Volume
1

QCM-I and eQCM-I

QUARTZ CRYSTAL MICROBALANCE WITH IMPEDANCE ANALYSIS

User Manual

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1. Safety

In no event shall Semilab ever be held responsible or liable for any direct, indirect, incidental, special or consequential damages or costs whatsoever resulting from or related to the use or misuse of the QCM-I instrument or components thereof, even if Semilab has been advised, knows of, or should be aware of the possibility of such damages. Semilab emphasizes the importance of consulting experienced and qualified professionals to assure the best results when using the QCM-I.

General Safety

WARNING!

The safety requirements listed in this manual must be followed in order to avoid personal injury and damage to the QCM-I instruments.

WARNING!

RISK OF ELECTRICAL SHOCK. Do not connect this instrument to electrical power if the enclosure is damaged or any of the covers or panels is removed. Make sure the voltage rating on the instrumentation matches the line voltage available in the lab. Connect only to outlets with safety earth ground. Make sure that the power cord is easily accessible when the equipment has been installed.

WARNING!

RISK OF ELECTRICAL SHOCK OR FIRE HAZARD. Switches may produce electrical sparks. Do not use the QCM-I instruments in the presence of flammable gases, fumes or liquids.

The instrument has been designed for indoor use only. Do not expose it to rain, snow or dust. During storage or transport the instrument should be kept dry. Temperatures below 0ºC and above 65ºC should be avoided. Do not operate at ambient temperatures below 5ºC and above 30ºC.

CAUTION!

Use only as specified in the operating instructions. Follow all instructions. Skipping steps can result in damage to the QCM-I instrument.

Handle carefully when removing the instrument from the transport packaging. The product must always be shipped in either the original packaging supplied with the QCM-I, or equivalent.

CAUTION!

Do not use force when connecting or disconnecting connectors as damage may occur.

Do not subject the equipment to external shocks.

Do not block or restrict ventilation slots.

Do not expose any parts other than the sample volume in the flow module(s) to water or other liquids.

CAUTION!

If liquid is spilled on the instrument, disconnect it from the power source and have it checked by an authorized person.

Refer to the safety information from the supplier and general safety regulations in your country when you work with chemicals.

Carry out appropriate decontamination if equipment is exposed to hazardous material.

Do not install substitute parts or perform any unauthorized modification to the product.

Return the product to Semilab or other qualified and authorized personnel for service and repair to ensure that safety features are maintained. Before returning the instrument it must be free of hazardous contamination.

For safety instructions and operation of peripheral equipment, e.g. the personal computer, read the safety instructions and the manual provided by the manufacturer carefully.

Turn the QCM-I or eQCM-I off when not in use. An appropriate risk assessment should be undertaken before the instrument is left operating unattended.

Measuring Head, Sensor Holder and Flow Cell

WARNING!

RISK OF FIRE HAZARD. Use only sample liquids with a self-ignition point higher than 85°C in the sample volume of the flow modules.

Parts of the sensor holder and flow cells can become hot.

Do not expose any parts other than the sample volume to water and other liquids.

If liquid is spilled inside the electronics part of the sensor holder, disconnect it from the electronics unit and have it checked by an authorized person.

2. Introduction

The QCM-I is a precision instrument for the determination of the mass and viscoelastic properties of thin films attached to the surface of a quartz crystal sensor. These films, which may be a wide range of molecular or atomic layers from metals to physisorbed polymers, surfactants or immobilized biological samples, are monitored in real time either in liquid or in the vapor phase. The measurement is made by monitoring the change in resonant frequency spectrum of the oscillating piezoelectric sensor crystal. In water the acoustic transverse wave created extends into the solution above the sensor surface, decaying rapidly with a penetration depth of ~250 nm for a 5 MHz crystal. The technique can measure changes in the layers over a nm to micron thickness range or ng/cm^2 to $\mu g/cm^2$ mass range, as well as changes in the solution viscosity. In solution, the mass determined is the “wet mass” or hydrated mass which corresponds to the solid material that makes up the film as well as solvent and ions etc. that are contained within the film and closely coupled to the oscillation of the film.

This manual describes the principles of operation and how to set up the instrument together with safety and technical information for the correct operation and maintenance of the QCM-I. It is important that the user familiarize themselves with these requirements if the equipment is to be operated correctly and to its best. Please read all sections before using the equipment.

As with all precision instruments, it is not recommended that the user undertake maintenance or calibration unless specifically trained to do so by the manufacturer. If for whatever reason the instrument ceases to operate correctly, the user should contact the vendor for guidance on whether the instrument needs to be serviced by a qualified service engineer or returned to the vendor for repair. Under no circumstances should the instrument be dismantled or operated without the fitted cover and attention should be taken at all times to the warnings detailed in the operator’s manual.

This User Manual (Volume 1) which focuses on the hardware aspects of the instrument should be read in conjunction with the Software Manual (Volume 2) also provided with the equipment.

3. QCM-I Principle of Operation

3.1 QCM-I MEASUREMENT PRINCIPLE

The Quartz Crystal Microbalance (QCM) technique monitors the resonant frequency of a piezoelectric quartz crystal sensor in response to an alternating voltage applied between electrodes on its two faces. The crystals are cut so that they oscillate in a thickness shear mode, with opposing faces travelling in opposite directions as shown in Figure 1. AT-cut quartz crystals are most commonly used as QCM sensors because of their superior mechanical and piezoelectric properties, and because they can be cut to give nearly zero temperature coefficients at room temperature. The resonant frequency corresponds to the excitation of the acoustic standing wave across the thickness of the quartz and top and bottom electrodes. If a thin rigid layer is added to the surface of one of the electrodes, the acoustic wave extends through this layer and the resonant frequency drops. The reduction in the frequency can be related to the change in areal mass ($\Delta m/A$) on the surface of one side of the crystal by the Sauerbrey equation[1]:

$$\Delta f_n = -2n.f_1^2.(\Delta m/A)/(\rho_q\mu_q)\tfrac{1}{2} \quad (\text{Hz}) \qquad (1)$$

$$\Delta m/A = \Delta f_n\ .(\rho_q\mu_q)\tfrac{1}{2}\ /\ (-2n.f_1^2)\ (\text{ng/cm}^2) \qquad (2)$$

Where Δf_n is the change in resonant frequency of the nth overtone of a crystal of fundamental frequency f_1, Δm is the change in mass (g), A is the area (cm^2), ρ_q is the density of quartz (2.648 g/cm^3) and μ_q is the Shear Modulus of quartz ($2.947\text{x}10^{11}$ gcm^{-1}s^{-2}).

For a crystal with fundamental frequency of 5 MHz, its mass sensitivity [$\Delta m/(\Delta f.A)$] is -17.7 ngcm^{-2}/Hz. The areal mass data from the Sauerbrey equation can also be expressed as a (Sauerbrey) thickness (d^s) by using an estimated density for the layer ρ, which is often taken as 1 gcm^{-3}.

$$d^s = (\Delta m/A)\ /\ (\rho.100) \qquad (\text{nm}) \qquad (3)$$

The crystal can also oscillate at overtone frequencies, which correspond to the odd harmonics; 3x, 5x, 7x etc. and measurements can also be made at these frequencies.

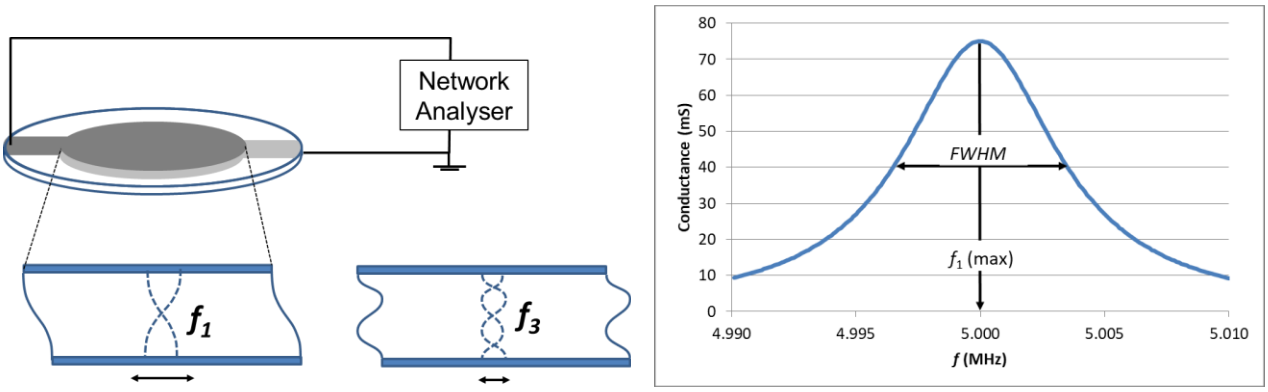

Figure 1: Schematic diagram of a QCM measurement, showing the shear displacement of the quartz at fundamental and 3rd harmonic frequencies. The plot shows a conductance-frequency response obtained from an impedance measurement with a network analyzer; resonant frequency and band width are marked.

In the QCM-I technique the resonant frequency is obtained using a network analyzer, which measures the impedance spectrum of the crystal as a function of frequency. The resonant peak obtained at the fundamental frequency is also shown in Figure 1. In addition to the frequency of the resonant maximum, the Full Width at Half Maximum (FWHM) is also obtained. The FWHM can be related to the dissipation (D, determined by QCM-D using the “ring-down” technique) and is inversely proportional to the Quality factor (Q) of the crystal:

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[1] Sauerbrey, G. *Z. Phys.* **1955**, *155*, 206.

$$\mathrm{FWHM} / f = D = 1/Q \qquad (4)$$

The FWHM/*f* measured from the impedance and D measured by the ring-down technique (QCM-D) have been shown to be the same parameter, just measured in two different ways[2].

When a rigid film is deposited on the sensor surface, the FWHM does not change and Δf/n is the same for the fundamental frequency and the overtones. However, if a bare crystal is immersed in a viscous liquid, or if a viscoelastic film is deposited on the sensor surface from solution, then as well as a reduction in the frequency, the FWHM will increase; this is shown in Figure 2. For a viscoelastic layer the frequency change, Δf_n/n, is also smaller for higher overtones.

The QCM-I signal Frequency and FWHM response to the viscosity and density of Newtonian solution (s) is given by[3]:

$$\Delta f_n = -n^{1/2} f_1^{3/2} (\nu_s \rho_s)^{1/2} / (\pi \rho_q \mu_q)^{1/2} \quad \text{(Hz)} \qquad (5)$$

$$\Delta \mathrm{FWHM} = 2\, n^{1/2} f_1^{3/2} (\nu_s \rho_s)^{1/2} / (\pi \rho_q \mu_q)^{1/2} \quad \text{(Hz)} \qquad (6)$$

This means that the response measured for a bulk solution change, due to different viscosity or density of the new solution follows the relationship: $\Delta \mathrm{FWHM}_n/\Delta f_n = 2$.

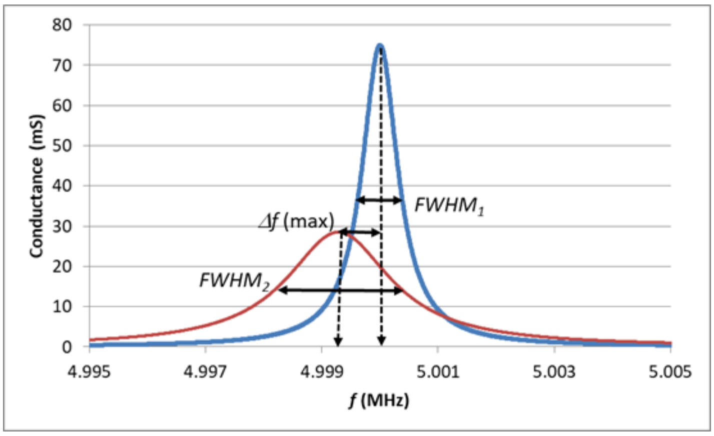

Figure 2: Change in fundamental resonance of a bare QCM sensor (blue) on immersion in a liquid (red).

3.2 LIMITS OF OPERATION

Assumptions

Measurements can be made for the deposition of a very wide range of layers, however analysis of film properties generally makes the following assumptions:

- Uniform film distribution – the surface is completely covered with a uniform film
- Good adhesion of the film to the surface
- Thin film approximation – the film thickness is significantly less than the thickness of the crystal
- Rigid layer – Sauerbrey analysis to directly determine the mass from the frequency change requires this, otherwise visco-eleastic models are required to stop underestimation of the mass change. The extent of the error is dependent on the film thickness as well as the solution viscosity, if the measurement is in solution.

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[2] D. Johannsmann, Viscoelastic, mechanical and dielectric measurements on complex samples with the quartz crystal microbalance. *Phys. Chem. Chem. Phys*. 10, 4516–4534 (2008)

[3] K. Kanazawa, J. G. Gordon, *Anal. Chim. Acta* **1985**, *175*, 99–105**.**

For data analysis and more complex modelling of QCM experiments where overtone data is available, the fundamental frequency is often not used because it does not always fit consistently with the overtone data. For some instruments it may also not be commonly measured due to issues with signal stability. The reason for this is likely to be due to the magnitude of displacement at the crystal surface, which is approximately inversely proportional to square of the overtone number. Ie. the surface displacement U_0 at the fundamental frequency is 9x that of the 3rd harmonic at the same Q.

$$U_0 = 4U_{el}Q\delta_q/(n\pi)^2 \qquad (7)$$

Where U_{el} is the electrical driving amplitude, Q the crystal quality factor, δ_q is the piezoelectric strain coefficient (3.1×10^{-12} m/V for AT cut quartz) and n is the overtone number.

This is likely to make it more sensitive to edge effects or stresses within the crystal. However for non-rigid layers, the lower the harmonic, the closer the calculated Sauerbrey mass will be to the actual hydrated mass. Indeed for some systems, such as coupled nanoparticles or vesicles, the reduction of the frequency response for the overtones can be so large that the fundamental and overtones give apparent mass changes in opposite directions and potentially wholly incorrect interpretation of the data if only the overtone data is collected. For this reason it is recommended that the fundamental frequency data is always collected.

Maximum Loads

QCM sensor crystals can be coated with virtually any material as long as it can be deposited in a sufficiently thin, uniform and well-attached layer. Layer thicknesses typically vary from a few Angstrom to a few micrometers. The maximum layer thickness depends on the viscoelastic properties of the coating material. As a general rule, thicker layers are possible for more rigid coating materials.

The maximum load on a crystal is limited by two factors: (1) total damping or (2) lost sensitivity. For highly viscous or solid materials, the damping of the crystal increases with increasing layer thickness. At a certain thickness (usually a couple of micrometers) the damping becomes so high that the crystal can no longer be driven, i.e. the measurement fails due to lack of oscillation. More viscoelastic materials do not couple completely to the crystal’s oscillation. With increasing layer thickness the outermost parts of the attached layer will couple weakly and at a certain thickness (usually a few micrometers) it is lost completely. Oscillation is still detected, and a frequency is still measured, but the equipment can only sense the part of the layer in the vicinity of the crystal-layer interface.

3.3 LOCATING RESONANT FREQUENCIES

In order to determine the resonant frequencies to track for a measurement, during the measurement initialization, the network analyzer scans through a wider frequency range measuring the sensor crystal admittance (1/impedance) based on the nominal crystal frequency. Once it has identified conductance maxima within this region it selects a narrower region to make measurements at smaller frequency intervals for a better defined resonance curve. The user can do a similar scan using the network analyser (Frequency Scan) between any frequencies from 0.05 to 80 MHz.

3.4 RESONANCE CURVE ANALYSIS

Resonance Modeling (Lorentz curve)

For each of the selected sensor resonances, the conductance (G) and susceptance (B) values as a function of frequency (the real and imaginary components of the admittance) are fitted to a Lorentzian model for the Crystal oscillator. The fit parameters are G_{max}, FWHM, Frequency, G_{off}, B_{off}, F_i and residual, derived from the equivalent circuit[4], shown in Figure 3. The resonant frequency and FWHM values are

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[4] D. Johannsmann, The Quartz Crystal Microbalance in Soft Matter Research: Fundamentals and Modeling, Springer International Publishing, Switzerland, 2015.

used for the film characterization. The parameters F_i and G_{off} account for effects of the connection of the sensor crystal to the analyzer or small errors in the instrument calibration.

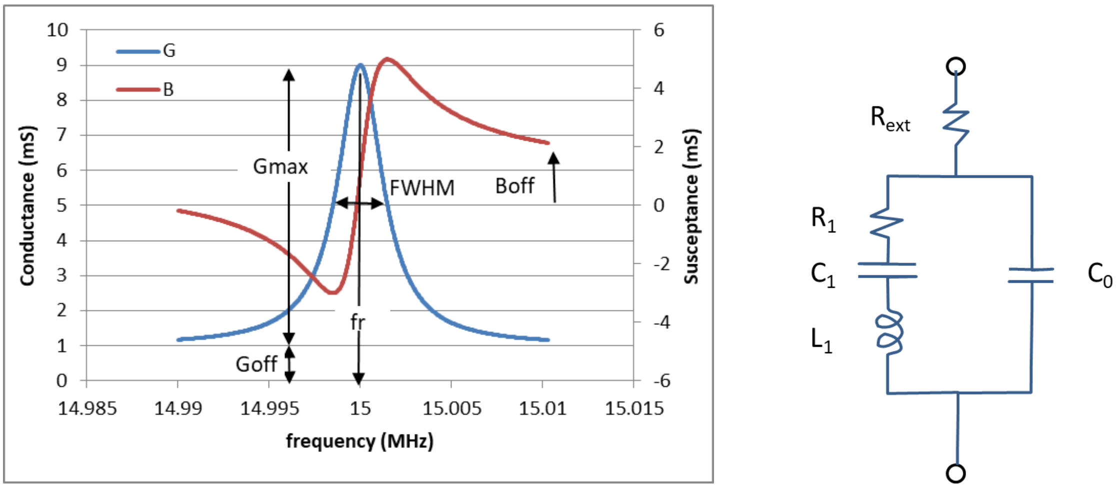


Figure 3: Simulated plot of conductance and susceptance from a crystal impedance measurement and equivalent electrical circuit on which the analysis is based.

The standard acquisition measures 200 frequency points for the curve fit, which limits the acquisition rate but gives high resolution. Fewer points are measured in Fast mode, 20, which increases the acquisition rate but also increases the noise.

Whilst the resonance curves (frequency spectra) can be saved during the experiment, in the interests of data file size, only the fitted parameters are recorded as the time dependent experimental data. The parameters returned from the fit of the resonance data and saved as the experimental data are:

- Frequency (the resonant frequency of the selected overtone, Hz),
- FWHM (full width half maximum of the resonance peak, Hz),
- G_{max} (conductance maximum from the fit of the resonance curve),
- G_{off}-s (conductance offset from the fit of the resonance curve),
- B_{off}-s (susceptance offset from the fit of the resonance curve),
- F_i (phase rotation of G and B components from the fit of the resonance curve),
- Residual (the difference between the fitted curve and the measured data from the Lorentz fit of the resonance curve).

From the fit parameters the following data can be derived and output:

- Q (Quality factor) and Dissipation,
- ΔFrequency (frequency change from start of experiment or baseline, Hz),
- ΔFWHM (change in resonant peak width, Hz,),
- ΔDissipation (change in dissipation from the start of the experiment),
- Sauerbrey Mass (Mass calculated using the Sauerbrey equation from the beginning of the experiment or the calculated baseline, ng/cm^2; if Sauerbrey is selected as the Calculation Model).

Other experimental data are also recorded from the experiment, depending on modules installed, such as:

- Temperature (measured on channel A and B for the 2 channel QCM-I),
- Flow (where fluidic pump control option is enabled).

3.5 QCM-I INSTRUMENT DESCRIPTION

General

The QCM-I instrument consists of the following modules:

- QCM-I measuring unit including
    - Impedance measurement circuit
    - Electronic signal processing and controlling unit
    - Temperature control unit
    - Built-in thermal chambers (Channel A and B) and sensor holders with flow-cell
    - Working electrode connector for electrochemical cell (2 mm banana socket)
- External Power supply
- External PC with installed Microsoft Windows OS operating system
- Pre-installed BioSense software for controlling QCM-I measurement

Figure 4: QCM-I measurement unit front view

Figure 5: QCM-I measurement unit’s underside view showing EC working electrode connector.

The signals are generated and data is collected in the QCM-I measuring unit before being sent to the computer.

The PC communicates with the QCM-I unit via Manufacturer supplied USB cable. Microsoft Windows OS operating system is installed on the PC.

The BioSense software controls the measuring unit, performs the data processing, computations and displays/saves/exports/imports the results.

Temperature Measurement and Temperature Control Module

The thermal chambers/ measuring heads (Channel A and B) of the QCM-I unit are heated/cooled by Peltier devices controlled by a temperature controller built-into the QCM-I instrument. The two channels are independently controlled between 4 °C and 80 °C with a stability of < ± 0.02 °C.

Power Supplies (External)

QCM-I is powered with a 2 DC power adapters, only use the manufacturer supplied Power Supply:

1. 12VDC 10A, mod: GlobTek TR9CE9000CCP-IM(R6B)

PC for Running BioSense Software

The PC is part of the QCM-I system. It is delivered by Semilab with pre-installed Microsoft Windows OS and BioSense software. For reliable and fast QCM operation this computer should only be used for running the BioSense software and only with the preinstalled software.

Do not install any third party software on this PC as it may affect the proper operation of the instrument.

BioSense Software

BioSense is Windows-based software for full control of QCM-I instrument.

Measurement Channels

Two QCM measuring channels are available with the QCM-I:Both **Channel A** and **Channel B** – temperature controlled built-in thermal chamber which takes a modular sensor-holder with flow cell, or an adaptor for external sensor-holder. Built-in Thermal Chamber and Sensor Holder with Flow-Cell.

The QCM sensor chips are placed in a sensor holder that supports the quartz crystal between two O-rings. The wetted part of this sensor holder is made of PEEK or stainless steel and serves as a flow cell for the QCM crystal. The sensor holder is placed in a temperature controlled measuring head that keeps the sensor and the flow cell at a well-controlled temperature.

External Sensor Holder

External sensor holders are available for different applications, where operating the sensors away from the instrument is required. A range of holders and custom holders are available for different applications, detailed in chapter 9 of this manual.

3.6 ELECTROCHEMICAL QCM-I

The QCM-I can be used as an electrochemical QCM (eQCM) for combined electrochemical and microbalance measurements. This requires electrochemical flow-cell and software modules. eQCM measurements enable the mass changes at the QCM sensing electrode surface to be monitored as a function of the electrochemical potential and the current and charge passed. The setup is shown schematically in Figure 6.

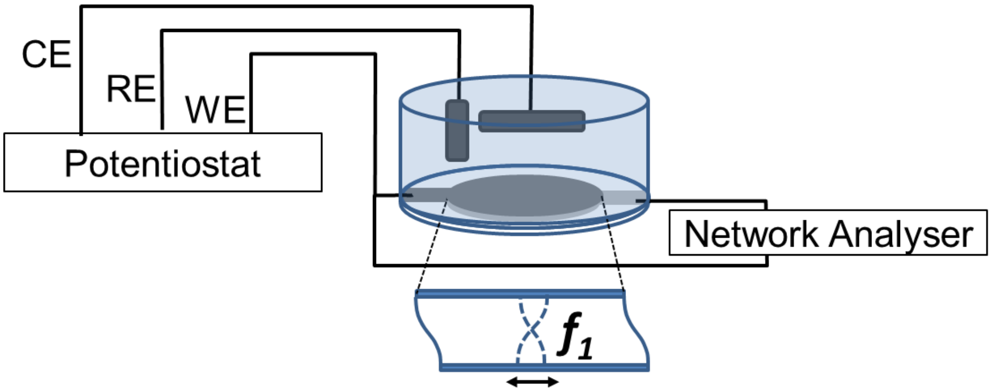


Figure 6: Schematic eQCM-I

Potentiostat

An external potentiostat is used to control the electrochemical measurement. An electrochemistry module is available for the BioSense 3 software to integrate measurements using Gamry and Semilab supplied potentiostats.

3.7 QCM-I SPECIFICATION

Technical Information	QCM-I
Measurement Channels	2 (Upgradable to 4)
Frequency Range	0.05 – 80 MHz, up to the 13th overtone for a 5 MHz Crystal
Measurement Modes	Frequency Scan, Resonance Spectra, QCM(t), QCM(t)-EC, EC
Frequency sensitivity in Liquid	≤ 2 x 10^{-1} Hz
Dissipation Sensitivity in Liquid	≤ 1 x 10^{-7}
Mass Sensitivity in Liquid *	≤ 1 ng/ cm^{-2}
Parameters Recorded for each Overtone	Resonance Curve, Frequency, ΔFrequency, FWHM, ΔFWHM, Q, Dissipation, ΔDissipation, Temperature, etc.
Temperature Control	
Thermal Zones	2, Independent Temperature Control
Working Temperature	4 ^{O}C to 80 ^{O}C with sample pre-equilibration on inlet
Temperature Stability	<± 0.02 ^{O}C
Temperature control	Set manually or via software
Fluidic and Sample	
Flow Cell Volume	~ 40 µl (typical with Ø14 mm crystals)
Wetted Parts	PTFE, PEEK, SS, VITON (or Kalrez)
Sample Loading	Manual and Software Controlled Injection or Selector Valve
Pump	Peristaltic, Pulse-free Independent Flow Control on each Channel
Other Sample Cell Options	Electrochemical flow-cell, Open Cuvette, Immersion, Vacuum, High-pressure, Remote Low-profile, Ellipsometry, Microscopy
Physical Dimensions (without the computer)	
Dimensions, weight	450 mm x 260 mm x185 mm, 5.5kg
Software	
BioSense	Universal software platform for QCM & EC measurements
Import / Export of data	Export to third party software Excel, JPG, BPM, WMF etc.
PC Control	USB 2.0, Windows® 10
Electrical and environmental	
Power supply	12VDC, 108W external power supply with universal input voltage (100V-240V AC / 50-60 Hz)
Fuse	10A, Slow-acting, glass cartridge
Overvoltage category	II.
Supply voltage fluctuations	±10%
Ambient temperature	+5°C…+40°C
Relative humidity	max. 80%
Altitude	max. 2000m
Pollution degree	2

Table 1: QCM-I Technical Specification

* Based on BioSense analysis using Sauerbrey equation and with data smoothing option enabled.

4. Getting the Equipment Ready for Use

4.1 UNPACKING QCM-I

The QCM-I is a sensitive instrument and should be handled with care. Take the QCM-I instrument out of the cardboard box, remove the plastic protecting cover and place it on the working bench.

The accessories are in a separate box. Please check the content according to the detailed part list enclosed in the box.

If any of the components are damaged, please contact the vendor immediately.

Install the QCM-I on a solid, clean, stable, laboratory bench away from direct sources of heat or draft.

⚠ Do not block the ventilation openings on the bottom and side of the equipment. Ensure that the laboratory power supply is suitable for the power adapters provided.

4.2 UNPACKING THE COMPUTER

Please follow the steps in the notebook Manual. The notebook is delivered with installed Microsoft Windows OS and BioSense software.

The QCM-I is supplied with either a standard desktop or NUC computer, or an Apple iMac PC. The following section details the configuration with the NUC computer and iMac.

4.3 INSTALLATION USING NOTEBOOK

Schematic layouts of the instrument cabling and fluidic connections are shown in **Error! Reference source not found.** and Figure . Step by step instructions are given below:

Step 1: Notebook

With the main power supply off, connect the power supply cable to the notebook.

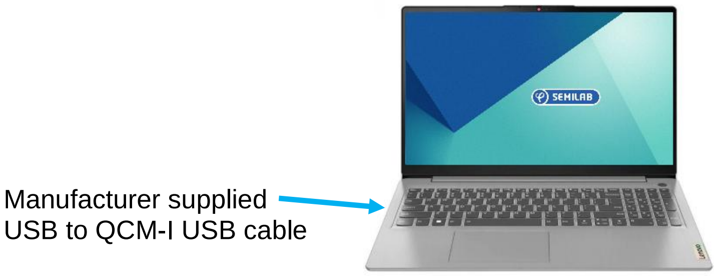


Figure 7: Connection on notebook

Step 2: QCM-I

Connect the QCM-I USB cable to the marked USB socket on the notebook. **Only use the white manufacturer-supplied (USB to screw-in USB) cable.** Connect the screw-in end of the USB cable to the QCM-I. Also connect the 12V QCM-I power supplies.

Figure 8: QCM-I rear view

Step 3: Pump

Connect the 24V Power adaptor supplied with the pump to the back of the peristaltic pump.

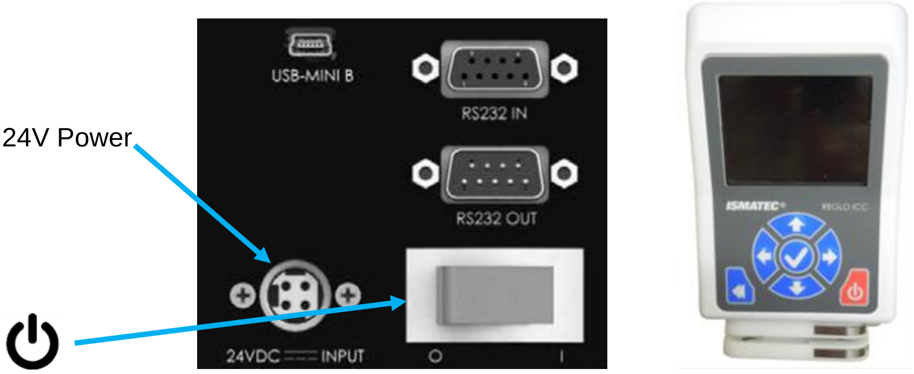


Figure 9: View of Ismatec ICC Peristaltic Pump rear panel and top view.

Step 4: Injection Valve

Connect the 24V Power adaptor supplied with the injection valve to the back of the valve. There is no on/off switch, this is turned on at the mains power.

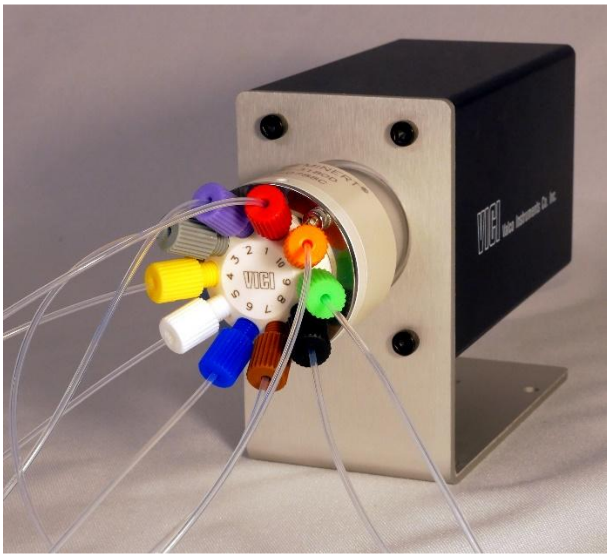


Figure 10: Front View of Vici Injection valve.

Step 5: Connect Fluidics

Connect the fluidics as shown in 11.

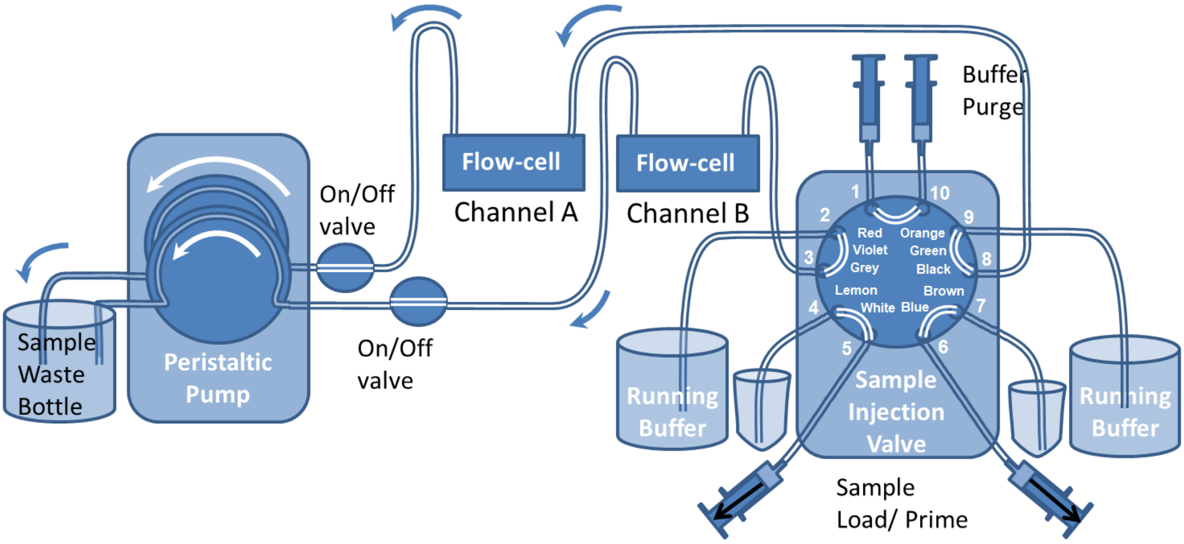


Figure 11: QCM-I Sample and flow setup.

Step 6: Turn On

Once all the cables are connected as shown in Figure 11 and Figure 2, turn on the power supplies and the PC. **Wait for Microsoft Windows OS to load fully before turning-on the QCM-I.** Turn on the QCM-I by pressing the on/off button on the temperature control panel, shown in Figure 4 for 2 s, or off for 4 s. The temperature control panel illuminates when on.

Start the BioSense 3 Software: Start the BioSense 3 software by double clicking on the icon on the Desktop or in the Start Menu. Every day you start the BioSense_3 software, a backup copy of your database is automatically generated. (See “DATABASE TOOLS” chapter in the Software Manual for more information.)

Log on with Username and Password. The installation is complete if the software loads without showing an error message. In the event of an error message, see the “Trouble Shooting” section at the end of this manual. The basic operation of the instrument can be tested using the “QCM-I Quick Start Guide”.

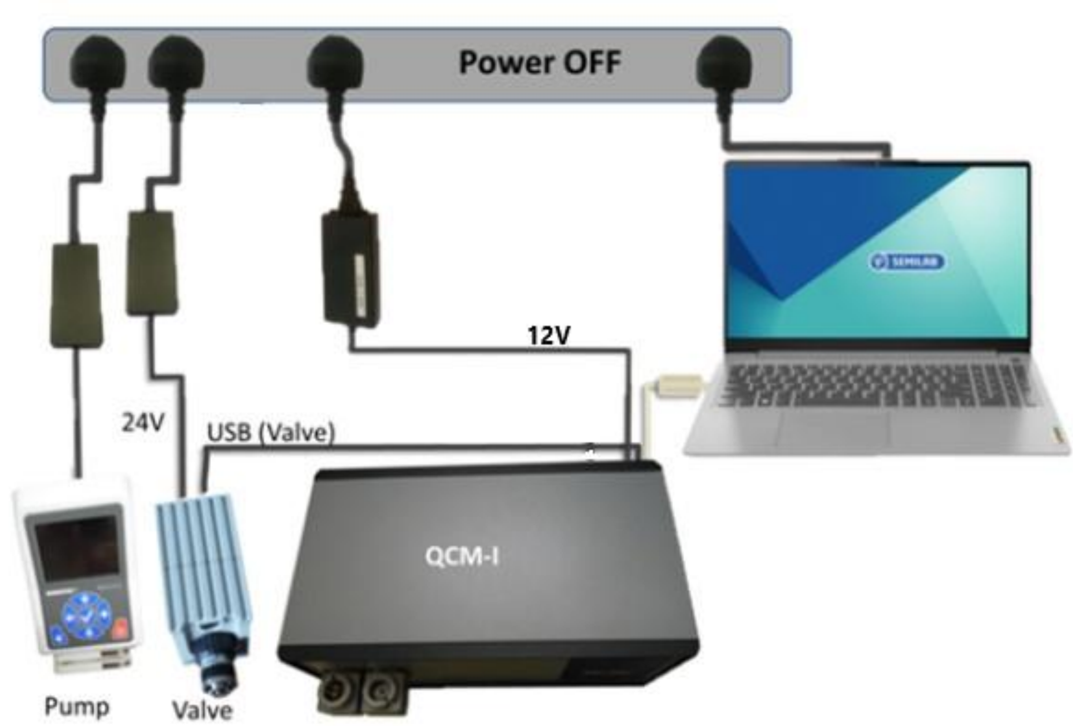


Figure 12: QCM-I with notebook schematic layout.

4.4 INSTRUMENT TESTING

Figure 8: MV-5MHz Dummy Sensor Holder

For learning to use the software or testing the instrument, you can use the dummy sensor module MV-5MHz instead of the flow-cell. The dummy sensor module contains a sealed, canned, 5MHz quartz crystal permanently mounted within it. Only 1, 3 and 5 overtones are available using this module.

4.5 eQCM-I INSTALLATION

The BioSense 3 software and QCM-I instrument can be upgraded to include an electrochemical module, BioSense EC 3. This can be done during a factory service or remotely by a service engineer with support from the Instrument Administrator using TeamViewer. Please see the *QCM-I Software Manual* for information about TeamViewer.

First install the QCM-I (detailed above). Next unpack and install the potentiostat, according to the manufacturers instructions. Connect it to the power supply and via USB to a USB port on the QCM-I computer or USB Hub provided. It can be connected to one of the USB ports on the QCM-I instrument, however in this case the instrument must be on to use the potentiostat, even if the QCM-I is not being used. If the potentiostat has not been preinstalled, the Manufacturer’s service engineer will configure the BioSense software and USB ports for the potentiostat.

After installation, when a compatible potentiostat is connected to the QCM-I computer, the BioSense 3 software will recognize it and the EC options will be displayed in the BioSense EC Software.

4.6 eQCM-I ELECTRODE CONNECTIONS

The electrical connections from the potentiostat to the eQCM-I are shown in Figure 94. Connect the working electrode directly via a 2 mm banana plug connector on the underside of the Channel B thermal chamber, shown in more detail in Figure 10. Connect the counter and reference electrode cables with the linking wires to the 1 mm pins of the RE and CE on top of the electrochemical flow cell sensor holder.

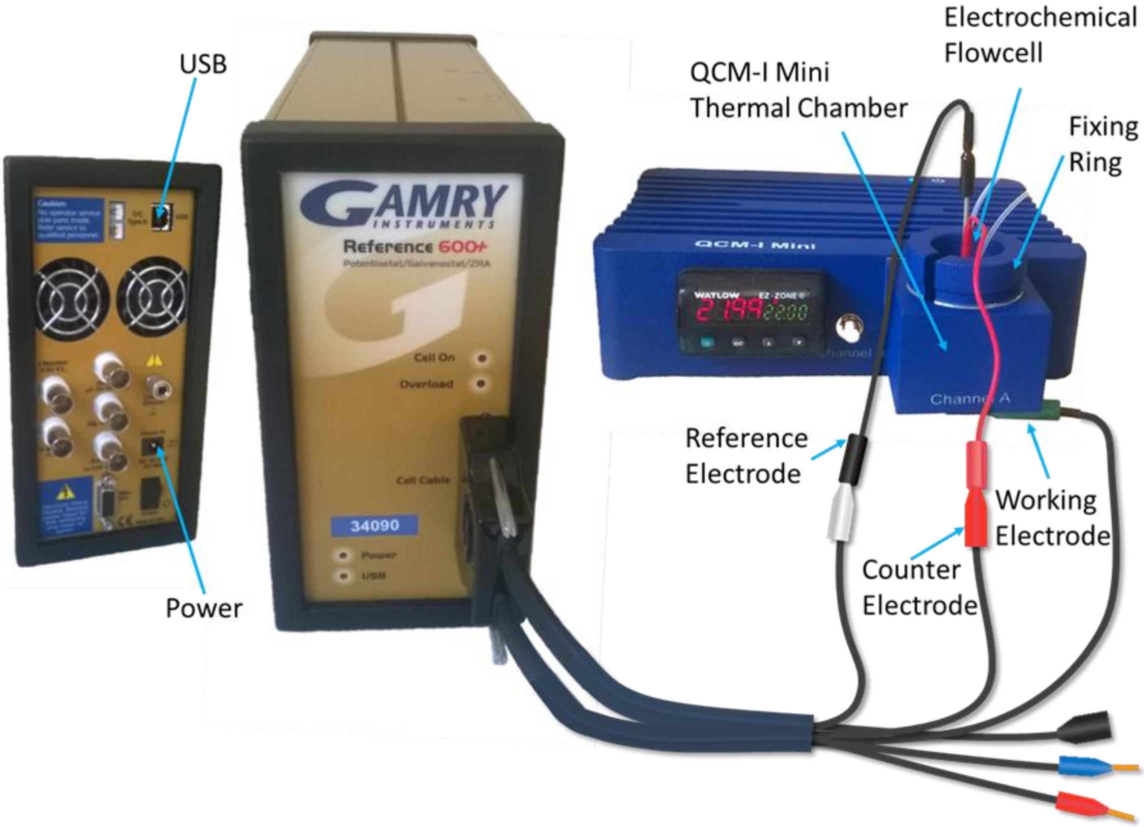


Figure 94: Gamry Potentiostat and QCM-I Mini schematic diagram, showing the Reference, counter and working electrode connections.

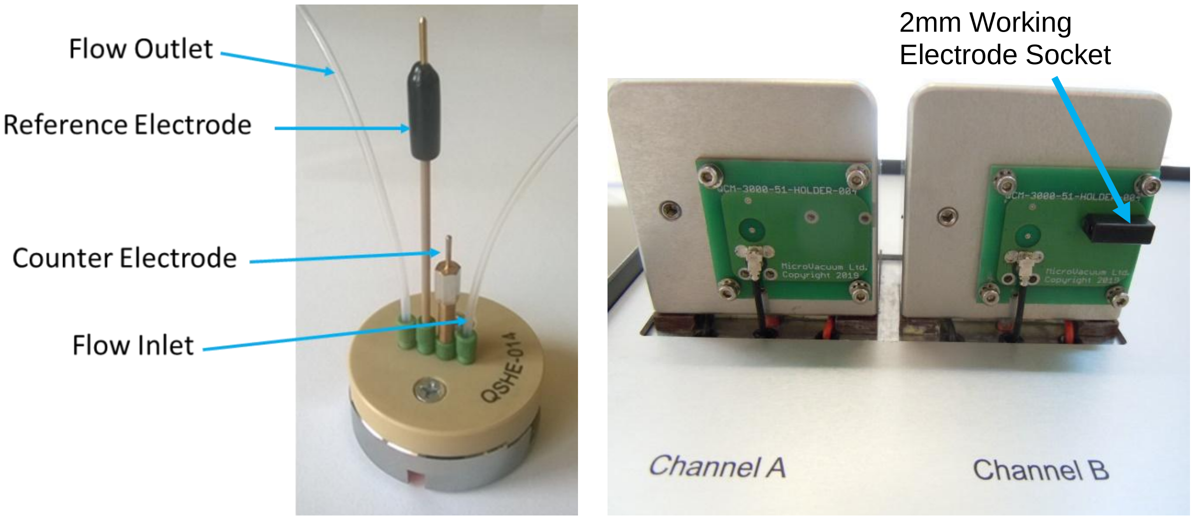


Figure 105: Electrochemical Flow-cell Sensor Holder, QSHE-014 (left) and underside of QCM-I thermal chambers showing the working electrode 2 mm banana connector socket on Channel B (right).

5. Temperature Control

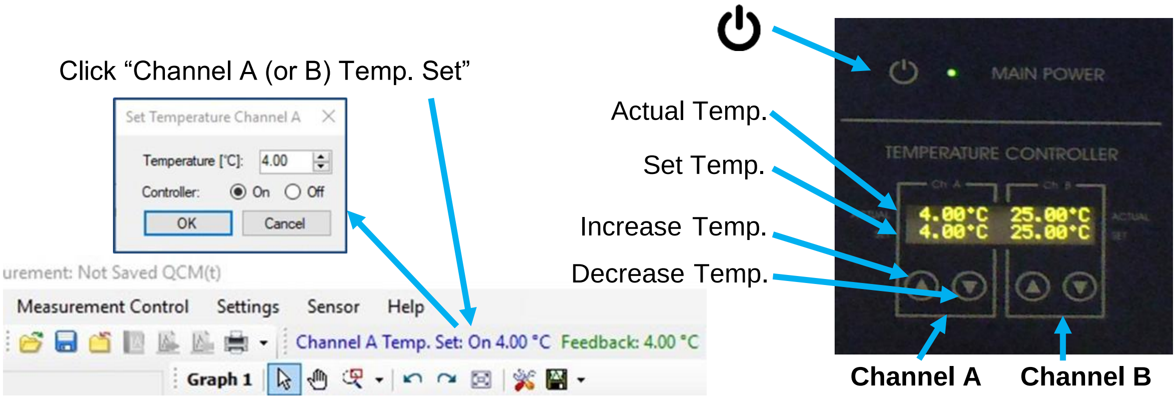
The sensor crystals themselves have little temperature sensitivity around room temperature due to their AT cut, however temperature changes can have significant impact on the QCM-I signal, which is why good temperature control is critical to the most stable measurements. In solution, the dominant effect is due to changes in the density and viscosity of the solution due to thermal expansion. In the vapor phase adsorption or desorption of water vapor from the sensor surface can also have a significant impact due to temperature dependent humidity changes.

The measuring heads (Channel A or B) of the QCM-I unit are heated/cooled by a Peltier device to a stability of better than ± 0.02 °C. They can be independently controlled to temperatures in the range 4–80 °C. The heating/cooling operation of the Peltier device is controlled by a temperature controller board built-into the QCM-I instrument.

The required temperature value can be set manually on the controller display panel, the measured temperature in the sensor holder block is displayed above and the set temperature below. The required temperature may be set by using the up and down arrows on the front panel.

The temperature setting for each channel can also be changed in the BioSense software, using the "Channel x Temp. Set" area of the task bar at the top of the BioSense window.

The temperature sensor (Pt100) is built into the measuring head. The temperature values measured by the Pt100 sensor are archived in the BioSense software database, together with the other measured experimental data.



Click "Channel A (or B) Temp. Set"

Set Temperature Channel A

Temperature [°C]: 4.00

Controller: ● On ○ Off

Channel A Temp. Set: On 4.00 °C Feedback: 4.00 °C

urement: Not Saved QCM(t)

Actual Temp.

Set Temp.

Increase Temp.

Decrease Temp.

Channel A **Channel B**

Figure 16: Software and manual temperature control options for the QCM-I.

Warning:

- **Take care if removing the sensor holder from the QCM-I thermal chamber after operating at elevated temperatures. It is recommended that you wait until the holder has reached ambient temperature before removing the sensor.**

6. Sensors

6.1 SENSORS

Geometry

Semilab offers QCM sensors with different geometries. The QCM-I is supplied with 14 mm 5 MHz sensors as standard, however the modular sensor-holders allow either 14 mm diameter or 1” diameter quartz crystals to be used with the QCM-I. The table below shows the geometry and electrode configuration of the 1” and 14 mm QCM sensors.

1”		14 mm	
TOP	BOTTOM	TOP	BOTTOM
			

Figure 17: 1” and 14 mm sensor crystal formats

The sensor parameters are given in Table 2.

Parameters	1”	14 mm
Nominal frequency	5050 ± 10 kHz	4950 ± 50 kHz
Crystal Cutting	AT	AT
Material	Pure Z quartz	Pure Z quartz
Angle	35° 15’ ± 30’	35° 15’ ± 30’
XX’ Angle	0° 00’ ±30’	0° 00’ ±30’
Diameter	25.4 ± 0.05 mm	14 mm
Electrode on the sensor side	Au or ITO	Au or ITO
Electrode on the contact side	Au or ITO	Au or ITO

Table 2: Sensor parameters

Electrode Materials

QCM sensors can be supplied with a range of electrode materials. These are available from stock:
Au (Cr or Ti adhesion layer),
ITO.

Au electrodes (100-1000 nm thick) are the most commonly used in QCM applications because of the ease with which gold is evaporated. A thin (2-20 nm) adhesion layer of either Cr, Ti or Si is often deposited directly on the quartz to aid in the adhesion of the metal electrode. Chromium is recommended for polished blank surfaces. Cr can be a problem in some electrochemical applications - spurious electrochemical responses can sometimes result if diffusion of the adhesion material to the electrode surface occurs. In that case Titanium is recommended as a substitute adhesive layer.

ITO sensor, transparent ITO electrodes are used providing a more stable electrochemical measurement and can be used for optical investigation as well.

Electrode Coatings

The QCM sensor electrodes can be coated with a non-conductive SiO_2 layer to emulate surfaces used in various applications.

6.2 SENSOR LIFE AND PERFORMANCE

Useful Life

Sensor crystals are reusable several times. However, reusing a crystal requires careful handling and cleaning procedures that do not harm the quartz material, the electrode pads and coatings. Some of the users consider their QCM crystals consumable items and discard them at the end of each experiment.

Some traces of consumption and wear can be detected visually:

- Edges of the sensor crystal might become cracked and the coating starts to show scratches and holes.
- In electrochemistry experiments it is not unusual to observe changes in the adhesion layer of the liquid surface electrode which ultimately result in peeling of the metal pad. A common problem is loss of the Cr adhesion layer in Au/Cr electrodes. These changes are visible from the contact side of the crystal.
- The liquid surface electrode might become irreversibly discolored or stained from chemical reaction with the analytes, buffers or solvent.

When a crystal is close to being consumed, the measurement signal will become noisy, possibly even shaky and it may be difficult to obtain a stable baseline. Contaminant peaks might become evident in electrochemical QCM experiments.

As the sensor crystal is coated, the FWHM often increases, with a corresponding a loss of Q. When this occurs, the circuit may occasionally resonate at one of the anharmonic frequencies. The oscillation may switch to an anharmonic mode, or it may alternate between the fundamental and anharmonic frequencies, a condition known as mode hopping. Notice that there is no outward evidence of mode hopping except for a discontinuity in the film thickness. Also, even though the film thickness changes dramatically, the mass sensitivity and rate of growth change by only a few percent.

Some experiments can cause irreversible changes to the crystal surface. Crystals exposed to etching solutions (i.e. Piranha solution) usually need to be replaced after two to three experiments.

Film stress can be particularly damaging. Stress can bend the crystal and induce a frequency change not related to mass. It can cause the electrode to tear from the quartz and, in the worst case, it can even cause the quartz itself to fracture.

Temperature Effects

QCM measurements are typically highly temperature sensitive due to a combination of different factors. The AT-cut quartz crystals used in QCM experiments have near zero temperature coefficients at room temperature. As a result, the intrinsic temperature dependence of the QCM sensor crystals is negligible at or around room temperature (~1-3 Hz/°C) and can often be ignored for monolayer adsorption/desorption processes in the gas phase. However, depending on the sensor coating, larger temperature dependent changes can be observed in ambient conditions due to changes in relative humidity with temperature causing adsorption or desorption of water vapor from the atmosphere.

For QCM sensors immersed in liquids, larger changes in frequency with temperature are expected. This is due to temperature dependent changes in the viscosity and density of the fluid. The temperature coefficient due to this effect is ~ -8 Hz/ºC for a 5 MHz crystal in water. As a result, for experiments in the liquid phase in which the frequency is to be monitored over an extended period of time, the temperature must be controlled to at least 0.1 °C, and preferably better. When samples are introduced thermal differences in the sample will be evident. This is also the case when, for example, the flow rate is changed or interrupted in a setup with continuous flow of running buffer.

Careful control of the temperature is required in high accuracy measurements to avoid frequency hysteresis effects - the dependence of resonator frequency at a specific temperature on its prior temperature history. For example, the frequency-vs-temperature curve obtained increasing the temperature by a few degrees will not coincide with one obtained immediately afterwards decreasing the temperature back to the original temperature. There are several potential causes of hysteresis such as changes in the strain of the mounted crystal, changes in the quartz, redistribution of contamination/water vapor in the crystal enclosure, and apparent hysteresis or retrace due to thermal gradients.

Each individual QCM user must determine the effect of temperature on the experiments being performed and control the temperature accordingly.

The most relevant static temperature coefficients for 5 MHz QCM crystals around room temperature are listed below:

- Temperature coefficient in air -1 to -3 Hz/°C
- Temperature coefficient in water -8 Hz/°C

Note

- **Temperature stabilization of flow cells better than ± 0.1 °C is generally required to eliminate temperature related transients and drifts in lengthy measurements.**

6.3 SENSOR HANDLING

Please follow these instructions about general handling of sensor crystals.

- Keep the crystals in a clean and dry place. When not in use store them in their original box and wrapper.
- Avoid touching the metal electrodes of the crystal.
- Rinse only with deionized water, or another appropriate residue-free solvent, before drying the crystal.
- Always use a flow of dry, oil-free, inert gas (e.g. nitrogen) to blow-dry the crystal. It is better to blow the liquid off the crystal than to let it evaporate on the electrodes.
- Do not handle the sensor crystal using bare fingers. Hold the sensor crystal with tweezers and only from its outer edge (outside the electrode area) to prevent scratches. The tweezers should have smooth gripping surfaces and preferably be made out of soft plastic material.
- Before starting a surface cleaning process confirm that the sensor materials will not be damaged by the cleaning solutions. Perform a test run on a practice crystal whenever possible.

For liquid treatment or cleaning processes a sensor holder basket can be used, which enables multiple sensors to be dipped into beakers of solution; shown in Figure .

Figure 18: Sensor cleaning and modification basket

6.4 SENSOR CLEANING

In order to ensure reproducible results, sensors should be treated in a consistent way before each experiment. For sensors coated with hard surfaces this usually involves cleaning immediately prior to use. For sensors which are going to be re-used, some cleaning steps can be started with the sensor still in the QCM-I to monitor removal of material deposited during the previous experiment. The cleaning steps required will also depend on whether the sensors are nominally clean or have been previously used and have been coated or contaminated by the experiment.

The QCM sensor itself can be used to measure the most suitable cleaning method for the experiments being undertaken. This also applies to experiments where the surface can be regenerated and reused several times during the course of a single experiment.

Several cleaning processes are described below. However, the user should determine the most suitable method for their application. A typical procedure may involve using several processes to remove all the contaminant material from the surface and re-generate a standard and reproducible surface condition e.g.:

1. Detergent clean,
2. Basic piranha,
3. UVO clean immediately before use.

Where sensors are transferred between different liquids they should not normally be dried in-between, as that can cause the deposition of residue or “drying marks”. Drying sensors is most effectively done with a stream of oil-free nitrogen, blowing the drop away from the sensor surface.

- **Safety: Solution cleaning steps often involve hazardous chemicals and should be undertaken by trained personnel, using the correct personal protective equipment and after carrying out an appropriate risk assessment with regard to local regulation on the safe handling and disposal of the materials.**

UV-Ozone Cleaning

This is a recommended cleaning method for most sensors, where the sensor surface is not detrimentally affected by oxidation (e.g. not for Ag or polymer surfaces). The method is suitable as an intermediate step on contaminated surfaces and as a final cleaning step for nominally clean sensors; it removes small amounts of organic contamination by exposure to UV light and the ozone created in the process. The process leaves the sensor surface hydrophilic, typically with a low water contact angle. Commercial UVO cleaners are available; please contact Semilab. for more information. This is not suitable for removing large amounts of contamination, for which a solution based clean or O_2 plasma cleaning is more appropriate.

- **Safety: Consult the UVO cleaner information before use. Typically it should be located in a well ventilated area, preferably in a fume hood to prevent inhalation of ozone.**

Method:

1. Rinse sensor in ultrapure water and high purity 2-propanol (without allowing to dry in-between) followed by blowing dry with oil-free N_2.
2. Place sensor in UVO cleaner with the sensing side up/ exposed to the UV light.
3. Turn on UVO cleaner for 10-15 minutes.
4. Rinse sensor in ultrapure water and dry with N_2 for storage, or place in QCM-I instrument for immediate use.

SiO_2 coated sensors will change contact angle as a function of time after UVO cleaning. For a minimum contact angle, the sensor surface should be immersed in water immediately after cleaning.

Basic Piranha

Basic piranha solution is used to remove organic and biological material from a surface by oxidative degradation and dissolution.

- **Safety: This cleaning step should be performed in a fume hood. The solution is very aggressive and should only be used by trained personnel after completion of the appropriate risk assessments etc. Protective clothing should be worn, such as laboratory coat, gloves and eye protection.**

1. Prepare cleaning solution by mixing High purity water 5:1:1 with ammonia (25%) and hydrogen peroxide (30%). A minimum quantity should be prepared, e.g. 10 ml.
2. Heat the solution to 75°C and immerse the sensor for 5 minutes.
3. Rinse sensor well with ultrapure water (without allowing to dry in-between) and dry by blowing with oil-free N_2.

Acid Piranha

Acid piranha solution is a highly effective method used to remove organic and biological material from a surface by oxidative degradation and dissolution. However, due to the aggressive nature of the reagents should not be the first method to try.

- **Safety: This cleaning step must be performed in a fume hood. The solution becomes very hot on mixing and is very aggressive and can be explosive if mixed with organic materials or solutions. It should only be used by trained personnel after completion of the appropriate risk assessments etc. Protective clothing should be worn, such as laboratory coat, rubber apron, gloves and eye protection. The solution should not be stored, but disposed of according to local advice once cooled after use.**

1. Immediately before use prepare the piranha solution by carefully adding 30% hydrogen peroxide 1: 3 to conc. Sulfuric acid. A minimum quantity should be prepared, e.g. 5-10ml. The solution becomes very hot on mixing and can exceed 100 °C.
2. Immerse the sensor for 5 minutes or pipette the mixture onto the sensor surface in a petri dish.
3. Rinse sensor very well with ultrapure water (without allowing to dry in-between). The cleaning solution is viscous and so will need copious rinsing to remove fully.
4. Dry by blowing with oil-free N_2.

Detergent

Detergents remove material by solubilization of hydrophobic material from the surface into aqueous phase. 2% Sodium Dodecyl Sulfate is most commonly used as a gentle detergent, 2% Hellmanex II is also often used and may slowly etch the surface of SiO_2 coated sensors. After immersion in detergent and rinsing, small amounts of material may also remain associated with the surface. This may require extended rinsing, which can be particularly relevant where e.g. SDS is used to clean and regenerate a surface during an experiment in high purity water. In this case ethanol or 0.1 M HCl and/or 0.1 M NaOH can be briefly added to displace material that is electrostatically bound to the surface followed by rinsing with water.

1. Rinse sensor in ultrapure water.
2. Soak in 2% SDS for 30 minutes.
3. Rinse with ultrapure water.
4. Soak in 0.1M HCl for 5 minutes.
5. Rinse with ultrapure water.
6. Blow dry with oil-free N_2.

Other Cleaning Methods

Sensors can be very effectively cleaned with an Oxygen plasma, using the appropriate plasma generating vacuum equipment. This will remove more substantial layer of contamination than the UVO method.

Sensors can also be soaked in and briefly sonicated (30 s) in a range of organic solvents, such as acetone or ethanol.

Some materials that are bound to the sensor surface with electrostatic interactions can be very effectively removed with rinsing in alternate HCl (1 M) and NaOH (1 M) solutions, however extended immersion in NaOH will damage the quartz crystal surface.

7. Flow Cell Assembly

7.1 STANDARD FLOW CELL ASSEMBLY

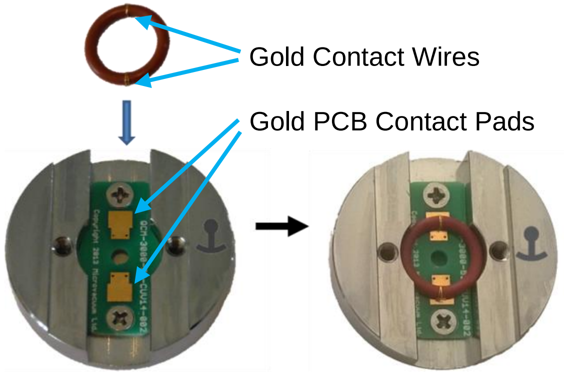
A quartz crystal sensor can be loaded for use in a flow-cell sensor holder and mounted in a thermal chamber in the QCM-I instrument, see Figure .

For software training or instrument testing, load the can-mounted test sensor MV-5MHz into the Channel A thermal chamber, instead of the fluidic cell shown in Figure .

To load a sensor crystal into the flow-cell, follow the sequence shown below:

Step 1: Place Red O-ring in Holder.

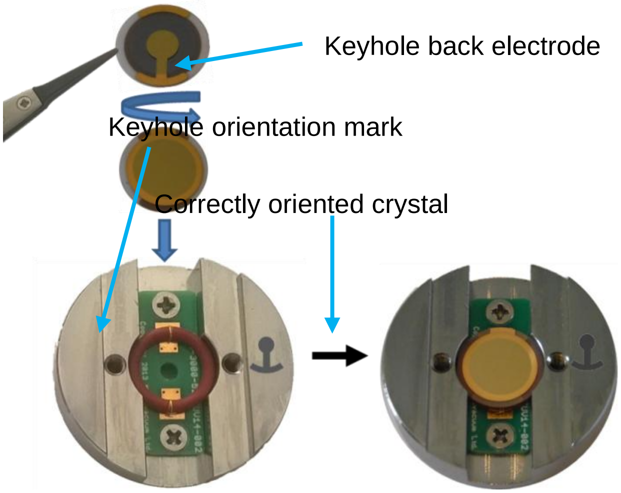
Ensure that the wound gold contact wires on the lower red O-ring are intact and place the O-ring into the flow-cell sensor holder base. Make sure the gold wires are aligned to the gold contact pads on the PCB.



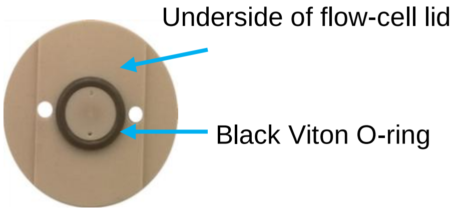
Step 2: Mount the Sensor

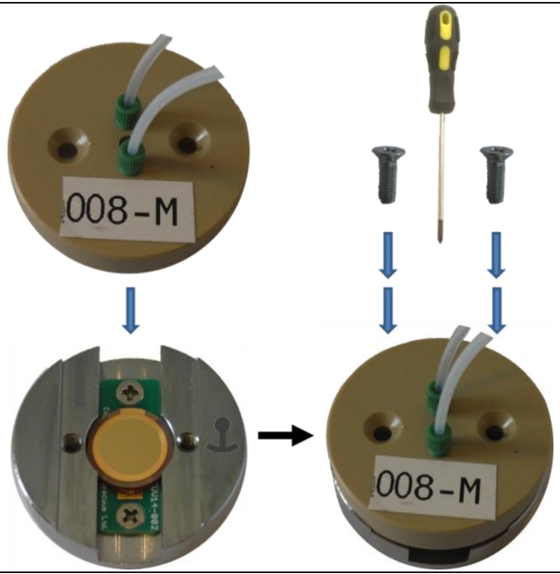
The crystal is fragile. Handle it gently using only plastic tipped tweezers. Take particular care not to touch or damage the electrode surface in the centre of the crystal which is the sensing region.

The orientation mark on the holder or PCB shows the correct orientation of the keyhole shaped electrode on the back of the sensor when it is mounted.



Step 3: Attach Flow-cell Lid





Make sure that the black O-ring in the PEEK flow-cell lid is clean, sits flat and is not damaged.

Place the PEEK flow-cell lid onto the holder base.

Tighten the screws alternately, to ensure that the O-rings are uniformly compressed onto the crystal.

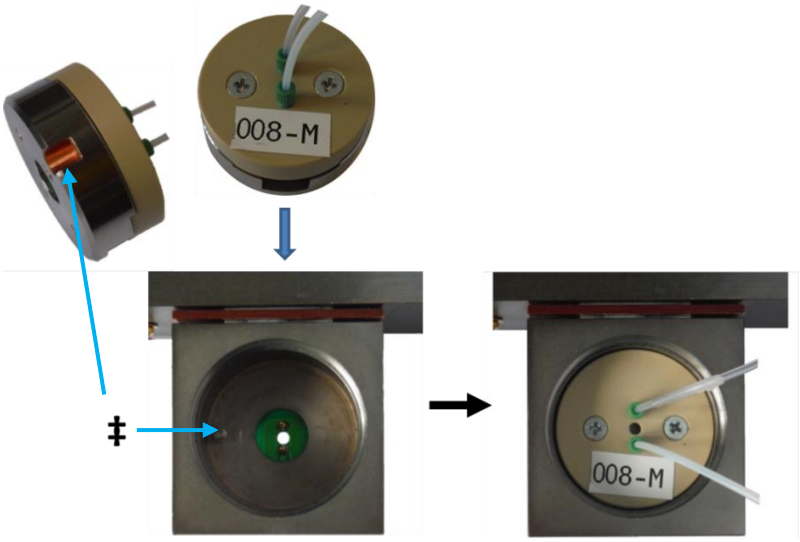
Figure 19: Mounting a sensor in the flow cell.

After mounting the sensor crystal in the flow-cell, it can be loaded into one of the thermal chambers in the QCM-I (Channel A or B), as shown in Figure .

Step 4: Place Flow-cell in Thermal Chamber

There is a notch in the underside of the flow-cell, which locates on a pin in the chamber, shown by **‡**.

Make sure the flow-cell sits down over the pin.



Step 5: Screw Down Fixing Ring

Place the fixing ring on top of the thermal chamber and screw it down to firmly clamp the flow-cell in the instrument.

If required, make fluidic connections to the flow-cell.

As supplied, connections comprise a luer fitting for a sample or waste syringe and tubing.

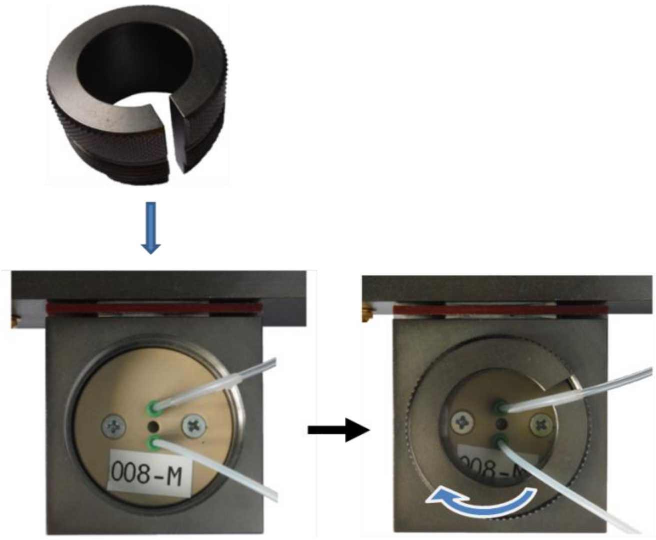


Figure 20: Mounting the Flow-cell in the QCM-I thermal chamber.

Once mounted in the thermal chamber, the flow-cell needs 5 to 10 minutes to reach the set temperature. Start the QCM measurement after the temperature has stabilized.

Alternatively, a sensor can be loaded into one of various external sensor holder accessories and connected to the instrument with an external holder adapter (see accessories section).

7.2 ELECTROCHEMICAL FLOW CELL ASSEMBLY

The electrochemical flow cell is assembled in the same way as the standard flow-cell, summarised below.

- (!) Ensure that the gold contact wires on the O-ring are aligned with the contact pads on the sensor holder base.
- (*) Orient the QCM Sensor so that the keyhole pattern of the back electrode matches the pattern on the PCB base.
- Tighten the screws alternately until fully closed.

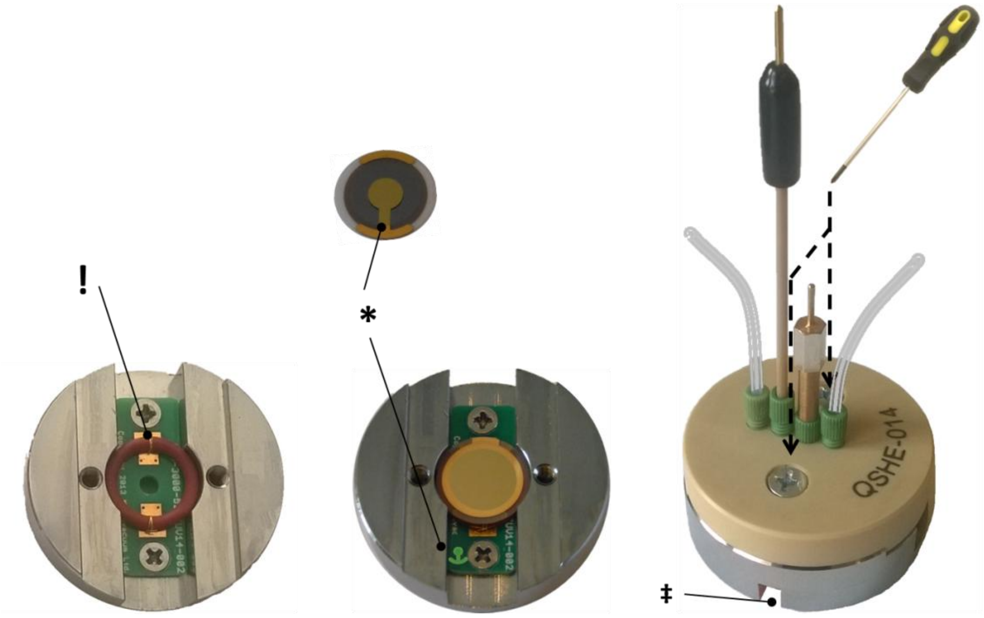


Figure 11: Electrochemistry Flow-Cell Assembly

The flow cell is also loaded into the QCM-I thermal chamber in the same way as for the standard flow cell. The notch on the base (‡) locates onto the pin in the base of the chamber and, as for the standard flow-cell, is held in place with the screw-in fixing ring. See Figure 19: Mounting a sensor in the flow cell.

After fixing in place into the QCM-I thermal chamber, the flow cell can be filled with liquid and should be allowed to stabilise for ~ 10 minutes.

When filling the flow cell, take care to flush the cell completely to ensure that there are no bubbles trapped in the outlet, so that there is a good electrical contact to the reference electrode.

8. Flow-cell Fluidic Configurations

The QCM-I flow-cell can be used with a variety of fluidic arrangements, depending on the application requirement. This section describes some of the configurations for the standard flow-cell supplied with each instrument. For each application consider the buffer solution and sample introduction requirements. You can change the tubing length and bore to accommodate the samples and buffers needed. For example, you may need to use wider bore tubing for more viscous samples. The flow rate used for sample exchange will also affect the pressure exerted on the sensor and may cause effects on the frequency measurement. For samples with large density differences from the running buffer gravity driven mixing can also have a significant effect. This is more pronounced with 0.75 mm ID and larger bore tubing than with 0.5 mm ID or lower.

8.1 PREPARING SOLUTIONS

The QCM-I signal can be affected by artefacts caused by the solution, such as changes in temperature, bubbles, solution composition.

Before introducing buffer or other liquids into the flow cell, ensure that they are suitable for the experiment. Usually they are of high purity, free of particulates, degassed and thermally equilibrated at the correct temperature for the experiment. The injector valve has a narrow bore and is not suitable for samples with highly viscosity, containing particulates or polymerizing materials.

One way to reduce the likelihood of bubble formation in the sensor chamber is to degas solutions before use; this is particularly important if the measurement is performed at elevated temperatures. Another method is to set the temperature of the QCM-I just below room temperature. This works because the solubility of gas in liquids increases as the temperature is lowered. Be aware that samples that are stored at low temperatures may have an excess of gas dissolved in them. Solutions should also be equilibrated to close to the QCM-I set temperature before introduction if possible to reduce changes due to thermal fluctuations.

8.2 STANDARD FLUIDIC CONFIGURATION

The standard QCM-I sample and flow setup is shown in Figure 12. In the simplest case shown on Channel B, buffer solution or the sample, is sucked up directly from the sample vial into the flow-cell, controlled by starting and stopping the pump. Alternatively, shown on Channel A, running buffer is sucked continuously from a buffer reservoir through the injection valve into the flow cell. The sample is loaded onto the fixed volume injection loop of the injection valve and injected during continuous buffer flow, controlled by the software; c.f. QCM-I Software Manual. More details on the how to operate the fluidic setup are given in the following sections, as well as in the Peristaltic Pump and Valve Manuals.

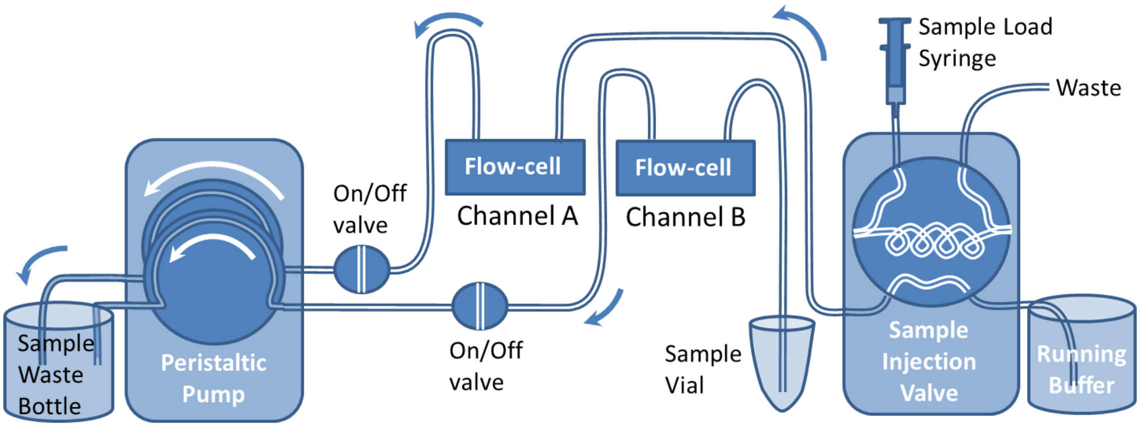


Figure 12: QCM-I Sample and flow setup.

8.3 PERISTALTIC PUMP

To make measurements where transport of material to the sensor surface may be a limiting factor, a peristaltic or syringe pump can be used to provide a well-defined and constant flow. Syringe pumps are typically used to push solution through the flow-cell and peristaltic pumps to suck the solution through. Most conventionally a peristaltic pump is used for QCM-I experiments as they can run continuously without having to be changed or refilled. The peristaltic pump supplied is able to set different flow rates and flow directions on the different fluidic channels.

By sucking the solution through, there is less chance of running buffer or sample leaking out of the fluidic system. However, if the tubing is long, the inlet is narrow bore, or the flow rate is high, there is an increased chance of forming bubbles in the fluidic line. This can be mitigated by ensuring that the solutions are degassed before use.

An On/Off valve between the pump and the flow-cell can be used if the flow needs to be stopped for an extended period during an experiment to ensure that there is no low level of residual flow/ syphoning (not generally an issue with a good quality pump) and means that the peristaltic tubing can be unclamped when not in use which will extend its operational lifetime.

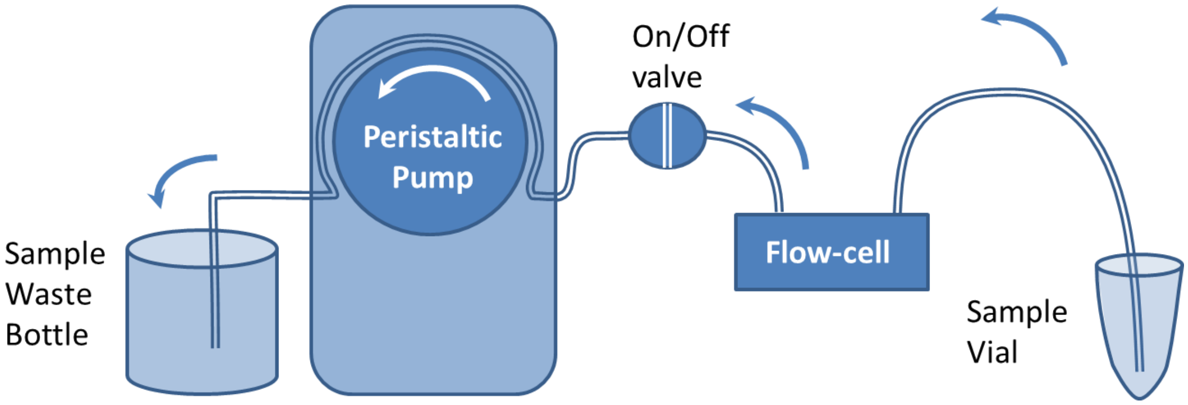


Figure 23: Schematic Diagram for sample introduction controlled by peristaltic pump.

Basic Peristaltic Pump Operation

For full instructions on operation of the Peristaltic pump, please refer to the peristaltic pump manual.

To introduce a running buffer into a flow cell:

1. With the whole fluidic path connected, place the inlet tube to the flow-cell (or injector valve) into the buffer.
2. With the cassette for the fluidic channel mounted on the peristaltic pump press down to close.

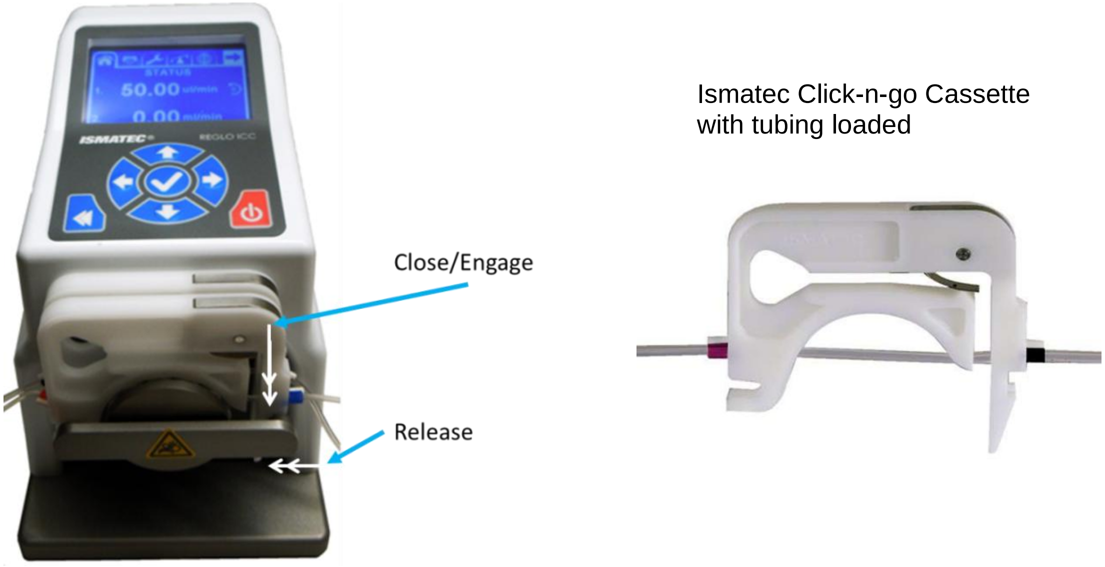


Figure 24: Peristaltic Pump and Tubing Cassette

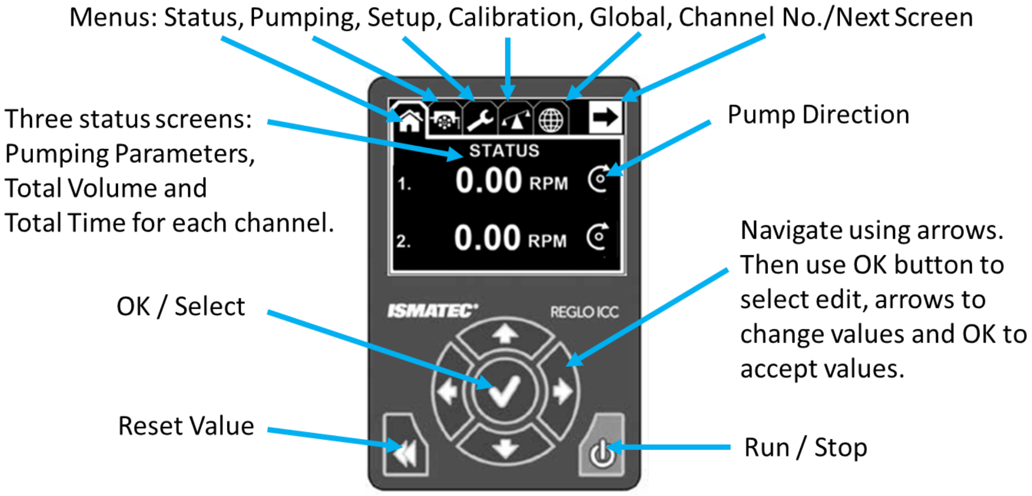


Figure 13: Ismatec Reglo ICC Peristaltic Pump Controlls

3. Open the on/off in-line valve.
4. Navigate to the Setup Menu on the pump and verify the correct tubing diameter is set (standard is 0.76 mm).

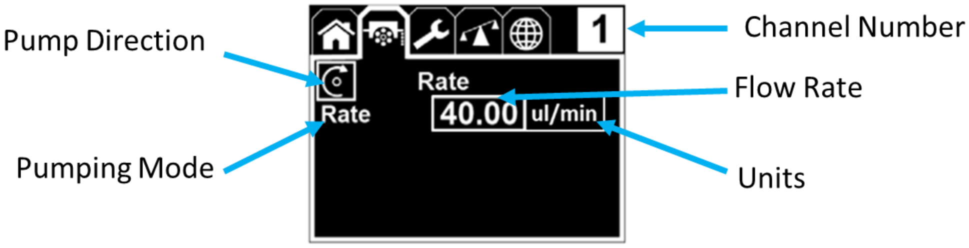


Figure 146: Pumping Menu

5. Navigate to the Pumping Menu and Set the Mode to “Rate”. Set the units to ul/min, the flow rate to 50-100 ul/min and pump direction so that the pump sucks the solution through the flow-cell – Anti-clockwise for the setup in Figure 12.

6. Start pump by pressing the Run/Stop button. The solution front can be seen travelling from the buffer reservoir, through the transparent tubing into and out of the flow-cell.
7. Sample can be introduced either with the injection valve (see below) or by stopping the pump, moving the inlet tube into a sample vial and restarting the pump. The pump can be reversed to remove bubbles inadvertently introduced into the tubing, or to return the sample to the sample vial. The Reglo ICC pump can set a different flow rate and direction for each fluidic channel.
8. At the end of operation the tubing should be rinsed, the on/off valve closed and the cassette released to prolong the life of the peristaltic tubing.

8.4 SAMPLE INJECTION VALVE

Samples can be introduced to the flow-cell using the 10-port sample injection valve, controlled by the BioSense software. The injection valve is typically used to introduce fixed volume samples of constant concentration under continuous flow conditions. By using a sample injection valve, you can inject multiple samples in a very reproducible way. It also reduces any effect of temperature fluctuations due to changes in flow rate on sample introduction. In this setup the sample inlet tubing is often a smaller bore than the outlet tubing to reduce the swept volume before the sample reaches the flow-cell. This maximizes the sharpness of the buffer to sample transition during sample introduction and wash-out. If the sharpness of buffer to sample exchange during wash-out is important, then the injection valve should also be switched back to load before the whole loop volume is injected, as the buffer flowing into the sample loop will dilute the sample towards the end of the injection.

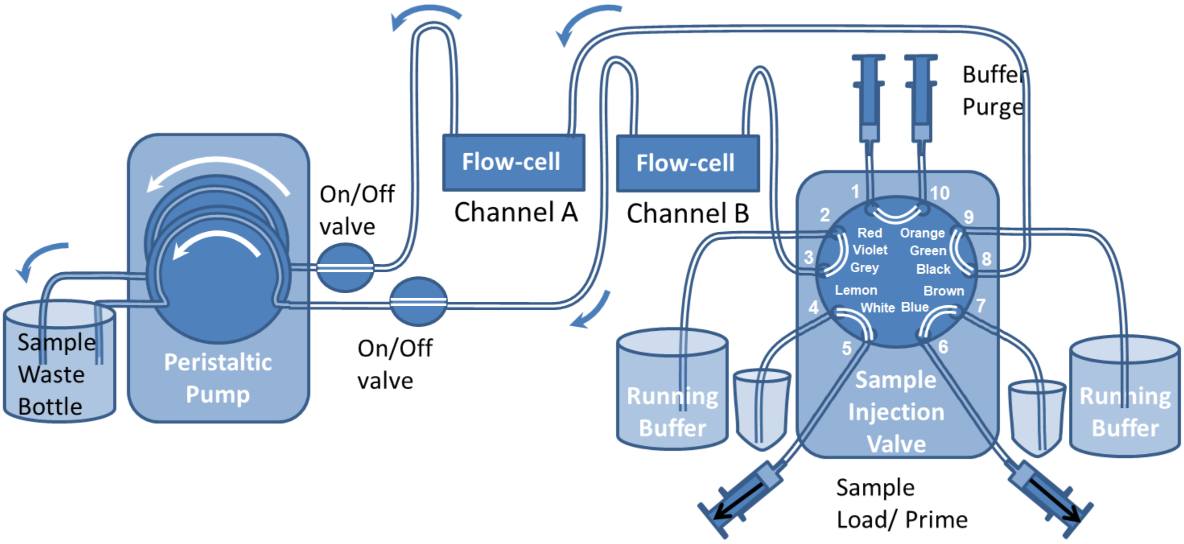


Figure 157: Schematic Diagram for fixed volume sample injection under continuous flow.

The fluidic connections in the injection valve are shown schematically in Figure for Load and Inject positions. In the load position sample can be loaded onto the sample loop, ready for injection into the fluid flow path.

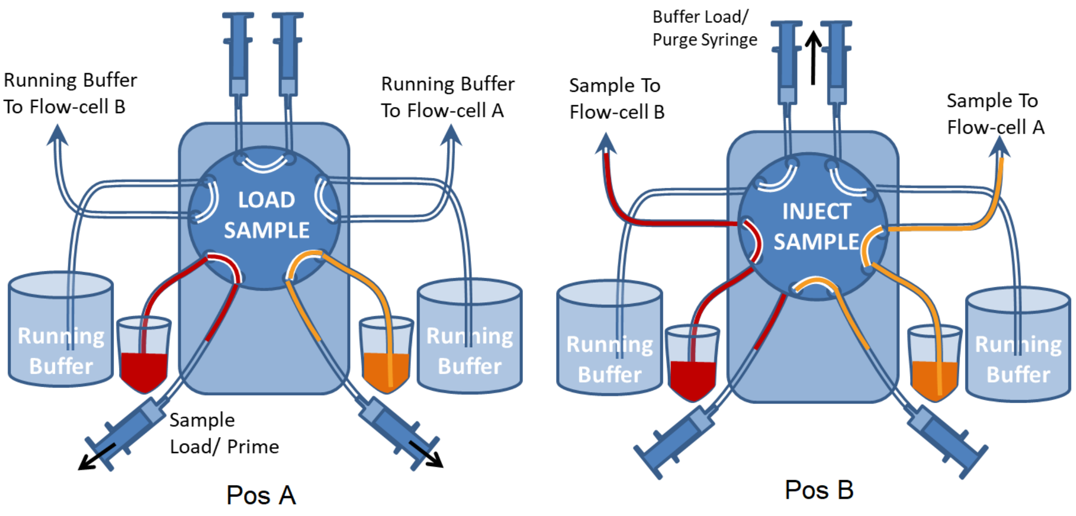


Figure 28: Schematic Diagram for Injection Valve in Load and Inject Positions.

"load sample onto the loop" and "inject sample into the flow-cell".

After sample injection, when the valve is returned to the Load position, the sample loop must be thoroughly washed/ rinsed so that all the previous sample is removed and cannot contaminate the next sample injection.

Injection Valve Operation

The injection valve is shown in Figure 29. It can be operated from the software when remote operation is turned on (remote light on), or manually when remote operation is turned off. The status of the valve is shown on the valve: 1 = Load, 2 = Inject.

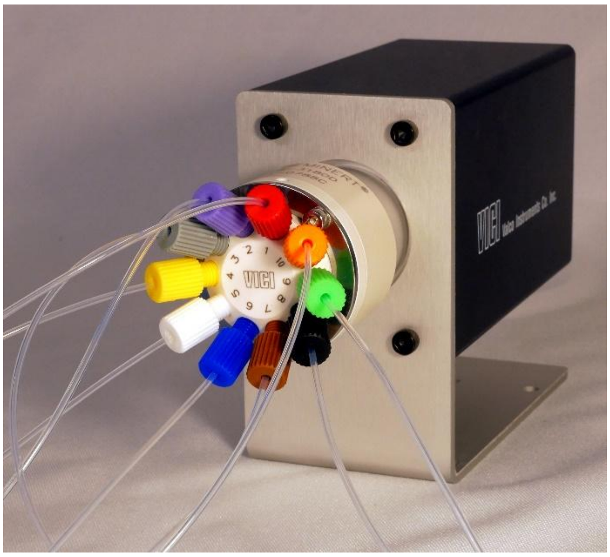


Figure 16: Injection Valve

Load sample onto the valve through the needle port, using a blunt tip syringe.

8.5 ALTERNATIVE FLUIDIC SETUPS

Manual Static Cell

Whilst it is not recommended due to lack of control, the QCM-I fluidic system can be operated without a pump or injection valve, but using a luer fitting for a syringe and an on/off valve. The syringe can be used to manually suck or push sample through the flow cell. When sucking the sample through, the open ended inlet tubing can be dipped into the sample vial and is a good way of drawing sample into the flow-cell without air bubbles and to ensure a clean sample to sample transition. Measurements are performed in a static mode where solutions are exchanged and then allowed to remain stationary on the sensor surface for the measurement. This will affect the sample adsorption characteristics where sample concentrations are low and mass transport to the sensor surface is also slow. An On/Off valve just before the syringe is used to prevent the sample from flowing when the syringe is not being used or whilst it is being emptied.

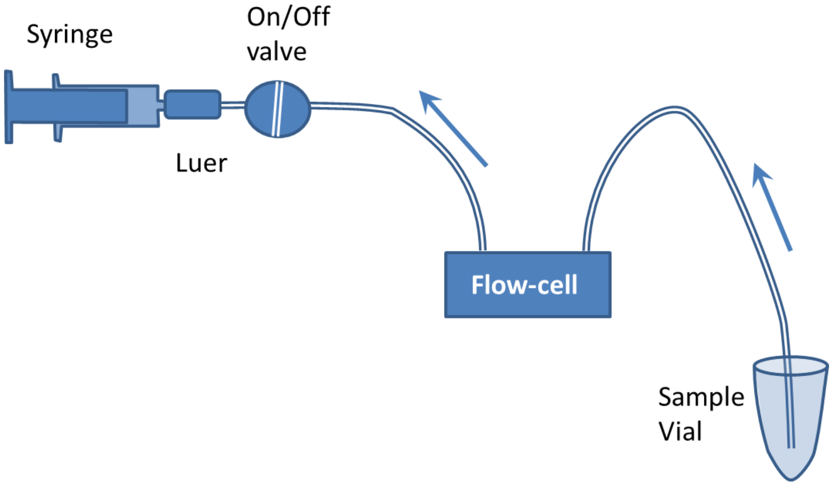


Figure 30: Schematic Diagram for a basic fluidic path for static flow-cell measurements.

An alternative arrangement is to use the syringe to prime the fluidic system and then turn the valve off and remove the syringe. The sample vial can then be placed higher than the luer fitting on the outlet and the valve can be used to control the flow of the sample through the cell under the force of gravity with a syphon as shown in Figure . This reduces the pressure effects of manually sucking with the syringe at too high a rate.

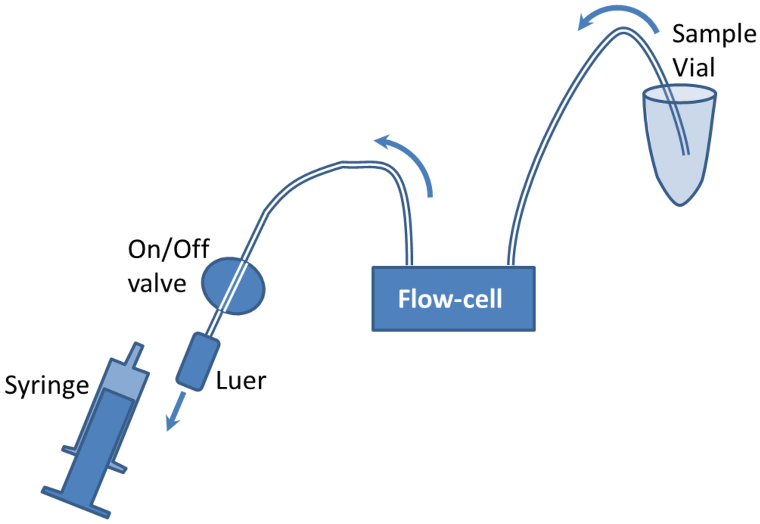


Figure 31: Schematic Diagram for a basic fluidic path for static flow-cell measurements.

Alternatively, the syringe without plunger can be used as a funnel for the sample to flow through the system in a gravity fed arrangement.

Peristaltic Pump and Selector Valve

Adding a selector valve to the standard configuration instead of an Injection valve means that different samples can be introduced automatically by switching between different sample vials. This allows e.g. the deposition of alternate multilayers with buffer rinse in-between. The samples can be switch under continuous flow conditions. The sample tubing and selector valve can be primed for each sample with a manual syringe before the start of the experiment as shown in Figure 32.

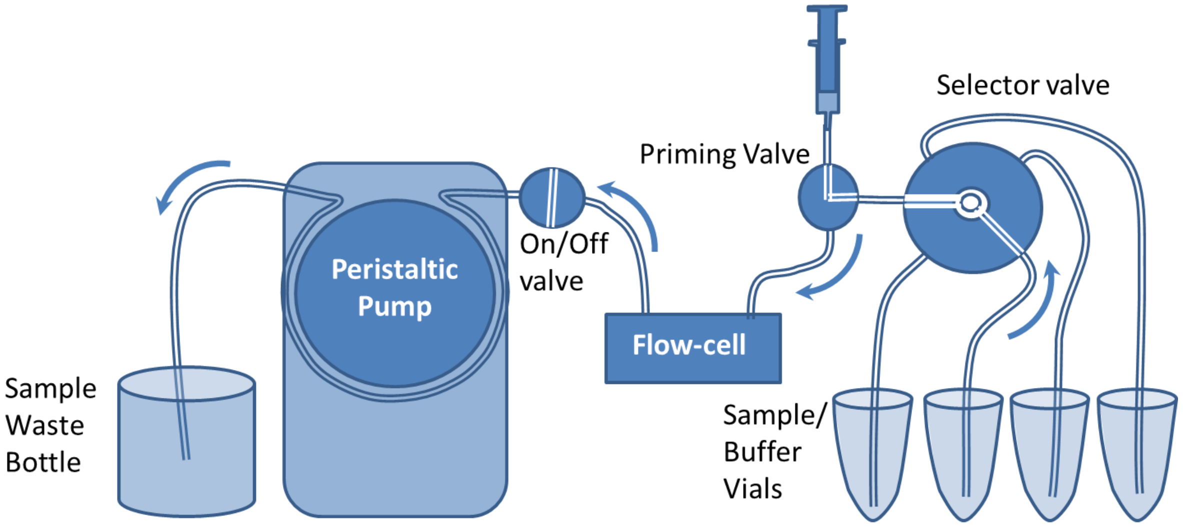


Figure 17: Schematic Diagram for multiple sample introduction using a selector valve.

9. Sensor Holders, Adaptors and Modules

9.1 HOLDERS AND ACCESSORIES FOR THERMAL CHAMBER

Standard Flow Cell

Part. No. QSH-014

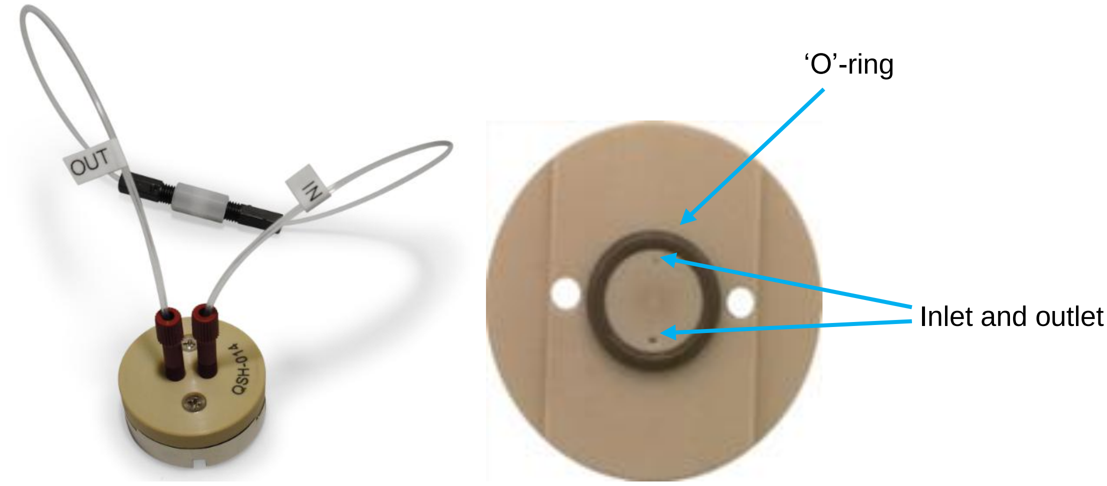


Figure 18: Flow Cell, assembled (left) and underside of PEEK flow-cell lid showing sealing 'O'-ring with inlet and outlet holes (right).

Dummy Sensor Module

Part. No. MV-5MHz

Figure 34: 5 MHz Dummy Sensor Module with alignment notch for Channel A thermal chamber.

The dummy sensor module contains a sealed canned crystal permanently mounted within it and can be used in channel A to produce a dummy signal for instrument test or training purposes. Only the fundamental, 3rd and 5th overtone frequencies are available with this module.

Calibration Kit

Part. No. MV-calkit

Figure 19: RF Calibration Kit for QCM-I Instruments.

The calibration kit is used to calibrate the line impedance of the QCM-I channels and is available for use by the system Administrator.

Electrochemical Flow Cell

Part No.: QSHE-014

The electrochemical flow-cell is shown schematically below in Figure 36. The Counter Electrode (CE) is a Pt disc above the QCM sensor Working Electrode (WE). The Reference Electrode (RE) is a Leak-free Ag/AgCl microelectrode situated in the exit flow path.

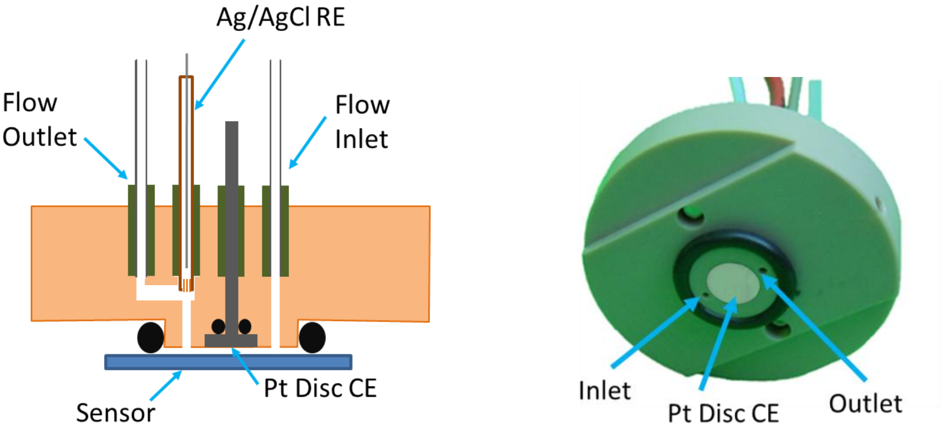


Figure 20: Schematic Diagram of the Electrochemical Flow Cell (left) and underside of flow cell lid (right).

Ag/AgCl Reference Electrode

Part No.: A11025425 (Innovative Instruments LF-1.6-48)

The Ag/AgCl leak-free reference electrode should be stored in aqueous solution. When it is not in use, screw the upper part of the flow cell onto the storage cup and fill it with aqueous 0.05-0.1 M H_2SO_4 in ~0.5M KCl solution. Seal the inlet and outlet tubing to prevent the solution from evaporating. If the electrode has been left dry it can recover after immersion in water.

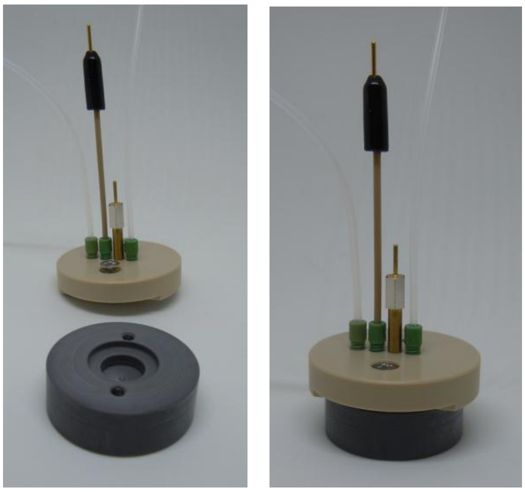


Figure 21: Electrochemical flow-cell lid with reference electrode and storage base.

According to the manufacturer’s recommendation (Innovative Instruments Inc. https://www.2in.com/), the electrode can be tested in the following ways:

- By measuring the conductivity of the reference electrode. This can be done in the storage holder in 1M KCl with an ionic conductivity meter or approximately with a digital volt meter and should be < 30 kOhm.
- The potential of the reference electrode should be within 20 mV of that of a Standard Ag/AgCl/KCl reference electrode and in any case within 50mV and corresponds to an intact electrode structure.

External Sensor-Holder Adaptor

Part. No. MV-QSH-Ext

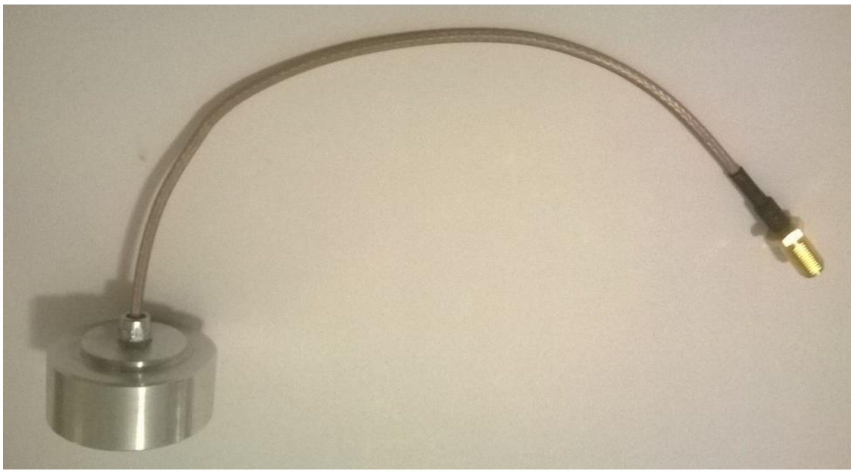


Figure 38: External Sensor-holder adaptor.

The external sensor-holder adaptor fits into the QCM-I thermal chambers (see section 7.1, step 4 and 5) and enables an external sensor holder to be attached to it. For both channels, the outer is grounded to the QCM-I case. A variety of external sensor-holders are available for different applications.

9.2 EXTERNAL SENSOR HOLDERS

Immersion and Open Sensor Holder

Part. No. QSH-dip

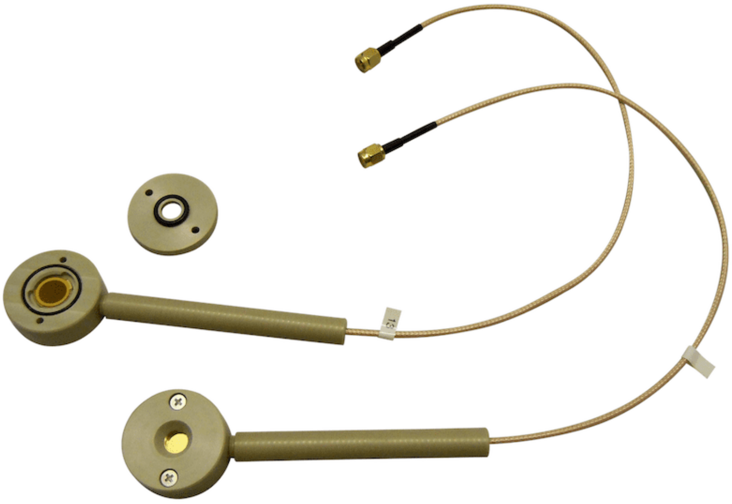


Figure 39: External Open Holder or Immersion Holder.

The external immersion sensor-holder exposes the sensing side of the crystal and is otherwise sealed, so that it can be immersed into a beaker of liquid, or can be used flat and filled with a small volume of solution.

High Pressure Sensor Holder

Part. No. QSH-HT-HP

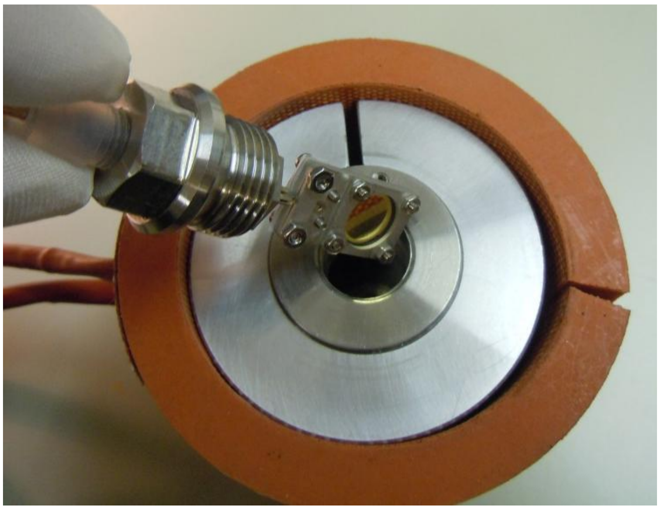


Figure 220: High temperature and pressure, heated chamber for liquids or gasses.

The high pressure sensor chamber allows the sensor to be taken to high temperature and/or pressure. Both sides of the sensor crystal are exposed so the response is double that obtained from a conventional single sided sensor and there is no net pressure difference across the sensor surface.

Vacuum Sensor Holder

Part. No. QSH-vac

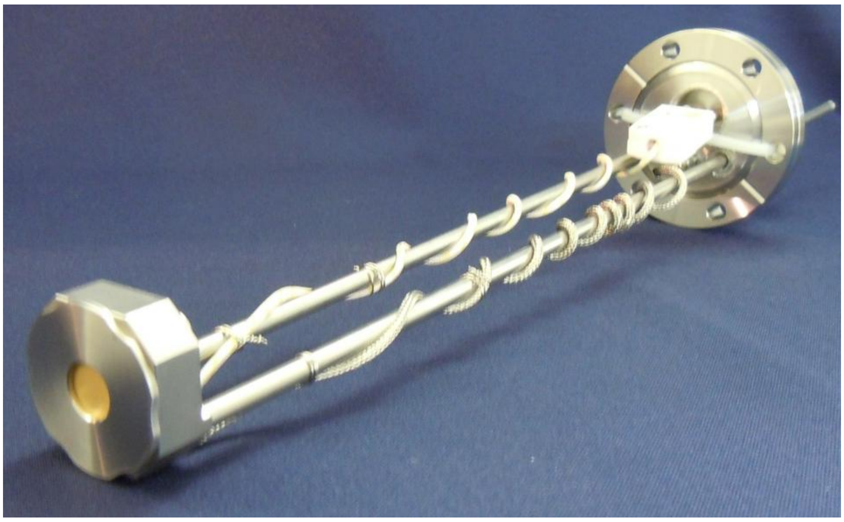


Figure 23: QCM sensor holder for vacuum application with CF feedthrough and temperature measurement.

Microscopy

Part. No. QSH-mic.

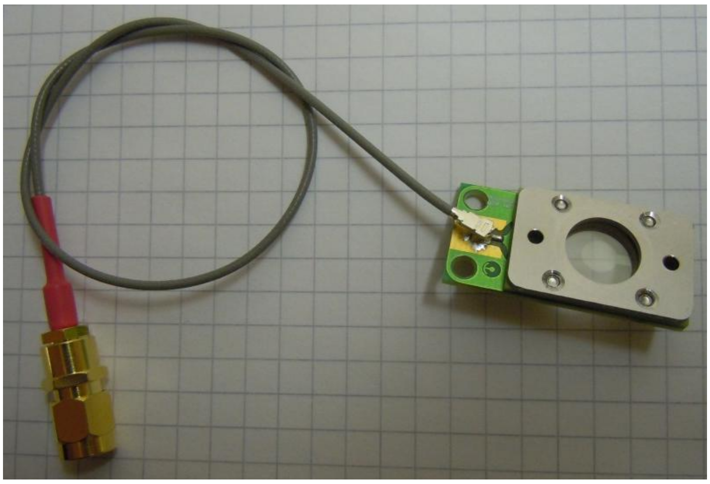


Figure 42: QCM sensor holder for microscopy with a transparent ITO coated sensor crystal for inverse microscopy.

Low Profile Holder

Part. No. QSH-thin

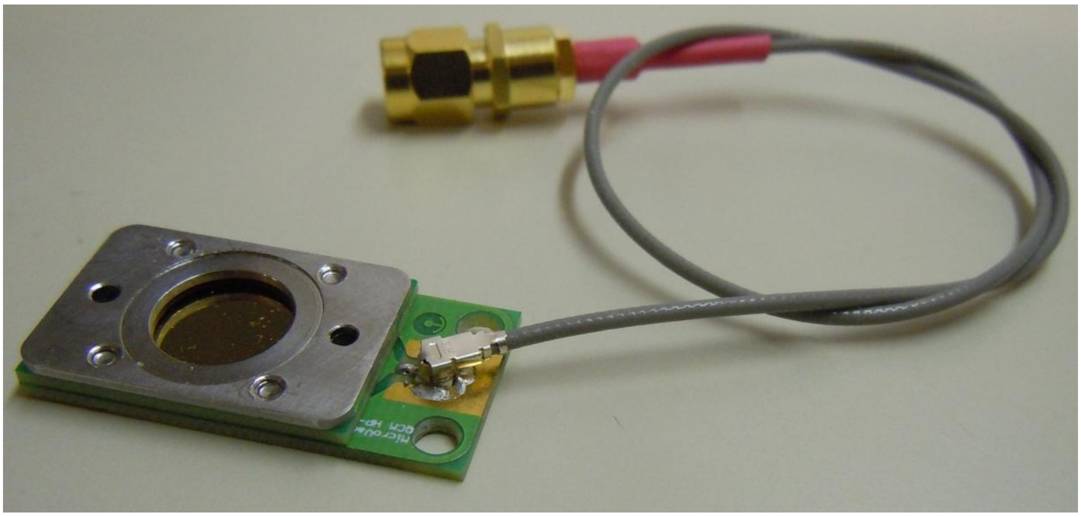


Figure 24: Low profile sensor-holder, 3 mm thick.

The low profile sensor-holder allows a sensor to be mounted away from the QCM-I instrument in a constrained location, primarily for the measurement of deposition from the vapor or gas phase, such as on the bed of a printer or spray coater or in a vacuum system.

Custom External Sensor-Holder

The QCM-I instrument is designed to allow a wide range of external sensor heads to be connected to it. These can be designed specifically for the required application and to be integrated into an external process tool. Please contact Semilab for more details: sales.support@semilab.hu

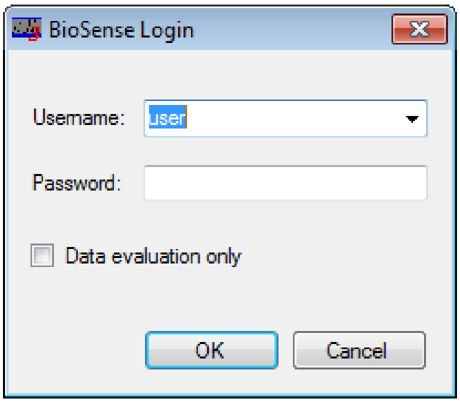
10. BioSense 3 software for QCM-I

10.1 USER LOGIN

After starting the software, the user is met by the login screen, where users are required to provide their login name and password. If the user has not been assigned an account by the Administrator, they can use default Username and Password.

Evaluation Mode

The software can be started without QCM-I instrument connected, in which case it will run only in evaluation mode, but the “Data evaluation only” box has to be selected.



Username: user

☐ Data evaluation only

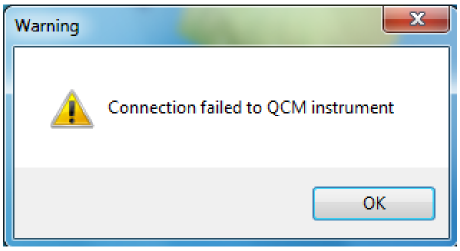
Figure 25: User Login Window

11. Troubleshooting

11.1 ERROR MESSAGES

“Connection failed to QCM instrument”

If QCM instrument is not connected or it is connected but not turned on and the evaluation mode is not selected, an error message will be displayed and the user will receive a warning about the failure (Figure 26.) and the BioSense starts running in data evaluation mode.



Connection failed to QCM instrument

Figure 26: Connection Failed Error Message

12. Support

Semilab offers remote customer support via preinstalled TeamViewer software. This support requires that the computer of QCM system is connected to the internet, and the QCM measurement system is switched on.

12.1 HOW TO ESTABLISH REMOTE CONTACT?

The date and time of the remote contact should be decided via e-mail. At the prefixed time please follow the steps bellow:

1. Please start the software (TeamViewerQS.exe) on your PC.
2. On the pop up window you will see an ID and a Password. Please send us the ID and the Password by e-mail (we will provide the e-mail of the service/support engineer when we arrange the support).

   Attention!!! Do not close this window!
3. After receiving the ID and the Password we can make the remote connection from our computer.

13. Warranty

Semilab warrants this product to be free from defects in material and workmanship for a period of one year from date of shipment. Semilab warrants the following consumable items for 30 days from the date of shipment: fuses, lamps and batteries. During the warranty period Semilab will, at its option, either repair or replace any product that proves to be defective.

To exercise this warranty, contact Semilab for RMA # at the address below. Returns will not be accepted without RMA #. The owner will send the product, transportation prepaid, to Semilab. Repairs will be made and the product will be returned to the owner with transportation prepaid. Repaired or replaced products are warranted for the balance of the original warranty period. For products not covered by warranty, the repair has a warranty of 90 days.

When a product is returned for examination and inspection, or for any other reason, Customer shall be responsible for all damage resulting from improper packing or handling, and for loss in transit, notwithstanding any defect or non-conformity in the Product, in all cases, Seller has the sole responsibility for determining the cause and nature of failure, and Seller's determination with regard thereto shall be final.

Limitation of warranty

This warranty does not apply to defects resulting from product modification without Semilab's express written consent, or misuse of any product or part. This warranty also does not apply to software, damage from battery leakage, or problems arising from normal wear or failure to follow instructions

this warranty is in lieu of all other warranties, expressed or implied including any implied warranty of merchantability of fitness for a particular use. the remedies provided herein are buyer's sole and exclusive remedies.

neither Semilab nor any of its employees shall be liable for any direct, indirect, special, incidental or consequential damages arising out of the use of its instruments or software even if Semilab has been advised in advance of the possibility of such damages. Such excluded damages shall include, but are not limited to: any lost profits or lost savings, costs of removal and installation, losses sustained as the result of injury to any person, or damage to property. Semilab does not and CANNOT warrant the performance or results obtained by using its equipment and software.

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