EQCM

User manual

Please read this manual carefully before starting to use the Autolab EQCM module

The next sections deal with appearance and use of the module and contain necessary information regarding operation and installation.

SAFETY PRACTICES

General

- The following safety practices are intended to ensure safe operation of the equipment and must be observed during all phases of operation, service and repair of the instrument.
- Failure to follow these instructions may cause unsafe operation.
- Metrohm Autolab is not liable for any damage caused by not complying with the safety requirements.
- Failure to follow these instructions may void any warranty provided to this module.

Electrical hazards

- To avoid electric shock hazard, always ground the instrument by using the provided power cable with earth connections.
- There are no user-serviceable parts. Module installation, component replacement and internal adjustments must be done only by qualified personnel.
- Removal of the module card from the Autolab PGSTAT and/or opening the external oscillator poses a risk of exposure to potentially dangerous voltages. Always disconnect the potentiostat from all power sources before removing protective panels.
- Please also refer to the Electrical Hazards described separately for the Autolab instrument used.

General precautions

- Use only stable surfaces for setting up the system.

- Do not expose the EQCM module and the Autolab instrument to damp or wet conditions.

Table of Contents

1 – Description of the EQCM module

This manual gives a detailed description of the Autolab EQCM kit, instructions for the installation of the module and EQCM cell, and also for the necessary software setup.

The EQCM consists of a module that fits inside the Autolab and its accessories, as shown in Figure 1.

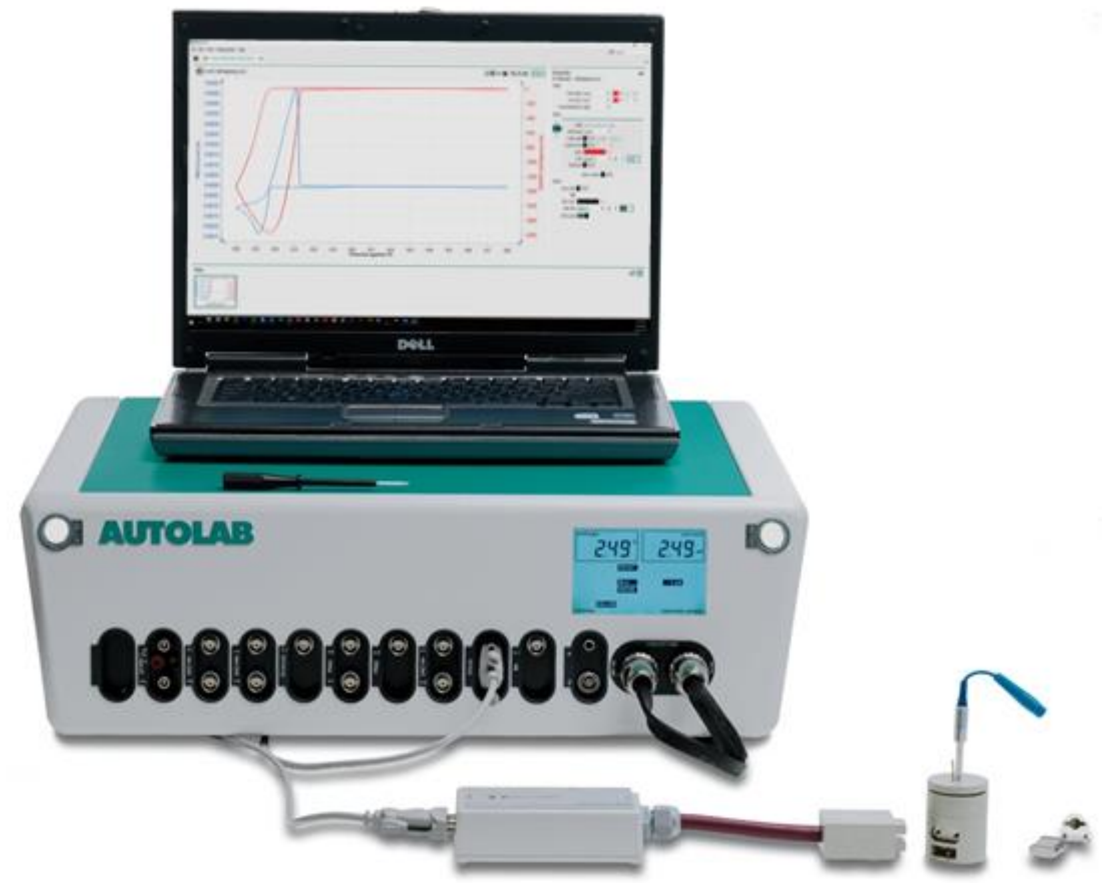

Figure 1 – The EQCM module, complete with oscillator, cell, electrodes and accessories

Shown in Figure 2 is a picture of all items which are included in the Autolab EQCM kit.

As shown in Figure 2, the Autolab EQCM kit contains the following:

1. EQCM module, to be installed in the Autolab PGSTAT or alongside the M101 module in a Multi Autolab Cabinet (Figure 2, A-1).
2. EQCM oscillator (Figure 2, B-2).
3. A 9 Pin Sub-D connector cable (2 m long) to connect the EQCM module and the oscillator (Figure 2, B-3).

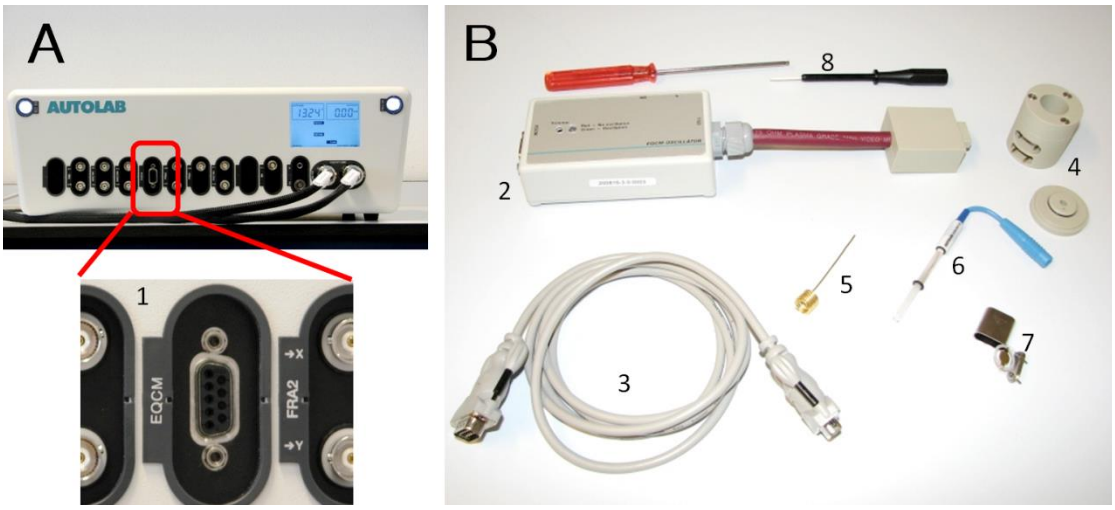

Figure 2 – Overview of the Autolab EQCM kit (A – Module, B – Accessories)

4. EQCM cell[1], detachable (Figure 2, B-4).
5. A gold counter electrode (Figure 2, B-5).
6. A Ag/AgCl in 3 M KCl gel reference electrode[2] with O-ring (Figure 2, B-6).
7. Two Au/TiO_2 polished EQCM crystals[3] (Figure 2, B-7).
8. Tool kit for the driving force adjustment and assembly/disassembly of the cell (Figure 2, B-8).
9. One set of spare O-rings (not shown in Figure 2).

[1] Please refer to Section 2.3 of this document for more information on the electrochemical cell.
[2] Please refer to Section 4.3 of this document for more information on the reference electrode and the care information of this electrode.
[3] Please refer to Section 2.2 of this document for more information on the EQCM crystals.

2 – Hardware installation

The EQCM module can be installed in any of the following Autolab PGSTAT which has a USB interface: PGSTAT 302N, PGSTAT 128N, PGSTAT 204. The EQCM module can also be installed in a Multi Autolab Cabinet, alongside a M101 or M204 module.

Note

The EQCM module cannot be installed in a 7-series instrument (PSTAT12, PGSTAT30, and PGSTAT302) or any earlier models.

In this manual, all the compatible instruments will be referred generically as PGSTAT.

2.1 – Installation of the EQCM module

Presented below is a step by step description for the installation of the EQCM module:

1. Connect the oscillator to the EQCM module (already installed in the instrument) with the provided 9 Pin Sub-D connector cable.
2. Prepare the EQCM cell (see Section 2.3 for more information).
3. Connect the cell cables of the PGSTAT (WE and S to the oscillator, CE and RE to the counter and reference electrode, respectively).

2.2 – The EQCM crystals

Figure 3 shows a picture of the EQCM crystal.

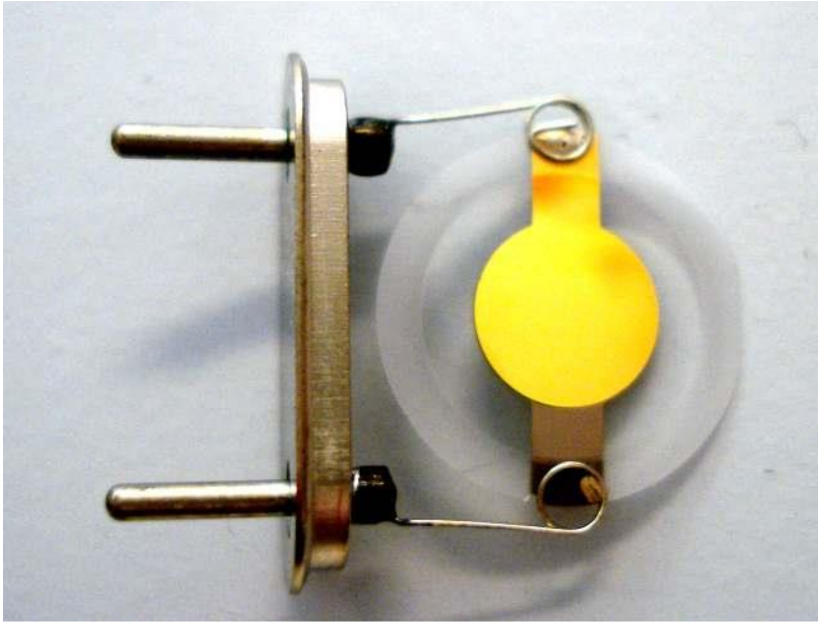

Figure 3 – Schematic view of the quartz crystals

The crystals are spring mounted and packed in a metallic casing. The two pins extending from the holder are used to provide contacts to the metallic layers located on both sides of the crystal. The crystals have a nominal frequency of 6 MHz. Typically, the metal layers have a thickness of 100 nm and an adhesion layer is used to attach the layer to the surface of the crystal. The adhesion layer has a typical thickness of 10 nm.

2.3 – The EQCM cell

A schematic representation of the EQCM cell is shown in Figure 4.

The main (1) and the upper body (2) of the cell, and the cover (3) are made of polypropylene[4] (PP), a chemical resistant material which is suitable for most of the electrochemical applications[5]. The detachable cover, which contains two holes, is designed to fix the Ag/AgCl reference electrode (6) and the Au

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[4] EQCM cells made of Kel-F (PCTFE) can be obtained on request (Item code: EQCM.CELL.PVDF).

[5] A chemical compatibility table for polypropylene is provided in Appendix 2 at the end of this document. Please check this table carefully before exposing the cell to a solvent for the first time.

counter electrode (7) during the measurement. Whenever needed, deaeration of the electrolyte is also possible by purging an inert gas through the electrolyte before measurements (using proper tubing and a third hole on the cover, not drilled).

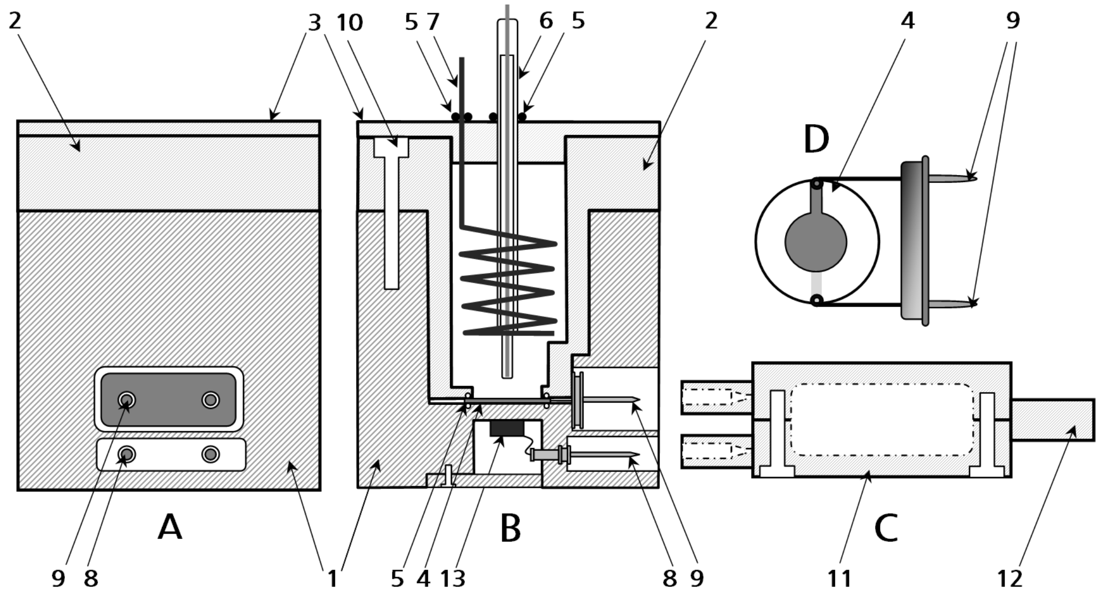

Figure 4 – Schematic representation of the EQCM cell: front view (A), section in the lateral view (B), connection socket to the oscillator (C) and quartz crystal, mounted, used in the measurements (D)

A full list of items is provided below:

1. Main body of the EQCM cell.
2. Upper body of the EQCM cell, removable.
3. EQCM cell cover (with holes for reference and counter electrode).
4. EQCM quartz crystal, mounted.
5. Viton O-rings.
6. Reference electrode (Ag/AgCl, 3 M KCl in gel).
7. Counter electrode (Au, spiral shaped).
8. Output pins from the temperature sensor.
9. Output pins from the mounted quartz crystal.
10. Fixing screws (set of three).
11. Connection socket, connecting to the EQCM oscillator.

12. Cable to the EQCM oscillator.
13. Temperature sensor.

The quartz crystal (4) is fixed between two O-rings[6] (5), between the upper (2) and the main body of the cell (1) by using 3 screws (only one shown in Figure 4 (10)). There is no need to over tighten the screws. In this way, a strong, liquid-tight assembly is obtained.

Note

It is possible to test the water tightness of the cell by adding a few ml of water into the cell and checking for leakage.

2.3.1 – Installing or changing the crystal

In order to install or change the quartz crystal, follow these steps carefully:

1. Remove the three fixing screws (10) on the top of the cell.
2. Remove the top of the cell.
3. Remove the old crystal (do not pull on too hard on the holder as it can easily break). The crystals can be used on both sides as they are totally identical (both sides of the crystal have a WE surface mounted).
4. Replace it with a new one.
5. Verify that the O-rings are positioned properly.
6. Retrace steps 2 and 1.

On average, a crystal can be reused about 20 times, supposing that no physical damage occurred.

[6] The O-rings are in Viton. Because of the possible swelling of the O-rings in organic solvents, there is a risk of applying extra pressure which can damage the crystal when working in these solvents. Please see Appendix 3, at the end of this document, for the chemical compatibility of Viton.

The life expectancy of the crystals depends on the following:

- The quality of the quartz.
- The amount of the deposited material and the stress generated due to it.
- The acoustic losses in the deposited material.
- The type of the deposited material.
- Formation of non-uniform films and flakes of the deposited material.
- Physical damage (scratches on the metal layer, cracks).
- Electrolysis of the deposited film material by using improper experimental parameters (i.e., applied potential).
- Accidental contact of the crystal with the counter electrode (CE) or the reference electrode (RE).

Note

The O-rings (5) on the reference and counter electrode must be used to prevent the electrodes from sliding down into the cell and eventually touching the crystal.

2.3.2 – Cleaning and handling the crystal

To reduce the measurement errors as much as possible, it is very important to keep the crystals very clean and free of any extraneous materials. The following guidelines can be used to extend the lifetime of the crystals:

- Do not touch the crystal with bare hands (use gloves and tweezers).
- Always store the crystals in their original package.
- Never touch the metallic layer of the crystal.
- Use always pure, deionized water or pure solvents for cleaning.

- Check the compatibility of the metal deposited on the crystal with the cleaning agent so that they will not react with each other.
- Do not wipe the crystal, always use a jet of clean gas to dry the crystal.
- If possible, use electrochemical cleaning to remove the deposited material.
- After the measurement, remove the crystal, rinse with clean water, dry it and store it in the original casing (not mounted in the cell).

Note

It is recommended to always dry the crystal using a clean and dry air (N_2, Ar) jet rather than leaving it to dry in air.

Warning

The EQCM crystals are spring-mounted. The metal clamps holding the crystal are very fragile and can be easily damaged when in contact with a corrosive environment. These clamps also serve as electrical contacts to the metal layers coated on the crystal. Proper care needs to be taken to prevent damage to these clamps since no valid measurements will be possible in case of damage.

When the cell is assembled, with the quartz crystal in its position, fill up the cell with clean water or electrolyte and inspect for any leakage around the contact pins. If leakage appears, disassemble the cell and start again. Do not over tighten the screws.

Note

The maximum volume of the cell is 3 ml.

3 – Software setup

If the cell has been assembled successfully, with the crystal properly installed and connected to the external oscillator, the next step is to set up the NOVA software[7]. The following step by step description will help to make the necessary settings in NOVA, before measurements can be performed.

3.1 – Installation of the EQCM module

Turn on the PGSTAT, run NOVA and select the EQCM module in the NOVA Hardware setup (see Figure 5).

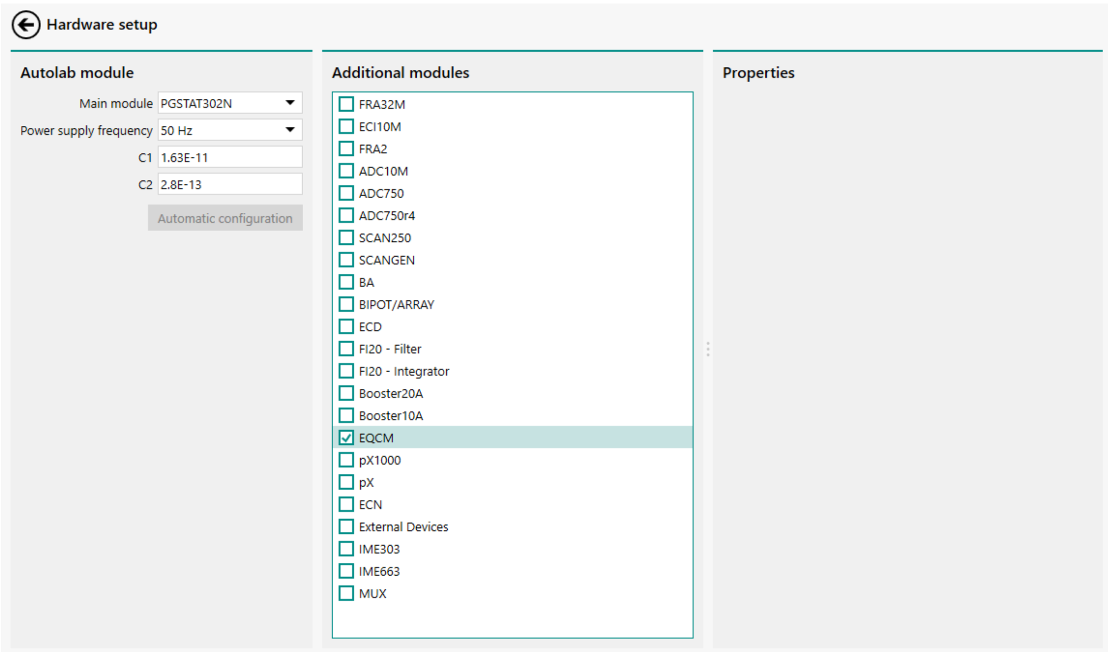

Figure 5 – Selecting the EQCM module in NOVA

3.2 – Quick test of the EQCM module

Nova provides a ready-to-use test procedure that can be used at any time to verify that the EQCM is working properly. This procedure is installed in the NOVA folder created in the Program Files folder during installation of the

[7] The general details about the NOVA software can be found in the NOVA User Manual.

software. From the Action section in the Nova main screen, select the Import procedure option (see Figure 6).

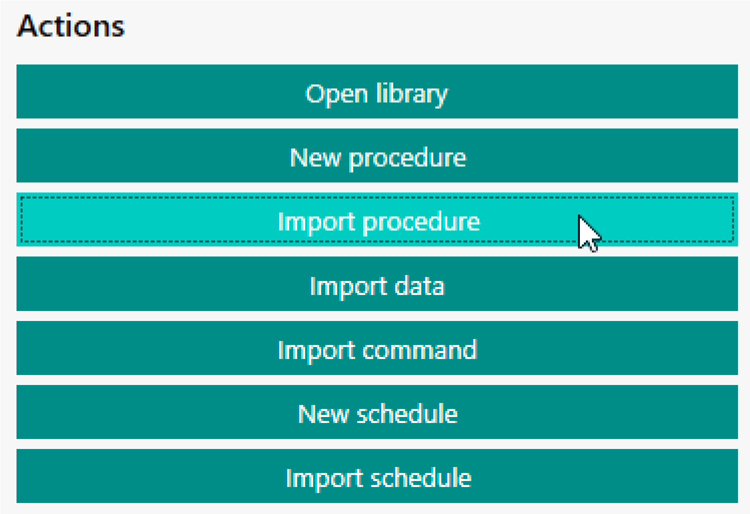

Figure 6 – Use the Import procedure option from the File menu to load the EQCM test procedure

The TestEQCM procedure can be found in C:\Program Files\Metrohm Autolab\Nova 2.1\Shared DataBases\Module test (see Figure 7).

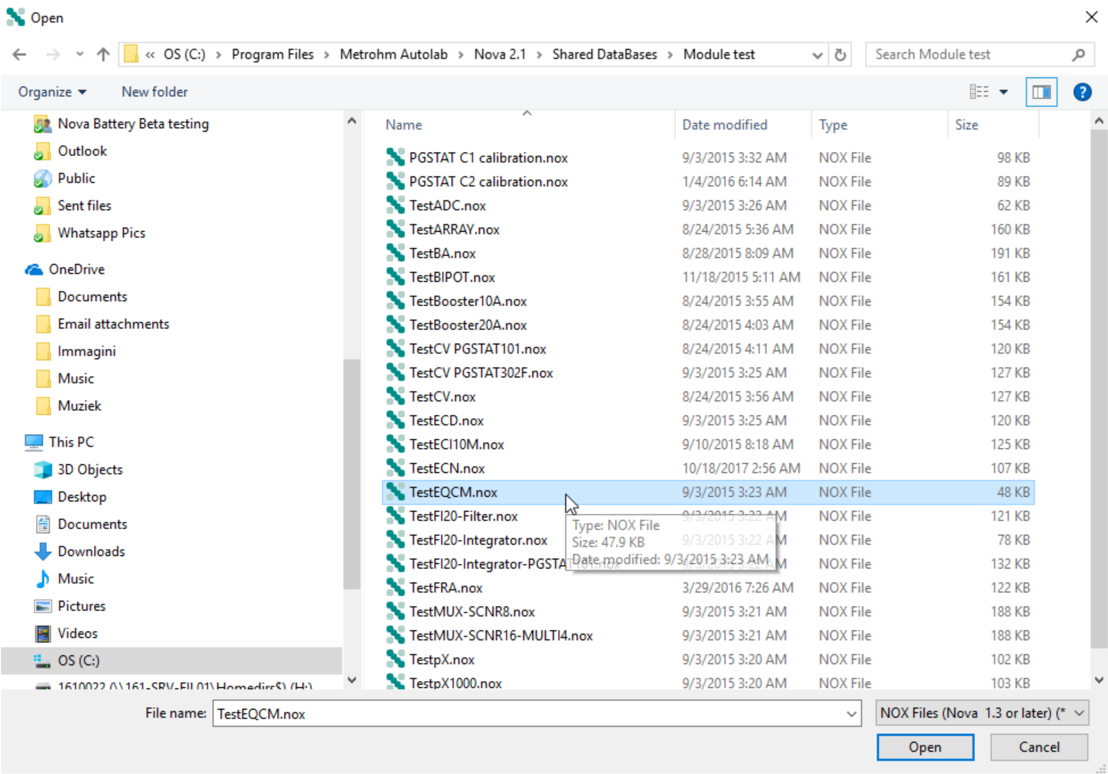

Figure 7 – The TestEQCM procedure can be found in the C:\Program Files\Metrohm Autolab\Nova 2.1\Shared DataBases\Module test folder

The TestEQCM procedure can be used to test the correct functionality of the filter circuit of the EQCM.

Insert a 6 MHz EQCM crystal in the EQCM cell as explained in section 2.3.1. Fill the cell with ca. 2 ml of water and check for leakage. Do not install the lid. Connect the cell to the EQCM oscillator and the oscillator to the Autolab PGSTAT using the provided cable. Leave the cell connectors from the PGSTAT disconnected.

Press the start button to start the measurement. Two messages will be displayed when the measurement starts (see Figure 8).

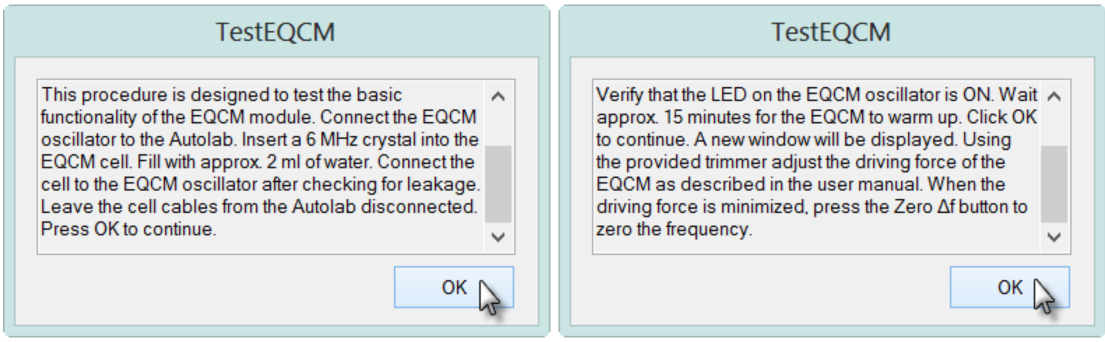

Figure 8 – Two messages are displayed at the beginning of the measurement

When the second message appears, verify that the LED on the EQCM oscillator box is **ON** (red or green). The LED is located on the front panel of the oscillator, next to the trimmer (see Figure 9).

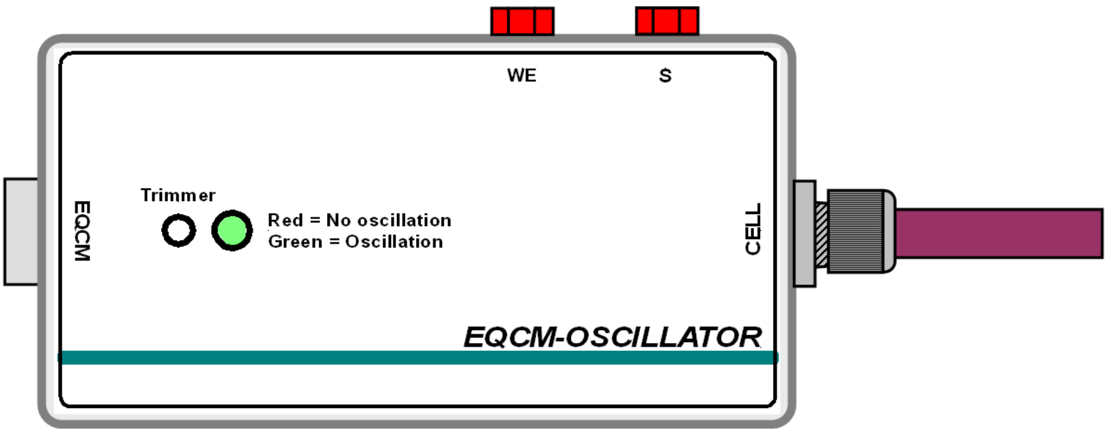

Figure 9 – The EQCM status LED is located next to the Trimmer

Note

Wait 15 minutes for the EQCM to warm up.

Click OK to continue. The *Determine EQCM zero frequency* window will appear (see Figure 10).

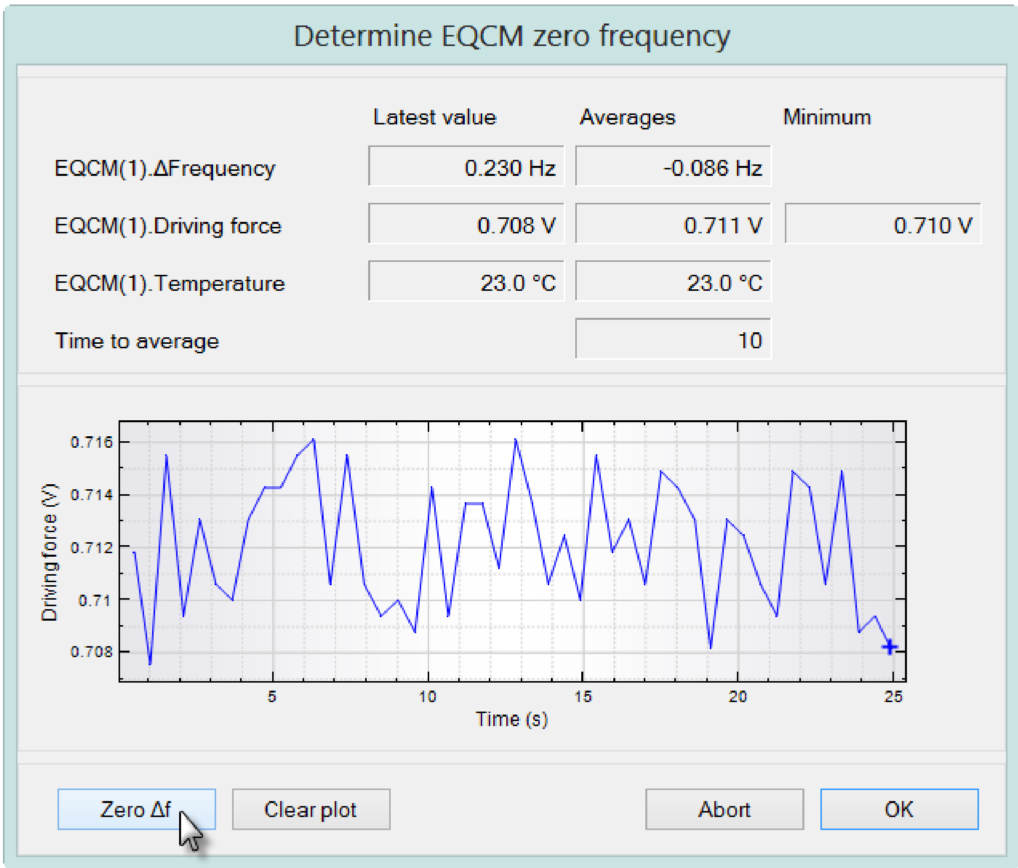

Figure 10 – The determine EQCM zero frequency window can be used to adjust the driving force

Using the provided adjustment tool, rotate the trimmer on the EQCM oscillator in order to minimize the driving force. The trimmer range does is not limited, it can be turned 360° in either direction. It recommended to slowly rotate the trimmer one full turn and then adjust the driving force in order to match the lowest recorded value displayed in the Minimum value field in the *Determine EQCM zero frequency* window.

When the driving force has been properly minimized, the LED on the EQCM oscillator must be green. Click the Zero Δf button in the *Determine EQCM zero frequency* window to zero the value of the EQCM(1).ΔFrequency signal.

After minimizing the ΔFrequency signal click the OK button to proceed with the measurement. The procedure records the three signals provided by the EQCM module during ten seconds. The EQCM(1).ΔFrequency (Hz) is shown on plot #1; the EQCM(1).Driving force (V) signal is shown on plot #2 and the EQCM(1). The EQCM(1).Temperature (°C) signal is shown on plot #3 (see Figure 11).

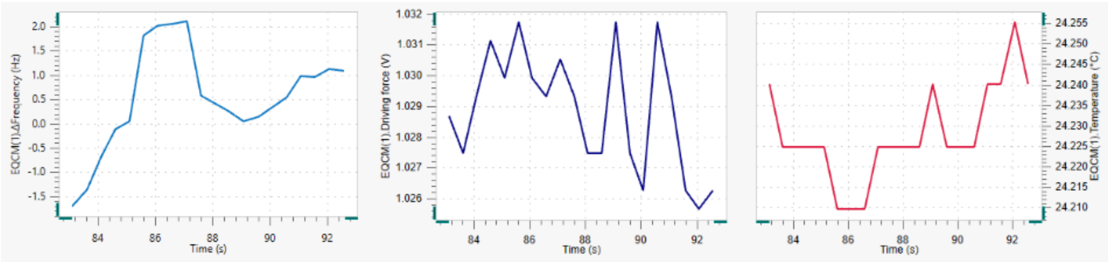

Figure 11 – The data recorded during the TestEQCM procedure

At the end of the measurement, a message is displayed, depending if the test was successful or not (see Figure 12 and Figure 13).

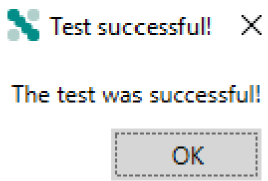

Figure 12 – The message in the case of a successful test

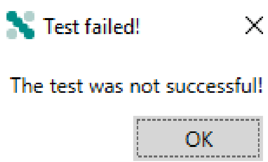

Figure 13 – The message in the case of an unsuccessful test

3.3 – Performing an EQCM measurement

In the following subsections, the connections between the EQCM cell, ECQM oscillator and the PGSTAT will be shown. Furthermore, it will be explained how to build up a procedure to perform an EQCM measurement.

Note

For more information on the use of the NOVA software, please consult the NOVA User Manual.

3.3.1 – Connections for electrochemical measurements

To perform electrochemical measurements, the crystal needs to be installed in the cell as explained in Section 2.3.1. The cell must then be filled with the solution and the lid, carrying the counter electrode must be fitted onto the cell.

Note

Remember that the maximum volume is 3 ml.

Warning

Be careful when installing the lid onto the cell that the electrodes (reference and counter) do not touch the surface of the crystal to prevent accidental damage.

If there is no leakage in the EQCM cell, connect the cell to the oscillator using the connection socket (11). Insert the reference electrode and connect it to the PGSTAT. Also connect the counter electrode to the CE plug of the PGSTAT using a crocodile clamp. Connect the WE and the S from the PGSTAT to their respective connectors on the EQCM oscillator (see Figure 14).

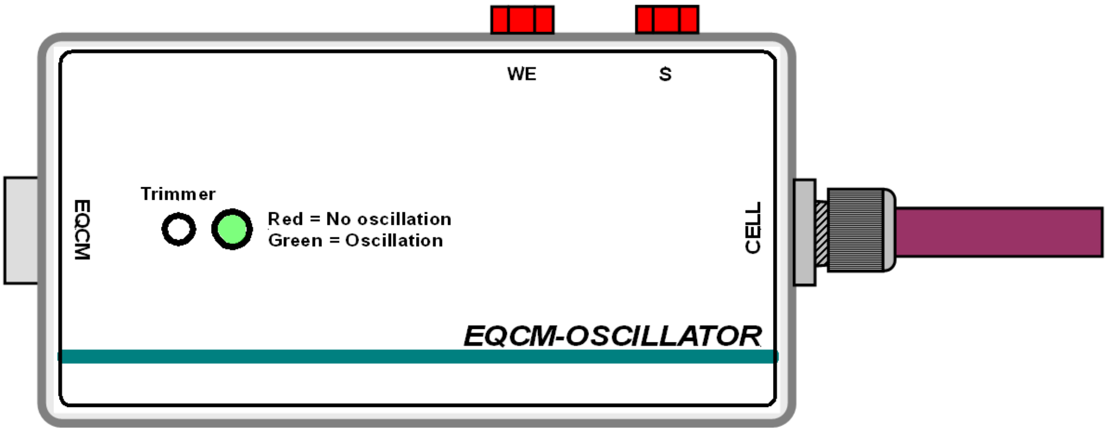

Figure 14 – The EQCM oscillator showing the WE and S connections on the side

Note

WE and S have different connections on the oscillator box.

3.3.2 – Signal sampler

Whenever a measurement involving the EQCM module is performed, the Signal sampler of the procedure must be modified in order to indicate which signals provided by the EQCM module have to be sampled alongside the usual electrochemical signals.

The EQCM module provides three different signals in the Signal sampler:

- **EQCM(1).Temperature:** the temperature signal is measured by the sensor located at the bottom of the EQCM cell. This signal is provided in °C.
- **EQCM(1).Driving force:** 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 should be 0.9 ± 0.25 V.

- **EQCM(1).ΔFrequency:** the ΔFrequency 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).

These three signals can be selected using the Signal sampler in the measurement command (CV or Record Signal). To edit the sampler, click the More button in the Properties section of the procedure or of the measurement command (see Figure 15).

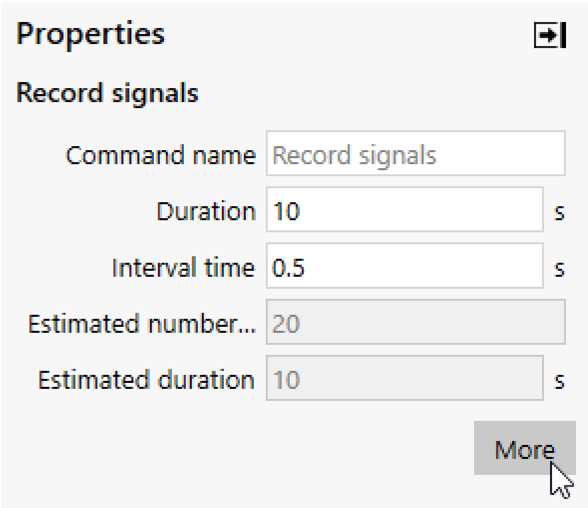

Figure 15 – Click the More button to open the signal sampler editor

In order to open the Edit Sampler window, click on Sampler on the list of Figure 16.

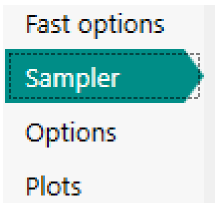

Figure 16 – Select Sampler

The Edit Sampler window will be displayed, indicating a list of signals available for the connected instrument. The three signals provided by the EQCM module can be found in this list (see Figure 17).

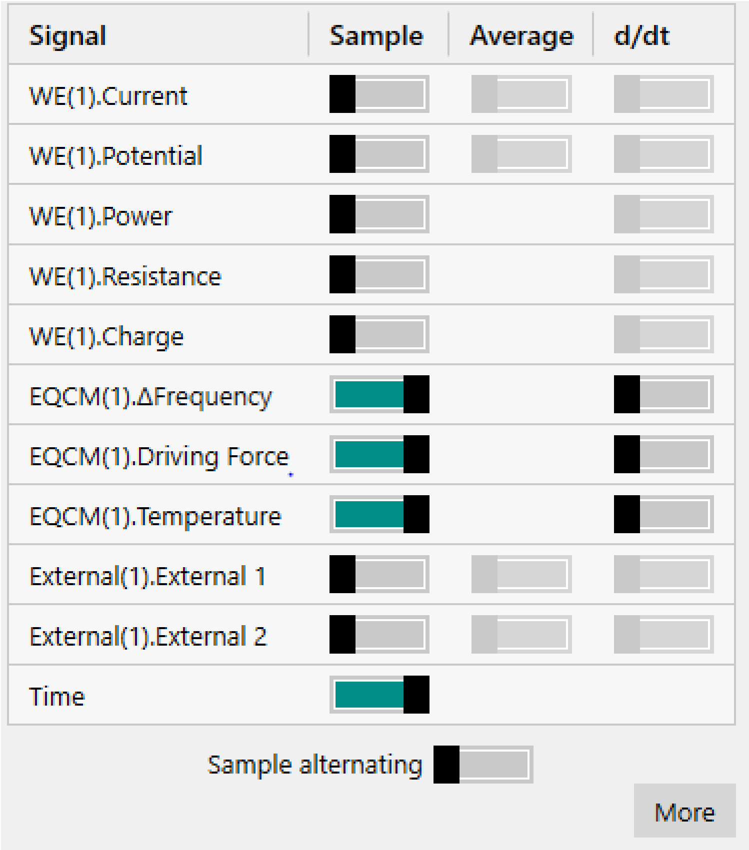

Figure 17 – The Edit Sampler window

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 'Average' 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.

It is possible to apply the sampler to a selection of measurement commands with the 'Apply global sampler to' (see Figure 18).

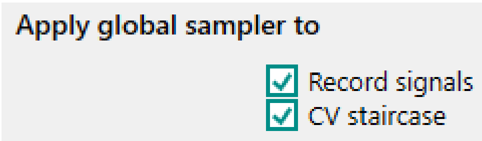

Figure 18 – The 'Apply global sampler to' section can be used to apply the modified sampler to one or more measurement commands in the procedure

Clicking the OK button validates the selected signals.

Note

Each measurement command has a local sampler that indicates which signals need to be acquired when that command is running during the measurement. It is therefore possible to adjust the signal samplers for each measurement command in order to customize the data acquisition. Please refer to the User Manual of NOVA for more information on the local and global signal samplers.

3.3.3 – Switching the EQCM on

Once the sampler is defined, the next step is to switch the EQCM module on. The default power up settings of the module keeps the module powered off until activated by the user.

Switching the EQCM on or off can be done at any time during a procedure using the *Autolab control* command[8]. The Autolab control command is a general purpose command that can be used to control all the instrumental settings of Autolab, including the settings of the modules installed in the Autolab.

Note

The *Autolab control* command can be found in the Measurement – general group of commands.

To switch the EQCM on at the beginning of the procedure, click the More button located on the Properties section of the *Autolab control* command (see Figure 19).

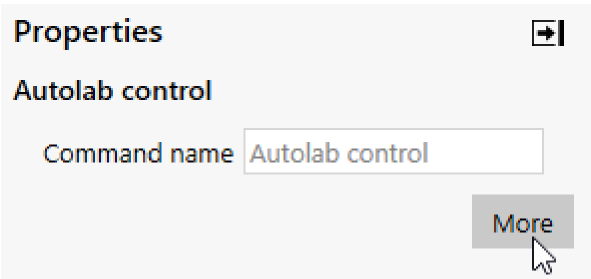

Figure 19 – Click the More button to open the Autolab control editor

The Autolab control window will be displayed. The on/off switch of the EQCM module can be found on the EQCM section (see Figure 20).

[8] More information on the Autolab control command can be found in the Autolab control tutorial, available from the Help menu.

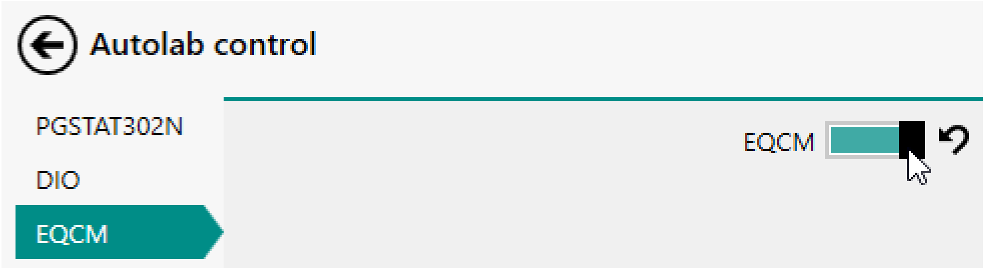

Figure 20 – The on/off switch of the EQCM module can be found on the EQCM section

Note

Once the EQCM module is switched on, it will remain powered on until the Autolab control command is used again to switch off the module. When the module is switched on, the LED located on the front panel of the external oscillator will be lit (green or red) when connected to the EQCM module.

Note

It is recommended to allow the EQCM to warm up for about 15 to 30 minutes before starting measurements. The EQCM can be left switched ON even when the measurements requiring the EQCM signals are finished, this will not interfere with experiments.

3.3.4 – Plotting the EQCM data

Since the signals recorded during the procedure can also be plotted in real time, additional plot can be added to the procedure. To add a plot to a procedure, the More button on the Properties section of the measurement command can be used. In the Plots section, the ΔFrequency vs. E plot can be added.

For example, click the *CV staircase* command, and then the More button on the Properties section. In the Plots section, toggle the ΔFrequency vs. E. A plot number can also be assigned (see Figure 21).

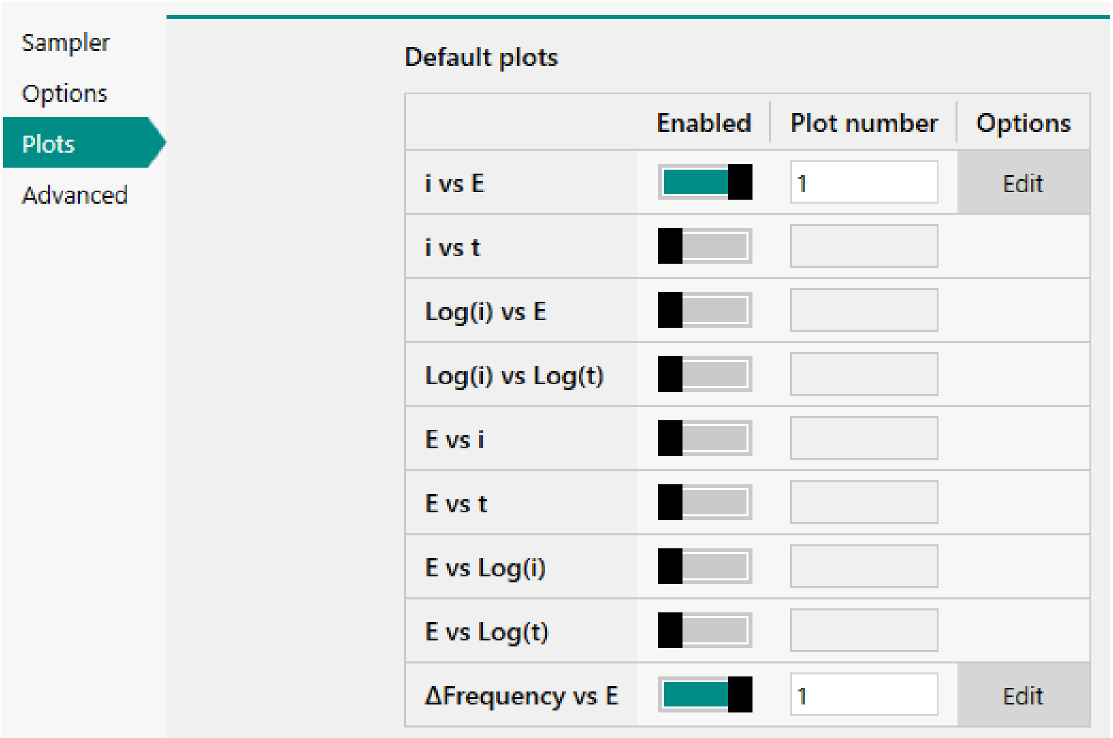

Figure 21 – Adding the ΔFrequency vs. E plot to the *CV staircase* command

3.3.5 – Adjusting the driving force and zeroing the EQCM ΔFrequency

The final item that should be included in an EQCM procedure, as illustrated in the *Cyclic voltammetry with EQCM* procedure, is the setting the ΔFrequency value measured by the EQCM module to zero Hz.

Additionally, whenever a measurement is performed using the EQCM, it is necessary to set the EQCM driving force to the minimum value. This **must** be done any time the environment to which the crystal is exposed is changed. The driving force needs to be minimized in order to maximize the measurable range of the EQCM and optimize the quality of the signal. This is an important adjustment that needs to be carried before zeroing the ΔFrequency.

> **Note**
>
> It is not necessary to set the driving force to the absolute minimum value. Any value close the minimum will be acceptable (qualitative adjustment)

Both adjustments can be done at any time in a procedure, using the *Reset EQCM ΔFrequency* command.

> **Note**
>
> The *Reset EQCM ΔFrequency* command can be found in the Measurement – general group of commands (see Figure 22).

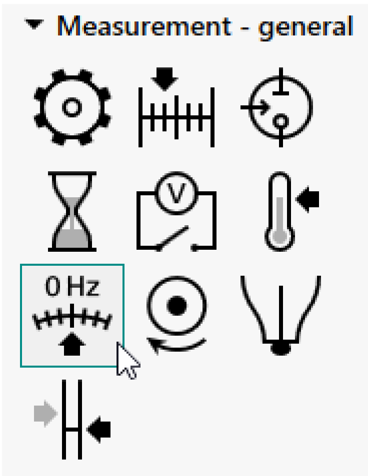

Figure 22 – The Reset EQCM ΔFrequency command

The usual strategy used in electrogravimetric experiments using the EQCM consists of zeroing the value of the ΔFrequency while the working electrode, located on the surface of the crystal, is kept in an electrochemical control condition. For metal deposition, or electropolymerization experiments, for example, this is typically done by keeping the working electrode at a potential with respect to the reference electrode at which no deposition occurs. The ΔFrequency value can then be zeroed in this condition and when the potential is changed with respect to this control situation, any change in ΔFrequency will be measured relative to this arbitrary zero Hz point.

Note

It is possible to zero the ΔFrequency and adjust the driving force as many times as required by adding the *Reset EQCM ΔFrequency* command to the procedure, in the required locations.

Whenever the software encounters the *Reset EQCM ΔFrequency* in the procedure, the Determine EQCM zero frequency window will be displayed (see Figure 23).

Both the driving force and the ΔFrequency value can be adjusted through the Determine EQCM zero frequency.

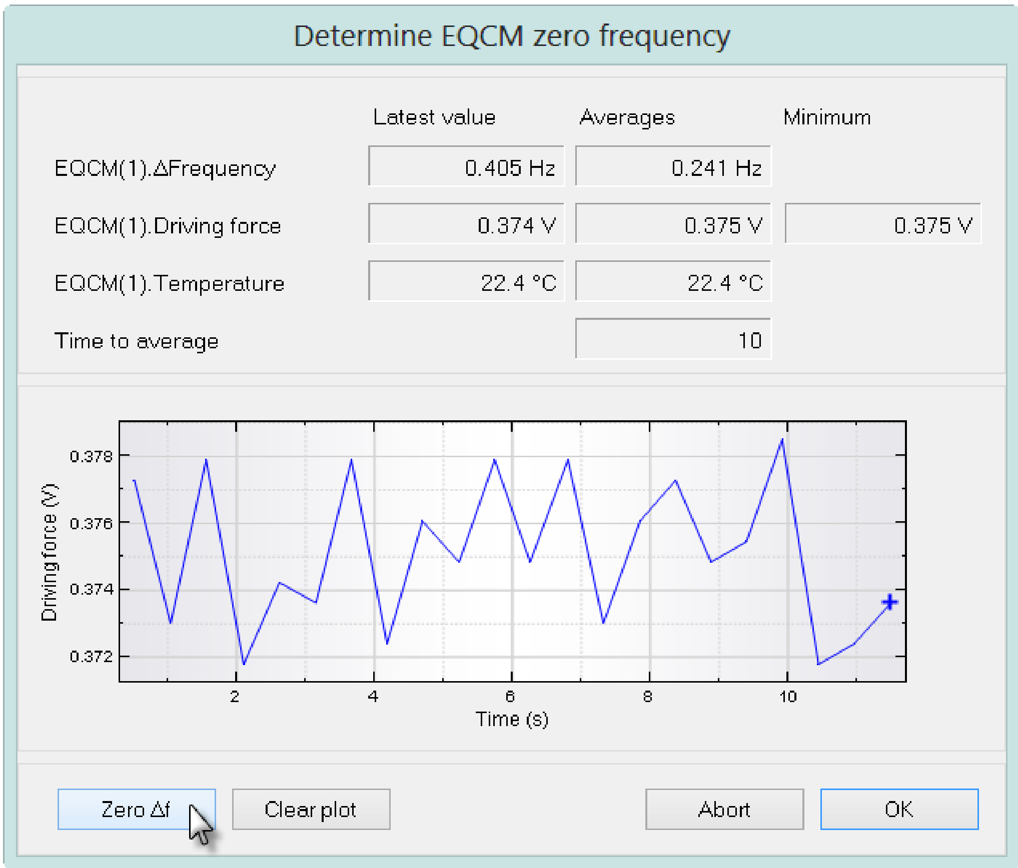

Figure 23 – The Determine EQCM zero frequency window appears each time the software encounters the *Reset EQCM ΔFrequency* command in the procedure

The *Determine EQCM zero frequency* window contains three sections:

The <u>topmost</u> section, shown in Figure 24, displays real time information on the measured signals provided by the EQCM:

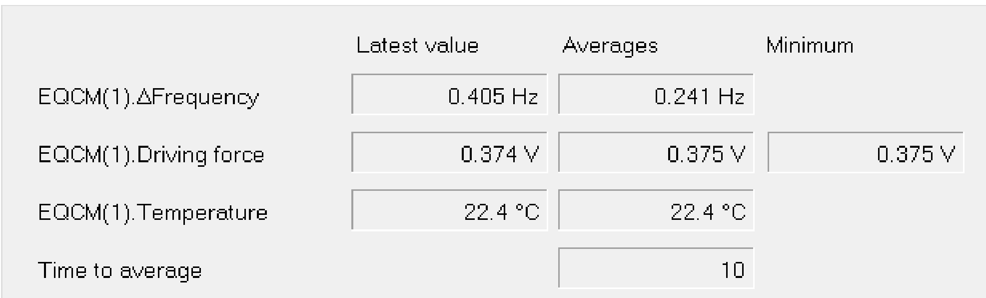

Figure 24 – The topmost section of the *Determine EQCM zero frequency* window displays the measured values in real time

- **EQCM(1).ΔFrequency (Latest value, Averages):** these fields show the latest and averaged ΔFrequency 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 25, displays the recorded values of the driving force plotted versus time.

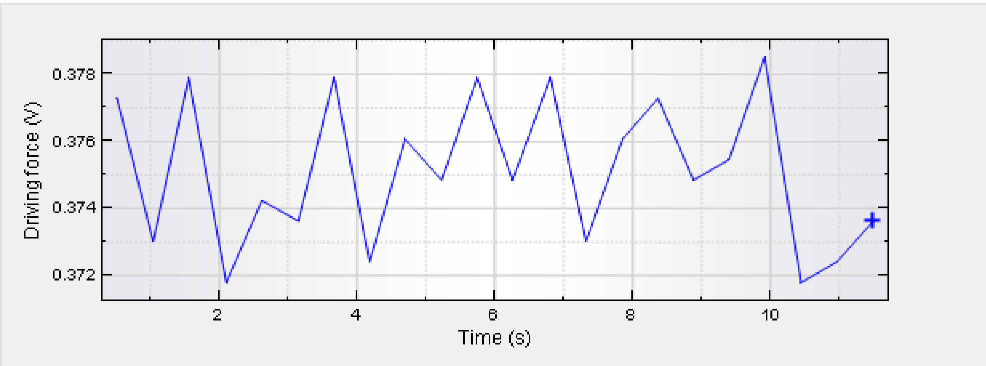

Figure 25 – The middle section of the *Determine EQCM zero frequency* window displays the measured driving force plotted versus time

The *bottom* section, shown in Figure 26, displays a series of buttons that can be used to control the behavior of the Determine EQCM zero frequency:

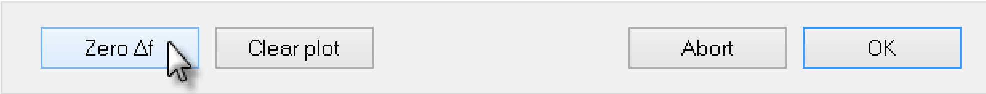

Figure 26 – The bottom section of the *Determine EQCM zero frequency* window displays the measured values in real time

- **Zero Δf:** set the value of the measured ΔFrequency to zero. Setting the value to zero requires five iterations. During this adjustment, the Zero Δf 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.

3.3.5.1 – Adjusting the driving force

The driving force is adjusted using the provided tool. Insert the tool vertically into the hole labelled Trimmer on the EQCM external oscillator and make sure that the tool fits into the trimmer located on the PCB enclosed in the EQCM oscillator.

Do not apply to much pressure. The trimmer should rotate without significant torque. If you find it difficult to rotate the trimmer, remove the tool and insert it again, paying careful attention to the position of the tool with respect to the trimmer.

Warning

To avoid damaging the trimmer, use only the provided tool for the adjustment.

Once the tool is properly inserted in the oscillator, rotate the trimmer slowly, while monitoring the driving force shown graphically and numerically in the Determine EQCM zero frequency window. At the same time, the LED located on the front panel of the oscillator will indicate the oscillation status:

- Green: stable oscillation is detected and the measurements can be performed.
- Red: unstable or unsustainable oscillation is detected. Measurements are not possible and the EQCM signals are invalid.

The trimmer range is not limited, it can be turned 360° in either direction (see Figure 27).

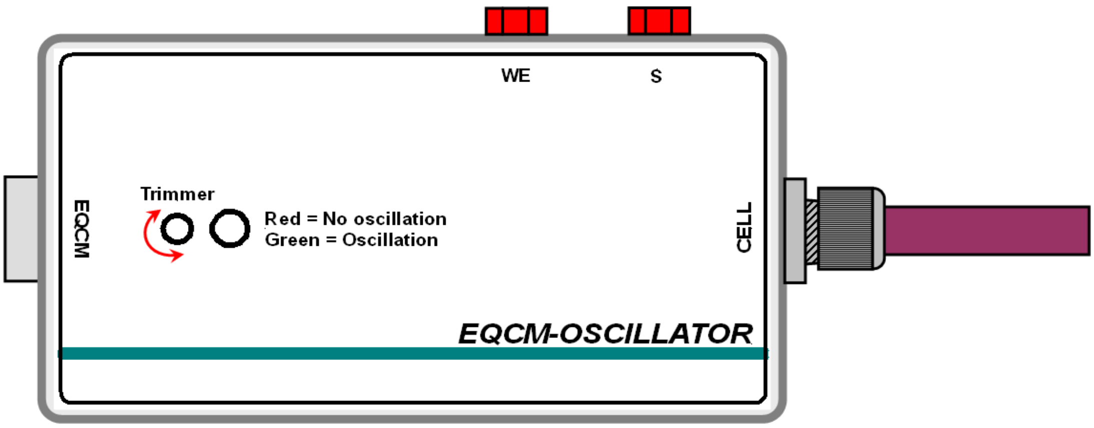

Figure 27 – The EQCM trimmer can be rotated in any direction 360°

It recommended to slowly rotate the trimmer one full turn and then adjust the driving force in order to match the lowest recorded value displayed in the Minimum value field in the *Determine EQCM zero frequency* window.

Note

It is possible to press the Clear plot button to clear the graphical display of the driving force.

3.3.5.2 – Adjusting the zero ΔFrequency

When the driving force has been properly minimized, the LED on the EQCM oscillator must be green. Click the Zero Δf button in the Determine EQCM zero frequency window to zero the value of the EQCM(1).ΔFrequency signal. While the ΔFrequency is zeroed, the Zero Δf button will be grayed out.

After minimizing the driving force and zeroing the ΔFrequency signal, if necessary, click the OK button to proceed with the measurement. The procedure records the EQCM signals during the cyclic voltammetry measurement.

3.3.6 – Example of Cyclic voltammetry with EQCM procedure

Figure 28 shows an example of a cyclic voltammogram recorded using the EQCM module[9]. This example corresponds to the bulk deposition (overpotential deposition) of lead on a gold-coated QCM crystal, in a 0.01 M Pb (II) perchlorate solution ($HClO_4$ 0.1 M) during a potential scan between -0.6 V and 1 V at a scan rate of 0.020 V/s. All frequency changes are measured with respect to the zero ΔFrequency which was set using *the Reset EQCM ΔFrequency* command while the working electrode at was kept at 0.8 V vs. Ag/AgCl (KCl 3 M) reference.

[9] The file corresponding to this measurement is included in the Demo database (Demo 02). Please refer to the NOVA User Manual for more information.

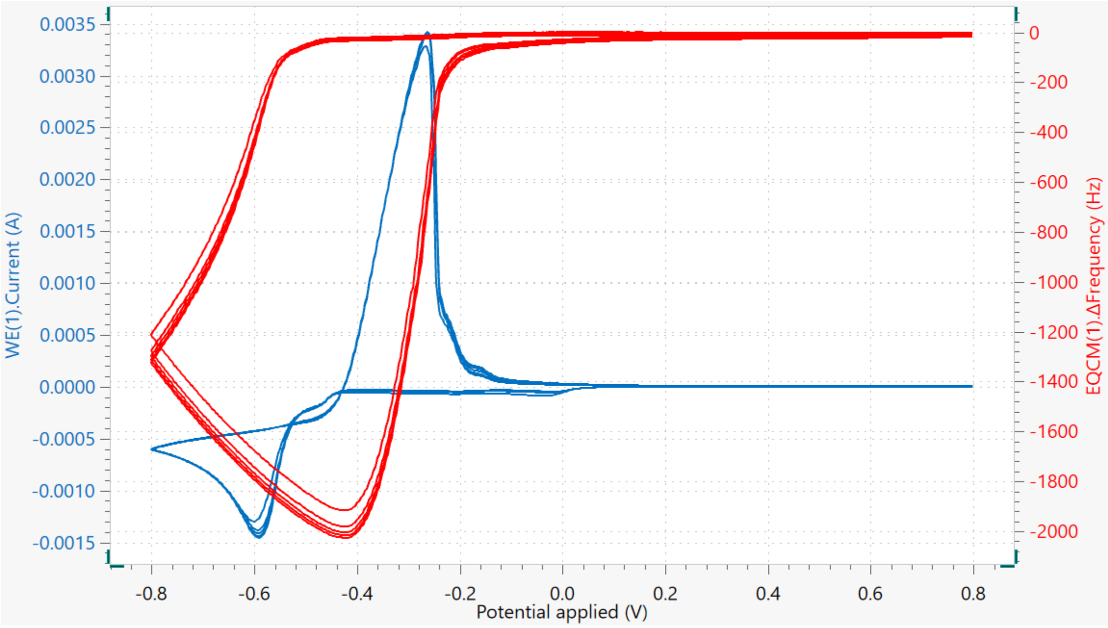

Figure 28 – An example of cyclic voltammetry (blue, left axis) recorded simultaneously with the EQCM signal (red, right axis) using the Cyclic voltammetry with EQCM procedure (0.01M lead (II) perchlorate in 0.1 M perchloric acid)

As the potential is scanned in the negative direction, the bulk deposition of lead onto gold is triggered at around -0.43 V. This is followed by a sharp increase of cathodic current at around -0.5 V, which is detected by a sharp decrease in EQCM ΔFrequency. The frequency continues to decrease after the lower vertex potential is reached until the current passes through 0 and become positive again. This triggers an increase of the frequency and the ΔFrequency value finally returns to roughly 0 Hz at the positive end of the scan as the lead adlayer is removed from the surface.

4 – Practical tips

The following section provides additional tips to consider when using the EQCM.

4.1 – Optimization of the signal to noise ratio

For the best signal to noise ratio, during the measurement, the EQCM cell should be placed in a grounded Faraday cage. The EQCM oscillator and cell will fit in the standard Autolab Faraday cage.

4.2 – Warming up of the EQCM oscillator

It is recommended to allow the EQCM oscillator to warm up before starting electrochemical measurement. Running a simple procedure like the one shown in Figure 29 can be used to switch on the oscillator and warm it up.

Figure 29 – A simple EQCM warm up procedure

Note

This procedure only used the Autolab control command to switch on the EQCM. No other commands are used and no measurement is performed.

4.3 – Caring for the reference electrode

The reference electrode included in the EQCM kit cannot be refilled and has a limited lifetime. The reference electrode, Figure 30, is based on a gel electrolyte (3 M KCl) that minimizes leakage. The electrode is shipped with a sealing cap, not shown in Figure.

Figure 30 – The reference electrode shipped with the EQCM kit

The cap contains excess electrolyte gel that ensures that the electrode will not dry out (estimated shelf life: 6 months). However, once the cap is removed for first use, the cap **must** be discarded and the electrode must be stored in a saturated aqueous solution of KCl (or 3 M KCl) to prevent the electrode from drying out.

Do not refit the cap onto the EQCM as this will trap an air bubble inside the cap that will significantly decrease the lifetime of the electrode.

4.4 – Prevent damage to the crystal surface and holding springs

When the measurements are finished, it is recommended to disassemble the cell completely, to clean the crystal surface and mounting spring and then dry the crystal surface and holding springs to prevent damage to the surface and extending the lifetime of the crystals. When the crystals are not used, it is best to keep them in the metallic enclosure they are shipped with.

Prevent accidental contact of the reference or the counter electrode with the surface of the crystal during the measurement or when handling the cables and connectors.

Remember that the crystals are double sided, both sides can be used.

5 – Measurement restrictions

Two restrictions apply when working with the Autolab EQCM module:

- The sampling rate of the EQCM is 50 samples/s.
- The measurable range is fixed to a mobile frequency window of 1000 Hz.

Both restrictions are illustrated in the following sections.

5.1 – Sampling rate

The EQCM module is capable of providing one new set of values for the measured signals (ΔFrequency, Driving force, Temperature) with an interval time of 20 ms (50 samples/s). When the sampling rate specified in the procedure is smaller than 20 ms, the EQCM module is not able to provide new data points quickly enough. In practice this means that last available data point provided by the EQCM module will be measured several times, until a new data point is available.

Figure 31 shows a practical example of a measurement in which the interval time defined in the procedure was set to a value smaller than 20 ms (the interval time is 1 ms).

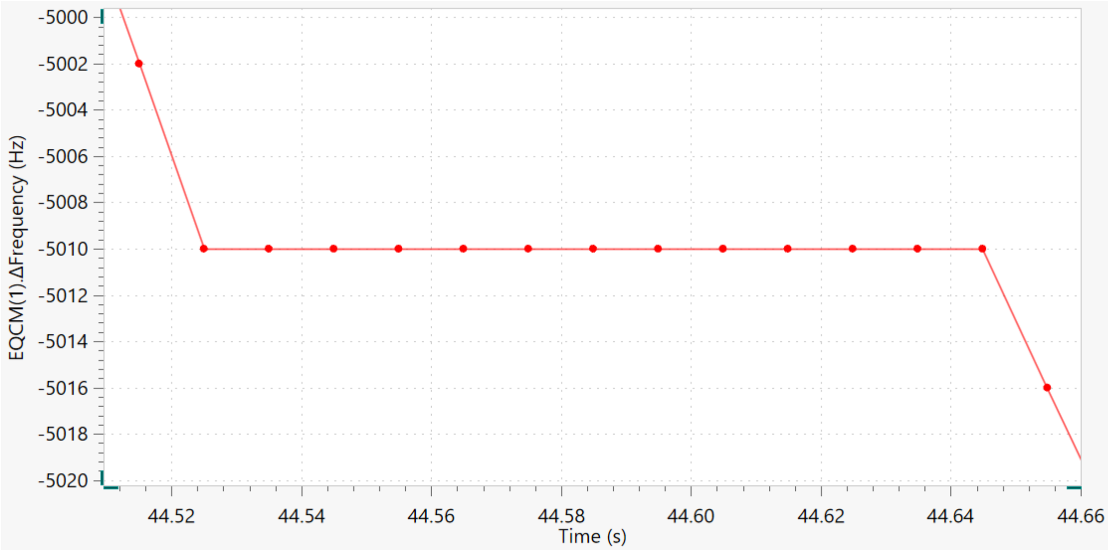

Figure 31 – An example showing multiple duplicates of the EQCM signals

Since the interval time is significantly smaller than the rate with which the EQCM can provide a new valid data point, the same data point can be displayed several consecutive times.

5.2 – Dynamic measurement window

The EQCM module uses a dynamic window of frequency of 1000 Hz. Rather than measuring the variation of frequency in the whole measurable range of 80000 Hz, the EQCM focuses on a sub-range, or window, of 1000 Hz. This ensures that the frequency is measured with the highest possible resolution. In practice, this means that no interruptions are observed as long as the variation of frequency is smaller than 1000 Hz during the course of the experiment.

However, when changes in frequency larger than 1000 Hz are measured, the software needs to readjust the measurement window downwards or upwards depending on the direction of the frequency change. This software rewindowing is triggered when measured ΔFrequency reaches the upper limit of the window (at 900 Hz) or the lower limit of the window (at 100 Hz). This ensures a 10% overlap between two consecutive ΔFrequency windows.

The duration of the window adjustment is 100 ms. During this adjustment, the EQCM is not able to supply new data points and this can be seen in the measured data, as shown in Figure 32.

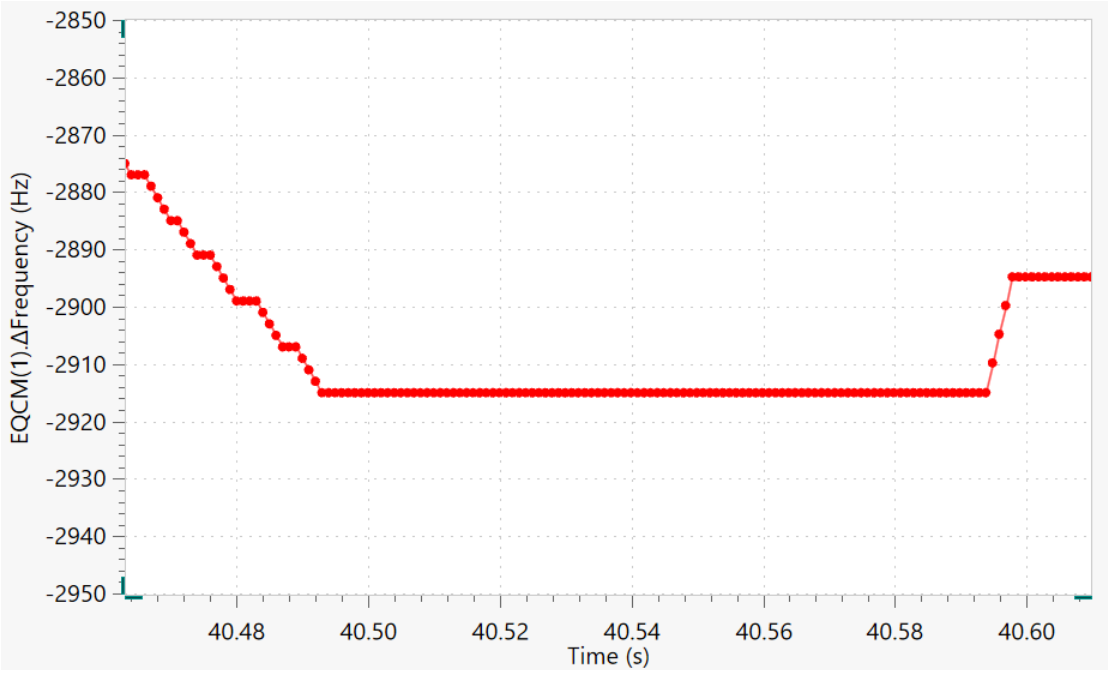

Figure 32 – When the EQCM needs to adjust the window, the data feed is interrupted during 100 ms

The windowing scheme is illustrated in Figure 33.

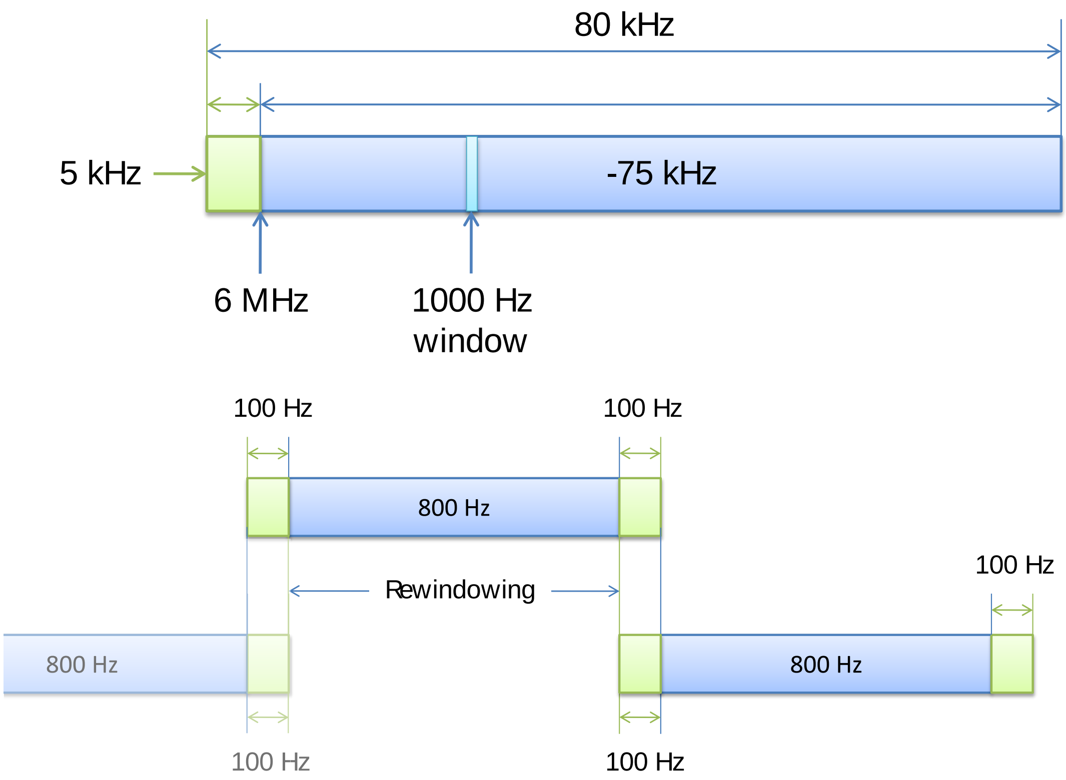

Figure 33 – Windowing scheme used in the EQCM (top: complete measurement range and measurement window; bottom: rewindowing adjustment)

The top graphic of Figure 33, shows the whole measurable range of the EQCM, relative to the nominal frequency of 6 MHz. The module can measure positive variation up to 5000 Hz and negative variations down to -75000 Hz. The actual measured range is 1000 Hz, represented by the small slice located in the 80000 Hz.

The bottom part of Figure 33 shows the details of the windowing adjustment. The measurable range is 1000 Hz. Whenever the variation of frequency reaches the first or last 100 Hz segment of the window, in absolute value, the EQCM detects that a readjustment of the window is required. The window is shifted upwards or downwards, depending on the variation of frequency, with an overlap of 100 Hz.

6 – Theoretical aspects

The Electrochemical Quartz Crystal Microbalance (EQCM) is widely used to monitor, simultaneously with the electrochemical signal, the change in frequency which is directly related to the mass changes due to deposition or adsorption of a species to or dissolution of a species from the working electrode.

The principle of operation of the EQCM relies on the piezoelectric properties of the quartz which will oscillate at a given frequency when a sinusoidal external electric field is applied to it. The oscillation frequency of the crystal depends on a number of parameters such as size, the thickness of the crystal, temperature and the oscillating media.

The crystals used for the system described are the so-called AT-cut[10] crystals (with a small temperature coefficient) with a base-frequency of $6\ MHz$. The crystals are covered with different metals (e.g., Au, Pt) on top of an adhesion layer (e.g., Ti or Cr oxides). The crystals will also act as working electrodes (WE) being in contact with the electrolyte solution, broadening in this way the application areas of this technique.

6.1 – The Sauerbrey equation

As mentioned above, the change on the frequency of the oscillation Δf is sensitive to the change in mass deposited on the crystal surface Δm, meaning that any variation in mass of the electrode or thickness of the deposited material will proportionally change the frequency at which the crystal oscillates. The relationship between Δf and Δm is given by the Sauerbrey[11] equation (1):

[10] The term AT describes the specific angle at which the quartz is cut.

[11] G. Sauerbrey, *Z. Phys.* **155**, 1959, 206.

$$\Delta f = -C_f \cdot \Delta m \tag{1}$$

Where $\Delta f\ (Hz)$ is the change in frequency, C_f $(0.0815\ Hz \cdot ng^{-1} \cdot cm^2$ for a crystal with the base frequency of $6\ MHz$, at 20 °C) is the sensitivity factor of the crystal and $\Delta m\ (g \cdot cm^{-2})$ is the change in mass per unit area.

C_f is provided by equation (2):

$$C_f = \frac{2n \cdot f^2}{\sqrt{\rho_q \cdot \mu_q}} \tag{2}$$

Where n is the number of the harmonic at which the crystal is driven (this factor is set to 1, by design), $f\ (Hz)$ is the resonant frequency of the fundamental mode of the loaded crystal, ρ_q $(2.648\ g \cdot cm^{-3})$ is the density of quartz and μ_q $(2.947 \cdot 10^{11}\ g \cdot cm^{-1} \cdot s^{-2})$ is the shear modulus of quartz.

From the equations (1) and (2), the change in mass can be calculated as following:

$$\Delta m = -\frac{\Delta f}{C_f} = \frac{(f_q - f) \cdot \sqrt{\rho_q \cdot \mu_q}}{2n \cdot f^2} \tag{3}$$

Note

It is possible to use the data handling commands in Nova to automatically calculate the values of interest by using the calculate signal tool and inserting the equations either directly in the procedure or in the data analysis window. For more details, please see the NOVA User Manual.

It is very important to keep in mind that the Sauerbrey equation is strictly applicable to uniform thin films, in vacuum as it assumes that the acoustoelastic properties of the deposited films are the same as of quartz.

6.2 – Z-match equation

In order to overcome the limitations of the Sauerbrey equations with its assumptions, the Z-match equation (4) was developed by Lu and Lewis where a new term is introduced, which takes into account the ratio of the acoustic impedance of quartz and the acoustic impedance of the deposited material[12].

$$\Delta m = \left(\frac{N_q \cdot \rho_q}{\pi \cdot R_Z \cdot f}\right) \tan^{-1}\left[R_Z \tan\left[\pi \cdot \left(\frac{f_q - f}{f}\right)\right]\right] \tag{4}$$

$$N_q = \frac{\sqrt{\rho_q \cdot \mu_q}}{2\rho_q} \tag{5}$$

$$R_Z = \sqrt{\frac{\rho_q \cdot \mu_q}{\rho_f \cdot \mu_f}} \tag{6}$$

where Δm $(g \cdot cm^{-2})$ is the change in mass per unit area , N_q $(1.668 \cdot 10^5\ Hz \cdot cm)$ is the frequency constant of the AT cut quartz crystal , ρ_q $(2.648\ g \cdot cm^{-3})$ is the density of quartz, R_Z is the Z-factor of the film material (acoustic impedance ratio), f (Hz) is the resonant frequency of the loaded crystal, f_q (Hz) is the resonant frequency of the unloaded crystal, μ_q $(2.947 \cdot 10^{11}\ g \cdot cm^{-1} \cdot s^{-1})$ is the shear modulus of quartz, ρ_f $(g \cdot cm^{-3})$ is the density of the material, and μ_f $(g \cdot cm^{-1} \cdot s^{-1})$ is the shear modulus of the film material.

When the acoustic impedance ratio R_Z is equal to 1 (quartz on quartz) then the new equation will become the Sauerbrey equation.

[12] C.S. Lu; O. Lewis, J. Appl. Phys. 43, 1972, 4385.

This equation applies strictly to elastic films and is considered to describe more accurately the experimental results for frequency changes up to 40% of the unloaded crystal. Films with viscoelasticity (thick layer of organic polymer) will exhibit significant deviations from both theories described above.

Furthermore, the thickness of the deposited layer TK_f (cm) can be also calculated using equation (7):

$$TK_f = \frac{\Delta m}{\rho_f} = \left(\frac{N_q \cdot \rho_q}{\pi \cdot R_Z \cdot f \cdot \rho_f}\right) \tan^{-1}\left[R_Z \tan\left[\pi \cdot \left(\frac{f_q - f}{f}\right)\right]\right] \tag{7}$$

where Δm $(g \cdot cm^{-2})$ is the change in mass per unit area calculated from Z-match equation, ρ_f $(g \cdot cm^{-3})$ is the density of the material, N_q $(1.668 \cdot 10^5\ Hz \cdot cm)$ is the frequency constant of the AT cut quartz crystal, ρ_q $(2.648\ g \cdot cm^{-3})$ is the density of quartz, f_q (Hz) is the resonant frequency of the unloaded crystal, f (Hz) is the resonant frequency of the loaded crystal, and R_Z is the Z-factor of the film material (acoustic impedance ratio).

6.3 – Measurements in liquids

The decrease in frequency Δ_f (Hz) due to the change of the viscosity and density of the liquid which comes in contact with the crystal is described by Kanazawa's equation[13] (8):

$$\Delta_f = \sqrt{f_q^3} \cdot \sqrt{\frac{\eta_L \cdot \rho_L}{\pi \cdot \mu_q \cdot \rho_q}} \tag{8}$$

Where $f_q (Hz)$ is the resonant frequency of the unloaded crystal, η_L $(N \cdot s \cdot m^{-2})$ is the viscosity of the liquid in contact with the electrode, ρ_L $(kg \cdot m^{-3})$ is the

[13] K.K. Kanazawa and J.G. Gordon, *Anal. Chim. Acta* 99: 1985, 175.

density of liquid in contact with the electrode, μ_q $(2.947 \cdot 10^{10}\ N \cdot m^{-2})$ is the shear modulus of quartz, and ρ_q $(2.648 \cdot 10^{3}\ kg \cdot m^{-3})$ is the density of quartz.

In Figure 34, the experimental change in frequency resulting from the exposure of the Ai/Ti crystal to different concentrations of glycerol in water measured with respect to the oscillation frequency in pure water (red curve) is compared to the theoretical plot calculated using the equation (8) (blue curve).

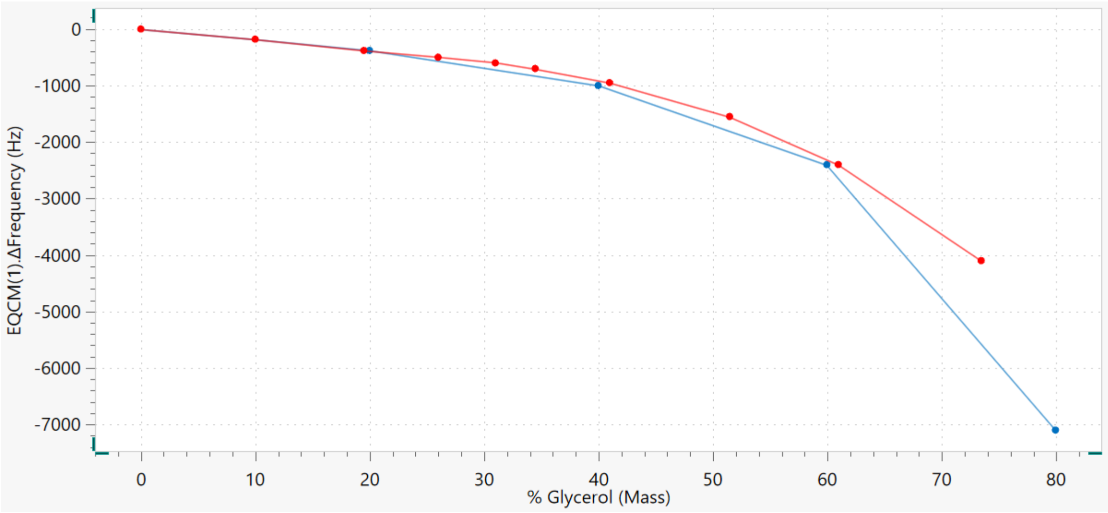

Figure 34 – Change in frequency measured during exposure to different water/glycerol solutions (red) vs. theoretical predictions (blue). The values of ΔFrequency were normalized with respect to water

Note

The EQCM is able to sustain stable oscillation in 100% pure glycerol.

Note

The deviation between the theoretical and the experimental plot is normal as the theoretical model fails to take into account the viscoelastic properties of the solution. As the % of glycerol increases, these properties become more dominant.

6.4 – Example of data analysis for metal electrodeposition on QCM crystals

In the case of experiments which measure relative change in frequency due to deposits of metal films on the electrode, measured in the same solution (electrolyte), the Sauerbrey equation can be accurately applied because the viscous loading of the liquid has a negligible effect. Therefore, for thin, lossless deposited films, it is possible to make quantitative correlation between the change in frequency Δf (Hz) and the total charge passed Q (C) by combining the Sauerbrey equation with the Faraday law. The total charge measured is directly proportional to the total number of electrons involved in the electrochemical process which is directly proportional to the total number of metal atoms (mass) deposited. Therefore, there is a linear relationship between Δf (Hz) and Q (C) (9).

$$\Delta_f = \frac{10^6 \cdot M_W \cdot C_f \cdot Q}{n \cdot F \cdot A_r} \tag{9}$$

Where M_W $(g \cdot mol^{-1})$ is the apparent molar mass of the deposited metal, C_f $(0.0815\ Hz \cdot ng^{-1} \cdot cm^2$ for a $6\ MHz$ crystal) is the Sauerbrey sensitivity factor for the used crystal, $Q\,(C)$ is the integrated charge during the electrodeposition, n is the number of electrons transferred during the deposition process, F $(96485\ C \cdot mol^{-1})$ is the Faraday constant, and A_r (cm^2) is the total deposition area of the working electrode.

This calibration procedure can be used with simple electrodeposition processes, e.g., Ag, Pb, Cu on Pt or Au EQCM crystals. Next, two examples of data analysis for Pb deposition on Au/Ti crystals are presented.

6.4.1 – Pb underpotential deposition on Au/Ti crystals

When the potential was stepped from 0.8 V (a value where no Pb is deposited on the Au surface) to -0.4 V (potential where Pb UPD occurs), the average change in frequency was measured as being $26.675\ Hz$ (see Figure 35). Using

Sauerbrey's equation (1), the change in frequency can be correlated to the change in mass:

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

If $C_f = 0.0815\ Hz \cdot ng^{-1} \cdot cm^2$ (the sensitivity factor of a 6 MHz crystal), the change of mass per unit of area Δm_{Pb}^{exp} $(g \cdot cm^{-2})$ of the Pb monolayer can be calculated using the measured value of $\Delta f = -37.17 - (-63.84) = 26.67\ Hz$:

$$\Delta m_{Pb}^{exp} = \frac{26.67\ Hz}{0.0815\ Hz \cdot ng^{-1} \cdot cm^2} = 327\ ng \cdot cm^{-2}$$

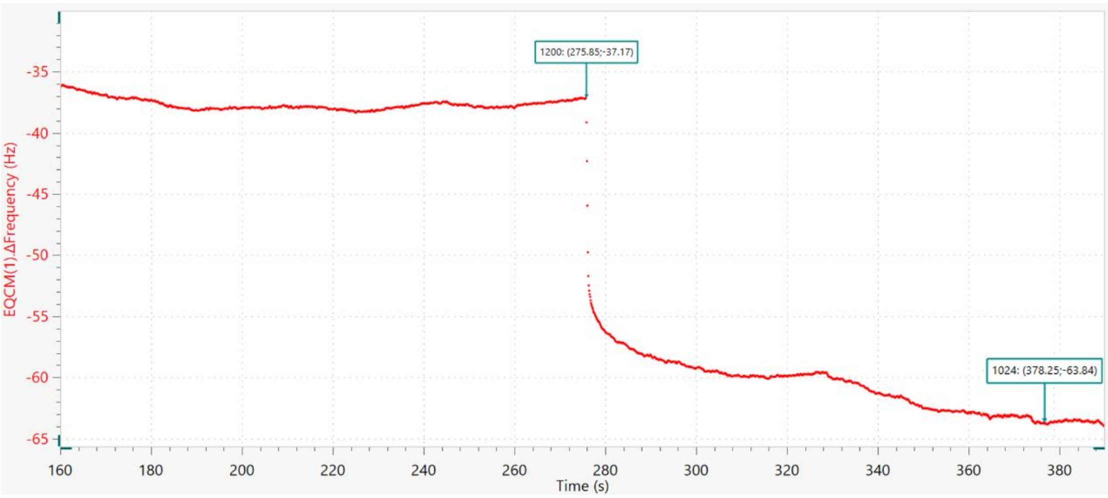

Figure 35 – The change in frequency due to the Pb UPD when the potential was stepped from 0.8 V to -0.4 V

The theoretical value for a Pb monolayer on Au(111) (using $Q_{Pb} = 302\ \mu C \cdot cm^{-2}$, a 2 electron transfer process, $n = 2$ and the molar mass of Pb $M_{pb} = 207.2\ g \cdot mol^{-1}$) is:

$$\Delta m_{Pb}^{th} = \frac{Q_{Pb}}{2F} \cdot M_{Pb} = 324\ ng \cdot cm^{-2}$$

Comparing the theoretical value (Δm_{Pb}^{th}) with the experimental one (Δm_{Pb}^{exp}), a very good agreement can be seen.

6.4.2 – Pb overpotential deposition on Au/Ti crystals

In Figure 36, the linearity of the change in frequency Δf (Hz) vs. charge Q (Hz) is shown for the Pb bulk deposition when a potential step was applied between 0.8 V and -0.6 V. Beside the clear indication of the linear dependence of the two parameters, there is the possibility to calculate the molar mass of Pb M_{Pb} $(g \cdot mol^{-1})$ from the slope of this plot and compare it with the theoretical value ($M_{Pb} = 207.2\ g \cdot mol^{-1}$).

The slope, in Hz/C can be reconverted into Hz/mol equivalent using the following formula:

$$\frac{d\Delta f_{QCM}}{dQ} \cdot zF = \frac{d\Delta f_{QCM}}{dn} \tag{10}$$

Where z is the electrovalence of the electroactive species (Pb) and F is the Faraday constant (96485 $C \cdot mol^{-1}$).

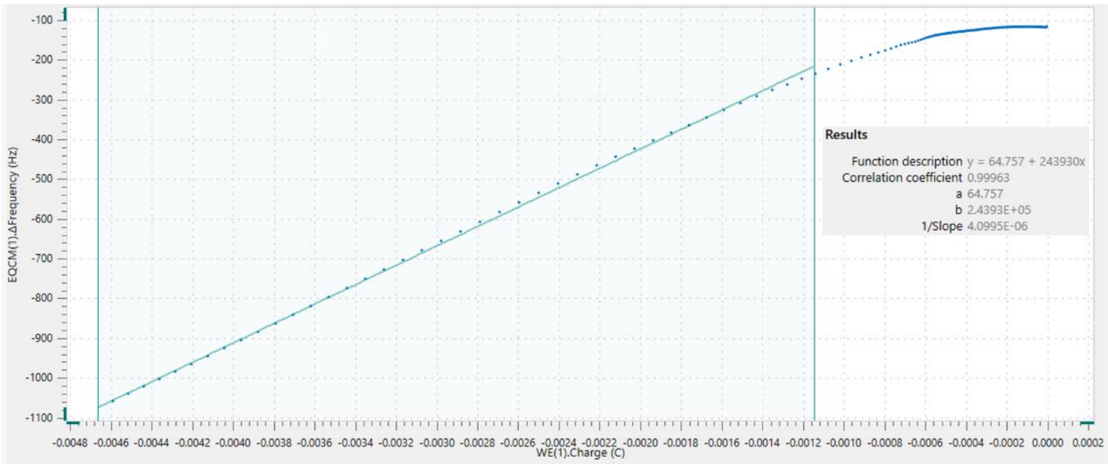

Figure 36 – Change in frequency vs charge (blue dots) and the linear regression through the experimental data points (green line) for Pb bulk deposition

From Figure 36, the slope of the linear regression of Δf vs Q is:

$$\frac{d\Delta f_{QCM}}{dQ} = 243930\ Hz/C$$

Applying equation (10),

$$\frac{d\Delta f_{QCM}}{dQ} \cdot zF = \frac{d\Delta f_{QCM}}{dn} = 47.1\ 10^9\ Hz/mol$$

Knowing the sensitivity factor of the crystal C_f ($0.0815\ Hz \cdot ng^{-1} \cdot cm^2$ for a 6 MHz crystal), it is possible to calculate the equivalent coefficient of the crystal for a known area ($A = 0.361\ cm^2$) making it possible to calculate the coefficient K ($g \cdot Hz^{-1}$):

$$K = \frac{A}{C_f} = \frac{0.361\ cm^2}{0.0815\ Hz \cdot ng^{-1} \cdot cm^2} = 4.429\ 10^{-9}\ g \cdot Hz^{-1}$$

With these two values, it is possible to calculate the experimental molar mass of the electroactive species:

$$M_{Pb}^{ex} = \frac{d\Delta f_{QCM}}{dn} \cdot K = 208.6\ g \cdot mol^{-1}$$

The comparison between the experimental value of the molar mass ($M_{Pb}^{ex} = 208.6\ g \cdot mol^{-1}$) and the theoretical one ($M_{Pb}^{theor} = 207.2\ g \cdot mol^{-1}$) shows a very good agreement.

Note

The main disadvantage of this quantitative method is that the exact surface area must be known (the real surface area is not always equal to the geometric surface area).

7 – General specifications

Oscillator

Oscillation frequency	6 MHz
Frequency resolution	0.07 Hz
Frequency accuracy	1 Hz

Available frequency range	Moving window of 1000 Hz. Absolute range: 80 kHz, from f_0 + 5000 Hz to f_0-75000 Hz
Temperature sensor resolution	0.1 °C
Temperature sensor accuracy	1 °C
Operation environment	10-40 °C
Input	WE + S electrode connections
Driving force adjustment	External trimmer
Housing	Autolab module

EQCM cell and electrodes

Connections to crystal holder	9 Pin Sub-D connector, 2 m long
Cell material	Polypropylene[14]
Cell volume	3 ml, maximum
Crystal diameter	1.36 cm (0.538")
Electrode diameter	0.67 cm (0.267")
Thickness of Au coating	1000 Å
Thickness of the adhesion layer	100 Å
Reference electrode	Ag/AgCl, 3 M KCl, in gel
Counter electrode	Au wire

[14] Please refer to Appendix 2 for more information on the chemical stability of Polypropylene.

Appendix 1 – Accessories and spare parts

Code	Description
EQCM	EQCM module installed in Autolab. Contains complete cell with temperature sensor, external oscillator box, 2 m long 9-Pin Sub-D connector cable
EQCM.AU	6 MHz EQCM crystal Au/TiO_2, polished
EQCM.AU.PCK25	6 MHz EQCM crystal Au/TiO_2, polished (25 pcs)
EQCM.PT	6 MHz EQCM crystal Pt/TiO_2, polished
EQCM.REF.EL	Reference electrode Ag/AgCl, KCl saturated
EQCM.CE	Gold counter electrode
EQCM.O.SET	O-ring set of EQCM cell (1·1 mm (1); 3.5·1.5 mm (1); 8·1.5 mm (4); 14·1 mm (1)
EQCM.O.CRSTL	O-ring set for crystal fixture 8·1.5 mm (10)
EQCM.SCRWS	Hex screws M3·16 (10)
EQCM.ADJ	EQCM driving force adjustment tool
EQCM.CELL	Polypropylene cell cover
EQCM.HEX25	Hex key, 2.5 mm
EQCM.CELL.PVDF	PVDF cell for EQCM
EQCM.CABLE	Cable to connect the EQCM with oscillator interface

Appendix 2 – Chemical resistance of polypropylene to common chemicals

The chemical stability tables for polypropylene are listed in this appendix. The resistance to a given medium is provided by a grade, between 1 and 5 (see Table 1).

Resistance rating	Indication
1	Excellent, no attack
2	Good, no significant attack
3	Acceptable, light attack, limited use
4	Unacceptable, significant attack
5	Inferior, cracking or dissolving

Table 1 – Overview of the grades used to indicate the chemical resistance of polypropylene towards different media

Polypropylene must not be exposed to media characterized by a rating of 4 or 5. Contact with media with a rating of 3 must be avoided, if possible. An alternative cell, in PVDF, is available on request (contact autolab@metrohm.com) for more information.

The following tables are provided in this appendix:

- Table 2 lists the resistance ratings towards common acids
- Table 3 lists the resistance ratings towards common bases
- Table 4 lists the resistance ratings towards common organic solvents

For a more comprehensive chemical resistance chart of polypropylene, please refer to https://www.coleparmer.com/Chemical-Resistance

Acids

Chemical	Resistance rating	
	20 °C	60 °C
C_6H_5COOH	1	2
H_3BO_3	1	1
HBr 25%	2	3
$C_6H_8O_7$ (citric acid)	1	1
HCN	2	2
HF	2	2
H_3PO_4 25%	1	1
H_3PO_4 85%	1	1
$C_8H_6O_4$ (phthalic acid)	1	1
H_2CrO_4	1	2
$C_4H_4O_4$ (maleic acid)	1	1
$C_{18}H_{34}O_2$ (oleic acid)	2	3
$C_2H_2O_4$ (oxalic acid)	1	1
HNO_3 5%	2	3
HNO_3 65%	4	4
HCl 10%	1	1
HCl 37%	2	3
H_2SO_4 10%	1	1
H_2SO_4 78%	2	4
H_2SO_4 93%	3	4
CH_3COOH 10%	1	1
CH_3COOH 50%	1	1
CH_3COOH 75%	1	1
CH_3COOH 100%	2	3
$HClO_4$	1	2

Table 2 – Chemical resistance ratings of Polypropylene towards common acids

Bases

Chemical	Resistance rating	
	20 °C	60 °C
NH_3	1	1
$Ca(OH)_2$	1	1
KOH	1	1
NaOH	1	1
K_2CO_3	1	2
$KMnO_4$	1	2
NaCN	1	1
$Na[Fe(CN)_6]_3$	1	2
NaClO	2	3

Table 3 – Chemical resistance ratings of Polypropylene towards common bases

Organic solvents

Chemical	Resistance rating	
	20 °C	60 °C
Acetone	3	4
Benzol	3	4
Petrol	4	4
Butyl alcohol	1	1
Ethyl acetate	2	4
Ethyl alcohol	1	1
Ethyl dichloride	3	4
Ethyl ether	4	4
Phenol	2	2
Formalin 37%	1	2
Heptane	3	4
Chlorobenzene	3	4
Chloroform	4	4
Carbon disulphide	4	4
Carbon tetrachloride	4	4
Methyl alcohol	1	1
Methylene chloride	4	4
Methylene dichloride	4	4
Methyl ethyle ketone	3	4
Nitrobenzene	3	4
Toluene	3	4

Table 4 – Chemical resistance ratings of Polypropylene towards common organic solvents

Appendix 3 – Recommendations regarding Viton

All the seals and gaskets used in the EQCM are made of Viton. This material will exhibit swelling when exposed to organic environments. The swelling will increase the pressure on the crystal and could damage the crystal if it becomes too significant.

Care must be taken when using Viton in the following organic environments:

- Acid anhydrides
- Acetone
- Acetonitrile
- Amines
- Dioxane
- DMF
- DMSO
- Ethylacetate
- Freon 22
- Methanol
- Pyridine
- THF

For a more comprehensive chemical resistance chart of Viton, please refer to https://www.aceglass.com/downloads/eccc.pdf

Appendix 4 – Troubleshooting guide

Table 5 displays a list of troubleshooting hints that can be followed when problems are encountered using the EQCM. If the hints provided in this table do not help in solving the problem, please contact autolab@metrohm.com.

Problem description	Suggested solution
Neither the red nor green LED does not light after the procedure is started	Check if the PCB card is inserted properly (it has to be fixed to the main Autolab frame with the provided screws
	Check all the connections
	Check if the Autolab EQCM is turned on in the "Autolab control" command
	Check if the crystal is not damaged and the pins make good contact with the metalized surface
Green LED will not light even after adjusting the trimmer.	Solution too viscous. Use a less viscous electrolyte
	Crystal damaged. Change the crystal
Noise and oscillations mostly in the electrochemical signal. Measurement is unstable	Make sure that the RE is not touching the WE (the crystal)
	Adjust the driving force. Make sure that the LED on top of the oscillator in green
	To avoid damaging the trimmer, use only the provided tool for the adjustment
The cell is leaking	Disassemble and reassemble the cell
	Check and, if needed, change the O-rings

Table 5 – Troubleshooting guide

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