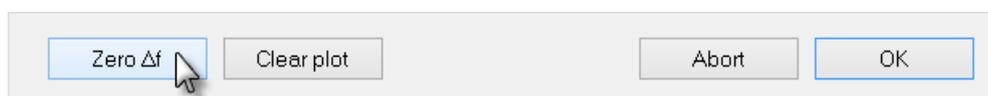


Figure 8 – The bottom section of the Determine EQCM zero frequency window displays the measured values in real time

- **Zero Δ f:** set the value of the measured Δ Frequency to zero. Setting the value to zero requires several iterations. During this adjustment, the **Zero Δ f** button will be grayed out.
- **Clear plot:** this button can be used to clear the plot displayed in the window. The measurement resumes after the button is pressed. The values shown in the topmost part of the window are not cleared.

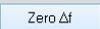
- **Abort:** closes the Determine EQCM zero frequency window and terminates the complete procedure.
- **OK:** closes the Determine EQCM zero frequency window and proceeds with the rest of the procedure.

Using the provided screw driver, the trimmer on the EQCM oscillator should always be adjusted in order to minimize the driving force of the QCM crystal. This should always be performed every time the environment of the crystal is changed. The driving force value is displayed in the plot area of the Determine EQCM zero frequency window.

The Clear plot button can be pressed at any time to clear the display. The  button can be used to zero the Δ Frequency signal. Pressing the Abort button stops the measurement.



Note

Pressing the  button will perform five consecutive adjustments to 0 Hz. While the Δ Frequency is zeroed, the  button will be grayed out.

6 – Measurements with the EQCM module

An EQCM 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.

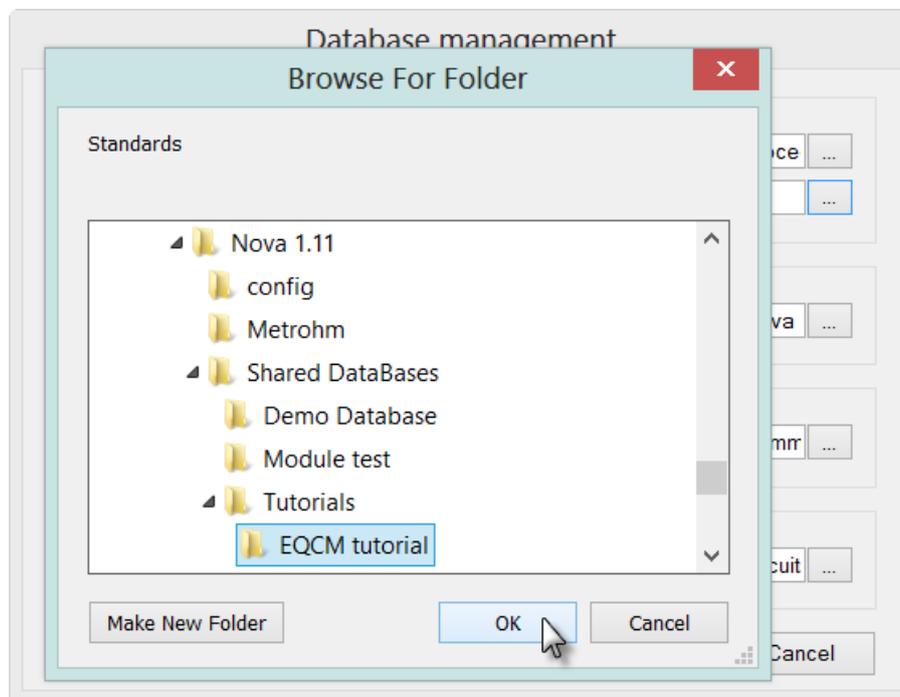


Figure 9 – Loading the EQCM tutorial database

The EQCM tutorial contains two procedures that can be used as examples of electrochemical quartz crystal microbalance measurements (see Figure 10).

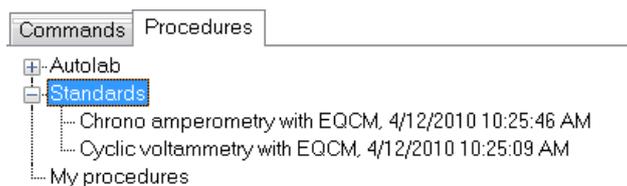


Figure 10 – Two procedures are provided in the EQCM tutorial

6.1 – Cyclic voltammetry with EQCM

Load the Cyclic voltammetry with EQCM procedure in the procedure editor. This procedure is designed to perform a cyclic voltammetry staircase measurement in potentiostatic mode. At the beginning of the procedure, the EQCM module is switched on, using the *Autolab control* command (see Figure 11).

Commands	Parameters	Links
Cyclic voltammetry with EQCM		
Remarks	EQCM Tutorial	...
End status Autolab		...
Signal sampler	Time, EQCM(1).Temperature, EQCM(1).Driving force, EQCM(1). Δ Frequency, WE(1).Current	...
Options	1 Options	...
Instrument		
Instrument description		
Autolab control		...
WE(1).Mode	Potentiostatic	
WE(1).Bandwidth	High stability	
WE(1).Current range	1 mA	
EQCM(1) Active	On	...
Set potential	0.800	
Set cell	On	...
Wait time (s)	5	
Optimize current range	5	
Reset EQCM Δ Frequency		
CV staircase	[0.800, 1.000, -0.600, 0.800, 2, 0.0200000]	
Start potential (V)	0.800	
Upper vertex potential (V)	1.000	
Lower vertex potential (V)	-0.600	
Stop potential (V)	0.800	
Number of stop crossings	2	
Step potential (V)	0.00244	
Scan rate (V/s)	0.0200000	
Estimated number of points	1322	
Interval time (s)	0.122000	
Signal sampler	Time, EQCM(1).Temperature, EQCM(1).Driving force, EQCM(1). Δ Frequency, WE(1).Current	...
Options	1 Options	...
Potential applied	<.array.> (V)	
Time	<.array.> (s)	
WE(1).Current	<.array.> (A)	
Scan	<.array.>	
EQCM(1).Temperature	<.array.> (°C)	
EQCM(1).Driving force	<.array.> (V)	
EQCM(1). Δ Frequency	<.array.> (Hz)	
Index	<.array.>	
i vs E		...
Δ Frequency vs E		...
Set cell	Off	...
<.>		...

Figure 11 – The cyclic voltammetry with EQCM tutorial procedure

During the cyclic voltammetry experiment, the three signals provided by the EQCM module are sampled alongside the WE(1).Current signal. The measurement starts by applying a pre-conditioning potential. Just before the cyclic voltammetry measurement starts, the *Reset EQCM Δ Frequency* is used to fine tune the settings of the EQCM module and to zero the Δ Frequency signal (see Figure 11).

Figure 12 shows an example of a cyclic voltammogram recorded using the Cyclic voltammetry with EQCM procedure. This example corresponds to the bulk deposition (over-potential deposition) of lead on a gold-coated QCM crystal, from a 0.01 M lead (II) perchlorate solution (HClO₄ 0.1 M). All frequency changes are measured with respect to the zero Δ Frequency which was set while pre-conditioning the working electrode at 0.8 V vs Ag/AgCl (KCl 3 M).

NOVA EQCM tutorial

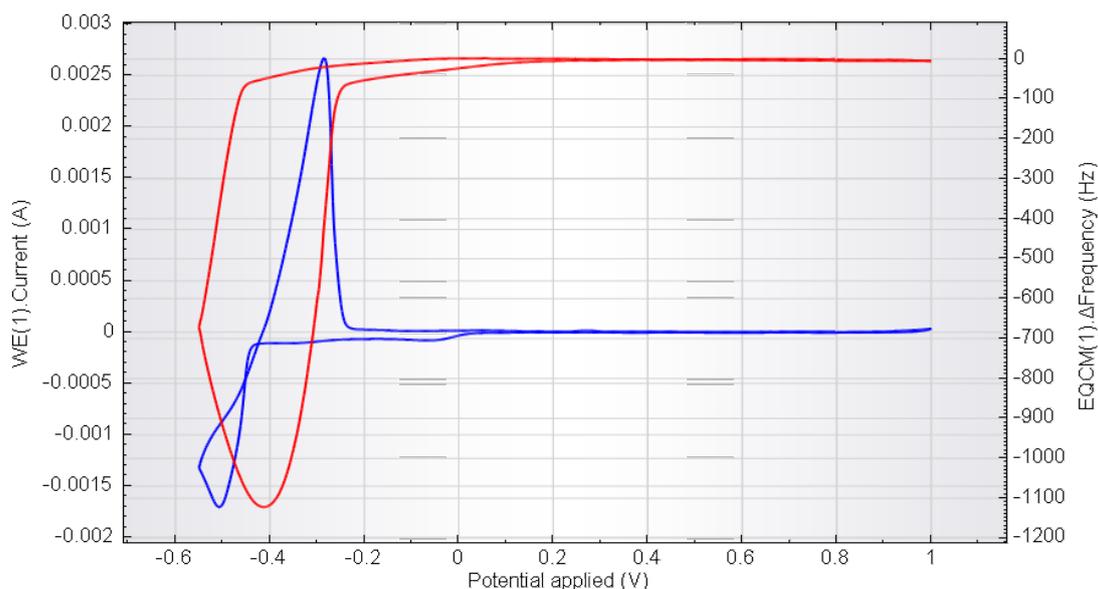


Figure 12 – An example of EQCM cyclic voltammetry recorded using the Cyclic voltammetry with EQCM procedure (blue curve: current, red curve: Δ Frequency)

6.2 – Chrono amperometry with EQCM

Load the Chrono amperometry with EQCM procedure in the procedure editor. This procedure is similar to the previous one. It is designed to perform a potential step experiment during which the signals provided by the EQCM module are sampled. At the beginning of the procedure, the EQCM module is switched on, using the *Autolab control* command (see Figure 13).

Commands	Parameters	Links
Chrono amperometry with EQCM		
Remarks	EQCM Tutorial	...
End status Autolab		...
Signal sampler	Time, EQCM(1).Temperature, EQCM(1).Driving force, EQCM(1). Δ Frequency, WE(1).Current	...
Options	1 Options	...
Instrument		
Instrument description		
Autolab control		...
WE(1).Mode	Potentiostatic	
WE(1).Bandwidth	High stability	
WE(1).Current range	1 mA	
EQCM(1).Active	On	...
Set potential	0.800	
Set cell	On	...
Optimize current range	5	
Record signals (>1 ms)	[10, 0.1]	-
Reset EQCM Δ Frequency		
Set potential	-0.400	
Record signals (>1 ms)	[10, 0.1]	-
Set cell	Off	...
<.>		

Figure 13 – The chrono amperometry with EQCM tutorial procedure

After the first potential value has been applied and the response of the cell has been recorded using the *Record signals (> 1 ms)* command, the *Reset EQCM Δ Frequency* is used to fine tune the settings of the EQCM module and to zero the Δ Frequency signal (see Figure 13). After the Δ Frequency signal has been zeroed, the procedure proceeds with the potential step and the response of the cell is sampled.

Figure 14 shows an example of a chrono amperometry experiment recorded using the Chrono amperometry with EQCM procedure. This example corresponds to under-potential deposition (UPD) of lead on a gold-coated QCM crystal, from a 0.01 M lead (II) perchlorate solution (HClO_4 0.1 M). All frequency changes are measured with respect to the zero $\Delta\text{Frequency}$ which was set while pre-conditioning the working electrode at 0.8 V vs Ag/AgCl (KCl 3 M).

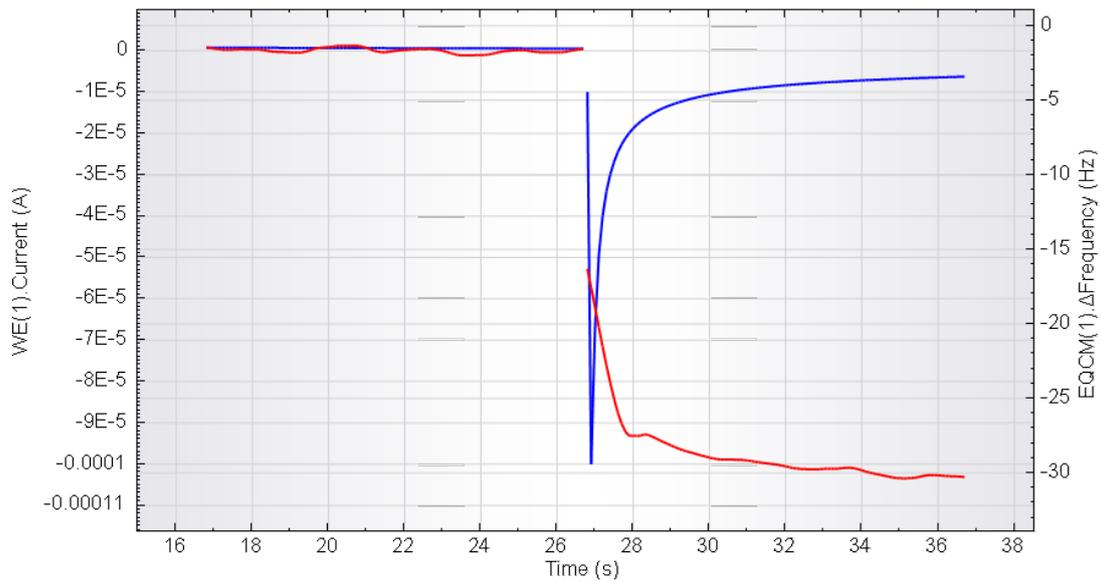


Figure 14 – An example of chrono amperometry experiment recorded using the Chrono amperometry with EQCM procedure (blue curve: current, orange curve: $\Delta\text{Frequency}$)

Hardware specifications

The EQCM module is an option module for the modular Autolab PGSTAT, with the exception of the PGSTAT100, PGSTAT100N and PGSTAT302F². The EQCM module is fitted with a 6 MHz crystal oscillator and it can be used to monitor changes in frequency, with a dynamic range of 80000 Hz.

The module is also fitted with a temperature probe, which can be connected to the temperature sensor embedded in the standard electrochemical cell provided with the module.

Table 1 provides an overview of some of the EQCM module specifications.

Specification	Value
Oscillation frequency	6 MHz
Frequency resolution	0.07 Hz
Relative accuracy	1 Hz
Absolute accuracy	10 Hz
Frequency range	80 kHz
Temperature sensor accuracy	1 °C
Temperature sensor resolution	0.1 °C

Table 1 – Overview of the specifications of the EQCM modules



Note

More information about the EQCM module can be found in the EQCM User Manual.

² The EQCM module cannot be fitted in the μ Autolab II/III and in the PGSTAT101.