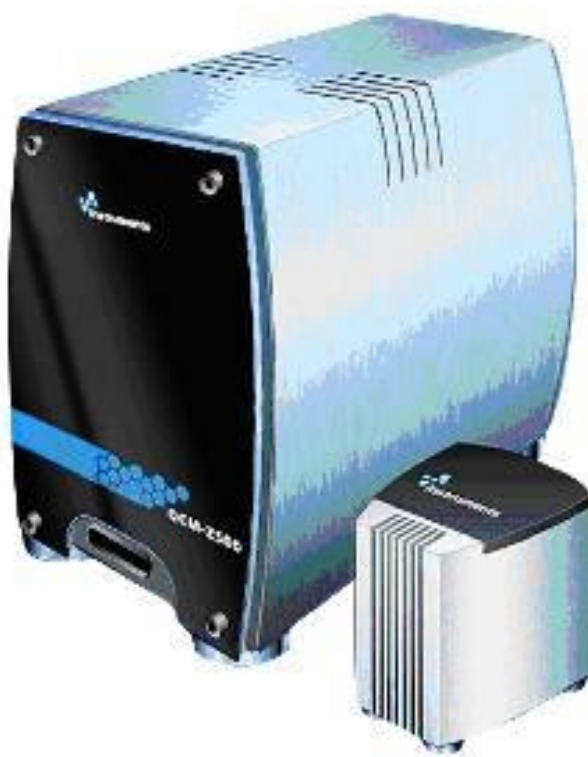




**Instruments**

## **Operation Manual**

### **QCM – Z500**



### **Quartz Crystal Microbalance**

Revision 3.0



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# 1. Introduction

The KSV QCM-Z500 microbalance is a computer controlled quartz crystal microbalance based on impedance analysis for determining the frequency ( $f$ ) and the quality of resonance ( $Q$ ) of quartz crystals in a gaseous or liquid environment. In other words, the QCM-Z500 microbalance is a mass sensing device with the ability to measure very small changes in mass on a quartz crystal resonator in real-time.

The KSV QCM-Z500 microbalance can measure the quality factor ( $Q$ ), dissipation ( $D$ ) and different harmonics of the quartz crystal giving additional information on the state of the layer adsorbed to the quartz crystal surface.

The KSV QCM-Z500 microbalance includes the main electronics unit with built-in impedance analyzer software, a measuring chamber for fluid phases, quartz sensor crystals with a variety of optional coatings and a Windows based program to control it all. A temperature control unit can be supplied if required.

The KSV QCM Impedance Analyzer software included with this instrument allows the easy operation of the experiments, which can be modified to any needs. The data is stored on the hard drive in a database and can be retrieved for analysis later. The data files can easily be exported in a variety of formats if another data reduction software is preferred.

## 1.1 Purpose of This Manual

This manual describes all the necessary steps to get the QCM-Z500 microbalance instrument operational, starting from the mechanical setup and through software installation, calibrating the instrument, making measurements and finally analyzing the data obtained. Please read this manual carefully before using the KSV QCM-Z500 microbalance and keep it available to ensure the maximum performance of the instrument.

## 1.2 Maintenance

The hardware of the QCM-Z500 microbalance is manufactured to the highest quality standards and when used properly it should yield a trouble-free use for a long time. There are no specific maintenance requirements or procedures for the instrument that can be taken in order to prevent breakdowns. If the instrument is set up and used as described in this manual only parts exposed to normal wear and tear might need to be exchanged.

**WARNING!** The original mains cables of the instrument and the computer must always be used and connected to a grounded wall socket. Ungrounded wall sockets may cause dangerous voltages between the instrument, the computer and the real ground.

## 1.3 Physical Description

The KSV QCM-Z500 microbalance consists of the main electronics unit and a measurement chamber, optionally a temperature control unit as well. The main electronics unit is the most central part of the KSV QCM-Z500 microbalance, it is in fact a Linux based computer with factory-installed software. It takes care of the communication between the measurement chamber and the data-collecting computer through a local area network connection.



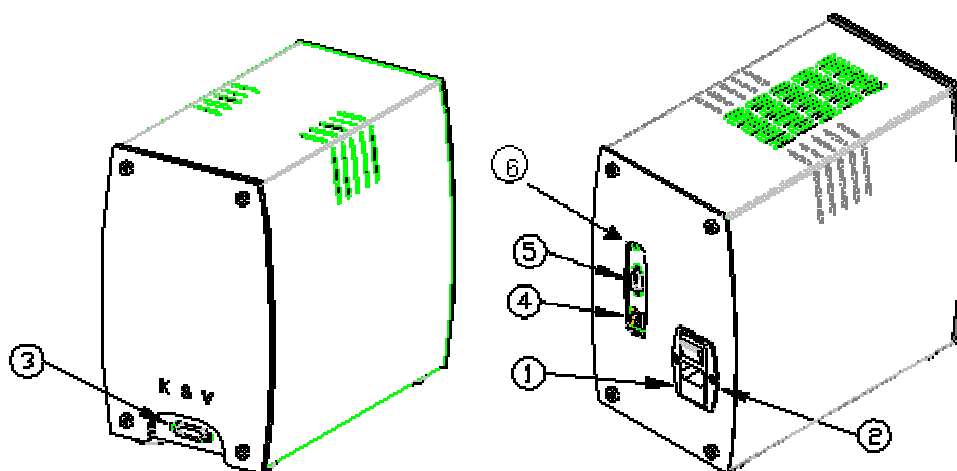
**Figure 1.1:** *The axial measurement chamber (left) and the main electronics unit.*

The axial flow measurement chamber is the standard chamber and is specially designed to ensure the best performance of the instrument by providing a controlled environment for the quartz sensor crystal during the measurements. It contains a temperature loop in which the sample fluid can be thermostated before it flows into the actual measuring chamber or into the waste channel. The tubing of the temperature loop is made of Viton, see

section 11. **Appendix A - Chemical Compatibility of Viton** of this manual for details on the chemicals that can be used with Viton.

### 1.3.1 Main Electronics Unit

The main electronics unit is a computer that sends and receives data from the measurement chamber. It connects to the measurement chamber with a 3-pin D-connector located on its front panel. A local area network is used to connect to the computer running the experiment, the network cable socket is located on the back panel. A power supply is also necessary, both 110-120VAC and 220-240VAC can be used but check that the fuse is on the correct setting before connecting to the mains (see section 3.1 **Mechanical Installation**).



**Figure 1.2:** Connections of the QCM-Z500 microbalance main electronics unit.

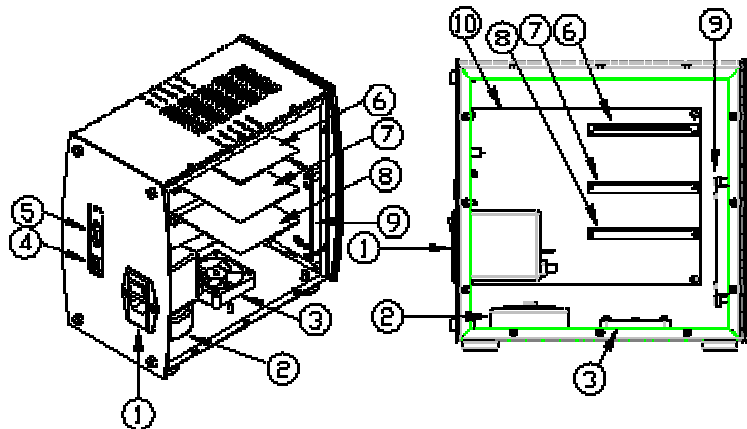
- |   |  |
|---|--|
| 1) Fuse   | 4) Network connection port to computer (RJ-42) |
| 2) Power connection and On / Off switch         | 5) Com port (RS-232, not for use with the TCU) |
| 3) Connection port to measuring chamber (3-pin) | 6) Reset button                                |

**NB)** The Com port (number 5 in figure 1.2) at the back of the main electronics unit is used *only* for loading the internal Linux program at the factory and not for use with the Temperature Control Unit (TCU)!

At the top of the front panel there is a green LED lamp which blinks when the instrument is turned on whilst the internal operating system loads. This LED will blink for about 1 minute. When the LED light stops blinking the Linux operating system has been loaded and the main electronics unit is ready for measurements.

The reset button (#6 in figure 1) reboots the main electronics unit.

The internal components of the QCM-Z500 main electronics unit are shown in figure 1.3 below.



**Figure 1.3:** *The internal components of the main electronics unit.*

- |  |                       |
|--|-----------------------|
| 1) Power switch and Fuse                       | 6) A/D-converter card |
| 2) Transformer                                 | 7) Oscillator card 2  |
| 3) Fan   | 8) Oscillator card 1  |
| 4) Connection port to computer (RJ-42)         | 9) Detector card      |
| 5) Com port (RS-232, not for use with the TCU) | 10) Processor board   |

### 1.3.2 Axial Flow Measurement Chamber

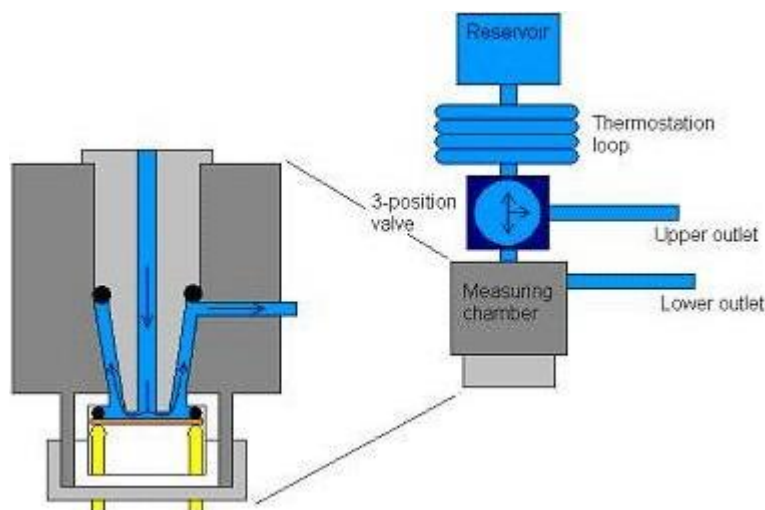
The measurement chamber is where the actual experiment takes place. There are several models available of which the axial flow measurement chamber is the standard one. Common to all is that a quartz crystal is cleaned and placed inside so that it rests on two electrodes. The electrodes provide alternating current that causes the crystal to move due to the piezoelectric effect inherent in quartz crystals. A fluid can flow across one side of the crystal.



**Figure 1.4:** *The axial flow measurement chamber.*

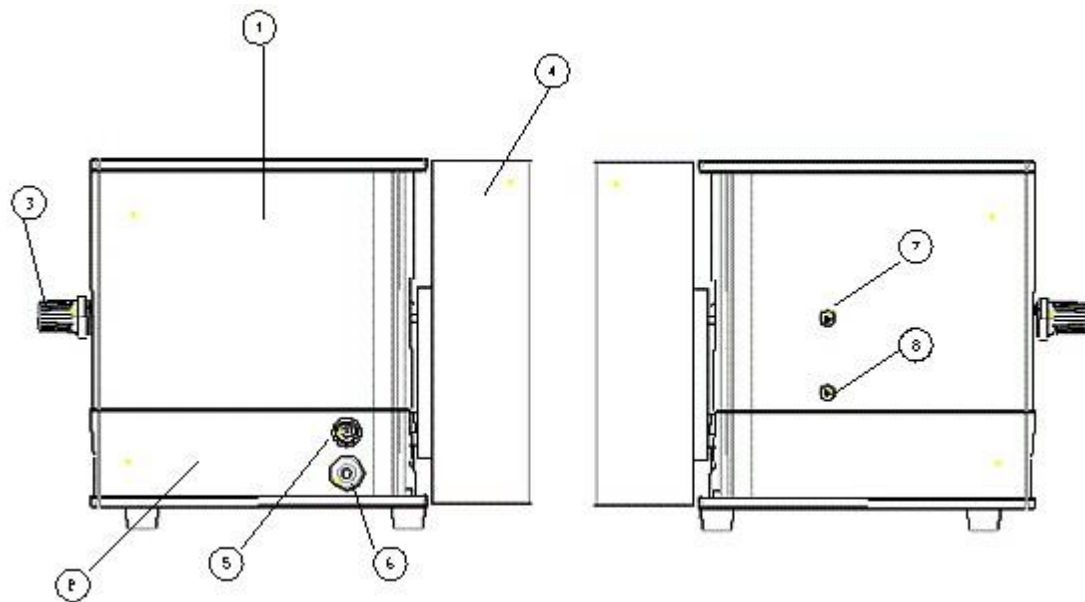
The name of the axial flow measurement chamber comes from the way the fluid moves through the unit. The inlet tube is at the top of the instrument, and the fluid flows down through a thermostation loop to either the crystal itself in the measuring chamber and then out or out directly (used for cleaning the tubing between samples).





**Figure 1.5:** *Flow direction of the sample in the axial flow measuring chamber.*

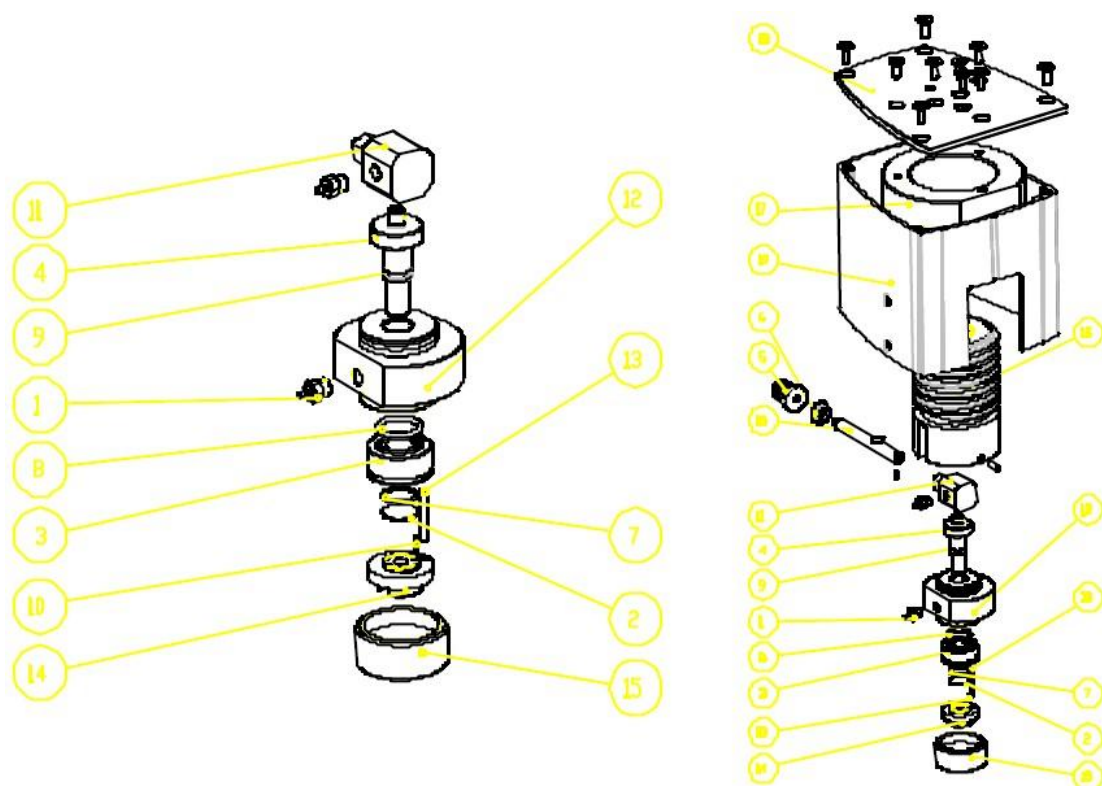
The volume of the temperature loop is around 3 ml, and the volume needed for flushing the actual measuring chamber is 1 ml. The flow direction of the fluid is controlled by a three-way valve. All parts of it in contact with the fluid sample are made of acid resistant stainless steel except the o-rings holding the crystal sensor, the tubing used in the temperature loop and the outlets from the measurement chamber which are all made of Viton. The o-rings and tubing can be easily exchanged to another material if needed, Viton has been chosen because of its high resistance to organic solvents. The actual measuring chamber is made of Teflon (PTFE) in order to meet the chemical compatibility standards and for ease of cleaning. The main body of the measurement chamber is made of aluminum to maximum heat transfer.



**Figure 1.6:** *Main components of the axial flow measuring chamber.*

- |                             |  |
|-----------------------------|--|
| 1) Top module               | 5) Temperature control socket              |
| 2) Bottom module            | 6) Grounding for crystal surface electrode |
| 3) 3-way valve control knob | 7) Top outlet for Bypass tube              |
| 4) Heat sink                | 8) Bottom outlet for Chamber tube          |

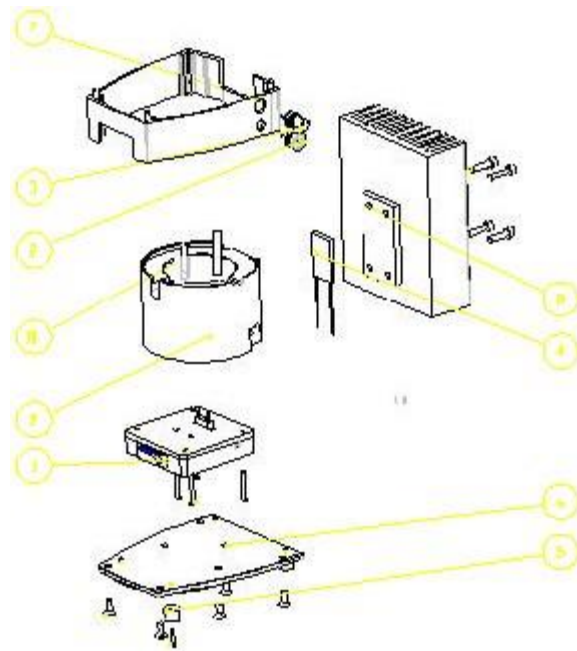
The axial measurement chamber also includes the sample inlet and the 3-pin D-connector socket on the bottom module which links the measurement chamber to the main electronics unit. The detailed components of the top module (#1 in figure 1.6) of the axial flow measuring chamber are shown below.



**Figure 1.7:** Components of the top module of the axial flow measuring chamber.

- |  |                                |
|--|--------------------------------|
| 1) Fitting                             | 11) 3-way valve                |
| 2) Crystal                             | 12) Crystal chamber body       |
| 3) Teflon crystal holder               | 13) Centering pin              |
| 4) Center tube                         | 14) Crystal support body       |
| 5) Knob                                | 15) Crystal support nut        |
| 6) Flange bearing                      | 16) Thermostating spiral block |
| 7) Viton O-ring                        | 17) Thermostating outer block  |
| 8) Viton O-ring                        | 18) Shaft                      |
| 9) Viton O-ring                        | 19) Top module cover           |
| 10) Crystal support spring-loaded pins | 20) Top plate                  |

The detailed components of the bottom module (#2 in figure 1.6) components are shown below.

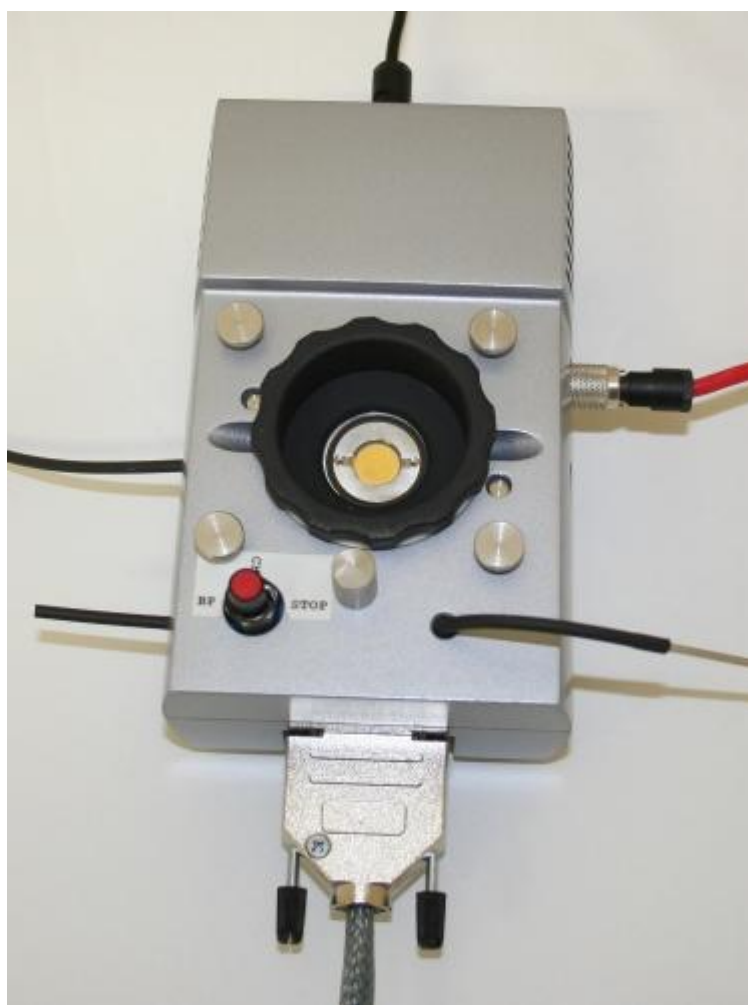


**Figure 1.8:** *Components of the bottom module of the axial flow measuring chamber.*

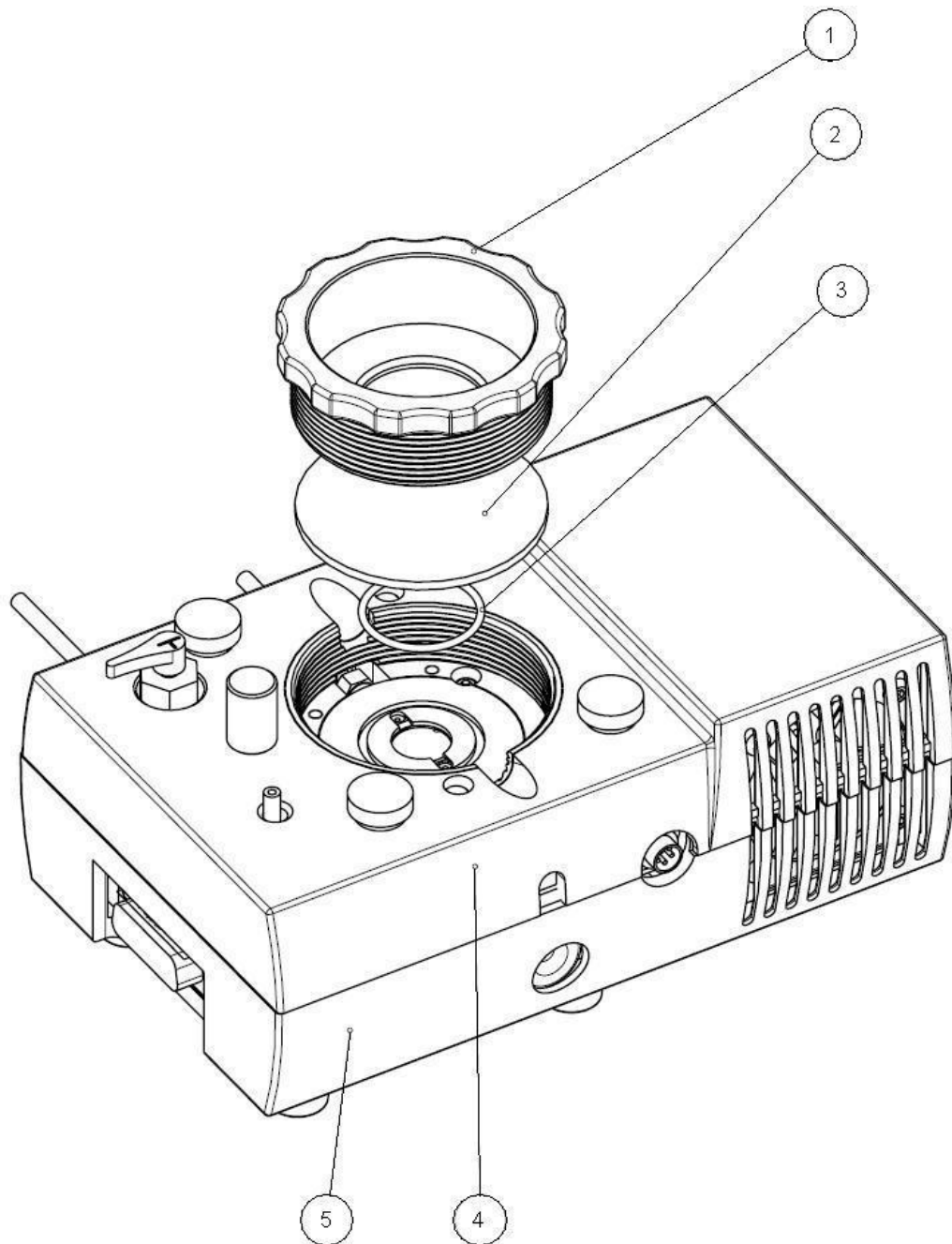
- |  |                               |
|--|-------------------------------|
| 1) Circuit board module                    | 6) Bottom plate               |
| 2) Grounding for crystal surface electrode | 7) Bottom module cover        |
| 3) Temperature control socket              | 8) Heat sink                  |
| 4) Peltier element                         | 9) Bottom thermostating block |
| 5) Rubber feet                             | 10) Centering pin             |

### 1.3.3 Parallel Flow Measurement Chamber

The parallel flow measurement chamber is an alternative to the axial flow measurement chamber. The principal concept of the parallel flow measurement chamber is the same as that of the axial flow one, that is the sample flows through a chamber where the crystal is housed. The advantages of the parallel flow measurement chamber are the smaller size, which means that smaller sample volumes are required, and a window directly to the chamber which allows the user to monitor constantly what is actually happening. It is also possible to use a microscope to observe the microscopic changes as a sample is introduced.



**Figure 1.9:** *The parallel flow measurement chamber.*

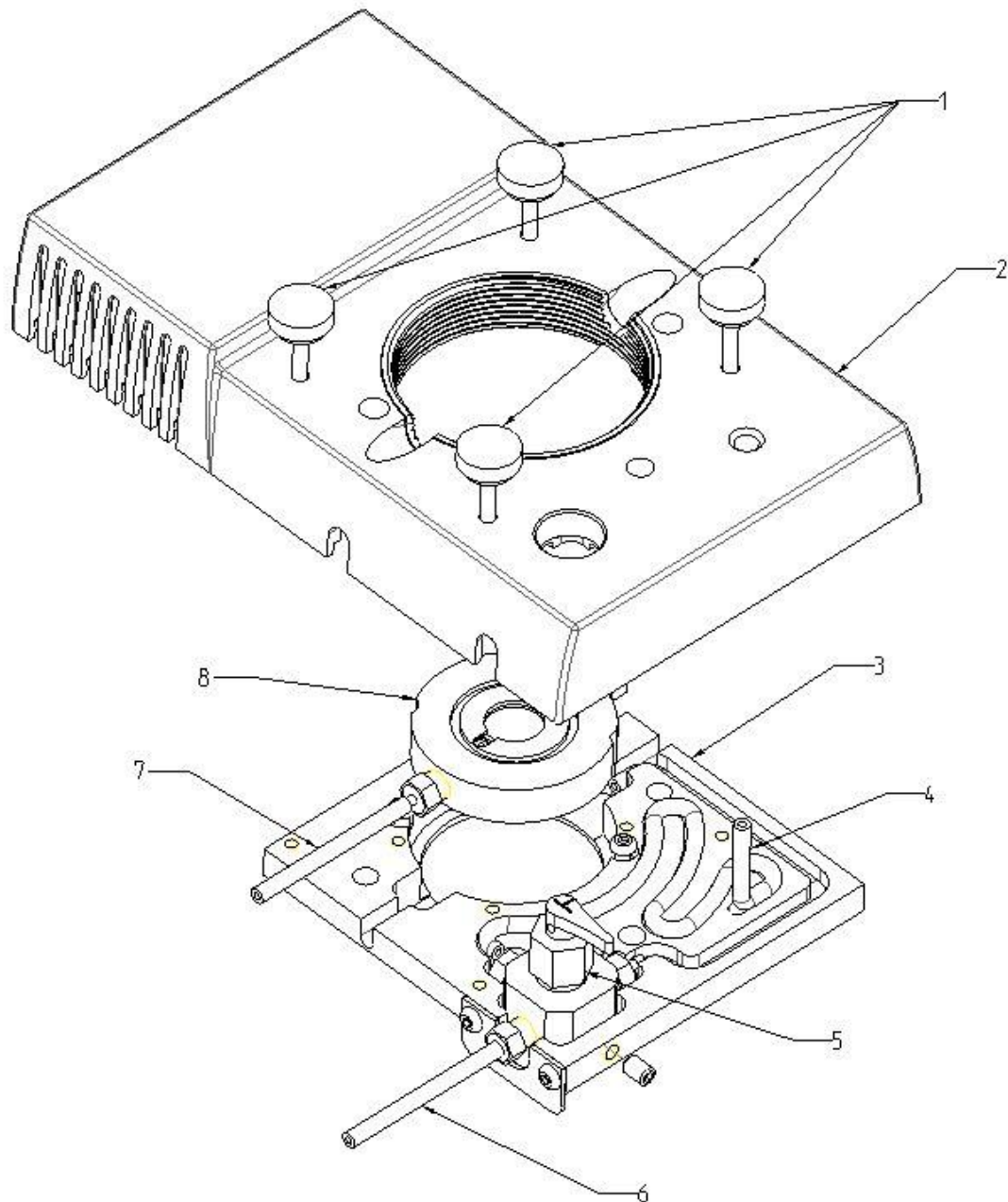


**Image 1.10:** *The window measurement chamber.*

- 1) Glass attachment nut
- 2) Glass window
- 3) Large o-ring
- 4) Top module
- 5) Bottom module

The window measurement chamber has two modules. The top module contains the main body of the measurement chamber, the chamber itself and the valve for controlling the flow direction of the sample whilst the bottom

module consists of the support platform for the measurement chamber, the heat sink, the electronics and the electrodes.



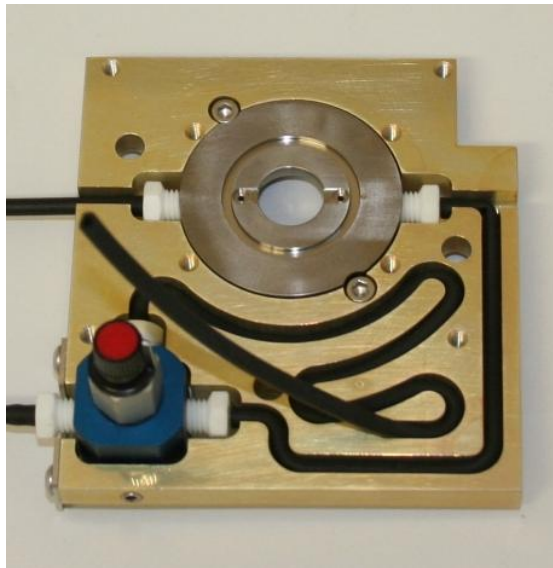
**Image 1.11:** *The top module.*

- |                          |                   |
|--------------------------|-------------------|
| 1) Lock screw            | 5) Valve          |
| 2) Top module cover      | 6) Bypass outlet  |
| 3) Chamber support stage | 7) Chamber outlet |
| 4) Feed                  | 8) Chamber        |

The main body of the top module is made of aluminum to maximise heat transfer. The internal parts of the valve are made of teflon (PTFE). The whole of the tubing and the o-rings are made of viton. The tubing supplied to



connect the sample reservoir to the valve is made of Viton as well. Please check that any sample or cleaning solution does not react with Viton from section **10. Appendix A - Chemical Compatibility of Viton**, if necessary alternative substances are available.



**Image 1.12:** *The chamber support stage.*

The tubing loops around the aluminum support stage to maximize the heat transfer.

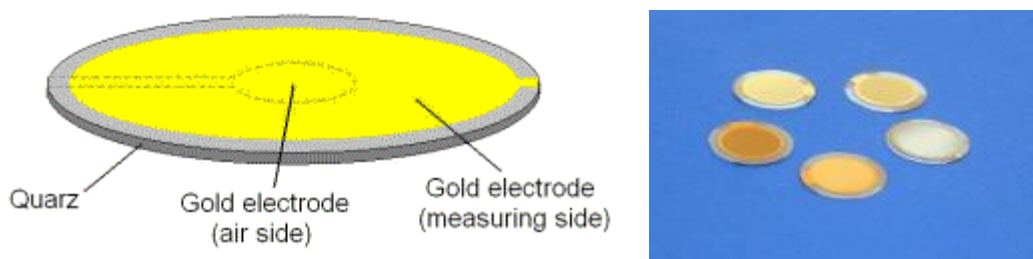
The axial measurement chamber also includes the sample inlet and the 3-pin D-connector socket on the bottom module which links the measurement chamber to the main electronics unit. The detailed components of the top module (#1 in figure 1.6) of the axial flow measuring chamber are shown below.



### 1.3.4 Quartz Crystal Sensors

The quartz crystal sensor is the heart of the instrument. The standard fundamental frequency of the crystals delivered with the QCM-Z500 microbalance is 5 MHz, although crystals with up to 50 MHz can be used with the instrument. KSV Instruments can also provide crystals with a fundamental frequency of 10 MHz. The electrodes on the crystals are made of gold and have a keyhole configuration where the contacts for the electrodes are on the same side. The electrode in contact with the sample fluid is grounded and much larger in order to make sure that the processes taking place on the quartz crystal surface are as similar as possible over the entire surface.

The gold surface of the electrodes can easily be modified for special applications or needs, for example by self-assembled monolayers, LB deposition, spin coating, vapor deposition etc.



**Figure 1.13:** *The quartz crystal electrodes and quartz crystals with different coatings.*

Apart from the standard gold-coated sensor crystals KSV Instruments can provide a variety of other surfaces upon request, these include:

**Metals:** Ag, Al, Ca, Cr, Cu, Li, Mg, Ni, Sn, Pt

**Inorganic:** ITO, LiF, MgF<sub>2</sub>, SiO, SiO<sub>2</sub>, TiO<sub>2</sub>, ZnS, Ti<sub>3</sub>NO

**Polymers:** PANi, Teflon, PMMA, PS, PC, PE, PP, AKD

The standard crystal sensor has a fundamental frequency of 5 MHz, a diameter of 14 mm and a gold coating. Other frequencies and coatings can be obtained by request.

### 1.3.5 Valve operation

The flow direction of the fluid is controlled by a three-way valve, connecting the sample reservoir, the waste container and the crystal chamber.

The recommended procedure in operating the valve either for filling the chamber with a sample is to have the valve in the Stop position (marker pointed down) before filling the reservoir. Fill the reservoir and then turn the marker to the Waste position (marker pointed left). Allow a few drops to come out, then turn the valve anti-clockwise through the Stop position to the

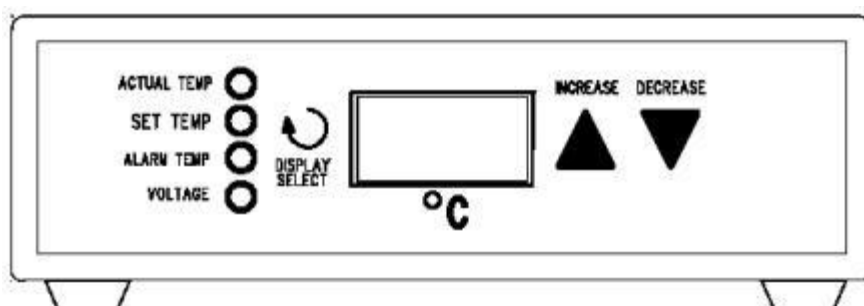
Chamber position (marker pointed right). Again allow a few drops to come out and turn the valve to the Stop position again.

To clean the tubing, set the valve to Cleaning (marker pointed up) and pour the cleaning solution into the sample reservoir. The cleaning solution will then flow along both tubes, be sure to do so above a sink or so that the chamber and the waste outlets are above a beaker

### 1.3.6 Optional Temperature Control Unit

The chambers supplied by KSV Instruments always contains a Peltier element, a heat sink, a temperature sensor inside the thermostation block parts and a fan, but in order to make use of these a separate Temperature Control Unit is required.

The Peltier element enables heating or cooling of the thermostation block and hence adjusting the temperature of the measuring chamber. The temperature can be either set manually from the Temperature Control Unit (figure 1.10) or with the computer by using the KSV QCM Impedance Analyzer software. The useful temperature range is between +10 and +50 °C with a resolution of 0.1°C for the axial flow measurement chamber.



**Figure 1.14:** Front panel of the optional Temperature Control Unit.

## 2. Brief Instructions

This section describes briefly the steps necessary to install the KSV QCM-Z500, calibrate it and perform a basic measurement. However, it is strongly recommended that this manual is read completely and thoroughly as it contains valuable information on the required procedures and the working of the instrument. Use this section as a checklist and a reference once the actual procedures are familiar.

### 2.1 Installation Procedure

- Lift the KSV QCM-Z500 microbalance instrument onto a steady table.
- Install the network card delivered with the instrument onto the computer.
- Connect the power cord and the network cross-cable to the instrument. Plug the power cord into a grounded wall socket and connect the network cross-cable to the installed network card. Connect the signal cable between the main electronics unit and the measuring chamber. If a Temperature Control Unit (TCU) is used connect it to the fan, measurement chamber, power supply and computer (note that the TCU connects directly to the computer, and *not* to the main electronics unit).
- Turn on the power of the main electronics unit and wait for at least 1 minute or until the light on the front panel stops blinking.
- Define the IP address of the installed network card as 192.168.168.1 and the Subnet mask as 255.255.255.0 in the Windows **Network Connections** screen.
- Install the KSV QCM Impedance Analyzer software from the software installation CD by running setup.exe from the root of the CD.
- Start the KSV QCM Impedance Analyzer software by choosing **Programs > QCMZ > QCMZ** from the Windows **Start** menu. Check that the **Status:** bar in the software says **Program ready for measurements**. If this is not the case check the IP address of the network card, the address of the QCM-Z500 microbalance (should be 192.168.168.168) from **Edit > Device Parameters** in the KSV QCM Impedance Analyzer software and that the internal program is loaded from **File > Load Program**. Also try rebooting.

### 2.2 Calibration

- From the menu bar of the KSV QCM Impedance Analyzer software open **Controls > Calibrate**.
- Insert the appropriate information and press **Calibrate**.

- Remove the top module of the axial flow measurement chamber and insert the calibration tool so that the short circuit part is in line with the electrodes and the guidance pole goes through the appropriate hole. Press down gently and press **OK**.
- Wait. When instructed to do so remove the calibration tool and press **OK**.
- Wait. When instructed to do so replace the calibration tool, this time with the known resistance in line with the electrodes and press **OK**.

## 2.3 Cleaning

- Remove the top module, unscrew the nut and take away the teflon chamber construction and the crystal.
- Let the cleaning and the rinsing liquids (often pure ethanol and ion-exchanged water are acceptable) flow through the Bypass and the Chamber loops.
- Wash the interior of the top module with the cleaning and the rinsing liquids.
- Wash the crystal with either chromic acid or a Piranha solution, and rinse with ethanol and ion-exchanged water.
- Wash the teflon chamber pieces with the cleaning and the rinsing liquid.
- Replace the chamber pieces and the crystal into the top module and screw on the nut. Replace the top module on top of the bottom module.

## 2.4 Measurement Procedure

- Check that the valve is set on Stop and fill the reservoir with the background liquid (often water). Turn the valve to the Bypass setting and after a few drops have come out return the valve to the Stop position.
- Turn the valve to the Chamber setting and after a few drops have come out turn the valve to Stop.
- If a Temperature Control Unit is used, set the target temperature from either the unit itself or the QCM-Z500 Impedance Analyzer program at **Controls > Temperature Controls**. Wait 30 minutes for the instrument to reach thermal equilibrium.

- Click the **New Experiment** icon. Fill in the relevant information in the **Experimental Setup** screen. Use **Edit Database** to add new items on the drop-down menus, press **Start** when finished.
- Select **Automatic** as the measurement **Method** and select all of the harmonics. Press **Start**. Wait for the frequencies of the resonances to settle.
- Empty the reservoir and open the Bypass. Let the background liquid drain and then pour the sample to the reservoir. When a few milliliters of the sample have come out from the bypass switch to Stop to wait for thermal equilibrium. Then turn the valve to Chamber.
- Allow a few milliliters to pass through the chamber to flush it. Close the valve and wait for the frequencies to stabilise. Flush with the background liquid again or introduce the next sample according to what is being measured. Press **Stop** when finished.

## 2.5 Data Analysis and Reduction

- Data analysis is carried out by another program called **Browse Experiments**. Open it from either the desktop (**QcmBrowse**) or from **Start > Programs > QCMZ > QcmZBrowse**.
- Set the search parameters for the experiment wanted if necessary and select it from the *Experiments* box. Right-click on it and select **Graph** to view the graph of the specified harmonic. Change the variable of the x-axis or the y-axis, or add another y-axis from the top right corner of the **Browse Experiments** window. Export a graph from **Graph > Show Menu > Export**.
- Export data either by pressing the **Copy to Clipboard** icon and pasting in another program (e.g. Notepad in order to save the data in ASCII format) or by selecting **File > Export/Delete Data**. Send the experiments to be exported to the **Destination List** and press **Export**. The file created is only useable by a KSV QCM-Z500 Impedance Analyzer program, use this feature to make backups or to transfer the data to another computer with the software. Import an experiment file from **File > Import Data**.

## 3. Installation

### 3.1 Mechanical Installation

The KSV QCM-Z500 instrument is delivered in one crate. The crate should be opened carefully and checked to see that it contains the following items:

- Main electronics unit
- Standard axial flow measuring chamber
- Calibration tool
- 5 gold coated quartz crystals
- Network card
- Power cord
- Network cross-cable
- Signal cable between the main electronics unit and the axial-flow measuring chamber
- Software and manual on CD

Unwrap the plastics around the unit and place the QCM-Z500 on a steady table, preferably with running clean (ion-exchanged) water nearby.

The KSV QCM-Z500 microbalance has an internal computer running a Linux operating system for taking care of the basic calculations during measurements and communications between the instrument and computer. The communication between the computer and the QCM-Z500 microbalance is carried out by a local network connection. This means that the computer used with the instrument needs to have a network card installed solely for the QCM-Z500 microbalance, and if the network card was already in use (for example to connect to the internet or an intranet) another one needs to be added. One is provided with the instrument.

The QCM-Z500 microbalance has been fitted with an IP address which is 192.168.168.168 . It can be changed but to do so please contact KSV Instruments directly.

#### 3.1.1 Installing the Network Card

Shut down the computer and open the cover of the computer's central unit. Find a free PCI slot and put the network card delivered with the instrument in this slot. Remember to attach the network card properly so that it cannot move in its slot. Start the computer, preferably with Windows 2000 or XP. Windows

will automatically install the network card and no drivers are needed. However, if it cannot be automatically installed (especially common with older versions of Windows) Windows will ask for drivers for the network card. Please insert the diskette or CD-ROM from the network card box and direct Windows to this media if that should happen.

### 3.1.2 Connecting Cables

The cables used with the KSV QCM-Z500 microbalance have been chosen so that no incorrect connections can be made. Before plugging in the power supply check whether the fuse (number 1 on Figure 2 of **1.3 Physical Description**) is in the correct setting. Two different voltage ranges are available, 100-120VAC and 220-240VAC. Look at the text at the bottom of the fuse next to the arrow pointing down, this indicates which voltage setting is currently in use. To change to the other setting remove the fuse, turn it so that the supplied voltage is indicated on the bottom and reattach it.



**Figure 3.1:** *Removing the fuse.*

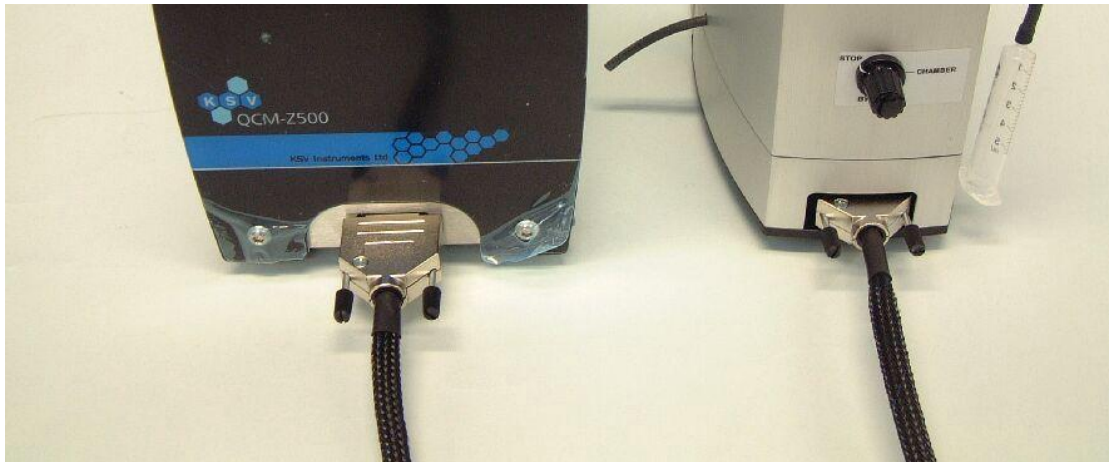
#### A) Power Supply

Plug in the power cord to the backside of the main electronics unit (#2 in figure 2 in section **1.3 Physical Description**). For safety reasons always use grounded wall sockets for the power supply. If the Temperature Control Unit is available then also connect a power cord to the backside of the unit (see Figure 8 in section **1.3 Physical Description**).

#### B) Measurement Chamber Communication



Connect the 3-pin signal cable between the 3-pin D-connector on the front side of the main electronics unit (#3 in Figure 2 in section **1.3 Physical Description**) and the 3-pin D-connector on the front side of the standard axial flow measuring chamber (#9 in Figure 4 in section **1.3 Physical Description**). The 3-pin D-connectors can only be connected one way, though if enough force is applied it is possible to attach them in the wrong way. Please avoid doing so. Remember to tighten the screws on the plugs to avoid accidentally removing the cable.



**Figure 3.2:** *The connector cable between the main electronics unit and the measurement chamber.*

### C) Network Cable

As this is a connection between two computers a cross network cable is required. Attach it to the RJ-42 connector (#4 in Figure 2 in section **1.3 Physical Description**) on the backside of the main electronics unit and then to the network card on the computer.

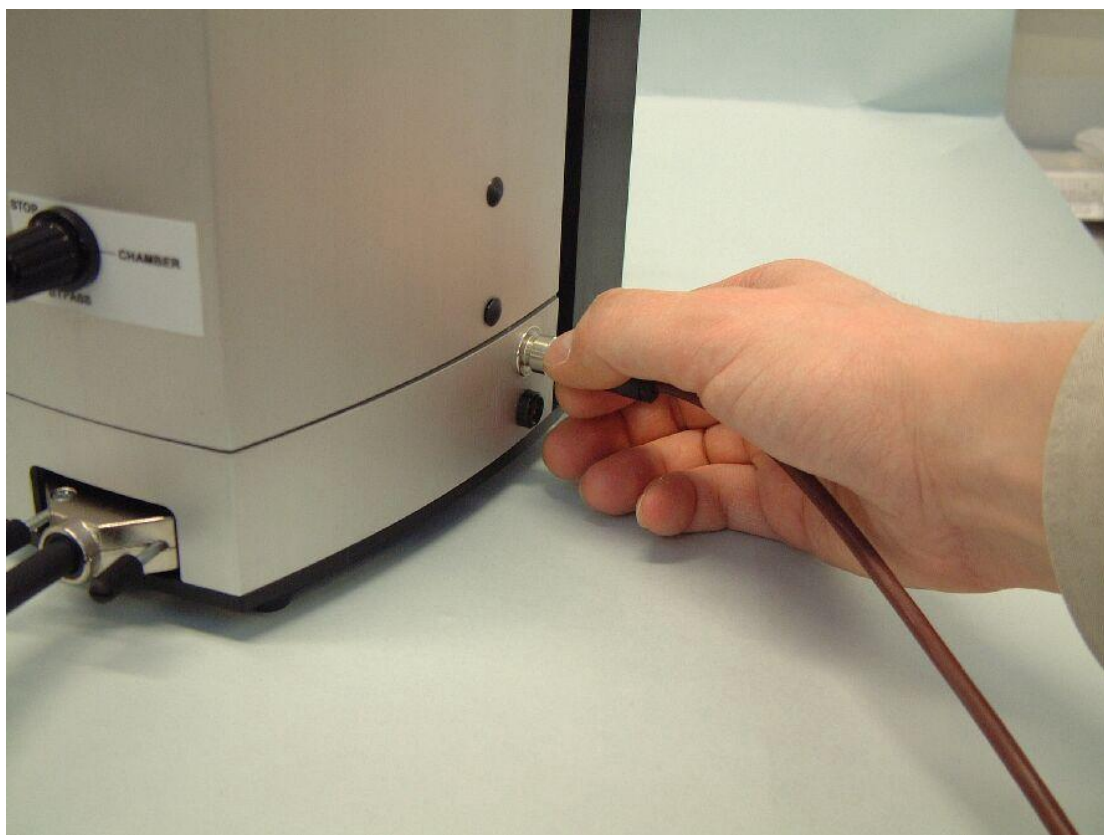


**Figure 3.3:** *The back of the main electronics unit.*



## D) Optional Temperature Control Cable

If the optional Temperature Control Unit (TCU) is available then two cables need to be connected from the TCU to the measurement chamber. These cables are ready connected to the TCU at the factory, the red cable connects to the bottom module of the chamber (#7 Figure 4 in section **1.3 Physical Description** for the standard axial flow measurement chamber) and the black cable connects to the fan. The red cable receives the temperature reading from the thermometer in the module and controls the Peltier element while the black cable controls the fan.



**Figure 3.4:** *Connecting the Temperature Control Unit to the measurement chamber.*

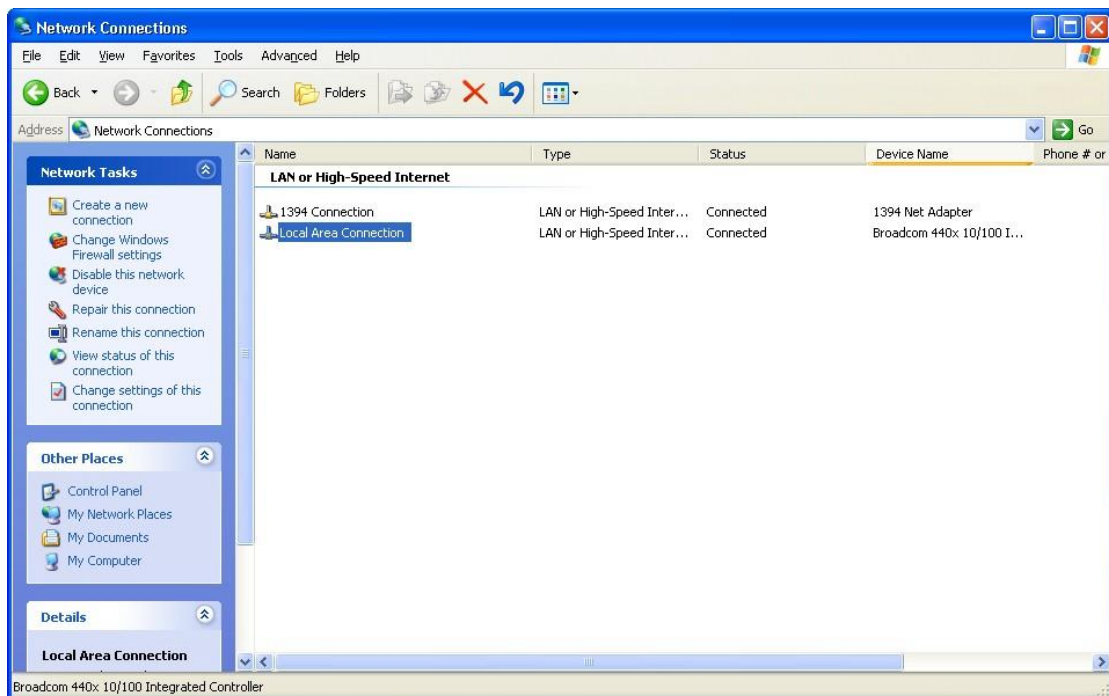
## 3.2 Software Installation

### 3.2.1 Setting Up a Local Area Network Connection

The QCM-Z500 microbalance is directly connected to the PC through a local area network connection. In order for the communication to work properly the local area network parameters for the installed network card should be set in Windows according to the instructions below.

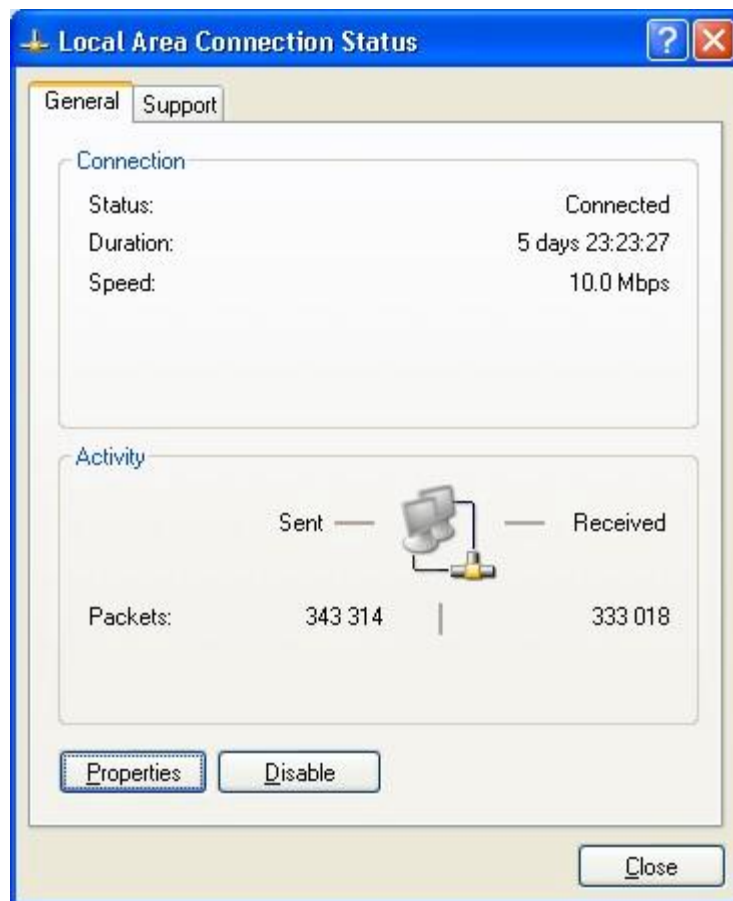
Make sure that the network card is installed in the computer and connected to the QCM with the cross network cable as explained in section **3.1 Mechanical Installation**. Turn on the power of the main electronics unit and wait for about 1 minute for the internal Linux operating system to load. The green light on the top of the front panel stops blinking once the main electronics unit is ready.

Open **Network Connections** from the **Control Panel**. The exact location depends on the version of Windows used, the **Control Panel** can usually be found from the **Start** menu. In the **Control Panel** the icon **Network Connections** exists either separately or under **Network and Internet Connections > Network Connections**.

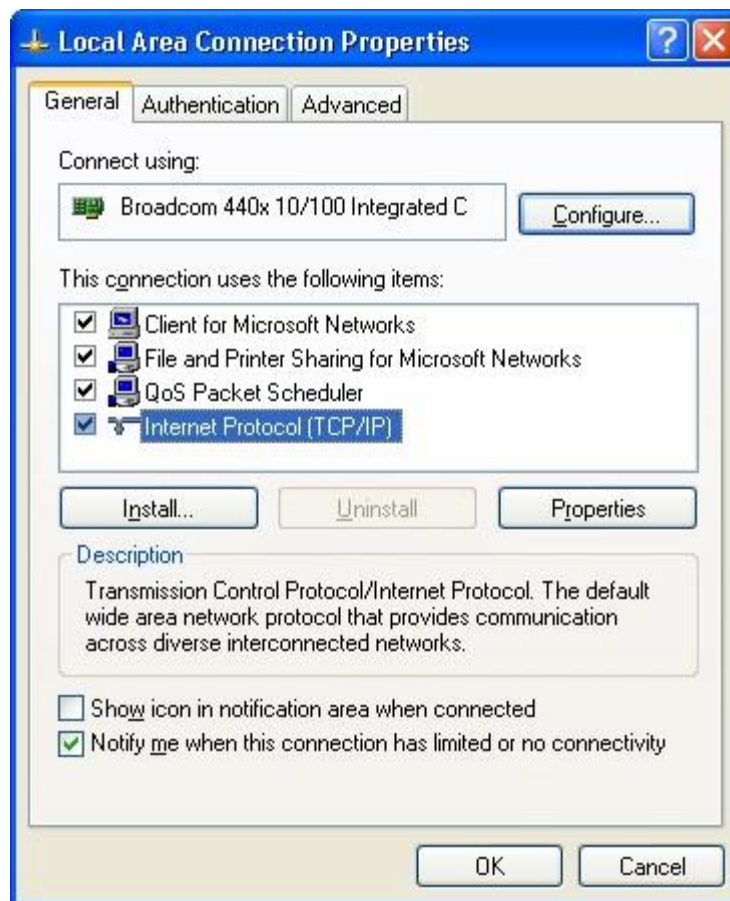


**Figure 3.5:** *The Network Connections window.*

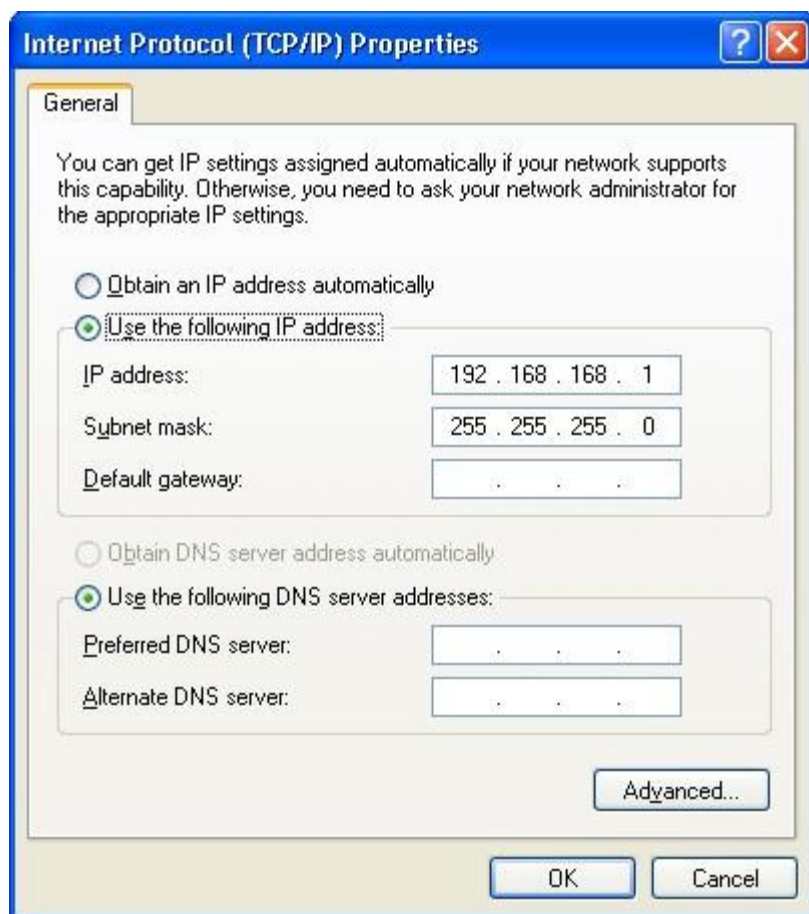
Double-click on **Local Area Connection**.



**Figure 3.6:** *The Local Area Connection Status window.*  
Press **Properties**.



**Figure 3.7:** *The Local Area Connection Properties window.*  
Select **Internet Protocol (TCP/IP)** and press **Properties**.



**Figure 3.8:** *The Internet Protocol Properties window.*

Select **Use the following IP address** option and fill in the **IP address** 192.168.168.1 and **Subnet mask** 255.255.255.0 as shown above. Press **OK**.

The communication path between the QCM-Z500 instrument and PC has now been defined. Sometimes it is necessary to restart the computer and the QCM-Z500 microbalance before the connection is activated.

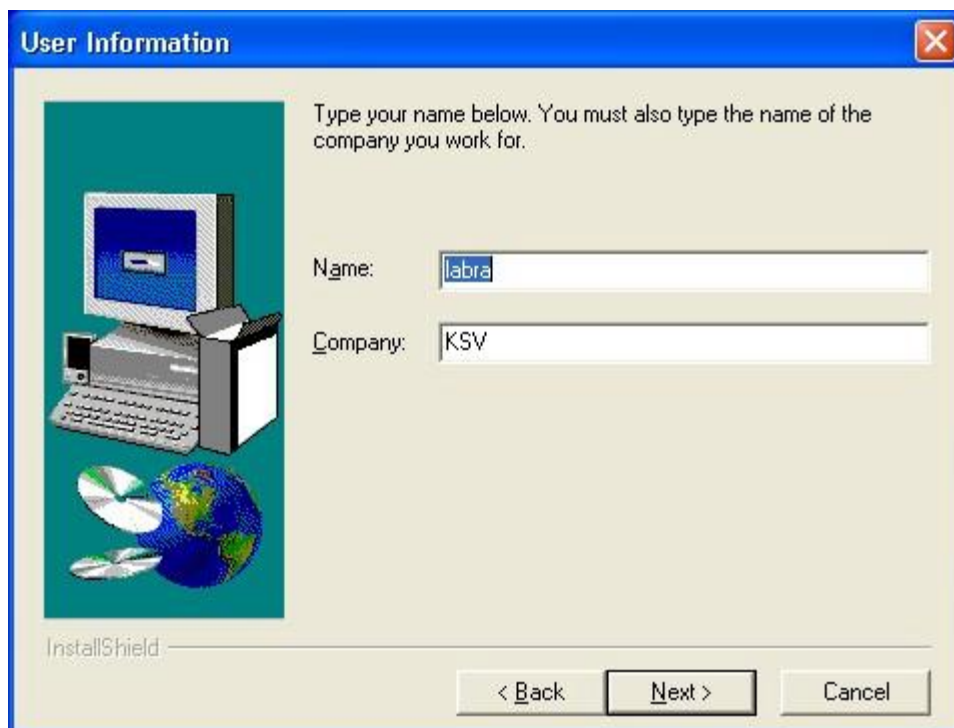
**NB!** It is also possible to connect the QCM-Z500 microbalance directly to a larger internal local area network (intranet). In such cases the QCM should have an individual IP address reserved for it so that it can be connected to the larger network in the same way as any other computer. This IP address is then programmed into the QCM-Z500 microbalance by KSV Instruments in cooperation with a local computer support person either before shipping or on-site during installation and training. However, the procedure for setting up this kind of connection is not described here.

### 3.2.2 Installing KSV QCM Impedance Analyzer Software

The KSV QCM Impedance Analyzer software is available on the CD-ROM delivered with the instrument. Insert the CD and open **My Computer**. Find the CD drive (D:\ on most computers) and open it. Double click on the file **setup.exe**.

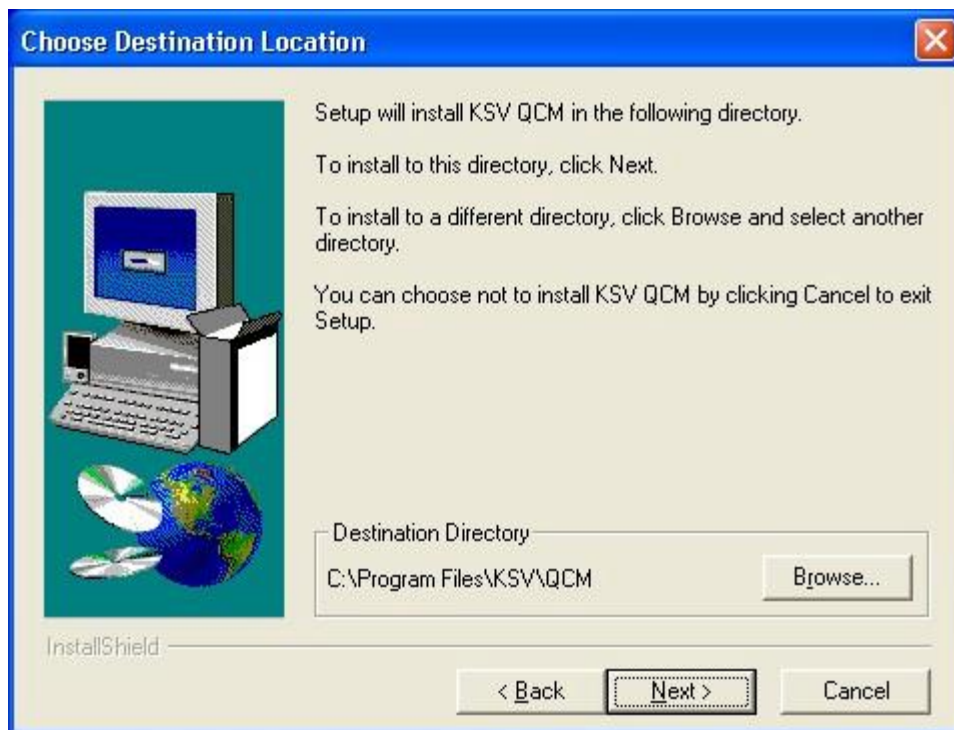


The installation program begins with this window. Press **Next** to continue.



Fill in the **Name** and **Company** fields, and press **Next**.





To change the installation directory press **Browse**, otherwise press **Next** to continue.



To change the folder name in the **Start** menu type it into the **Program Folders** field, otherwise press **Next** to continue.

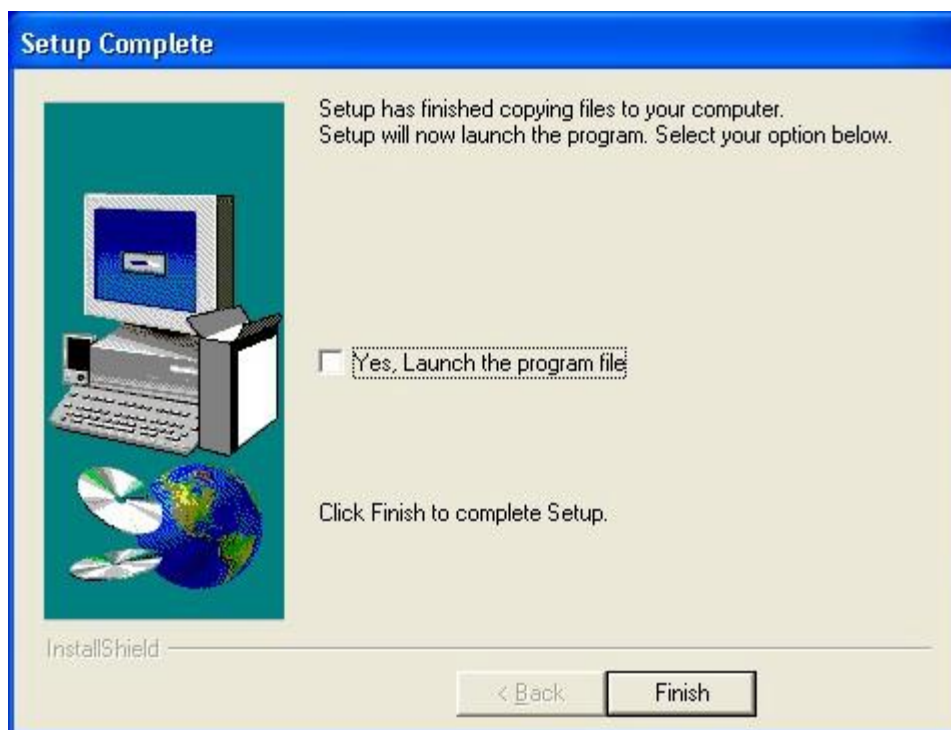


Press **Next** to continue.



Wait for the installation to complete itself.



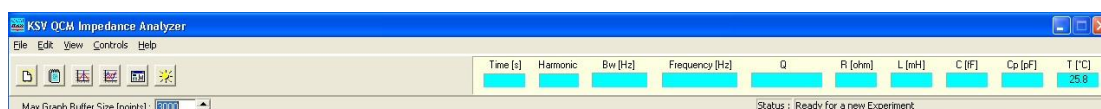


Press **Finish** to complete the software installation process. To create a shortcut to the QCM program open **My Computer** and select the folder to which the QCM software was installed (by default **C:\Program Files\KSV\QCMZ**). Right-click on the file QCM.exe and select **Send To > Desktop (create shortcut)** from the drop-down menu.

To start the program either double-click on the shortcut on the desktop or from the **Start** menu at **Start > Programs > QCMZ > QCMZ**. This opens the main menu of the KSV QCM Impedance Analyzer software.

### 3.2.3 Checking Software Installation and Communication

First turn on the power of the main electronics unit and let it load its internal programs for ca. 1 minute (once loaded the blinking green light changes to a steady green light). Start the software by double-clicking on the QCM shortcut on the desktop or choose **Start > Program > QCMZ > QCMZ** from the **Start** menu. If the connection between the main electronics unit and the computer is working the **Status:** field in the lower right corner will state that the instrument is **Ready for a new Experiment**.



**Figure 3.9:** The QCM Impedance Analyzer main window.

If this is the case then the instrument needs to be calibrated before measurements can be performed. The calibration procedure is described in section **3.3 Calibration** below. However, if the main electronics unit is not

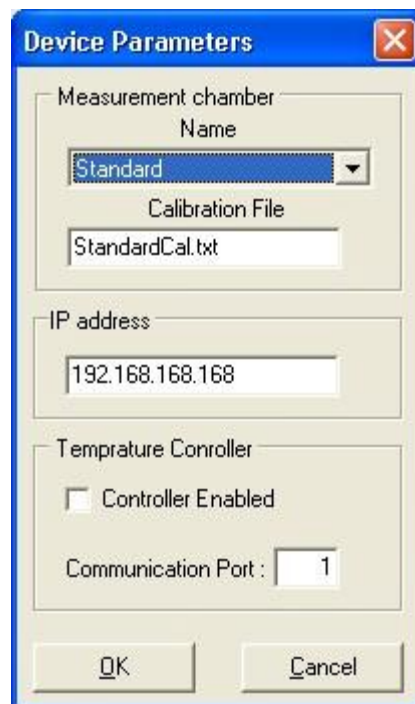
turned on, the IP address in the KSV QCM Impedance Analyzer software for the QCM-Z500 microbalance is not correctly defined or there is a problem with the cables connecting the main electronics unit to the computer the following window will appear:



**Figure 3.10:** *The Error! message.*

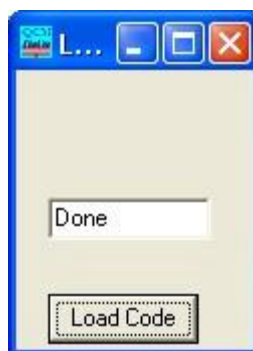
If this window appears check that the power is turned on and then press **OK** to continue. In the main menu if the **Status:** field says **Program not loaded for QCM unit** then first try to close and restart the program. If the problem persists then try the following, though do not hesitate to contact your local distributor or KSV directly. Often with Windows based programs a problem can be fixed by restarting the computer so that should be attempted as well.

- Check that the green light on the top of the front panel of the main electronics unit is on and that it is not blinking. If it is not on check the power cable for the unit and check that the switch in the back of the unit is in the "on" position, that is with the I pushed towards the unit and O sticking out. If the light is blinking the processor inside the unit is still starting up (like turning on the computer it takes time) and wait for it to stop blinking. This should take about a minute.
- Check the IP address in the local area network connection by repeating the steps described in section **3.2.1 Setting Up a Local Area Network Connection**. Make sure that the **IP address** is defined as 192.168.168.1 and that the **Subnet mask** is 255.255.255.0.
- Check the cable connecting the main electronics unit to the computer. Do this for example by removing the network cable from another computer connected to the internet or an intranet and replacing it with the one connecting the unit and the computer. If the connection works then reconnect the cable and try restarting the software.
- Check the IP address in the KSV QCM Impedance Analyzer software. Do this by selecting **Edit > Device Parameters** from the main menu.
- Check that the IP address is 192.168.168.168. If necessary the last three digits can be altered as long as they do not match the IP address of the local area network connection. Press **OK** and restart the software.



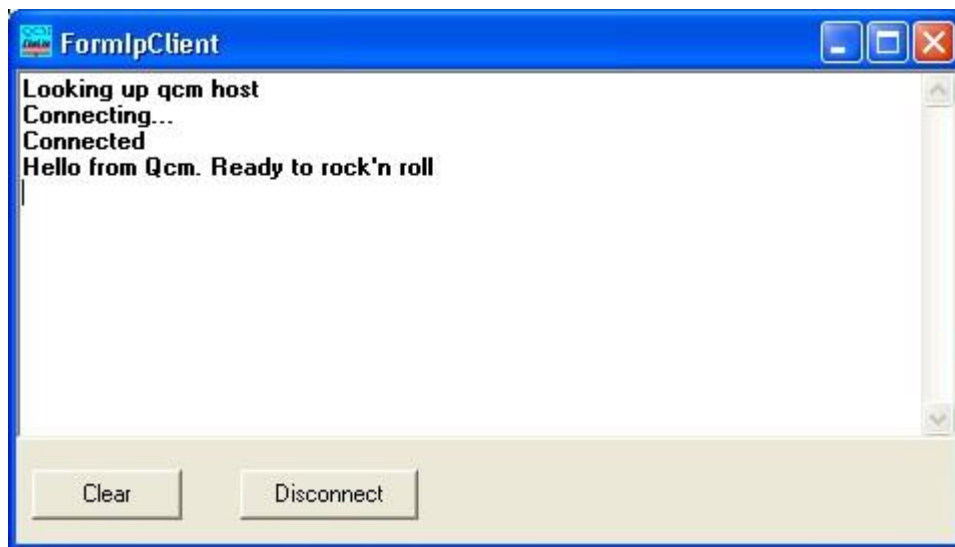
**Figure 3.11:** *Device Parameters. Indicate which measurement chamber is connected and whether a Temperature Control Unit is available.*

- Check if the internal program for the QCM is loaded. Select **File > Load Program** from the main menu. If the text field says **Done** that means that the internal QCM software has been successfully loaded. If the field is empty press **Load Code** to attempt to load the program manually. This will only work if the connection between the main electronics unit and the computer is working.



**Figure 3.12:** *Load. If the field is empty press **Load Code** and wait for the text **Done** to appear.*

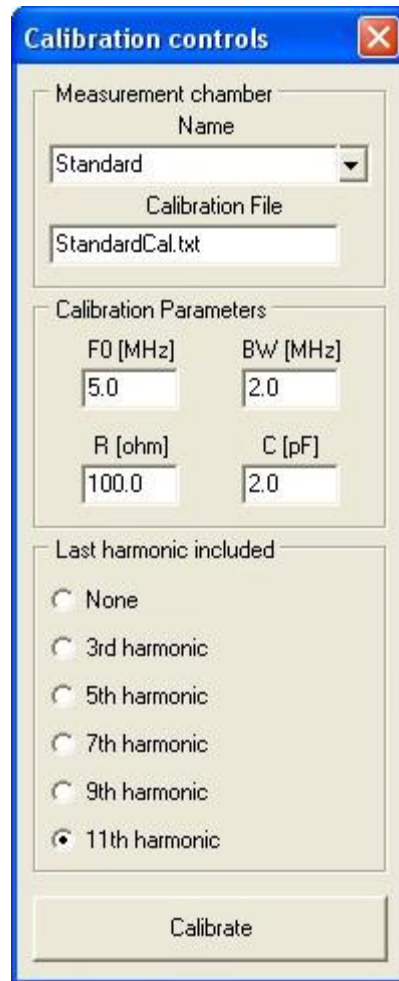
- Check if the connection between the main electronics unit and the computer is working. After loading the code successfully select **File > Connect** from the main menu. Press **Connect Qcm** if no text is visible. If the connection is working the following text will appear “**Looking up qcm host, Connecting..., Connected, Hello from QCM. Ready to rock’n roll**” will appear.



**Figure 3.13:** *FormIpClient. Check the connection to the QCM, receiving the above message indicates that the connection is fine.*

### 3.3 Calibration

After installing the software and checking that the KSV QCM Impedance Analyzer software and the QCM-Z500 microbalance instrument are communicating with the computer the instrument has to be calibrated. Each measurement chamber type has to be individually calibrated, and the following procedure applies to all chambers. The calibration is done in 3 steps, with a short circuit, an open circuit and a known resistance. Select **Controls > Calibrate** from the main menu window to open the **Calibration controls** window.



**Calibration controls**

Measurement chamber  
Name  
Standard

Calibration File  
StandardCal.txt

Calibration Parameters

F0 [MHz]	BW [MHz]
5.0	2.0
R [ohm]	C [pF]
100.0	2.0

Last harmonic included

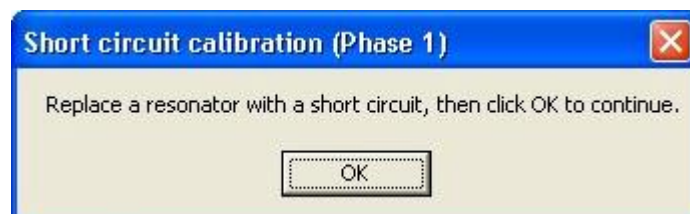
☐ None  
☐ 3rd harmonic  
☐ 5th harmonic  
☐ 7th harmonic  
☐ 9th harmonic  
☒ 11th harmonic

Calibrate

**Figure 3.14:** *Calibration controls. Select the measurement chamber available and press **Calibrate**.*

If an alternative measurement chamber is in use indicate so in the *Measurement chamber* box. With a new chamber remember to add it to the database first, select **Edit > Database** or see section **6. The Database** for details. In the *Calibration Parameters* box fill in the values for the fundamental frequency **F0** (usually 5 MHz), the bandwidth **BW** (usually 2 MHz) and the known resistance **R** (usually 100 Ohm).

In most circumstances the harmonics are very useful so it is advisable that the **11th harmonic** is chosen in the *Last harmonic included* box. Press **Calibrate** to begin the calibration.



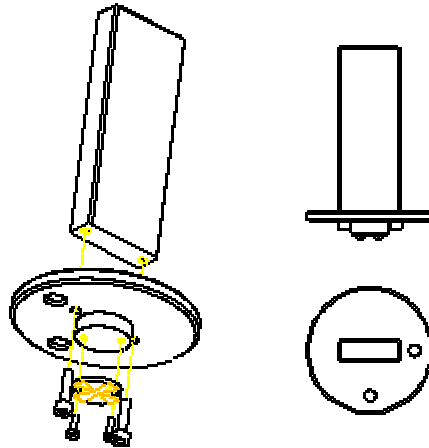
**Short circuit calibration (Phase 1)**

Replace a resonator with a short circuit, then click OK to continue.

OK

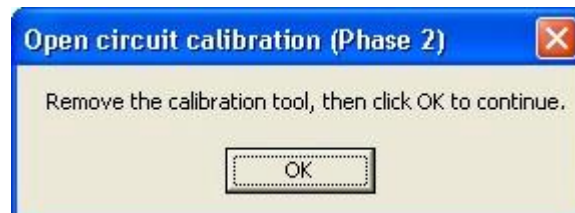
**Figure 3.15:** *Calibration instructions, phase 1.*

Lift the top module away from the standard axial measurement chamber to expose the electrodes. Insert the calibration tool so that the short circuit part of it is in line with the electrodes and the guidance pole goes through the designated hole on the tool. Press the calibration tool down gently and press **OK**.



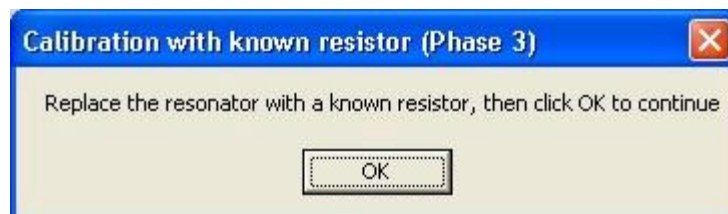
**Figure 3.16:** *The calibration tool.*

The mouse cursor changes to show an hourglass. After a while (even up to 1 minute) the following window will appear.



**Figure 3.17:** *Calibration instructions, phase 2.*

Remove the calibration tool from the measuring chamber and press **OK**.



**Figure 3.18:** *Calibration instructions, phase 3.*

Wait until this window opens. Replace the calibration tool into the measurement chamber, this time with the known resistance part in line with the electrodes. Press the calibration tool down gently and press **OK**.



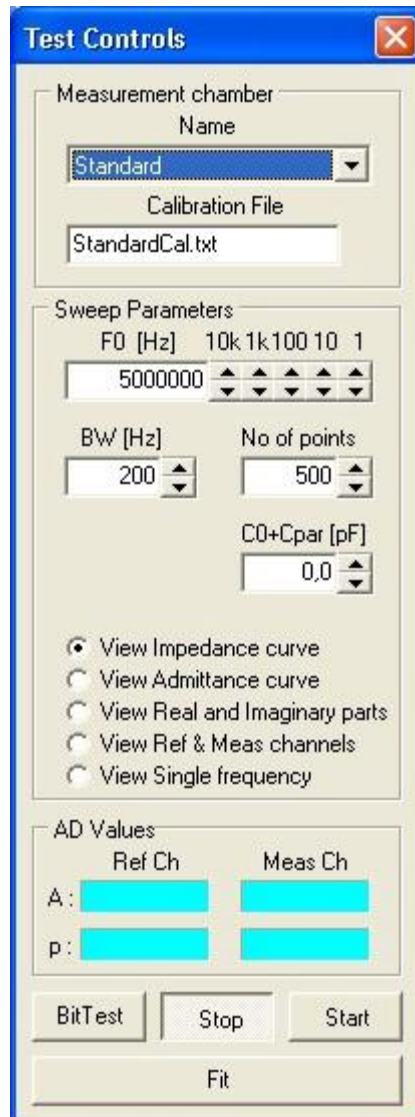
**Figure 3.19:** *Calibration complete.*

Calibration has been completed, press **OK** to start making measurements with this chamber.

Calibration of the QCM-Z500 microbalance should only be necessary the first time the instrument is installed. However it is recommended that the instrument is recalibrated every 6 months and each time the instrument is moved, even from table to table.

The calibration of the instrument can easily be checked by selecting **Controls > Test** from the main menu.





The **Test Controls** dialog box is used to configure measurement parameters. It includes sections for Measurement chamber, Sweep Parameters, View options, and AD Values.

**Measurement chamber**

Name: Standard

Calibration File: StandardCal.txt

**Sweep Parameters**

F0 [Hz]: 5000000

BW [Hz]: 200

No of points: 500

C0+Cpar [pF]: 0,0

**View options:**

- ☒ View Impedance curve
- ☐ View Admittance curve
- ☐ View Real and Imaginary parts
- ☐ View Ref & Meas channels
- ☐ View Single frequency

**AD Values**

	Ref Ch	Meas Ch
A:		
p:		

Buttons: BitTest, Stop, Start, Fit

**Figure 3.20:** *Test Controls. Select the test conditions and press **Start**.*

Press **Start** to see the impedance and phase curve as a function of frequency. By placing the calibration tool in the shortcut orientation impedance should show a value close to zero, while changing to the resistance orientation of the calibration tool should show an impedance value of the known resistance (usually 100 Ohm). If this is the case the instrument calibration is fine, if not then it is recommended to recalibrate the instrument.

For more information on the **Test Controls** screen please see section 7. **Testing and Troubleshooting**.



## 4. Measurement

### 4.1 Overview

Once the QCM-Z500 microbalance instrument has been installed and the communication between the instrument and the computer is established the instrument is ready to make measurements. Using the QCM-Z500 microbalance is straight forward, but there are certain steps that have to be done in order to obtain good and reproducible results and those are: cleaning the measuring chamber, cleaning the quartz crystal, assembling the measurement chamber, preparing the samples, filling the flow system and measuring chamber with a background liquid, starting the software and collecting the datapoints.

Each step is described in detail below in order to guide the user through making a complete measurement. It is advisable to make the first measurements with either pure liquids or a series of glycerol solutions in order to get a feeling for the instrument before starting with the actual measurements.

The **KSV QCM Impedance Analyzer** software is an easy to use Windows based program capable of being used for various types of experiments, to log data with real-time graphing and to review results from previous experiments.

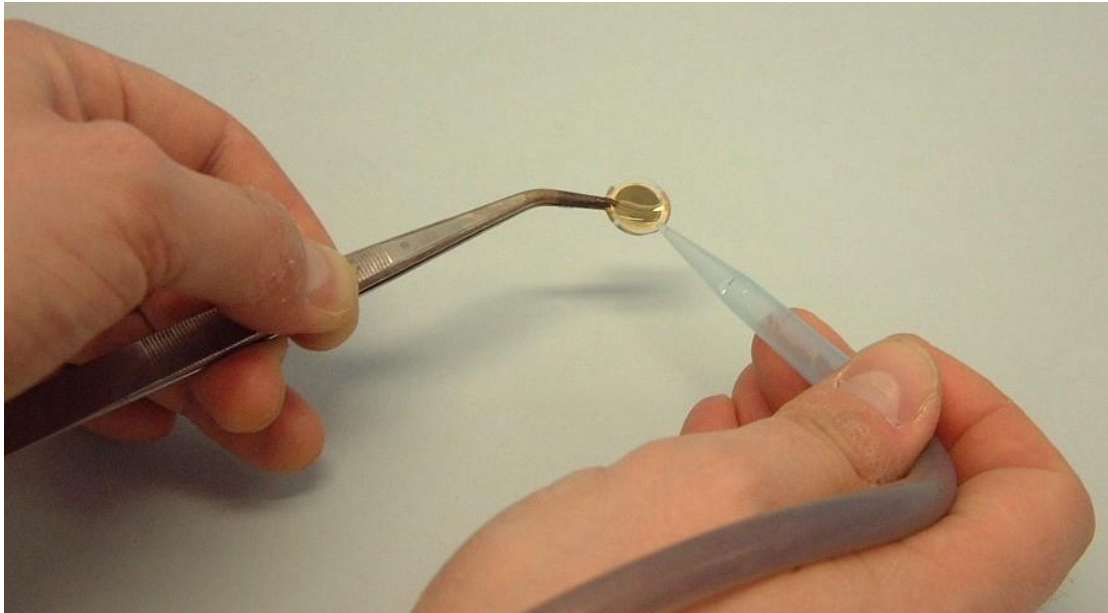
The software should be used with Windows 2000 or XP operating systems. Experimental data is stored directly to the hard drive in a single database library during an experiment. To access previous measurements an additional program, the **Browse Experiments**, is available. Through it specific measurements can be found by searching with the user name, file name, substance used or date of the experiment. Data can be exported as an image of the graph, as comma or tab delimited lists for use with a spreadsheet program or in ASCII format.

### 4.2 Cleaning the Quartz Crystal

Much of the stability and reproducibility of measurements made with the QCM depend on how well the crystal has been cleaned before use. There are several well-known cleaning procedures for quartz crystals and these can easily be found in literature. Here are 3 ways of cleaning the crystal:

- Place the crystal in a Piranha solution (1:3  $\text{H}_2\text{O}_2$ : $\text{H}_2\text{SO}_4$ ) for a couple of minutes and rinse the crystal afterwards thoroughly with ion exchanged water. Dry the crystal by blowing with nitrogen or use an aspirator to suck it dry. **Warning!** Piranha solution is very corrosive and utmost care should be taken and proper protective clothing should be used when handling it.

- Bring a 1:1:5 solution of  $\text{H}_2\text{O}:\text{H}_2\text{O}_2:\text{NH}_3\text{OH}$  to boil and place the crystal in it for about 5 minutes. Dry the crystal by blowing with nitrogen or use an aspirator to suck it dry.
- Leave the crystal inside a UV-ozone cleaning chamber for about 10 minutes. This method is very effective against organic contaminants. The crystal is ready to use straight from the chamber with no rinsing or drying necessary.



**Figure 4.1:** *Sucking the crystal dry.*

After any of these cleaning procedures the crystal can be used for measurements immediately.

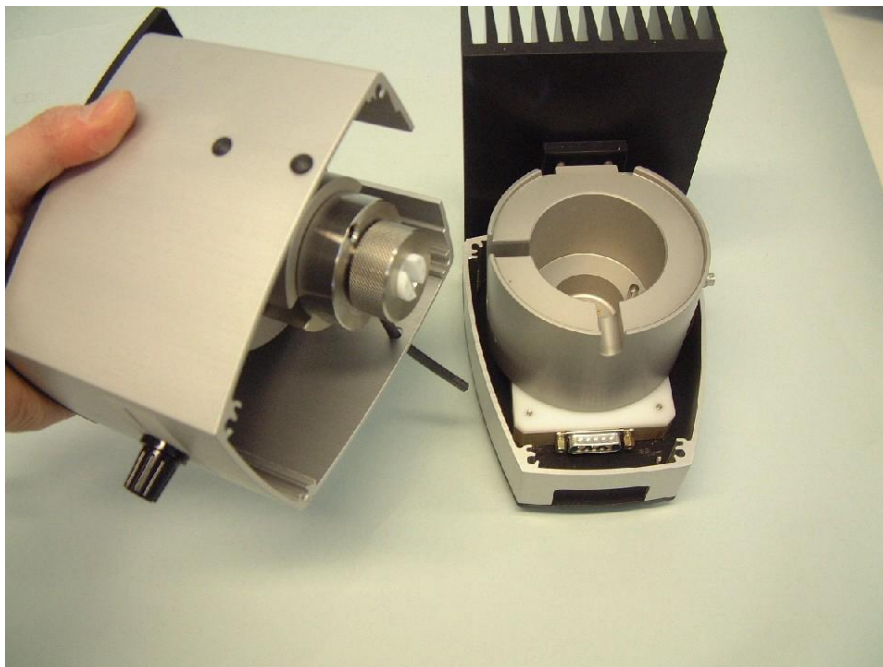
### **4.3 Cleaning the Axial Flow Measuring Chamber**

In order to have stable and reproducible measurements it is necessary to use a good cleaning procedure for the measuring chamber, i.e. its flow system and the parts in contact with the sample fluids. The cleaning of the flow system and the measuring chamber parts is therefore recommended before and immediately after each measurement.

The standard axial flow measurement chamber usually requires a rinse of the flow system and the measuring chamber parts with extensive amount of ethanol followed by ion-exchanged water to be sufficiently clean. However it might be necessary to use other liquids for cleaning, and finding the appropriate way of cleaning depends largely on the type of experiments so proper cleaning procedures develop by experience.

Here is the recommended method for cleaning the axial flow measuring chamber:

1. Lift the top module separate from the bottom module and take it to a sink. Set it down upside-down, unscrew the crystal support nut and remove all of the teflon chamber parts and the guidance pole.



**Figure 4.2:** *Separating the top module of the axial flow measurement chamber.*

2. Set the top module upright again, turn the valve to the Chamber position, fill the reservoir with an appropriate cleaning solution and let the liquid pass through the flow system. Repeat this for each cleaning and rinsing solution (often pure ethanol and ion exchanged water are enough) at least 3 times.
3. Turn the valve to the Stop position and turn the top module of the axial flow measuring chamber upside down so that the crystal chamber body is upwards. Rinse the inner compartment of the crystal chamber body first with the cleaning solution and then with the rinsing solution.
4. Dry the flow system and the inner compartment of the crystal chamber body either by using an aspirator or by blowing nitrogen through the system.
5. Clean the 2 Viton o-rings and the teflon crystal holder with appropriate cleaning and rinsing solutions.



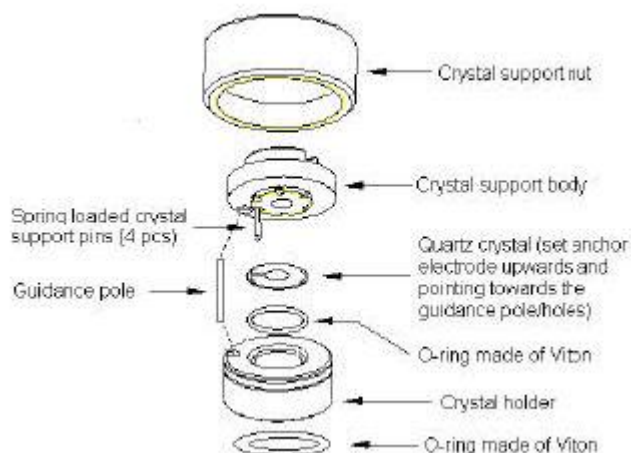
**Figure 4.3:** *The crystal support nut, o-rings, teflon chamber, crystal and guidance pole.*

6. Dry the o-rings and teflon crystal holder by either using an aspirator or blow them dry with nitrogen.

**NB!** Check to be sure that the cleaning agent is chemically compatible with the measurement chamber (see the **Chemical Compatibility of Viton** section at the end of this manual).

#### 4.3.1 Reassembling the Axial Flow Chamber

After all parts of the measuring chamber and the crystal have been cleaned the standard axial flow measuring chamber is reassembled. Please remember that cleanliness is very important during the assembly process as the slightest contaminations can spoil a measurement. Therefore it is strongly suggested to use clean tweezers and laboratory gloves when handling the o-rings, crystal holder and the crystal itself as these parts will be in direct contact with the sample. The crystal support nut, the crystal support body and the guidance pole are not in direct contact with the sample so cleanliness is not as critical.



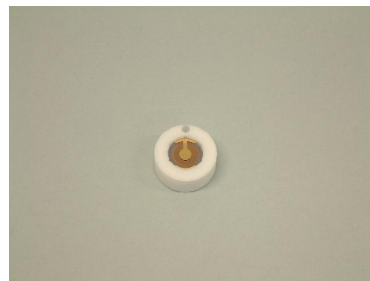
**Figure 4.4:** The components of the crystal support chamber of the axial flow measurement chamber.

Start the assembly process by placing the larger o-ring into the crystal holder.



**Figures 4.5 and 4.6:** Placing the larger o-ring in the crystal holder.

Turn the crystal holder around and place the smaller o-ring in the center of the crystal holder. Take the crystal and place it on top of this o-ring so that the larger gold electrode faces downward and that the anchor shaped electrode points towards the centering hole.



**Figures 4.7, 4.8 and 4.9:** Placing the crystal on the smaller o-ring in the crystal holder.

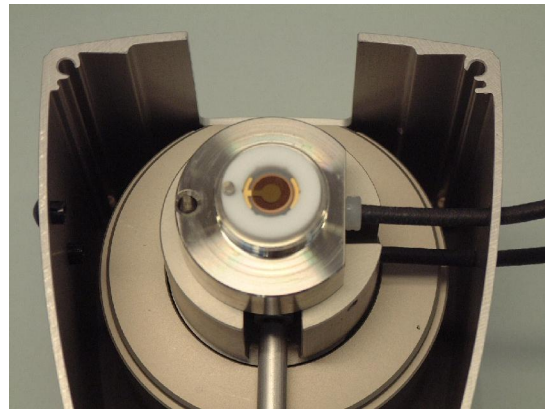
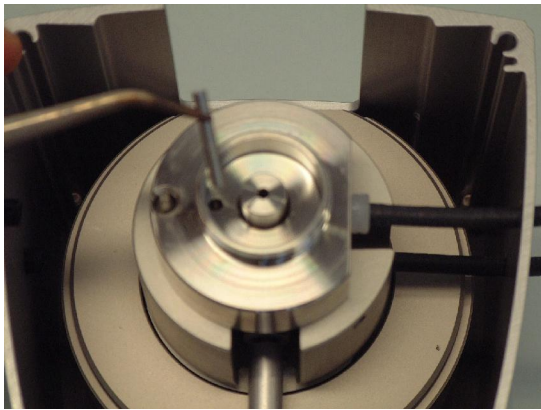
**NB!** It is very important that the crystal is loaded into the crystal holder as described because the larger plated electrode of the quartz crystal has to be



grounded when it is in contact with the sample fluid. No successful measurements can be performed with the crystal facing the wrong way.

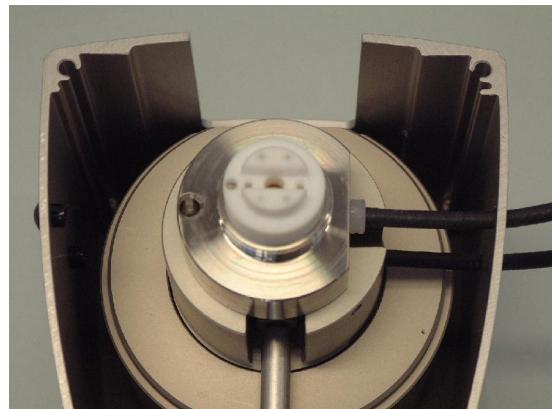
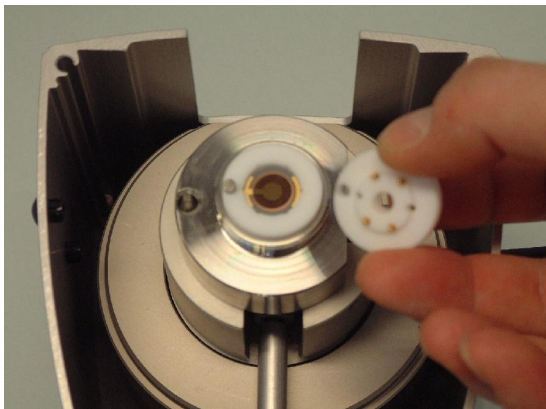
Be careful when handling the crystal, use only tweezers and gently hold the crystal from its edges. Do not touch the crystal or the plated electrodes directly as this will easily contaminate the crystal which will lead to unstable and irreproducible results. If it is necessary to touch the crystal then plastic gloves should always be worn.

The next step in the assembling process is to place the guidance pole in its position on the top module and then load the crystal holder with the o-rings and the quartz crystal into its position.

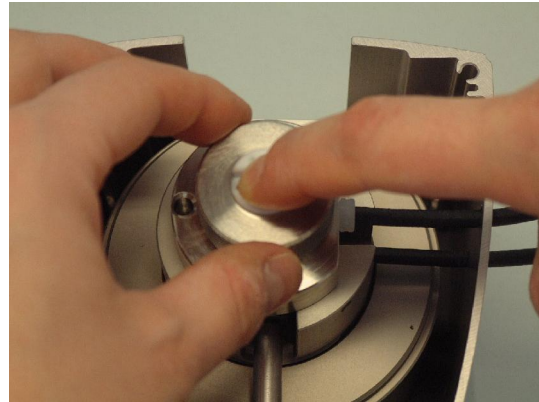
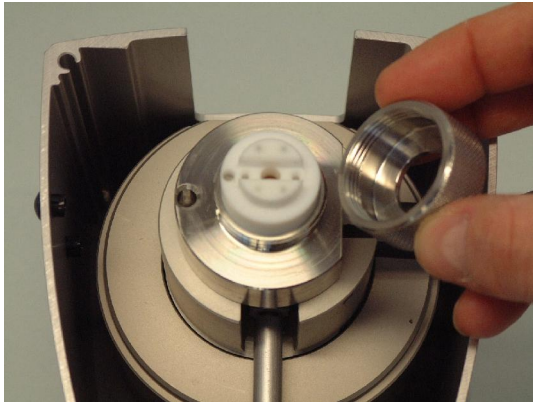


**Figures 4.10 and 4.11:** *Placing the guidance pole and the crystal holder back into the top module.*

Fit the crystal support body with the spring-loaded pins on the crystal so that the pins press the crystal against the o-ring and the guidance pole goes through the crystal support body. Place the crystal support nut on top of the crystal support body and screw it tightly to make the o-ring seal hold.

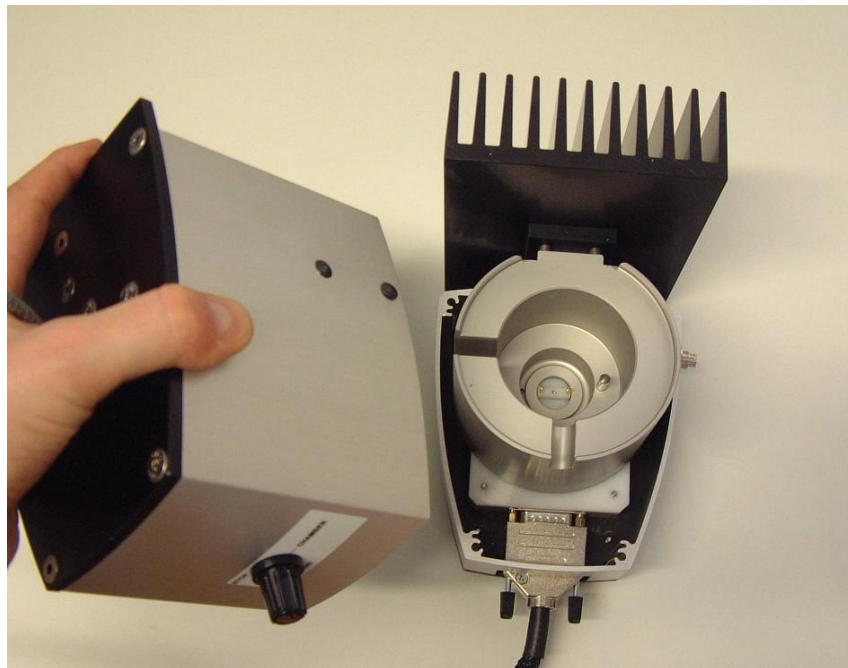


**Figures 4.12 and 4.13:** *Placing the crystal support body.*



**Figures 4.14 and 4.15:** *Placing the crystal support nut.*

Take the top module of the standard axial flow measuring chamber and place it on top of the bottom module. The guidance pole which sticks up from the bottom module prevents any false assembly of these two modules, i.e. the top module only fits into the bottom module one way. On the bottom of the bottom module there are 2 spring-loaded pins which will be in contact with the electrodes of the quartz crystal through holes in the crystal support body.



**Figure 4.16:** *Placing the top module back on the bottom module.*



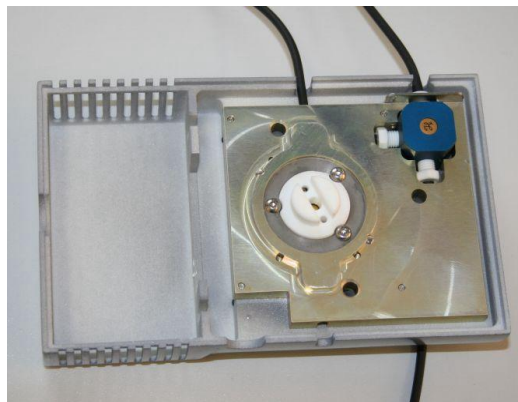
## 4.4 Cleaning the Parallel Flow Measuring Chamber

### 4.4.1 Disassembling the Parallel Flow Chamber

The measurement chamber usually requires a rinse of the flow system and the measuring chamber parts with extensive amounts of ethanol followed by ion-exchanged water to be sufficiently clean. However it might be necessary to use other liquids for cleaning, and finding the appropriate way of cleaning depends largely on the type of experiments so proper cleaning procedures develop with experience.

Here is the recommended method for cleaning the parallel flow measuring chamber:

1. Open the lock screw on top of the chamber. Lift the top module separate from the bottom module and take it to a sink. Set it down upside-down, open the crystal holder by pushing it gently and turning anticlockwise. Remove the crystal and the o-ring.



**Figures 4.17 and 4.18:** Separating the top module of the parallel flow measurement chamber.

2. Set the top module upright again, turn the valve to the Chamber position, fill the reservoir with an appropriate cleaning solution and let the liquid pass through the flow system. Repeat this for each cleaning and rinsing solution (often pure ethanol and ion exchanged water are enough) at least 3 times.
3. Turn the valve to the Stop position and turn the top module of the axial flow measuring chamber upside down so that the crystal chamber body is upwards. Rinse the inner compartment of the crystal chamber body first with the cleaning solution and then with the rinsing solution.

4. Dry the flow system and the inner compartment of the crystal chamber body either by using an aspirator or by blowing nitrogen through the system.
5. Clean the Viton o-ring with appropriate cleaning and rinsing solutions.
6. Dry the o-ring by either using an aspirator or blow them dry with nitrogen.

**NB!** Check to be sure that the cleaning agent is chemically compatible with the measurement chamber (see the **Chemical Compatibility of Viton** section at the end of this manual).

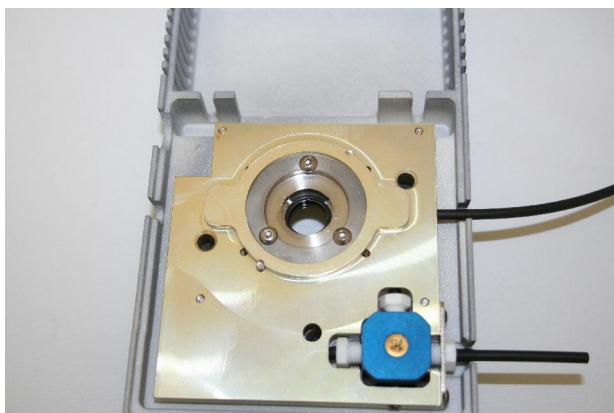


**Figure 4.19:** *The removable parts of the chamber: crystal holder, o-ring and the crystal.*

#### 4.4.2 Reassembling the Parallel Flow Chamber

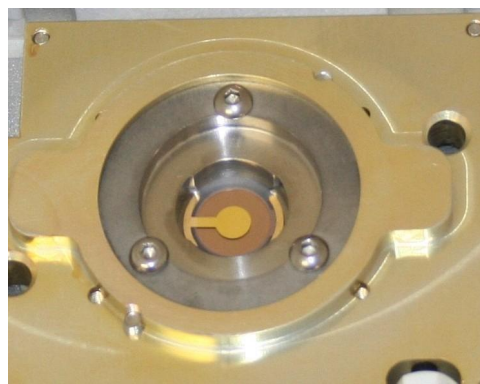
After all parts of the measuring chamber and the crystal have been cleaned the parallel flow measuring chamber is reassembled. Please remember that cleanliness is very important during the assembly process as the slightest contaminations can spoil a measurement. Therefore it is strongly suggested to use clean tweezers and laboratory gloves when handling the o-ring and the crystal itself as these parts will be in direct contact with the sample. The crystal holder is not in direct contact with the sample so cleanliness is not as critical.

Start the assembly process by placing the o-ring into the crystal chamber.



**Figures 4.20 and 4.21:** *Placing the larger o-ring in the crystal chamber.*

Place the crystal on top of the o-ring so that the larger gold electrode faces downward and that the anchor shaped electrode is on the left side.

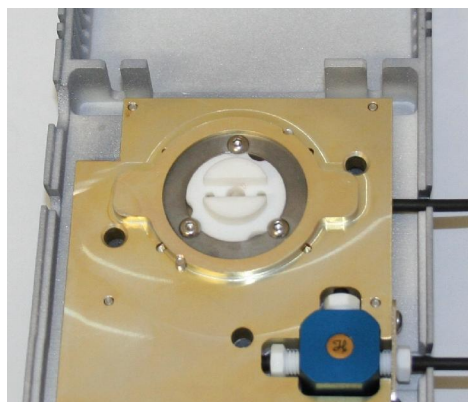


**Figures 4.22 and 4.23:** *Placing the crystal on the o-ring in the window chamber.*

**NB!** It is very important that the crystal is loaded into the crystal chamber as described because the larger plated electrode of the quartz crystal has to be grounded when it is in contact with the sample fluid. No successful measurements can be performed with the crystal facing the wrong way.

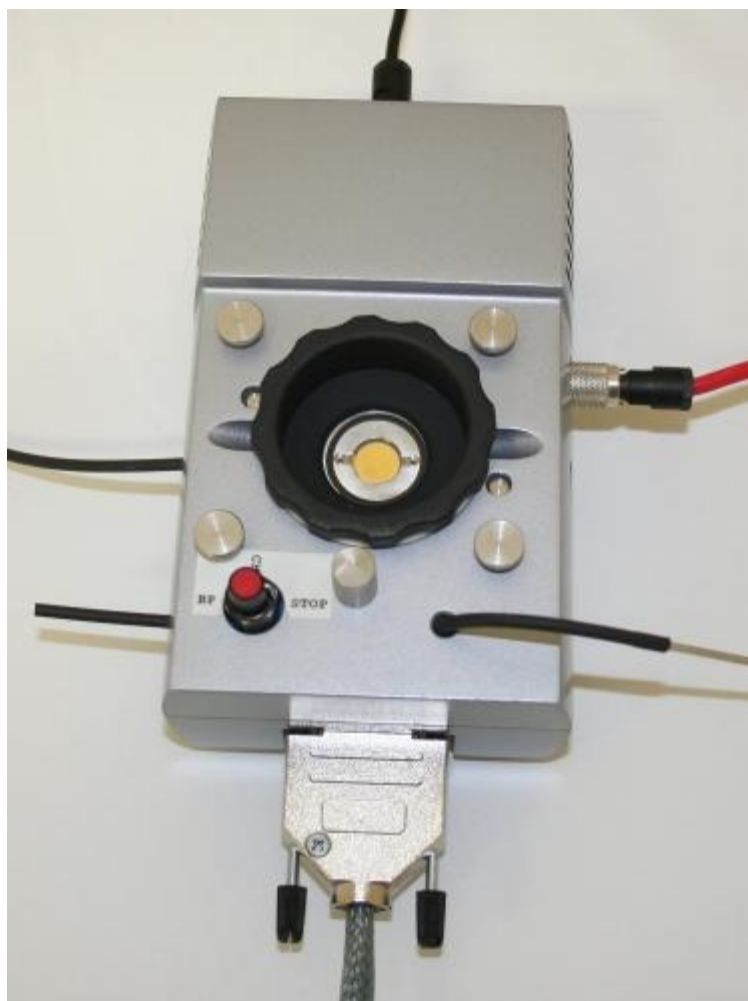
Be careful when handling the crystal, use only tweezers and gently hold the crystal from its edges. Do not touch the crystal or the plated electrodes directly as this will easily contaminate the crystal which will lead to unstable and irreproducible results. If it is necessary to touch the crystal then plastic gloves should always be worn.

The next step in the assembling process is to place crystal holder on top of the crystal. The crystal holder fits only in one way. Once the holder is in its place push it gently and turn it clockwise. The crystal holder is properly set when the electrode holes in the middle are horizontal.



**Figures 4.24 and 4.25:** *Placing the crystal holder back into the top module.*

Set the top module on top of the bottom module and tighten it with the locking screw.



**Figure 4.26:** *The fully assembled and connected parallel QCM ready to use.*

The temperature sensor (red cable) is connected to the right side of the chamber and the fan power cable (black cable) to the back of the chamber. The computer connection is connected to the front of the chamber.

## 4.5 Pre-filling the Temperature Loop

It is advisable to start the temperature control of the instrument 20 to 30 minutes before the actual measurement to improve its stability and reproducibility. This can be done with the Temperature Control Unit if available, but even if not it is important to fill the temperature loop and the actual chamber with the background liquid, follow this procedure to do so.

1. Check that the valve is set to Stop and fill the reservoir with the background liquid (often water).
2. Turn the valve to the Bypass setting, wait for a few drops to come out and return the valve to the Stop position. Fill the reservoir as necessary, no air bubbles should be let into the chamber and thus into the tubing.
3. Turn the valve to the Chamber setting and after a few drops have come out turn the valve to Stop.
4. If a Temperature Control Unit is available set the target temperature from the QCM-Z500 Impedance Analyzer program by opening **Controls > Temperature Controls** and selecting the appropriate temperature.

Wait 30 minutes before starting the experiment, use this time to fill in the **Experimental Setup** and otherwise ready the software side of the experiment.

### 4.5.1 Finalizing the Mechanical Setup

When all of the parts have been cleaned and the axial flow measurement chamber has been assembled check that

- All of the cables are connected, especially the one connecting the measuring chamber to the electronics unit, and that the electronics unit is on.
- If a temperature control unit is present make sure that it is connected to the measuring chamber and the computer directly (and not to the main electronics unit).
- The outlet tubes have a waste beaker under them so that the waste liquid is collected and disposed of appropriately.
- The temperature loop is filled with the background liquid, and if a Temperature Control Unit is available then it is set to the target temperature.

## 4.6 The Measurement Process



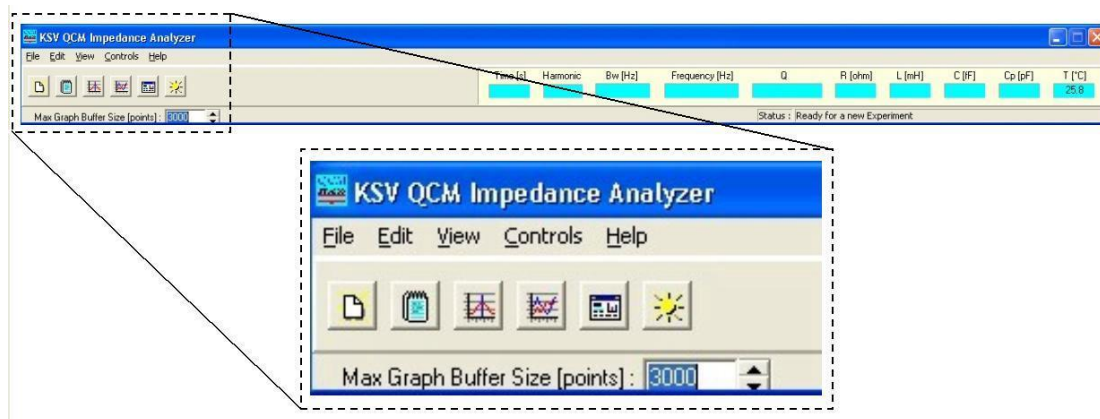
### 4.6.1 Starting up the QCM-Z500

When the power of the main electronics unit is turned on, the QCM-Z500 microbalance starts to boot up the internal Linux computer. A flashing green light on the front panel of the unit indicates that the computer is still loading, much like starting up a computer takes a few minutes. The booting process takes about 1 minute. Do not open the KSV QCM Impedance Analyzer software before booting has finished and the green light has stopped flashing or the connection cannot be made and the software must be restarted. \*\*\*






### 4.6.2 Software Overview

The KSV QCM Impedance Analyzer software has an easy and user-friendly interface. Experiments and any other communication between the computer and the main electronics unit are conducted from the program labeled **QCMZ**, and the data from previous measurements can be viewed and analysed from the program labeled **Browse QCMZ**. This section of the manual is only concerned with taking a measurement, analysing the data is explained in the following chapter of this manual, **5. Data Analysis**. Once these procedures are familiar use the checklist in section **2. Brief Instructions** to ensure the proper use of the instrument when running experiments.

To start the QCM program double-click the QCM icon on the desktop or choose **Start > Programs > QCMZ > QCMZ**. This will open the main menu of the program.



**Figure 4.27:** The QCM Impedance Analyzer main window.

-  Start a New Experiment
-  Experimental Setup
-  Show Sweep Graph
-  Show Graph
-  Show Measurement Controls



### Show Temperature Controls

A new experiment is begun from the **Start a New Experiment** button. This opens the **Experimental Setup** screen which contains the basic identifying data of the measurement, like user, resonator type, etc. After that the **Measurement Controls** window along with a **Sweep Graph** opens.

The **Sweep Graph** shows impedance and phase against frequency, the normally used **Graph** shows frequency change against time. A graph of the **Calculated Results** will open on top of the **Sweep Graph** once an experiment is underway with separate **Graphs** for each harmonic.

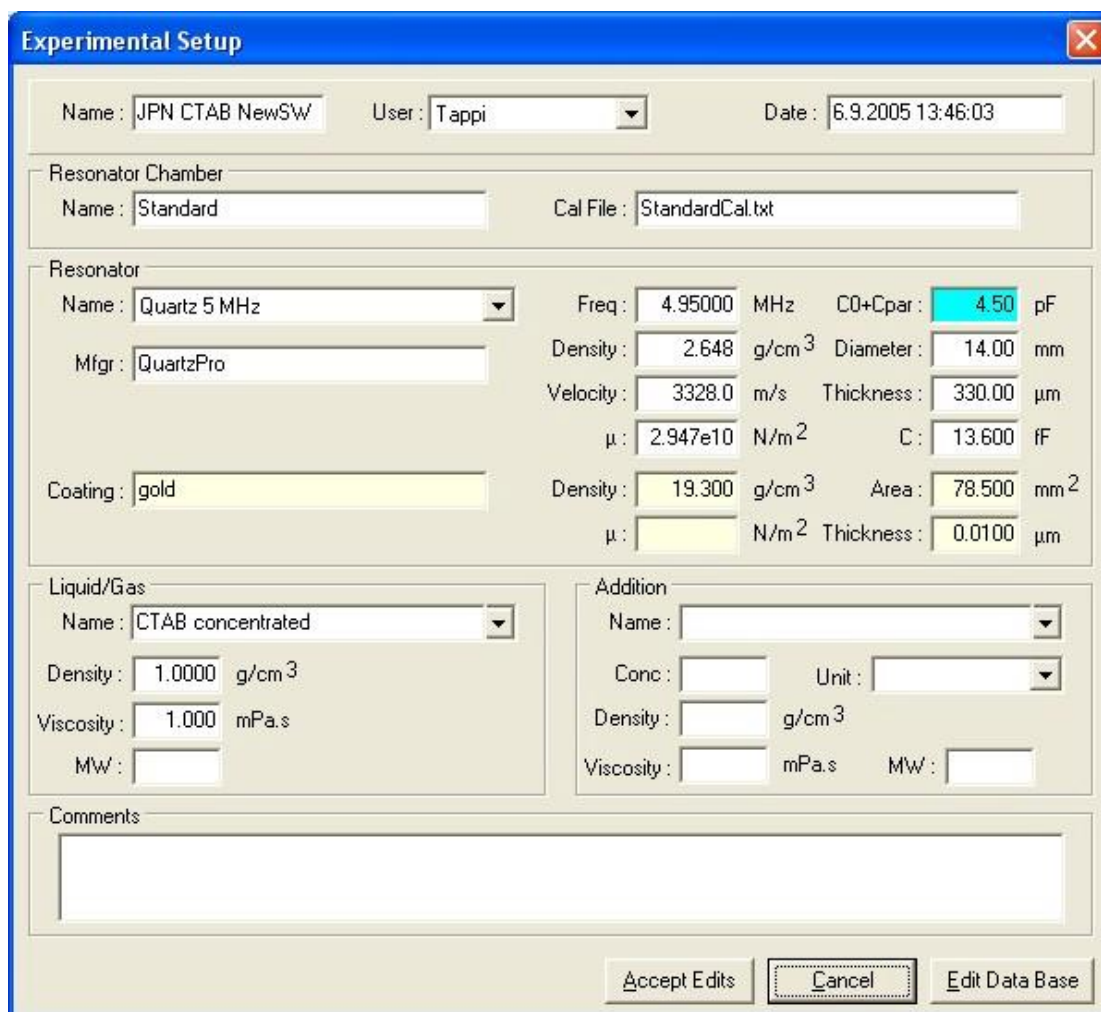
**Temperature Controls** is only available when a Temperature Control Unit is attached, use this to control the temperature of the measuring chamber with the computer. Alternatively it can be controlled directly from the Temperature Control Unit itself.

To start a new experiment choose **File > New Experiment** from the main menu window.

## 4.6.3 Experimental Setup

Fill in the information in the **Experimental Setup** window to comply with the measurement. Double-check the **Resonator Chamber** choice as the automatic choice might not always apply, and remember that a calibration must be run with each **Resonator Chamber** separately. For details on calibration, please see section **3.3 Calibration**. Several fields (like **User**, **Resonator Chamber**, etc) have a drop-down menu available. To add items onto the menu open the **Edit Data Base** and select the appropriate tab, for more details please see the **5.2 Edit Database** section of this manual.





The screenshot shows the 'Experimental Setup' window with the following fields and values:

- Name:** JPN CTAB NewSW
- User:** Tappi
- Date:** 6.9.2005 13:46:03
- Resonator Chamber:**
  - Name:** Standard
  - Cal File:** StandardCal.txt
- Resonator:**
  - Name:** Quartz 5 MHz
  - Mfgr:** QuartzPro
  - Freq:** 4.95000 MHz
  - Density:** 2.648 g/cm<sup>3</sup>
  - Velocity:** 3328.0 m/s
  - μ:** 2.947e10 N/m<sup>2</sup>
  - Coating:** gold
  - Density:** 19.300 g/cm<sup>3</sup>
  - μ:** (empty) N/m<sup>2</sup>
  - C0+Cpar:** 4.50 pF
  - Diameter:** 14.00 mm
  - Thickness:** 330.00 μm
  - C:** 13.600 fF
  - Area:** 78.500 mm<sup>2</sup>
  - Thickness:** 0.0100 μm
- Liquid/Gas:**
  - Name:** CTAB concentrated
  - Density:** 1.0000 g/cm<sup>3</sup>
  - Viscosity:** 1.000 mPa.s
  - MW:** (empty)
- Addition:**
  - Name:** (empty)
  - Conc:** (empty)
  - Unit:** (empty)
  - Density:** (empty) g/cm<sup>3</sup>
  - Viscosity:** (empty) mPa.s
  - MW:** (empty)
- Comments:** (empty text area)
- Buttons:** Accept Edits, Cancel, Edit Data Base

**Figure 4.28:** The Experimental Setup screen. Fill in identifying information on the experiment.

**Name** is the identifying name of the measurement, used to help locate the specific experiment later.

**User** is the person conducting the measurement.

**Date** records the time and date for future reference. It cannot be altered.

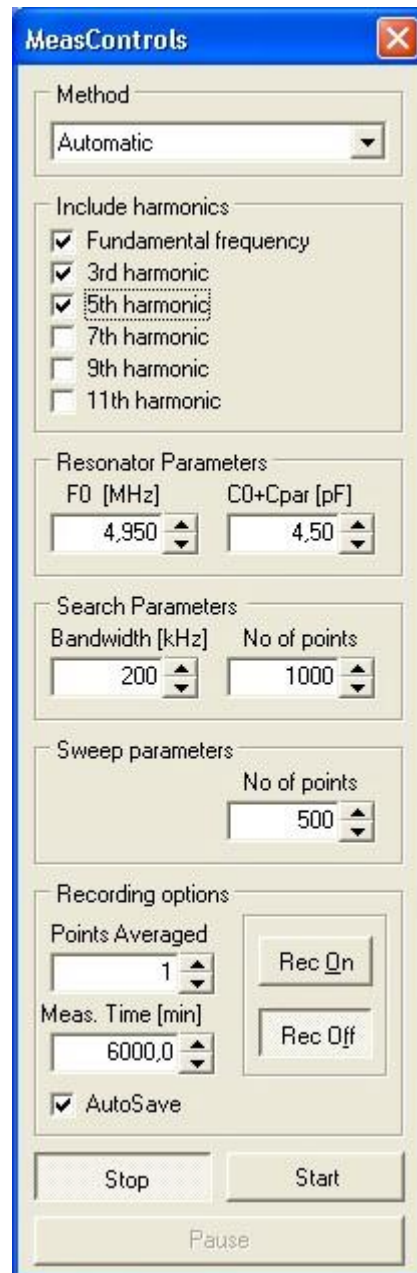
By selecting a **Resonator** (a quartz crystal) all of the required fields are automatically filled. If a new **Resonator** is added fill in the relevant data about it into the **Database** so as to avoid having to fill them in manually each time an experiment is run. Information in the **Liquid/Gas** and the **Addition** fields are for use when analysing the data as well as for reference.

Once all of the required information is filled out press **Start** to continue.

#### 4.6.4 Software Control of the Measurement

When the **Experimental Setup** has been completed, two windows will open, the **Measurement Controls** window and the **Sweep Graph** window. The **Sweep Graph** plots impedance and phase against frequency, and once the

experiment is begun a **Graph** of frequency change against time will open on top of it. If harmonics are selected they will all be shown on separate graphs. The **Measurement Controls** window controls the measurement chamber, how it resonates and what data is sent back to the computer. In most cases very little needs to be done in this screen except choosing all of the harmonics and pressing **Start**.



The screenshot shows the 'MeasControls' window with the following settings:

- Method:** Automatic
- Include harmonics:**
  - ☒ Fundamental frequency
  - ☒ 3rd harmonic
  - ☒ 5th harmonic
  - ☐ 7th harmonic
  - ☐ 9th harmonic
  - ☐ 11th harmonic
- Resonator Parameters:**
  - F0 [MHz]: 4,950
  - C0+Cpar [pF]: 4,50
- Search Parameters:**
  - Bandwidth [kHz]: 200
  - No of points: 1000
- Sweep parameters:**
  - No of points: 500
- Recording options:**
  - Points Averaged: 1
  - Meas. Time [min]: 6000,0
  - ☒ AutoSave
  - Buttons: Rec On, Rec Off
- Control Buttons:** Stop, Start, Pause

**Figure 4.29:** The Measurement Controls screen. Select measurement setup and press **Start** to begin an experiment.

There is only one measuring **Method** to choose from by default. This method, *Automatic*, sets the parameters for the measurements (that is, the **Resonator**, **Search** and **Sweep Parameters**) to fixed values that have been found to work

in most cases for measurements involving a gas, a liquid of either high or low density or soft films.

The **Resonator**, **Search** and **Sweep Parameters** cannot be changed when using the Automatic method. To change the parameters of the experiment create a new **Method** and fill in the parameters as wanted in the **Database**. From the **Edit** menu select **Database** to access it, please see section **5.2 Edit Database** for details.

What must be determined before the measurement are the **Recording Options** and the **Included harmonics** (overtones). The harmonics are selected by checking the respective box, the measurement data will be more complete and easier to analyse with more harmonics so it is advisable that they are all chosen.

The **Measurement Time** should be longer than the experiment is expected to last so that all of the interesting phenomenon will be recorded. With **AutoSave** checked the data will automatically be recorded, if unchecked begin and end recording with the **Rec On** and **Rec Off** buttons. The **Rec** buttons will only be active if **AutoSave** is not selected.

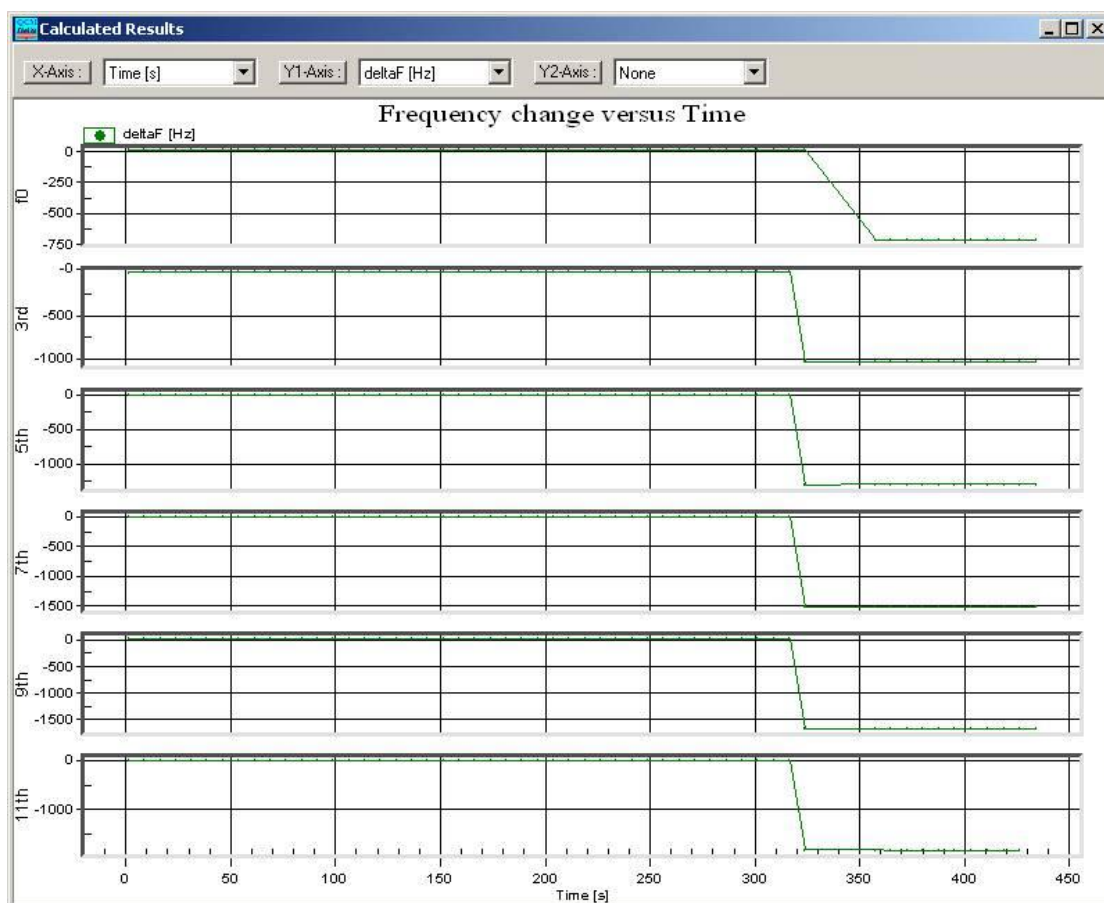
The software side of beginning the experiment is complete, it is now time to ready the chamber for the experiment if this has not yet been finished.

#### 4.6.5 The Measurement Process

Check now that all of the steps in **4.2 Preliminaries** have been completed. This means checking that

- All of the cables are connected and the electronics unit is on.
- If a temperature control unit is present make sure that it is connected to the measuring chamber and to the computer directly (and *not* to the main electronics unit).
- The outlet tubes have a waste beaker under them so that the waste liquid is collected and can be disposed of appropriately.
- The temperature loop is filled with the background liquid, and if a Temperature Control Unit is available then it is set to the target temperature.

When ready begin the experiment by pressing **Start**. The Sweep Graph should now activate and scan for the capacitance of each harmonic separately. Once that is finished the Sweep Graph is replaced by the normal Graph which by default shows change in frequency against time.



**Figure 4.30:** Graph of change in frequency against time for all harmonics.

Once the frequencies have stabilised it is time to introduce the actual sample into the chamber. Follow these steps to do so

- Empty the reservoir and open the Bypass. Let the bypass drain the background liquid.
- Pour the sample liquid into the reservoir. When a few milliliters of the sample have come out from the bypass outlet switch the valve to Stop and wait a few minutes to ensure thermal equilibrium.
- Turn the valve to Chamber. Allow a few milliliters to pass through the chamber to flush it and then put the valve on Stop.
- Again wait for the frequencies to stabilise. Flush with the background liquid another time or introduce the next sample according to what is being measured. Press **Stop** when finished, obtaining data for the measurement is now complete.

The measurement can be stopped at any time before the chosen **Measurement Time** has been reached by pressing **Stop**. This action will bring up a query of whether to keep the experiment data or not. If the measurement data collected so far should be stored in the database for further analysis press **Yes**, but if the measurement data is not useful (for example if waiting for frequencies to stabilise before the actual experiment) then press **No**.

#### 4.6.6 Useful Tips

Whenever operating the valve some key points about the working of the tubing should be kept in mind. When the sample is a liquid, it is important that no air bubbles reach the chamber. Thus whenever something is to be introduced to the chamber it must run through the bypass loop first. Also whenever anything is flowing out of the reservoir to either the chamber or the bypass checks should be kept on the level of the liquid. It should always have a few milliliters in reserve.

When changing liquids first empty the reservoir, set the valve to Bypass and allow it to empty. Then flush the bypass loop with the new liquid by filling the reservoir and allowing the liquid to flow down the bypass for several milliliters. It might be necessary to allow more liquid to flow down to clean the tubing.

Whenever changing from the Bypass to the Chamber position or visa versa always go by Stop.

The volume of liquid in the bypass loop is slightly above 2 ml, so by careful liquid handling it is possible to exchange the liquid in the actual measuring chamber with 2 ml of the sample liquid. This can be done by letting a small amount of air into the bypass loop and replacing the actual sample liquid with a less expensive liquid like water, and then with the help of measuring the amount of this substitute water make sure that the air bubble between the actual sample liquid and the substitute water never reaches the actual measuring chamber. This method however requires careful measuring and concentration to be successful.

The Sample Interval in the Recording options box can be reduced to 0.2 seconds i.e. 5 data points can be collected per second. However, this will increase the noise level of the measured signal and should not be used if there is not a real need for fast measurements.

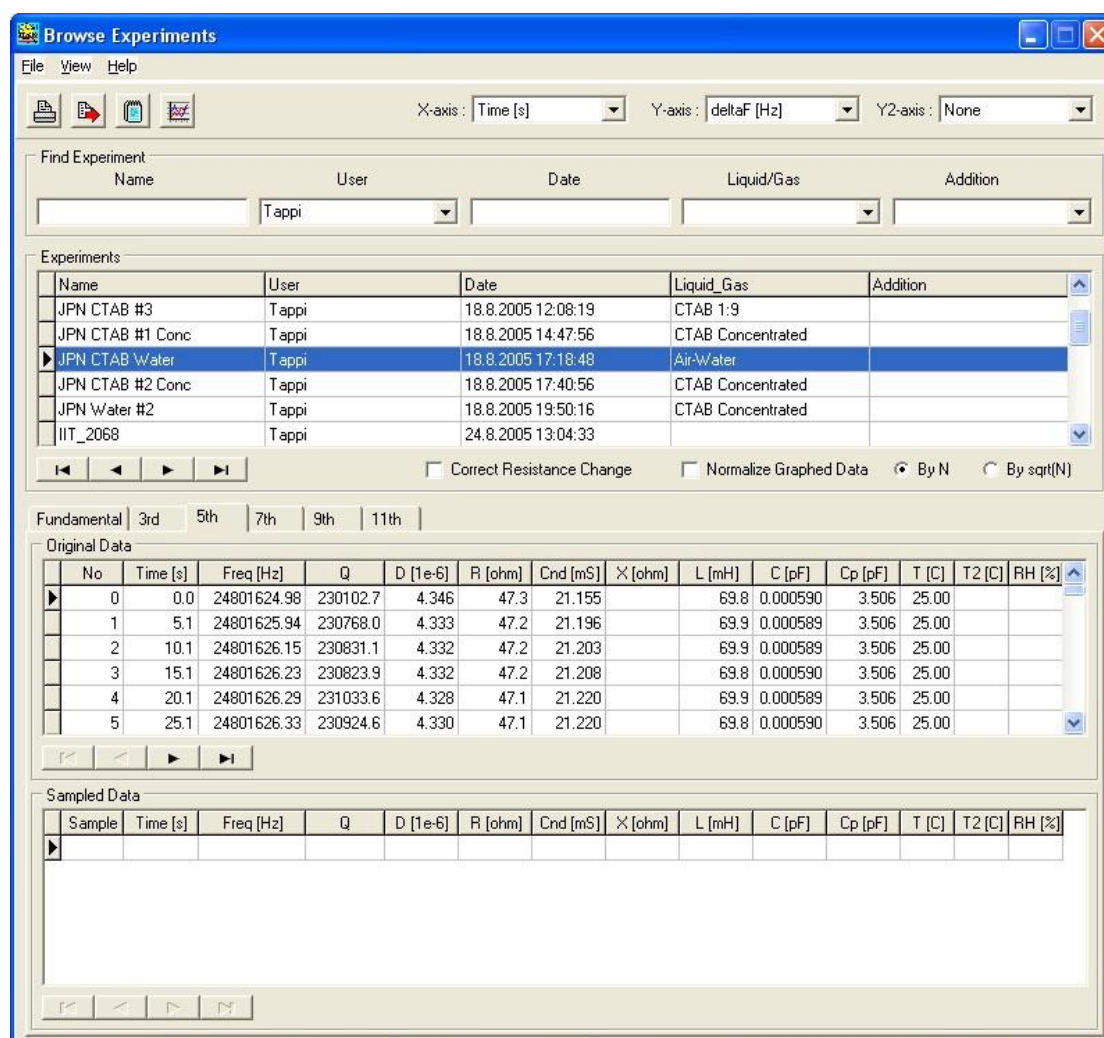
To check that everything is working correctly before starting an actual measurement it is possible to check the status of the QCM. Start a new experiment but do not let any liquid into the chamber, and check what resistance is measured across the crystal. The standard 5 MHz gold plated quartz crystal when clean and dry has a resistance of about 20 Ohm. Let water into the chamber and check the change in frequency. The change from air to water should be about -700 Hz. If either of these figures are off then there might be a problem with the cleanliness of the crystal, the water or some part of the QCM.

To view other graphs during the measurement choose different parameters for the x- and y-axis from the drop-down menu at the top of the Graph window. An additional curve can be plotted on the same graph by choosing a y2-axis parameter, click on the respective button to change the scale.

## 5. Data Analysis and Reduction

### 5.1 Overview

Handling the data obtained by QCM-Z500 microbalance measurements is all done with the separate **Browse Experiments** program. Use it to review data, print reports, view and manipulate graphs or to export data to another application. A separate **Analysis** program exists within the **Browse Experiments** screen, the use of which is described in section 5.5 Analysis.



**Figure 5.1:** Use the *Browse Experiments* screen to locate and analyse experiments.



## 5.2 Browse QCMZ Measurements

Open the QCMZ **Brows Experiments** by clicking on the icon on the desktop or selecting **Start > All Programs > QCMZ > QCMZBrowse** from the **Start** menu. It can also be found from the installation folder, open **My Computer** and select **C:\Program Files\KSV\QcmZBrowse.exe**

The main window is split into four boxes. The *Experiments* box lists all of the experiments that are on the database and fit the search criteria inserted in the *Find Experiment* box. The data sent by the QCM of the selected experiment is shown in the *Original Data* box, and if an analysis is run of the experiment then the results will be shown in the *Sampled Data* box.

The menu bar includes these options.

### File

- Search Experiments: adds all of the experiments in the selected folder to the *Experiments* box.
- Import Experiment: adds a single experiment to the *Experiments* box.
- Export Experiments: saves the selected experiment in a specific folder.
- Make a Copy of Experiment: copies all of the measurement data of the selected experiment.
- Copy Data to Clipboard: copies the data of the highlighted experiment to the clipboard for pasting in another program.
- Print: Opens a **Print Preview** screen of a report of the experiment containing all of the vital information.
- Remove Experiment from Browser: removes the selected experiment from the *Experiments* box but does not delete the measurement data.
- Delete Experiment: deletes selected experiment.
- Exit: Closes the **Browse Experiments** window.

### View

- Experimental Setup: Opens the **Experimental Setup** window of the highlighted experiment for viewing and editing purposes.
- Graph: Opens the latest graph viewed, will be blank until some data has been graphed.

The icons have the most commonly used functions readily available.



**Print** a report of the highlighted experiment.



**Copy** the **Data** of the highlighted experiment to the clipboard for pasting in another program.



**View Experimental Setup** window of the highlighted experiment for viewing and editing purposes.



**View** the latest **Graph** opened.



The axis of the graph can be chosen directly from the top of the **Browse Experiments** screen using the x- and y-axis selectors. Next item down is the *Find Experiment* box with search parameters that can be filled as far as necessary. The search fields limit the experiments visible in the *Experiments* box, select an experiment either by clicking on it or by scrolling with the arrows. Double-click on an experiment to display measurement data in the *Original Data* box. Use the tabs to select a specific harmonic. The following information about the measurement is shown.

No: Data point identification number.

Time [s]: Time at which the data point was taken.

Frequency: The measured frequency.

Q: The measured Q-value.

D: The measured dissipation value.

R: The measured resistance value.

Cnd: The measured conductivity value.

L: The measured induction value.

C: The measured capacitance value.

Cp: The measured parasitic capacitance value.

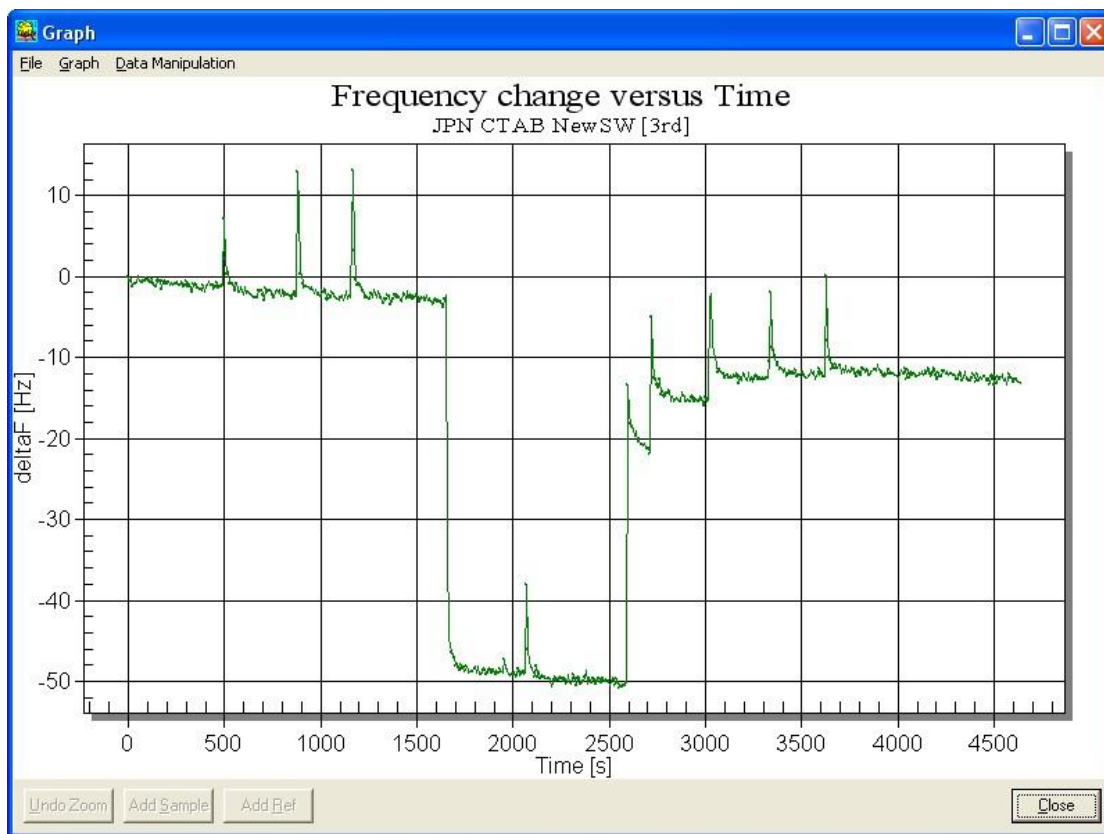
T: The measured temperature.

T2: The measured temperature from a second probe

RH: The measured relative humidity.

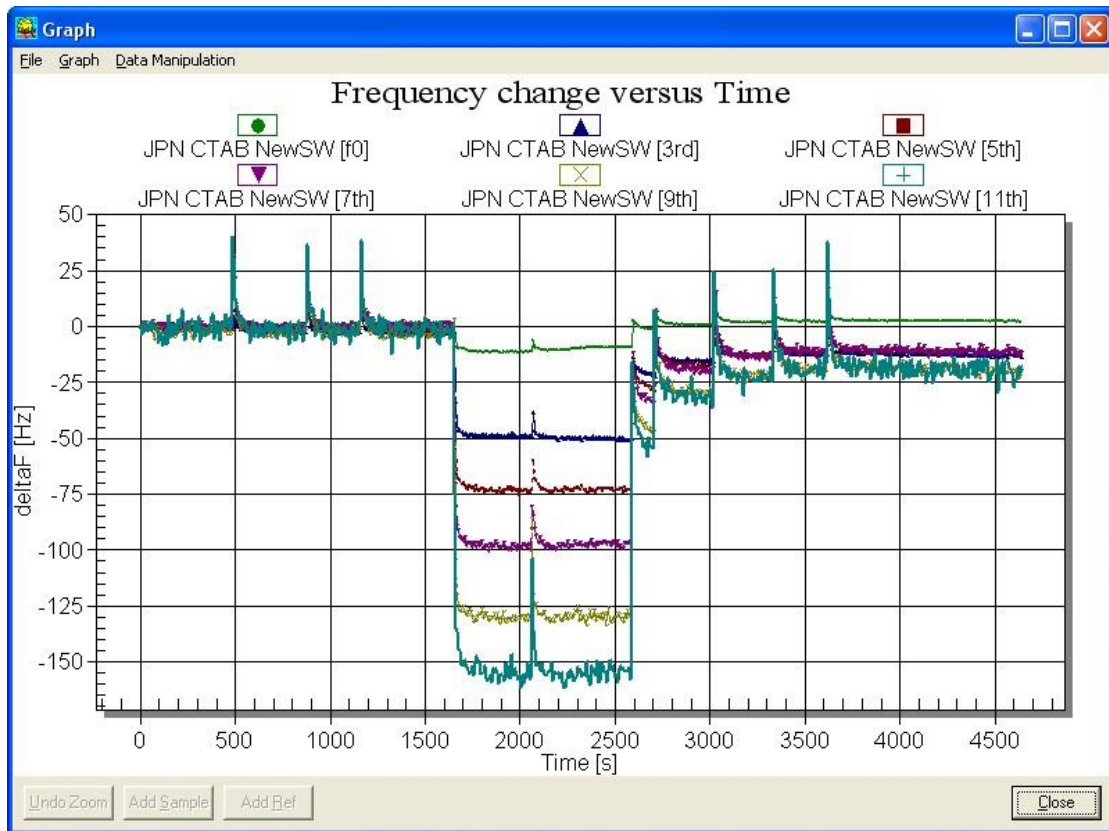
## 5.3 Data Graphing

The graphs of the **Browse Experiments** program are very versatile. The same graph can show simultaneously two separate variables plotted against a third variable for any number of experiments. To view the basic graph, right-click on an experiment in the *Experiments* box and select **Graph > Fundamental** or **Graph > Nth harmonic** where N is replaced by the number of the harmonic.



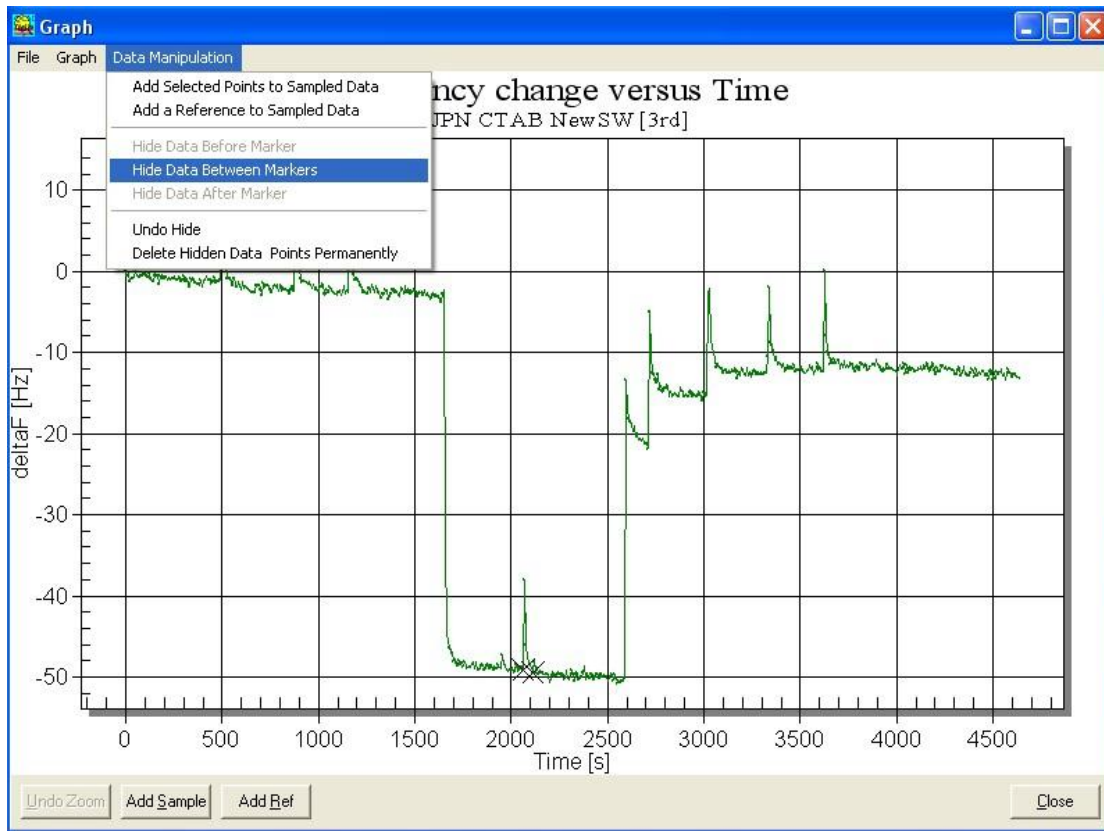
**Figure 5.2:** Graph of change of frequency against time for the third harmonic.

This is the same graph as is open during an experiment, plotting the change in frequency against time. To view the frequency change of another experiment on the same graph right-click on the experiment and select **Add to Graph > Fundamental**. To view the frequency changes of all of the harmonics of an experiment at the same time select **Graph > All**. To change the variable of an axis select a new one from the top of the **Browse Experiments** screen, right-click on an experiment and select **Graph**. Below is an example of all of the harmonics for an experiment.



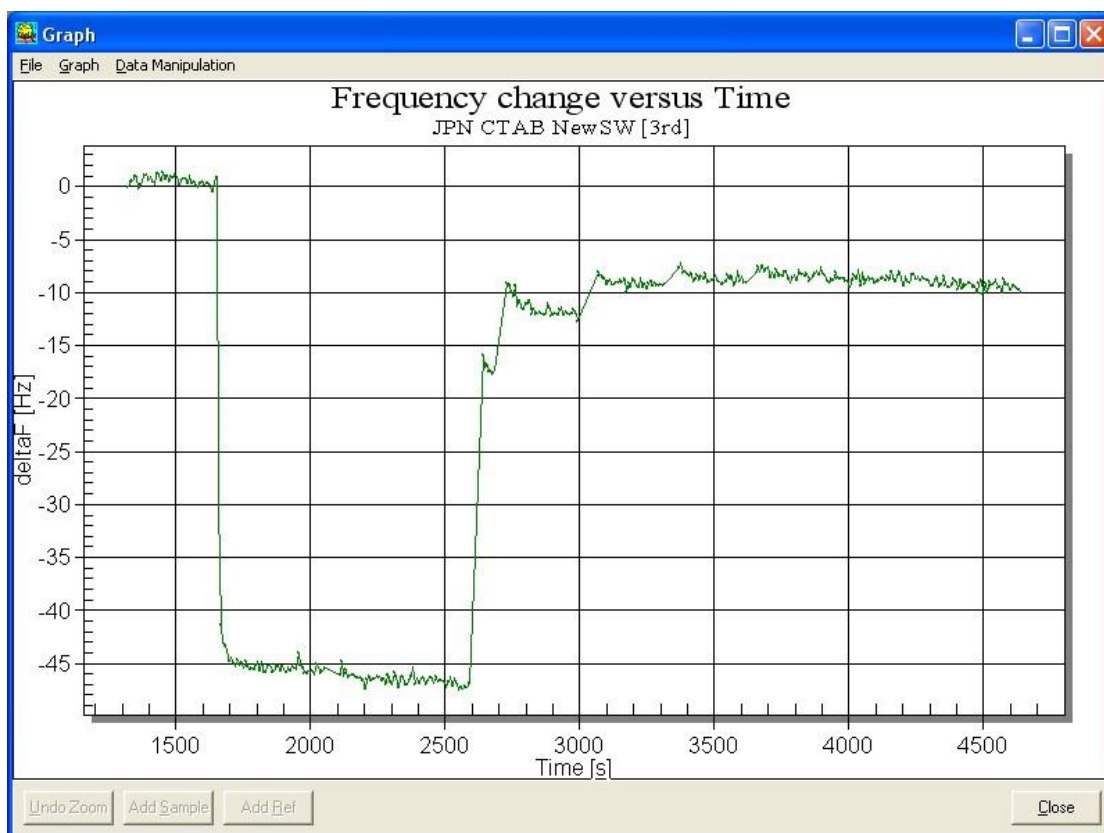
**Figure 5.3:** Graph of change of frequency against time for the all harmonics.

To alter the data visible the **Data Manipulation** menu gives the possibility to ignore selected data points. The options are to hide data before a selected point, after a selected point or between two selected points. Hidden data is not considered when running an **Analysis**. The **Data Manipulation** menu is also used to select sampled data, this is explained below. To select a point double-click on it.



**Figure 5.4:** *Removing data spikes from view to simplify analysis.*

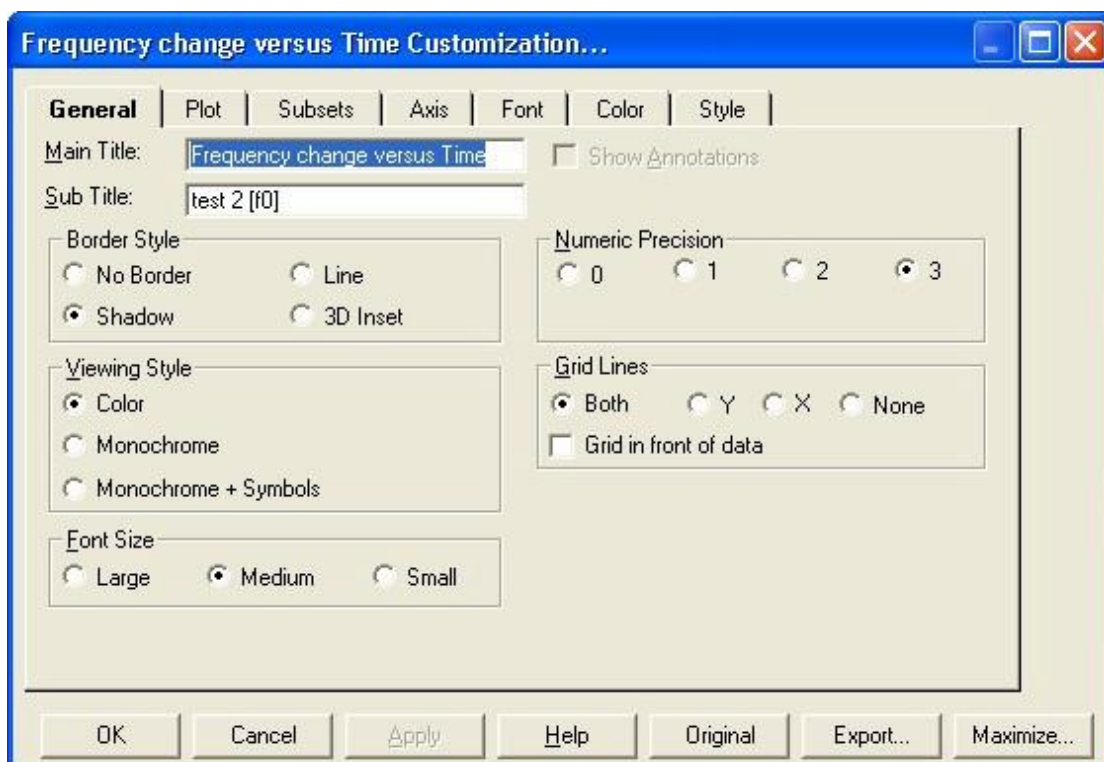
After hiding all of the irrelevant spikes (caused by operating the valve) the graph looks like this.



**Figure 5.5:** *Graph of change of frequency against time for the third harmonic, data spikes hidden.*

From the **Data Manipulation** menu this action can be cancelled by clicking **Undo Hide**, or made permanent by clicking **Delete Hidden Data Points Permanently**.

Once a graph is closed it can still be retrieved using the **Graph** icon on the top of the **Browse Experiments** screen, this brings up the last graph that was opened. To alter the display appearance of the graph or to export it select from the **Graph** menu **Show Menu**.



**Figure 5.6:** The graph Menu can be used to alter the appearance of the graph as well as to export the data.

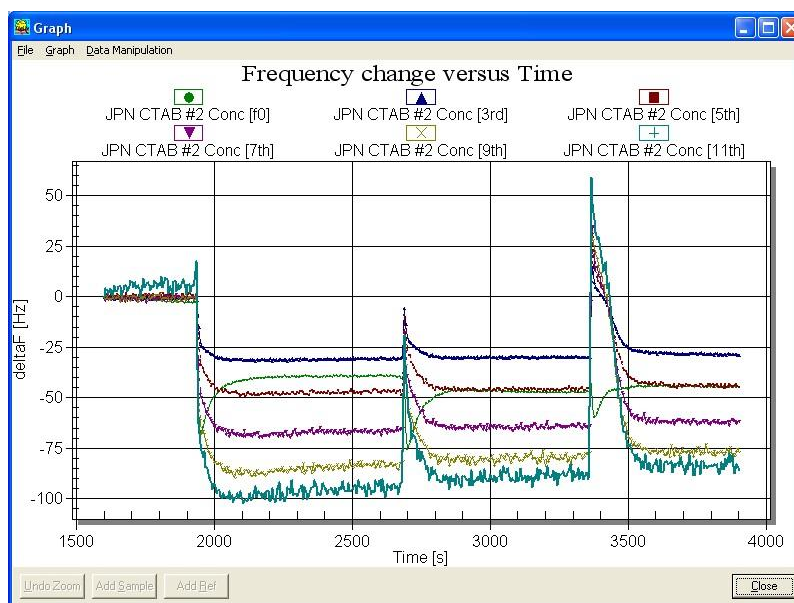
This section features seven tabs: **General**, **Plot**, **Subsets**, **Axis**, **Fonts**, **Color** and **Style**. The tabs have settings ranging from visual aspects of the graph to varying the values on the axis, and as most adjustments are familiar from other applications they shall not be explained in this manual. There is however a help file which can be accessed by clicking **Help**.

There are two extra buttons on the menu window. **Maximize** displays a full screen version of the graph and **Export** is used to export data to other applications.

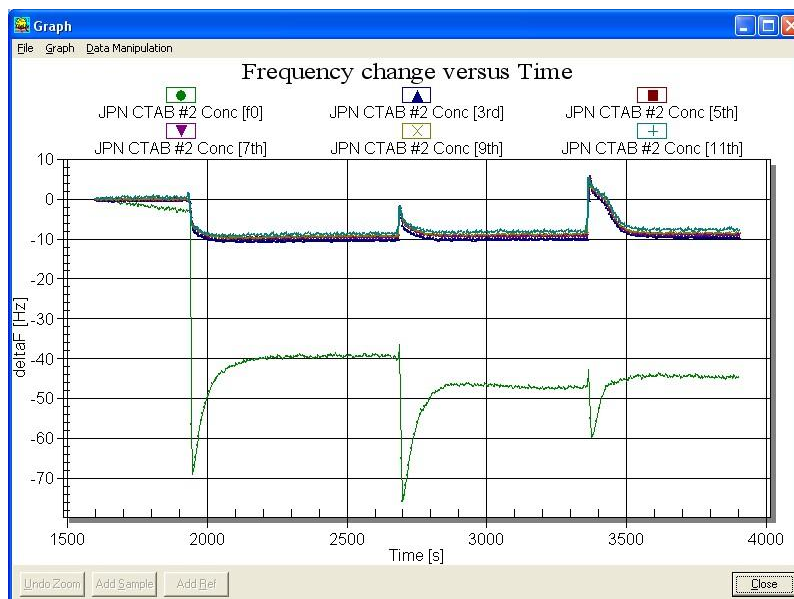
An **Analysis** window can be accessed from the menu which opens when right-clicking on an experiment in the *Experiments* box. This can use the normal continuous data or *Sampled data*, where specific data is selected from the graph of the experiment. This uses the **Add Sample** and the **Add Ref** buttons on the bottom of the graph, and is explained in section **5.5 Analysis**.

Below the *Experiments* box in the **Browse Experiments** window is the option to **Normalize graph data**. The purpose of normalising is to make the harmonics comparable to one another by either multiplying or dividing with the chosen variable, either N (number of harmonic) or the square root of N as the normalising term. Use N when dealing with a rigid film and square root N when dealing with changes in viscosity. Below is a demonstration of how normalisation works.

**Standard  
graph**



**Graph  
normalised by  
N**



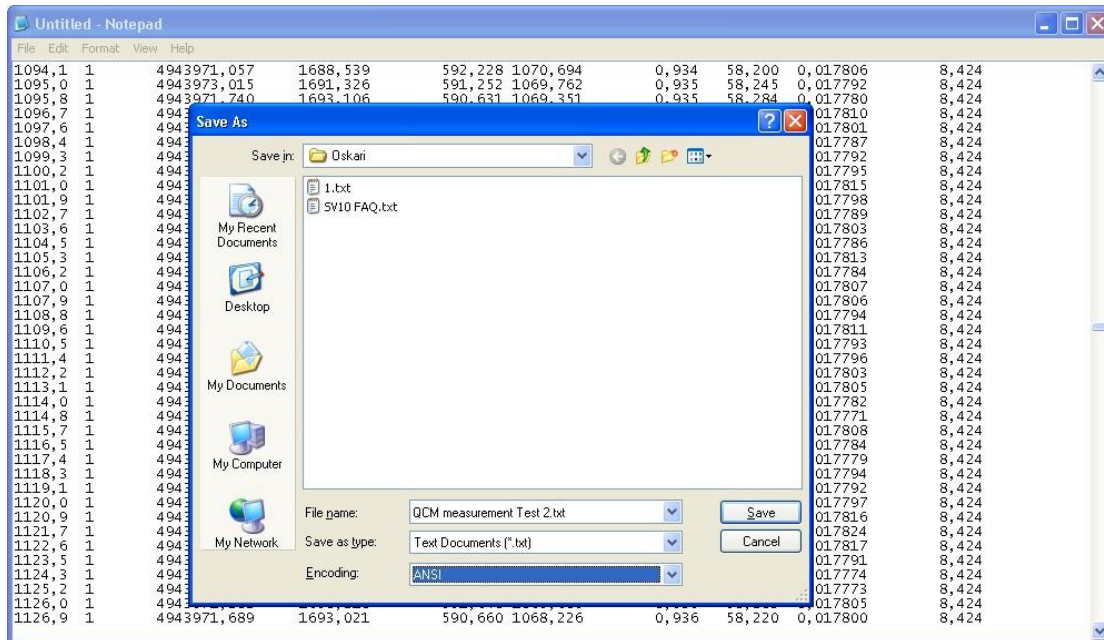
The normalised graph clearly demonstrates that the fundamental frequency exhibits curious differences to the other harmonics. It is often recommendable to ignore the fundamental in the analysis of QCM measurements.

## 5.4 Exporting Data

Data can be exported either as numbers in a data file or as a graph. The easiest way is to click on the **Copy Data to Clipboard** icon, open a spreadsheet program and then paste the data (often from **Edit > Paste** or by pressing **Ctrl + V**). To export the data in ASCII format click on **Copy Data to Clipboard**, open Notepad (located by default in **Start > Programs > Accessories > Notepad**), paste the data by pressing **Ctrl + V** in Notepad and

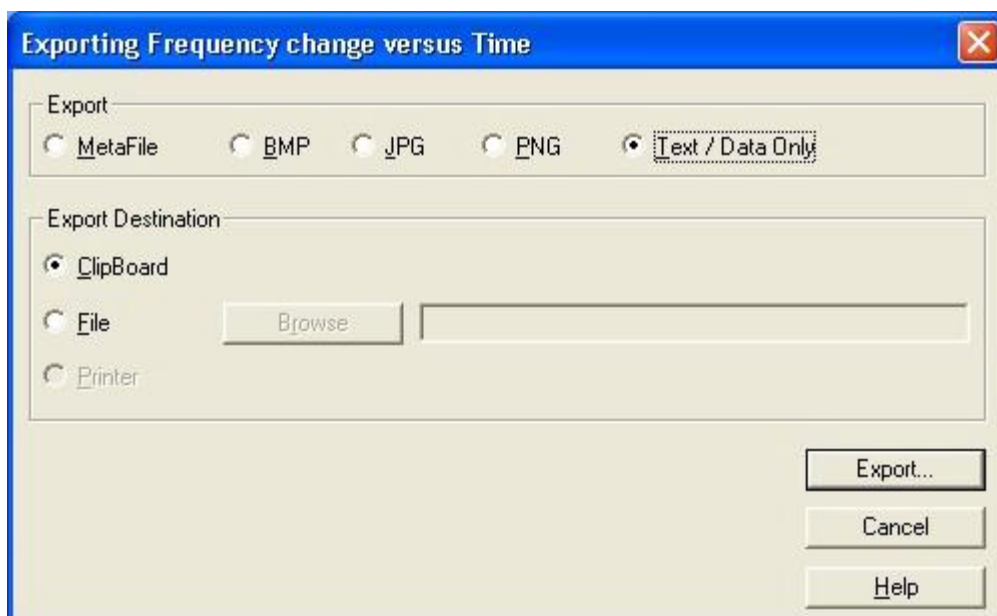


save. The lists of experimental data is in the same order as the data in the *Original Data* box in the **Browse Experiments** screen.



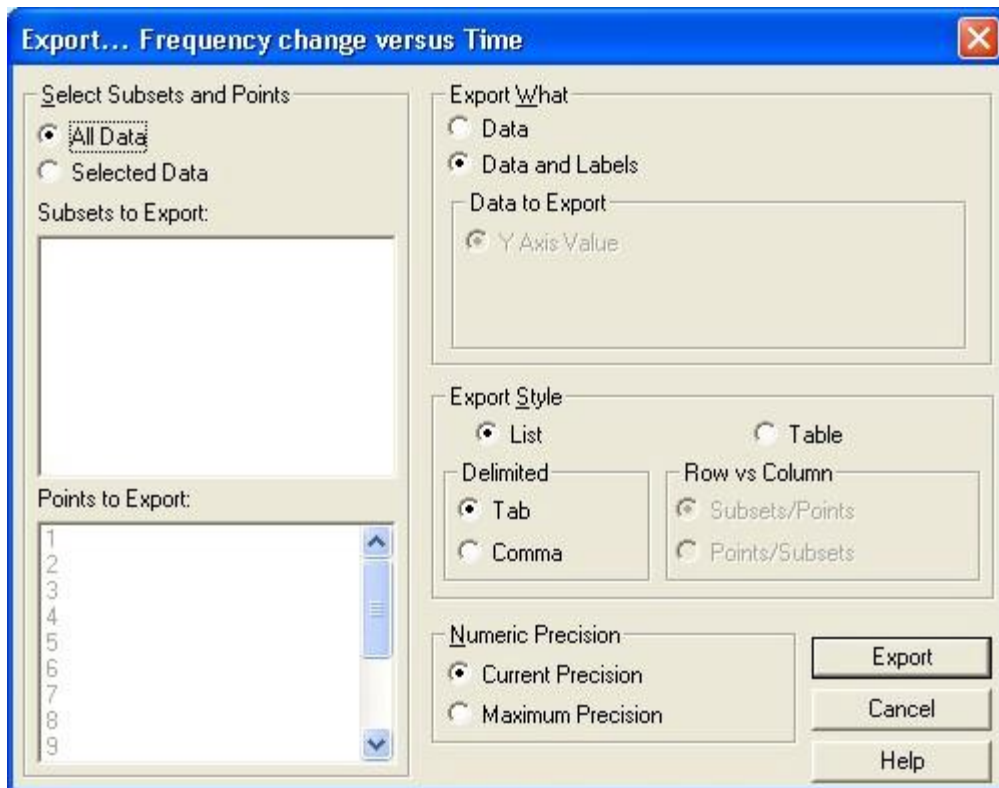
**Figure 5.7:** Pasting data onto **Notepad** to save it in ASCII format.

The data is tab delimited, for a comma delimited list open the **Export** menu of the graph of the required data. Do so by selecting **Graph > Show Menu** and clicking on **Export**.



**Figure 5.8:** Export data as an image or text file from the graph Menu's **Export** screen.

Choose **Text / Data Only** from the top and select whether to place the data on the clipboard (for pasting in another program) or to make a .dat file of it. Press **Export** to continue.

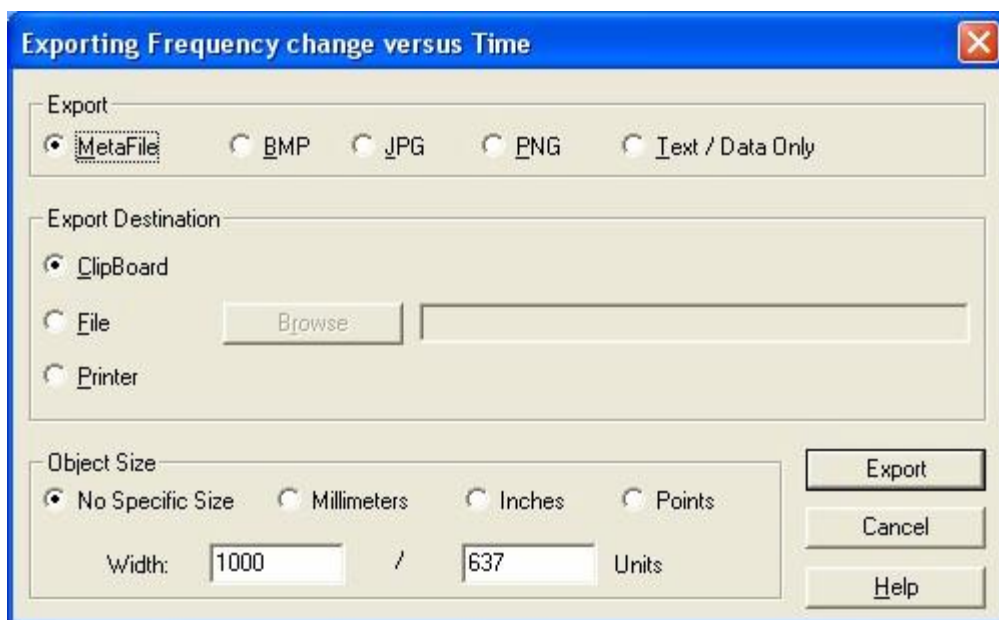


**Figure 5.9:** Exporting data as a text file, indicate format styles and press **Export**.

This menu has more specified information on what to export and in what format. When finished selecting press **Export** to continue, either by manipulating the .dat file created or pasting the data to another program.

To export the graph as an image use the same screen as shown above. First open the desired graph and from the **Graph** menu select **Show Menu** and then click on **Export**. The **Exporting [Name of Graph]** window opens and several options as to the image file type are given. Most often JPG will be fine. If the image is to be used within a document simply select **Clipboard** in the *Export Destination* box and **Paste** the image onto the document. If saving the image for later use select **File** and indicate the folder wanted by clicking **Browse**.

When an image file type is selected the *Object Size* box is visible, giving various options on size restriction methods. The default values should be fine in most cases and need not be adjusted.



**Figure 5.10:** *Exporting a graph as an image file. Select type, location, size and press **Export**.*

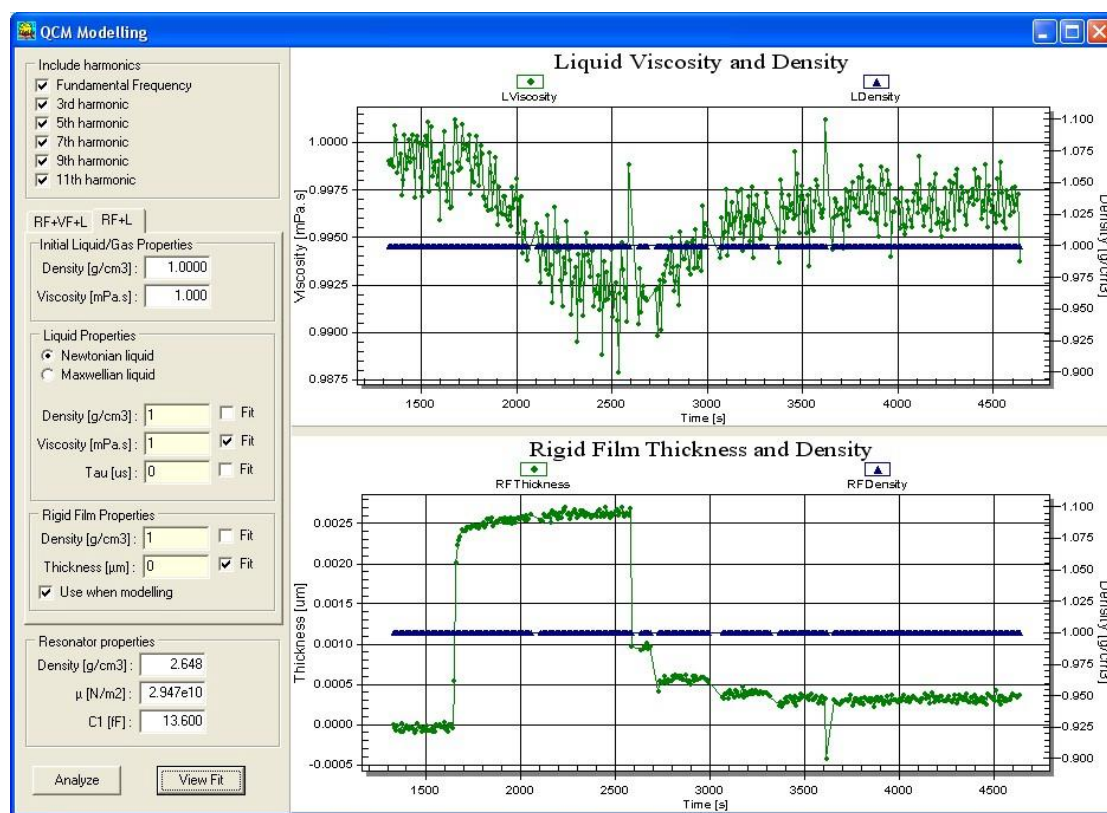
Alternatively just use the **Export Experiments** command in the **File** menu to save the selected experiment in the specified location. This saves the data in a format that only another QCMZ Browse Experiments software can read. Use this command to transfer measurement data to another computer with QCM software.

## 5.5 Analysis

The **Analysis** window provides useful tools to investigate QCM-Z500 microbalance measurements. It can be used to calculate for example the thickness of the film on top of the crystal and the viscoelastic properties of the sample. Additionally the measured frequency change and resistance can be compared to the theoretical values of each harmonic separately, calculated from the given experimental data.

Access the **Analysis** window by right-clicking on an experiment in the *Experiments* box and selecting **Analyze**.

### 5.5.1 Description



**Figure 5.11:** The *Analysis* window. Select modeling method, fill in the parameters and press **Analyze**.

The *Include harmonics* box in the top left corner of the window selects the harmonics to be used in the analysis. Often the fundamental includes peculiar phenomena that is not visible in the other harmonics and thus it might improve results to leave it out.

Two modeling methods are available, one in which the crystal is covered by a rigid film (**RF**) and a liquid (**L**) and one in which there is also a viscoelastic film

(VF) between the two. The *Resonator properties* box is filled automatically from the **Database** and thus cannot be altered from this screen.

Use **RF+VF+L** to observe the rigid and viscoelastic films of liquids.

Use **RF+L** to study viscosity changes in liquids or the rigid films in liquids.

The different tabs present different options and properties used in the analysis. For more detailed explanation on the differences and the equations used please see section **8.3 Theory of Impedance Analysis**. Most of the fields are filled from the **Experimental Setup**, others are to be filled with known or estimated data.

In each *Properties* box there are several fields, some which have a faint yellow background and can be altered from this screen, some which have a white background and need to be altered from the database if necessary. To add or change a value in these fields access the **Database** by closing the **Analysis** window, opening the **Experimental Setup** screen and pressing **Edit Database**. Due to the equations used (see section **8.3 Theory of Impedance Analysis** for details) some variables can not be fitted simultaneously so a choice between two has to be made. Some variables present a choice of whether to fit it or not, those not selected for fitting will be considered constant and those selected will use the given value as the first term in the modeling.

## A) RF + VF + L

In the **RF+VF+L** tab are three boxes, one for the properties of each layer.

The *Initial Liquid/Gas Properties* box has two fields, Density and Viscosity, which are filled automatically from the data in the **Database**.

The *Liquid Properties* box has several fields that can be adjusted from this screen. These are the Density, Thickness,  $G'$  and either Viscosity or  $G''$  of the film. Each variable presents a choice of whether to **Fit** it or not. Select whether to use viscosity or  $G''$  in the model from the top of the box.

The *Rigid Film Properties* box has two fields that can be adjusted. Those are the Density and the Thickness of the film. There is also a choice of whether to use that information when modeling or not.

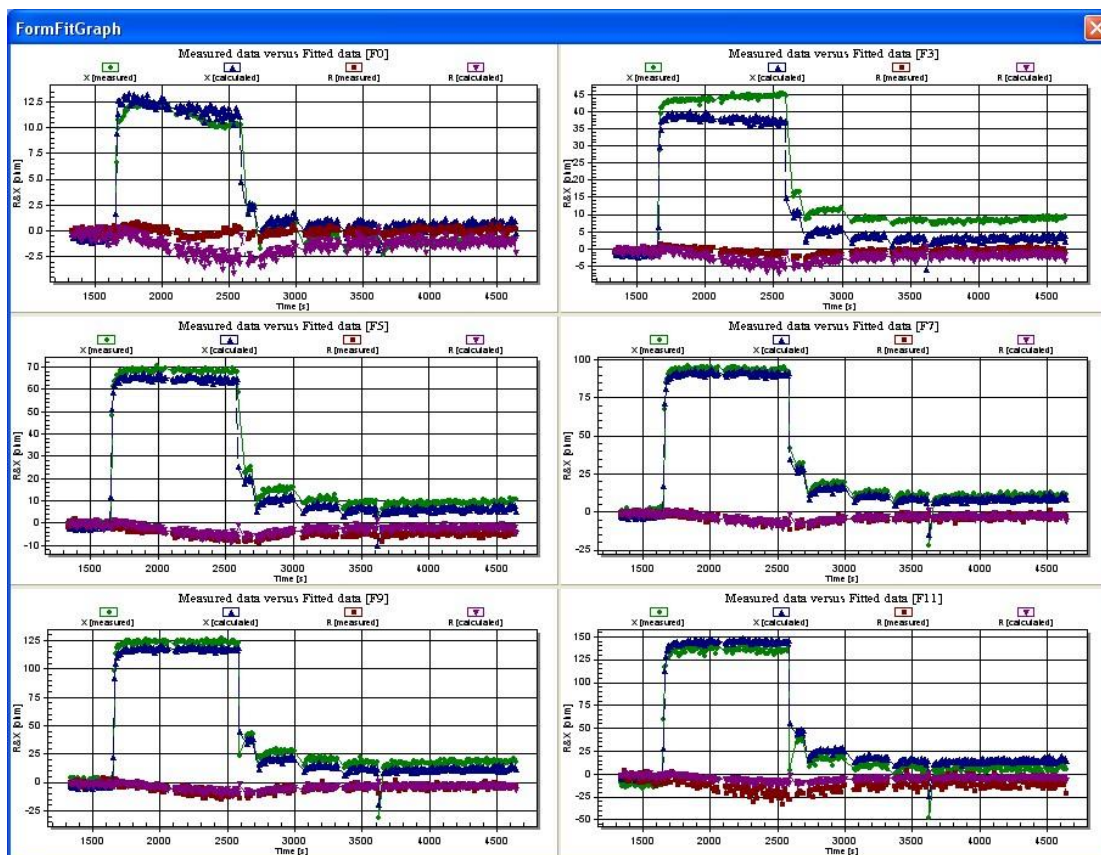
## B) RF + L

The **RF+L** tab is almost the same as the **RF+VF+L** tab, the main difference being the absence of the *Viscoelastic Film Properties* box. The *Liquid Properties* box has three adjustable fields which are Density, Viscosity and Tau. There is also a choice of whether the liquid is Newtonian or Maxwellian.



The *Rigid Film Properties* box has two fields that can be adjusted, the Density and the Thickness of the rigid film of which only one can actually be used in the fitting.

The **View Fit** button opens a new window displaying graphs of the harmonics individually. The graph displays both the resistance  $R$  and the reactance  $X$  against time, and for both variables a measured value and a calculated value are shown. This can be useful to compare the accuracy of the model against the experimental data.



**Figure 5.12:** The View Fit screen compares the calculated and measured values for each harmonic separately.

The **Analyze** button runs the modeling program, and the results are displayed on the two graphs on the right side of the screen. The **Film thickness** graph simply plots the thickness, in micrometers, of the film on top of the crystal as a function of time. The **Elastic shear modulus and shear viscosity** graph has two values, the elasticity in mega Pascals and the viscosity in Pascal seconds against time.

### 5.5.2 Sampling Data

Experimental data is imperfect, in the above example changing the position of the valve caused spikes in the readings. The way to remove these known errors from analysis was to hide them from the graph. Another method which

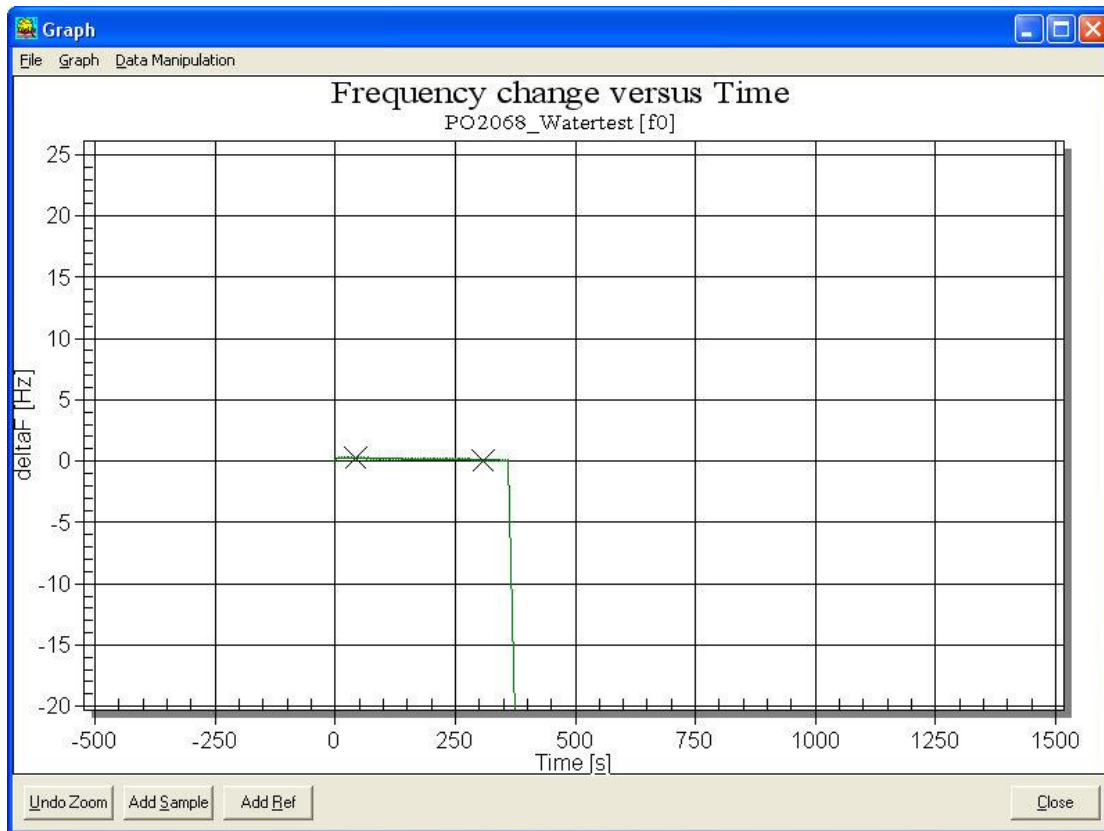


improves the quality of readings and is to be recommended in most cases when running an analysis is to sample the data. Note that in experiments with a large number of data points (e.g. overnight experiment with a reading taken every second) data sampling significantly reduces the time taken to calculate an analysis.

Data sampling works by selecting data sets from the graph of a measurement of the change in frequency of a harmonic against time. Successive samples are taken from an experiment and compared against a reference reading. Two alternate methods are available, depending on whether the reference value is taken from this experiment or another. If the reference reading can be taken from this experiment then first select the reference value (usually from the beginning of the experiment) and check that it is designated **Sample Number 0**. Then select successive samples with sequential numbering starting from 1 are taken from the measurement.

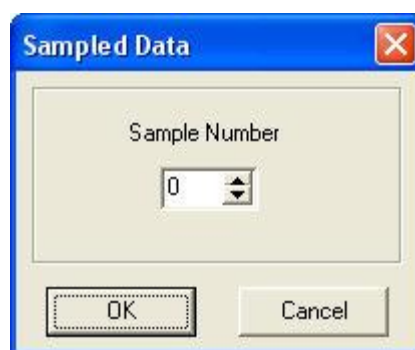
If however the reference reading is to be taken from another experiment then it must be taken *last*. Thus first select the samples with sequential numbering starting from **1** from the measurement. Then open the measurement from which the reference reading is to be taken from and select the reference reading, ensuring that it has **Sample Number 0**.

Samples (and references) are obtained from the graph of a single harmonic at times when the frequency has stabilised. Zoom in on the chosen frequency by clicking and dragging a box around it. Double-click on the points that mark the limit of the data set to select it. The actual recorded sample point is the average of all the values between the markers, and it will be automatically calculated for all harmonics.



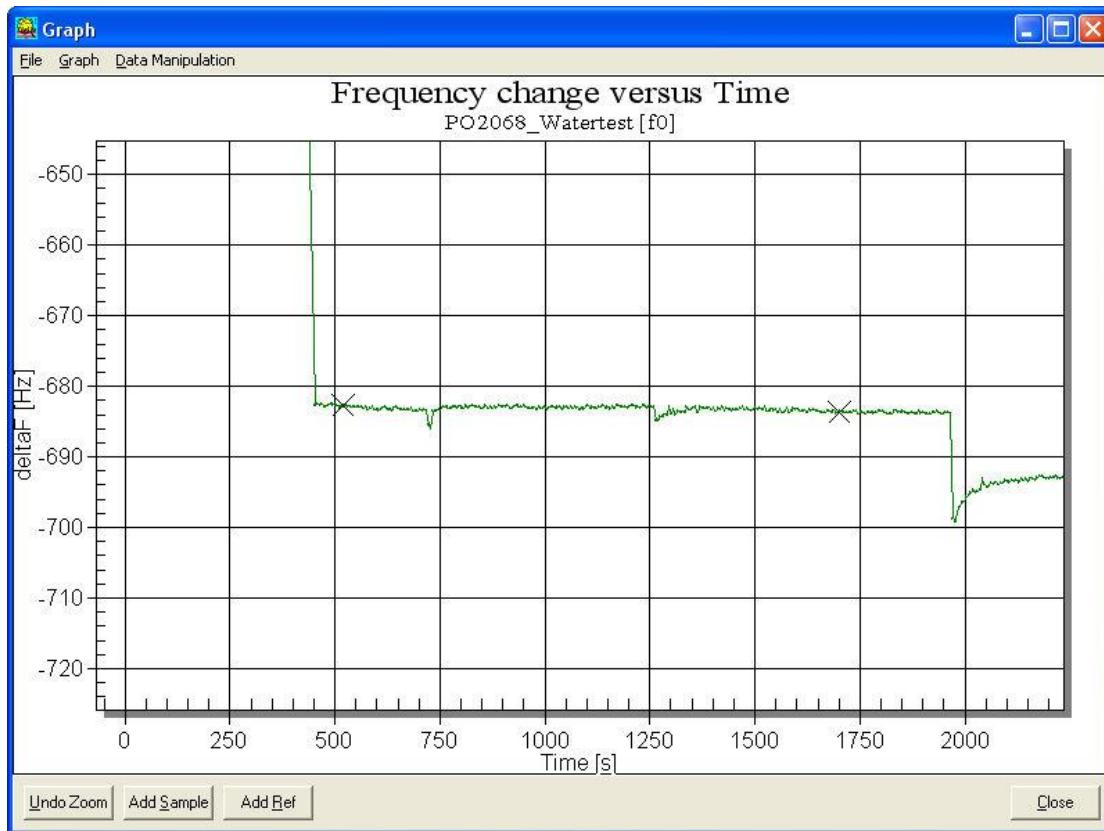
**Figure 5.13:** Sampling data from a graph.

If the reference is taken from the same experiment then select the reference data set and click the **Add Ref** button or selecting **Add a Reference to Sampled Data** from the **Data Manipulation** menu. This brings up the **Sampled Data** screen. The reference reading must be chosen as number 0, which should be displayed automatically. All sample data is then calculated in comparison to this reading.



**Figure 5.14:** Sampled Data number selection box.

Press **OK** to continue. Zoom in on the next stable frequency, the first actual sample reading, and select a new data set.



**Figure 5.15:** Sampling data from a graph.

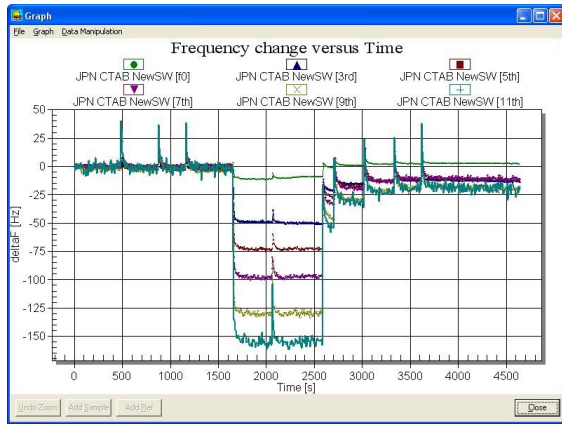
Press the **Add Sample** button or select **Add Selected Points to Sampled Data** from the **Data Manipulation** menu. The **Sample Number** should now be 1, click **OK** and continue until all of the relevant data sets have been selected.

Remember that if the reference is to be taken from another experiment then the correct order is to first select the data samples, starting from number 1, then open the other experiment and select the reference reading with **Sample Number 0**.

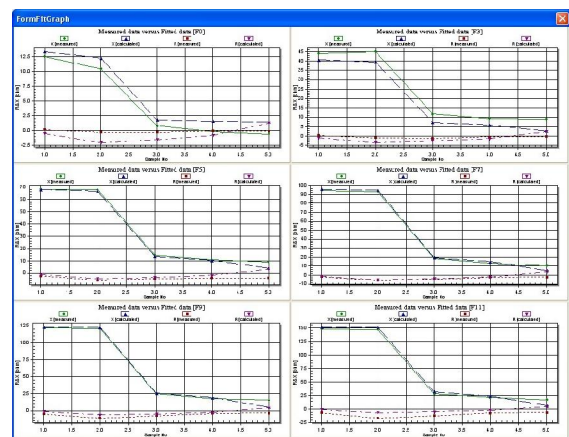
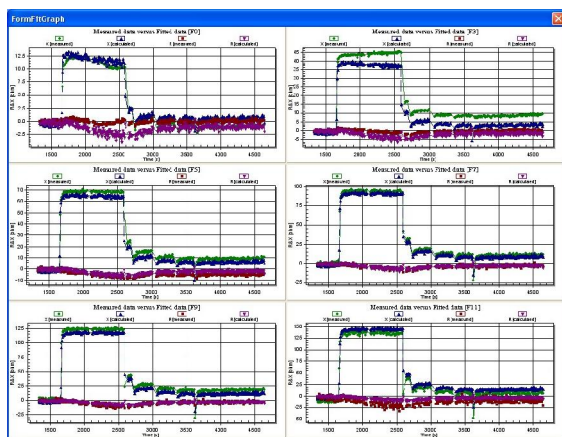
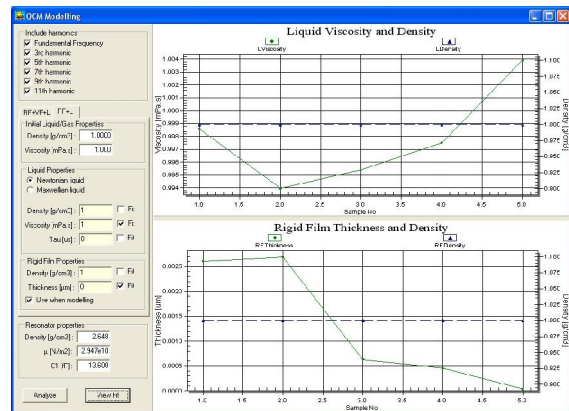
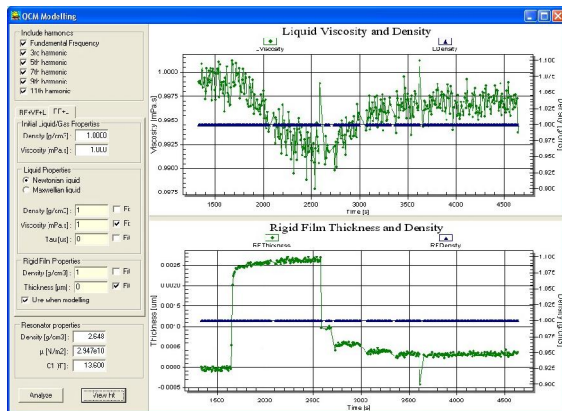
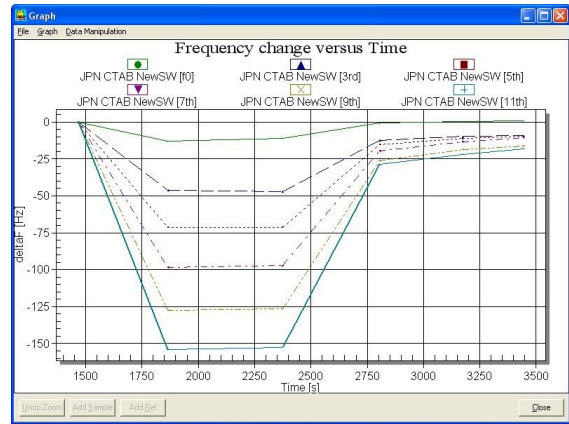
To view the sampled data right-click on the name of the experiment in the *Experiments* box of the **Browse Experiments** screen and from under --- **Sampled Data**--- select **Graph > Nth harmonic**. To then run an analysis of this data simply right-click on the name of the experiment and from under --- **Sampled Data**--- select **Analyze**.

For comparison below are several screenshots of the same experiment, on the left is the original data and on the right is the sampled data.

## Original Data



## Sampled Data

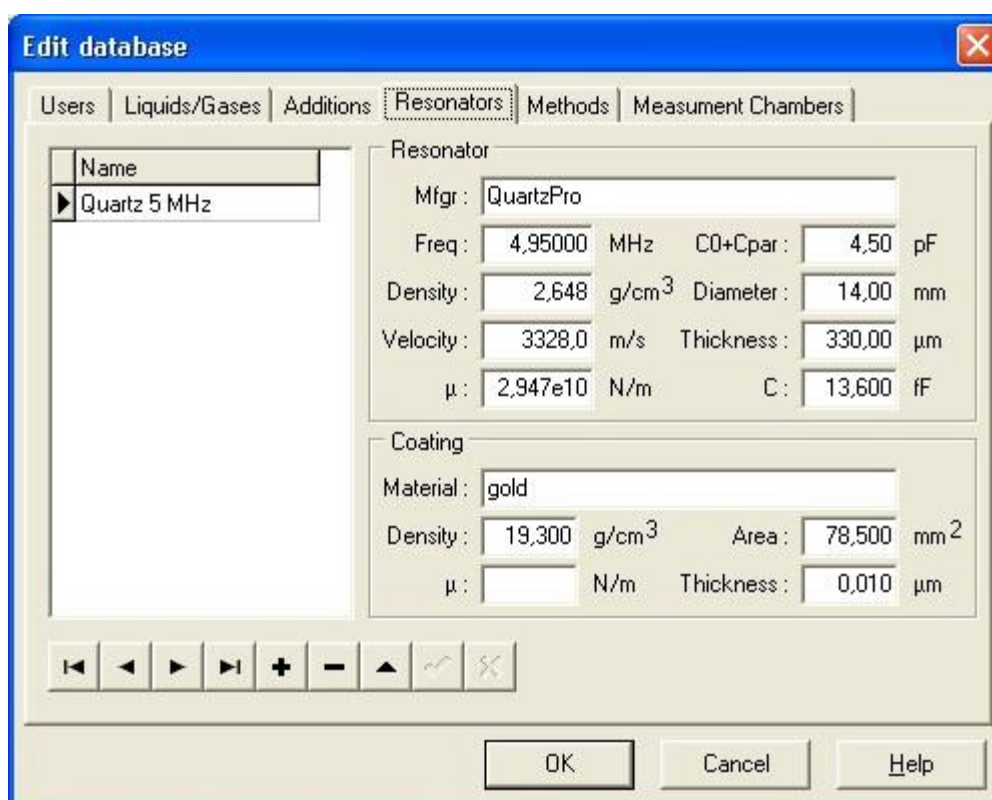


### 5.5.3 Step-by-Step Guide to Analysing Data

- If all of the data can be used for analysis, right-click on the experiment name and select **Analyze**. Otherwise select the *Sampled Data* as instructed below.
  - Select the reference frequency either from the same measurement as the one for which the sample data will be selected from or another experiment run under the same conditions.
  - Select the sample sets at each relevant stable frequency. Right-click on the experiment name and select the **Analyze** which is under *Sampled Data*.
- Choose whether to include the viscoelastic film in the analysis, and select the appropriate tab. Check that all of the relevant information has been included, and if not either fill it in from this window or from the **Database** accessible from the experiment's **Experimental Setup** screen.
- Select the harmonics to be included in the calculations. Press **Analyze**. The graphs on the right now display the results of the analysis.
- Press **View Fit** to view the data and the theoretical value of each harmonic separately.

## 6. The Database










The database stores the library of information the QCM has of possible users, liquids and solids. When the **Experimental Setup** window is open the software will reference the information stored in the database to supply the choices in the drop-down menus. Use the **Edit Database** to add, remove or alter the information in the database. The database is divided into six tabs: **Users**, **Liquids/Gases**, **Additions**, **Resonators**, **Methods** and **Measurement Chambers**.



**Figure 6.1:** *The Database screen holds all of the information on available users and materials.*

Open the **Edit Database** window from either the QCM menu bar under **Edit > Database** or from the **Experimental Setup** screen by clicking **Edit Database**. Each page has a row of buttons near the bottom that can be used for scrolling and editing.



	Jump to top of list
	Move one space up
	Move one space down
	Jump to bottom of list
	<b>Add New item</b> to list
	<b>Delete item</b> from list
	<b>Edit item</b> on list
	<b>Post new item</b> entered
	<b>Cancel edit</b>

## 6.1 Users

In the **Users** tab a list of current users will appear. To add a new user press the **New item** button, enter the new name in the field space and press **Post new item**. Press **OK** to continue.

## 6.2 Liquids/Gases

The available names of the fluids are edited like those of users. The additional fields give more information about each substance.

**Density:** Density of fluid  
**Viscosity:** Viscosity of fluid  
 $\gamma$ : Surface tension of fluid  
 $\gamma_d$ : Dispersive component of surface tension  
 $\gamma^+$ : Acid component of surface tension  
 $\gamma^-$ : Base component of surface tension  
**MW:** Molecular weight of fluid

## 6.3 Additions

The available names of the additions are edited like those of users. The additional fields give more information about each substance.

**Density:** Density of addition  
**Viscosity:** Viscosity of addition  
**MW:** Molecular weight of addition  
**Concentration & Unit:** Concentration of component added, include units

## 6.4 Resonators

The resonator is the quartz crystal. The available names of the resonators are edited like those of users. The additional fields give more information about each resonator.

In the *Resonator* box:

**Mfgr:** Manufacturer of the resonator.

**Freq:** Fundamental frequency of the entered resonator.

**Density:** Density of quartz, literature value 2.648 g/cm<sup>3</sup>

**Velocity:** Speed of sound in quartz, literature value is 3328 m/s

**m:** Stiffness coefficient of the resonator material

**Cpar:** Parasitic capacitance for the entered resonator

**Diameter:** Diameter of the entered resonator

**Thickness:** Thickness of the entered resonator

In the *Coating* box:

**Material:** Material of the electrodes on the resonator

**Density:** Density of electrode material on the resonator

**m:** Stiffness of the electrode material on the resonator

**Area:** Active area of the electrode between which the resonator is oscillating.

**Thickness:** Thickness of the electrode material on the resonator

## 6.5 Methods

The available names of the methods are edited like those of users. The additional fields give more information about each method.

In the *Search Parameters* box:

**Bandwidth:** The bandwidth used when searching for the fundamental and overtone frequencies at the start of a measurement.

**No of points:** Number of points used for plotting the **Impedance** and **Phase Shift** curves during the search process.

In the *Sweep Parameters* box:

**Bandwidth:** The bandwidth used when sweeping around the fundamental and overtone frequencies during measurement. If this bandwidth is left at zero, the instrument automatically determines a 3 dB wide bandwidth as the sweep width for the fundamental and overtone frequencies during the measurement.

**No of points:** Number of points used for plotting the **Impedance** and **Phase Shift** curves shown in the sweep graph. Also defines the number of points on the **Impedance** and **Phase Shift** curves used for fitting the Butterworth-van Dyke equivalent circuit model to the data to obtain the electrical components, and hence calculate the frequency, Q, and dissipation changes.



**Allow Edits:** Sets permission of changing the **Search** and **Sweep Parameters** in the **MeasControls** window for this method. Check to allow editing.

## 6.6 Measuring Chambers

The available names of the measuring chambers are edited like those of users. Specify a file name where the calibration information for this specific chamber will be stored, this file will be created by the program once a calibration is run with this chamber.

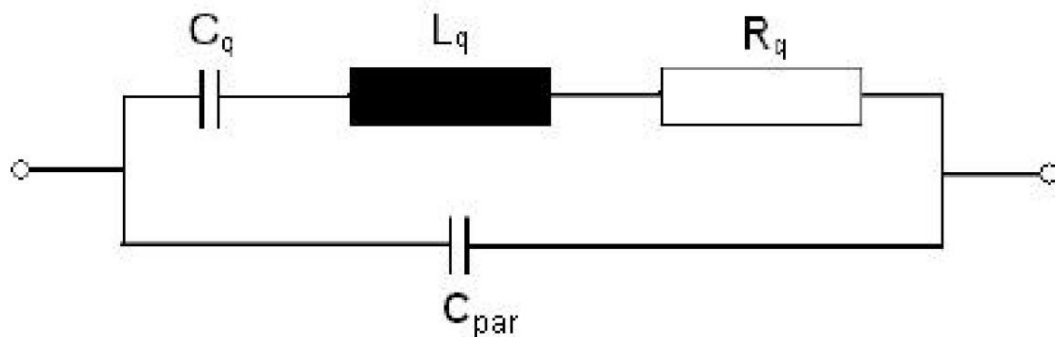
## 7. Testing and troubleshooting the QCM

Sometimes it is necessary to look at the impedance spectra of the quartz crystal and determine if the instrument is working properly, whether it is finding the optimum parasitic capacitance  $C_{\text{par}}$  of the crystal and possibly altering the instrument setup by hand.

The KSV QCM software is written so that it automatically finds the optimum parasitic capacitance for the fundamental and all the chosen overtone frequencies. However in problem solving situations looking at the impedance spectra and determining the parasitic capacitance can speed up the process tremendously.

The background of the parasitic capacitance (procedure also known as the electrode capacitance cancellation) is that the total quartz crystal impedance includes a parasitic (or shunt) capacitance in parallel with the series resonant arm (see figure 7.1 below) of the crystal. This parasitic capacitance originates from the capacitance of the crystal electrodes, cables and crystal holder.

The total current through the crystal is the sum of the current through the parasitic (shunt) capacitance plus the current through the series resonant arm. The physical motion of the crystal is reflected in the values of the  $L$ ,  $R$  and  $C$  in the series arm of the crystal only, and therefore we want to subtract out or otherwise cancel the current through the parasitic (shunt) electrode capacitance. By canceling this electrode capacitance we ensure that the measured crystal current does not include the current through the electrode capacitance and therefore the measured current is essentially the current through the series resonant arm of the crystal only i.e. only the changes at the electrode surface is detected without any contributions from the instrument set-up and connections.

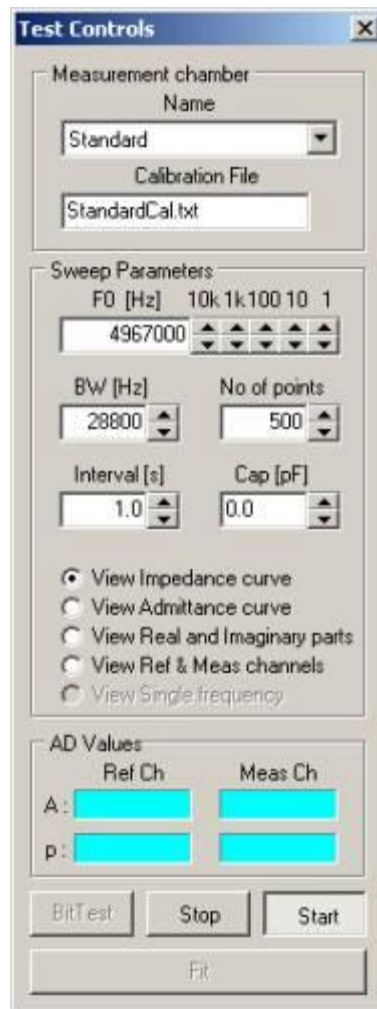


**Figure 7.1:** A circuit equivalent model for the crystal.

In order to test the apparatus first ensure that the instrument is calibrated properly and then prepare the instrument as if to conduct an experiment. This

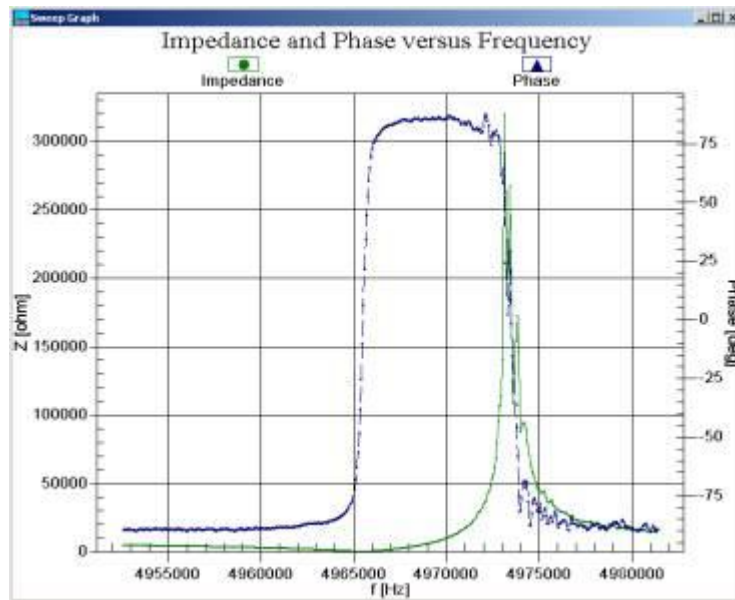
means disassembling, cleaning and reassembling the various parts and starting up the main electronics unit. Do *not* fill the instrument with any liquid, leave the chamber with air.

Start the QCM measurement program from the Windows **Start** menu, choose **Start > Programs > QCM > QCM**. From the **Controls** menu select **Test**. This will open the **Test Controls** window.



**Figure 7.2:** *The Test Controls screen.*

Fill in the values as shown above and press **Start**. The graph that appears should have curves similar to those shown below.

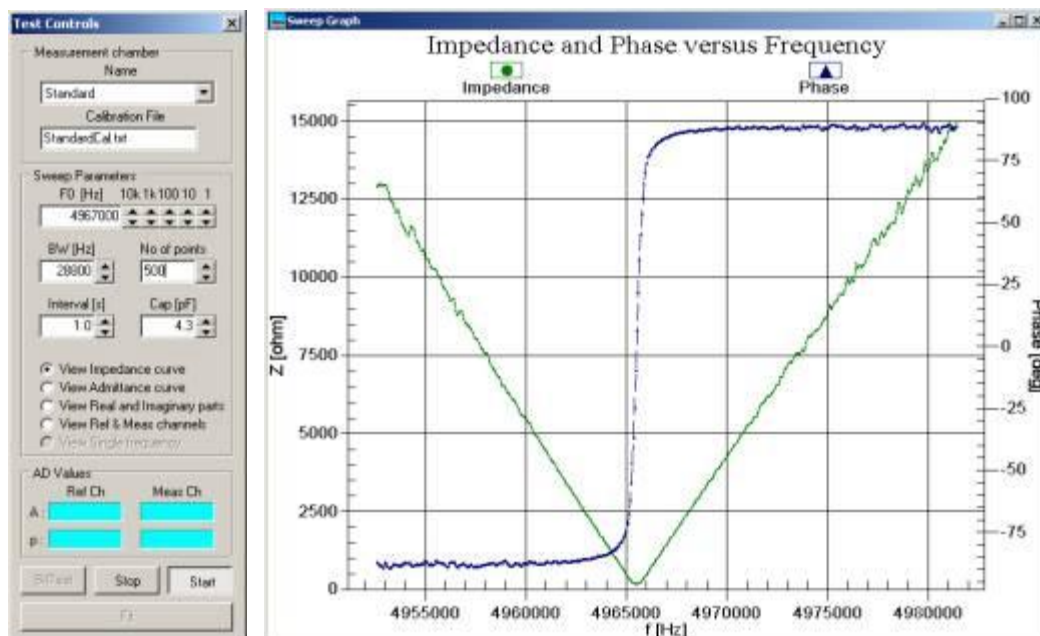


**Figure 7.3:** Graph of impedance and phase against frequency.

If the error message **No calibration** appears then check that the F0 value is correctly defined i.e. around 5 000 000 Hz.

If the curves does not look like those shown above try to change the F0 and BW parameters in the *Sweep parameters* box so that it would look as close as possible to the above curves. Remember to check that the Cap value is 0 at this point.

When this is completed start to increase the Cap value so that it reaches 4-5 pF, and the Impedance curve changes to a V-shape. Try to obtain as good a V-shape as possible.







**Figure 7.4:** *Test Controls and graph of impedance and phase against frequency.*

The obtained Cap value is the capacitance needed to compensate for the parasitic capacitance for the specific crystal used at that moment in the measuring chamber. This capacitance is usually different when the measuring chamber is filled with liquid and can be found in the same way as described above.

This test is not necessary for making a measurement, the KSV QCM Impedance Analyzer software will automatically determine the parasitic capacitances for all of the chosen harmonic frequencies when a measurement is started as the Cap values tend to change a little bit at different overtones.

If the Impedance and the Phase Shift do not look as smooth as in the above figures, then there might be a problem with the instrument. In such a case please contact the nearest KSV distributor (see **Appendix: Contacts and Support**) for further assistance.

When finished with the testing press **Stop** in the **Test Controls** window.

## 8. Theory

### 8.1 Background

Pierre and Marie Curie showed in 1880 that crystals of Rochelle salt could produce electricity when pressure was applied in certain crystallographic directions. Later they also showed the converse effect i.e. production of strain by application of electricity. These findings mark the discovery of the piezoelectric effect.

Piezoelectricity did not receive a lot of interest in the beginning and a more detailed study of piezoelectricity was not started until 1917 when it was shown that quartz crystals could be used as transducers and receivers of ultrasound in water. In 1919 several devices of everyday interest based on the piezoelectricity of Rochelle salt were described, these being loudspeakers, microphones and sound pick-ups. In 1921 the first quartz crystal controlled oscillator was described.

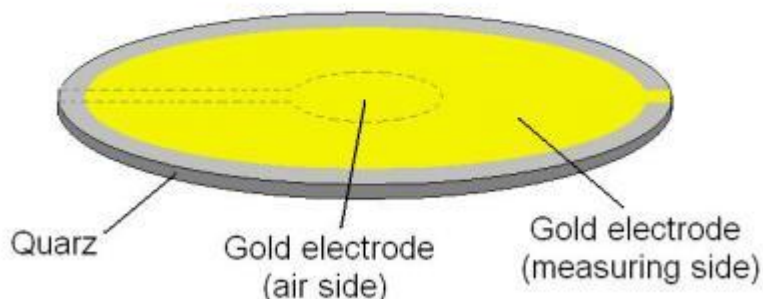
These first quartz crystal controlled oscillators were based on X-cut crystals which have the drawback of being very temperature sensitive. Therefore, the X-cut crystals are now used in applications where the large temperature coefficient is of little importance, such as transducers in space sonars.

The dominance of the quartz crystal for all kinds of frequency control applications started in 1934 when the AT-cut quartz crystal was introduced. The advantage of the AT-cut quartz crystal is that it has nearly zero frequency drift with temperature around room temperature. From the very beginning of using quartz crystal resonators as frequency control elements it was common to increase the frequency of the resonator by drawing pencil marks on the electrodes and to decrease the frequency by rubbing off some of the electrode material with an eraser.

This mass induced frequency shift was only understood on a qualitative basis until 1959, when Sauerbrey published a breakthrough paper which showed that the frequency shift of a quartz crystal resonator is directly proportional to the added mass. Sauerbrey's work is generally taken as the first step towards a new quantitative tool to measure very small masses i.e. the quartz crystal microbalance (QCM).

Hence, one can describe the QCM to be an ultra-sensitive mass sensor. The heart of the QCM is the piezoelectric AT-cut quartz crystal, sandwiched between a pair of electrodes. When the electrodes are connected to an oscillator and an AC voltage is applied over the electrodes the quartz crystal starts to oscillate at its resonance frequency due to the piezoelectric effect. This oscillation is generally very stable due to the high quality of the oscillation (high Q factor).

## Quartz crystal - The heart of the QCM



**Figure 8.1:** *The quartz crystal.*

If a rigid layer is evenly deposited on one or both of the electrodes the resonant frequency will decrease proportionally to the mass of the adsorbed layer according to the Sauerbrey equation:

$$\Delta f = -[2 \times f_0^2 \times \Delta m] / [A \times (\rho_q \mu_q)^{1/2}]$$

Where

$\Delta f$  = measured frequency shift

$f_0$  = resonant frequency of the fundamental mode of the crystal

$\Delta m$  = mass change per unit area ( $\text{g}/\text{cm}^2$ )

$A$  = piezoelectrically active area

$\rho_q$  = density of quartz,  $2.648 \text{ g}/\text{cm}^3$

$\mu_q$  = shear modulus of quartz,  $2.947 \times 10^{11} \text{ g}/\text{cm s}^2$

There are situations where the Sauerbrey equation does not hold, for example when the added mass

A) is not rigidly deposited on the electrode surface(s),

B) is not deposited evenly on the electrode(s) or

C) slips on the surface.

Therefore, the Sauerbrey equation is only strictly applicable to uniform, rigid, thin-film deposits. Due to this the QCM was for many years just regarded as a gas-phase mass detector. Not until the beginning of the 1980's scientists realized that a quartz crystal can be excited to a stable oscillation when it was completely immersed in a liquid. Much of the pioneering work in liquid phase QCM measurements has been done by Kanazawa and co-workers, who showed that the change in resonant frequency of a QCM taken from air into a liquid is proportional to the square root of the liquid's density-viscosity product:

$$\Delta f = -f_u^{2/3} [(\rho_L \eta_L) / (\pi \times (\rho_q \mu_q))]^{1/2}$$

Where

$\Delta f$  = measured frequency shift

$f_u$  = resonant frequency of the unloaded crystal

$\rho_L$  = density of liquid in contact with the crystal

$\eta_L$  = viscosity of liquid in contact with the crystal

$\rho_q$  = density of quartz, 2.648 g/cm<sup>3</sup>

$\mu_q$  = shear modulus of quartz, 2.947x10<sup>11</sup> g/cm s<sup>2</sup>

After it was found that excessive viscous loading would not prohibit the use of a QCM in liquids and that the response of the QCM is still extremely sensitive to mass changes at the solid-liquid interface, QCMs have been used in direct contact with liquids and / or viscoelastic films to assess changes in mass and viscoelastic properties. Even in air or vacuum (where the damping of layers have been considered to be negligible or small) the QCM has been used to probe dissipative processes on the quartz crystal. This is especially true for soft condensed matters such as thick polymer layers deposited on the quartz surface.

## 8.2 Applications for QCMs

A quartz crystal microbalance is basically a mass sensing device with the ability to measure very small mass changes on a quartz crystal resonator in real-time. The sensitivity of the QCM is approximately 100 times higher than an electronic fine balance with a sensitivity of 0.1 mg. This means that a QCM is capable of measuring mass changes as small as a fraction of a monolayer (single layer of atoms). The high sensitivity and the real-time monitoring of mass changes on the sensor crystal make the QCM a very attractive technique for a large range of applications. Especially the development of QCM systems for use in fluids or with viscoelastic deposits has dramatically increased the interest towards this technique. A major advantage of using a QCM in liquid analysis is that it allows a label-free (not necessary to add a label to the substance) detection of molecules . This also means that it is possible to make measurements from samples that are not transparent. A partial list of the application areas of the QCM is shown below, and in truth it seems that the application areas are only limited by imagination.

- Thin film thickness monitoring in thermal, e-beam, sputtering, magnetron, ion and laser deposition.
- Electrochemistry of interfacial processes at electrode surfaces.
- Biotechnology
  - o Interactions of DNA and RNA with complementary strands
  - o Specific recognition of protein ligands by immobilized receptors, immunological reactions
  - o Detection of virus capsids, bacteria, mammalian cells
  - o Adhesion of cells, liposomes and proteins
  - o Biocompatibility of surfaces
  - o Formation and prevention of formation of biofilms
- Functionalized surfaces
  - o Creation of selective surfaces
  - o Lipid membranes
  - o Polymer coatings
  - o Reactive surfaces

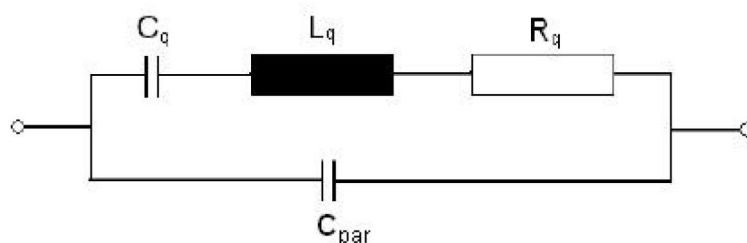
- o Gas sensors
- o Immunosensors
- Thin film formation
  - o Langmuir and Langmuir-Blodgett films
  - o Self-assembled monolayers
  - o Polyelectrolyte adsorption
  - o Spin coating
  - o Bilayer formation
  - o Adsorbed monolayers
- Surfactant research
  - o Surfactant interactions with surfaces
  - o Effectiveness of surfactants
- Drug Research
  - o Dissolution of polymer coatings
  - o Molecular interaction of drugs
  - o Cell response to pharmacological substances
  - o Drug delivery
- Liquid plating & etching
- In situ monitoring of lubricant and petroleum properties

## 8.3 Working Principle of KSV's QCM-Z500

The KSV QCM-Z500 measurement principle is based on the impedance analysis of the quartz crystal. This measurement principle means that the quartz crystal is not resonating all the time, but the crystal is swept with potential perturbations with various frequencies close to the quartz crystal's resonant frequency. The potential (U) over the crystal and the electricity (I) flowing through the crystal are recorded. The ratio of U and I then give the impedance (Z), and the result of the sweep is the so-called impedance curve (the inverse curve is called admittance).

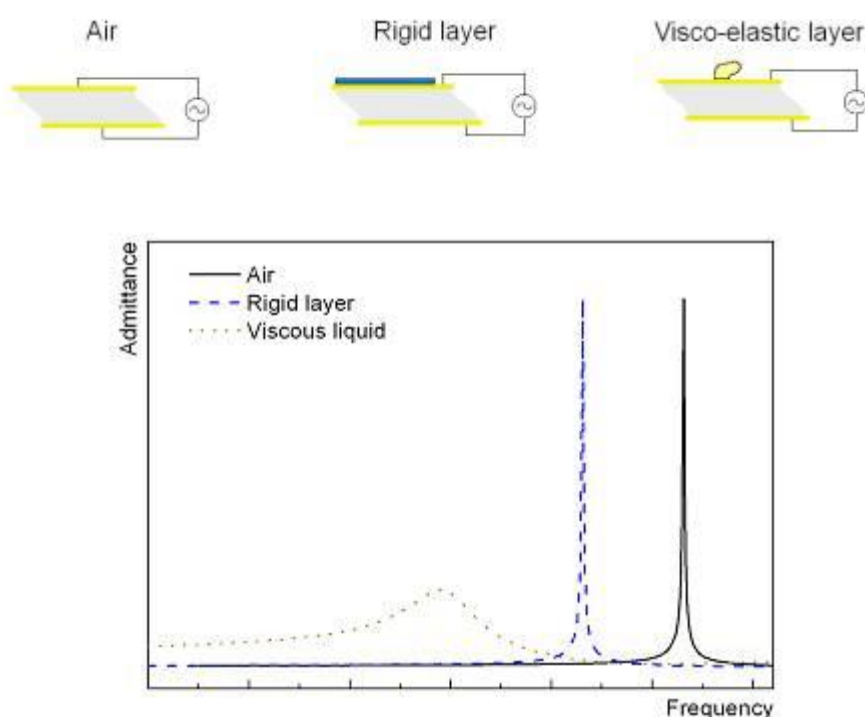
The impedance (or admittance) curve holds all of the information concerning the properties of the quartz crystal and the layer deposited on the crystal (see figure below). This sweep can be done as a function of time, which enables either the measurement of mass changes happening at the quartz crystal electrode surface, or only once in steady state case studies. The KSV QCM-Z500 sweep generator technology is specially designed for QCM applications and it enables fast real-time monitoring of adsorption processes and kinetics.

Normally an equivalent circuit model (as shown in below) is fitted to the impedance curve and the obtained parameters can be used for calculating the resonance frequency and quality factor (Q) or dissipation (D) of the quartz crystal (i.e. masses and visco-elastic properties of the deposited layers).



**Figure 8.2:** A circuit equivalent model for the crystal.

The admittance curve displays relevant information on the crystal. The broader and lower the admittance curve is the lower the Q-value and the more dissipation is taking place. Admittance peaks occur at resonance frequencies.



**Figures 8.3 and 8.4:** The crystal in three different environments and the admittance against frequency graph for each.

The above admittance curve shows how admittance is affected by a rigidly deposited layer or a viscous liquid as compared to air. Additionally the QCM-Z500 can measure different harmonics of the quartz crystal, which gives additional value for determining viscoelastic coefficients of the coating. Due to the specially designed sweep generator technology of the QCM-Z500 the jump between the different overtones can be made very quickly, and up to the 11th overtone can be measured for a 5 MHz quartz crystal.

In most cases quartz resonators are integrated to oscillator circuits to form a QCM for micro-weighing applications. While this is a cheap and convenient way of determining the resonance frequencies of quartz crystals, it will not give any information about the quality of the resonance (Q value) which would



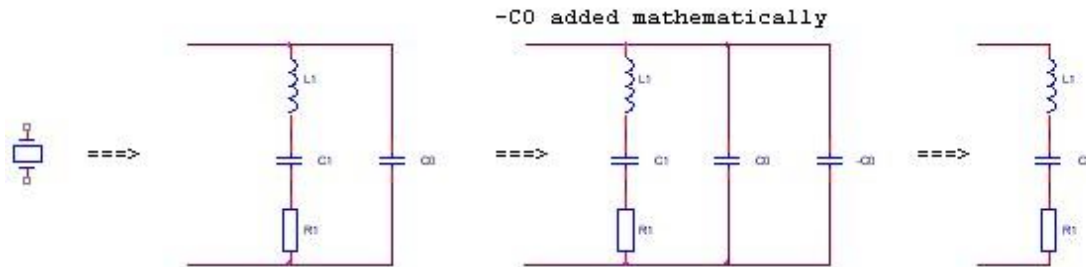
help for viscoelastic analysis. The advantages of determining the impedance (or admittance) curve are:

- Both frequency (f) and quality of resonance (Q factor) or dissipation are accessible.
- Different harmonics can be quickly and sequentially measured.
- Undesired anomalies including skewed resonance curves or distorted resonances due to the interference of anharmonic sidebands are directly detected.

## 8.4 Theory of Impedance Analysis

### 8.4.1 Electrical Impedance Model

An unloaded quartz crystal close to its resonating frequency can be modeled by the following equivalent circuit.



**Figure 8.5:** The crystal and its equivalent circuit. Unwanted capacitance subtracted to calculate impedance.

As introduced in the previous section, the crystal can be considered equivalent to an inductor, a capacitor and a resistor in series: the motional branch. Parallel to it is a capacitance  $C_0$  which is caused by the capacitance between the two electrodes that connect to the crystal. Real measurements also have some parasitic capacitance ( $C_{par}$ ). Let

$$C_0^* = C_0 + C_{par}$$

As the interesting phenomena happen on the motional branch, the effects of  $C_0^*$  must be eliminated. The method used is to first determine the value of  $C_0^*$  and then adding a capacitor of capacitance  $-C_0^*$  to the circuit.  $C_0$  is constant but the value of  $C_{par}$  has to be continuously measured as it changes with varying conditions (conductivity of liquid, etc.).

The value for  $C_0$  can be determined by

Now the motional branch can be examined. The motional impedance of an unperturbed quartz crystal can be calculated with this equation.

$$Z_m^0 = R_1 + j \left( \omega L_1 - \frac{1}{\omega C_1} \right) = R_1 + jX_1$$

Where

$$X_1 = \omega L_1 - \frac{1}{\omega C_1} ,$$

$$\omega = 2\pi f \text{ and}$$

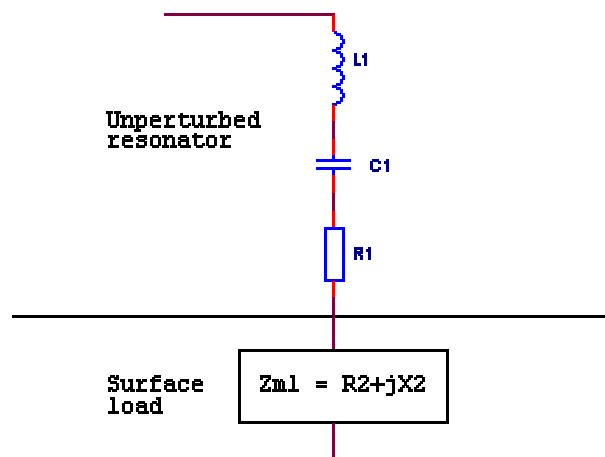
$f$  is the frequency.

When close to the resonance frequency the following simplification can be made.

$$X_1 = 2L\omega = \frac{2\omega}{\omega_0^2 C_1}$$

Where  $\omega_0$  is a resonant angular frequency.

If the crystal is loaded then an impedance component caused by the surface load must be added to the motional branch model.



**Figure 8.6:** *The equivalent circuit of a loaded crystal.*

The additional impedance is labeled  $Z_m^0$ . The total motional impedance is then

$$Z_m = Z_m^0 + Z_m^1 = (R_1 + R_2) + j(X_1 + X_2)$$

### 8.4.2 Converting Electrical Impedance to Mechanical Impedance

The impedances covered above were electrical impedances, that is the values measured when investigating the electrical properties of a crystal. Placing a load on the crystal surface actually alters the mechanical impedance ( $Z_s$ ). All changes in the mechanical impedance are thus actually recorded as changes

in the electrical impedance and so must be converted to the mechanical impedance. Electrical impedance is directly proportional to mechanical impedance, and the exact equation is as follows.

$$Z_m^1 = \left( \frac{N\pi}{4K_0^2 \omega_0 C_0 Z_q} \right) \times Z_s$$

Where

- $N$  = Number of harmonic (1,3,5,7,9 or 11)
- $K_0^2$  = Electromechanical coupling factor
- $\omega_0$  =  $2\pi f_0$
- $f_0$  = Fundamental resonance frequency
- $C_0$  = Parallel capacitance of the crystal
- $Z_q$  = Mechanical impedance of unloaded crystal
- $Z_q$  =  $\sqrt{\rho_q \mu_q}$
- $\rho_q$  = Density of quartz
- $\mu_q$  = Quartz shear stiffness

As

$$C_0 = C_1 \times \frac{(N\pi)^2}{8K_0^2}$$

the conversion equation from electrical to mechanical impedance can be simplified to the following.

$$Z_m^1 = \left( \frac{1}{N\pi^2 C_1 f_0 Z_q} \right) \times Z_s$$

Let the term  $zm2ze$  be used for this coefficient. Thus

$$zm2ze = \frac{1}{N\pi^2 C_1 f_0 Z_q}$$

and

$$Z_m^1 = zm2ze \times Z_s$$

Furthermore the real and complex components of the mechanical impedance can be separated into the equations below.

$$\begin{aligned} R_2 &= zm2ze \times \text{Re}(Z_s) \\ X_2 &= zm2ze \times \text{Im}(Z_s) \end{aligned}$$

As

$$X_2 = \Delta X = -\frac{2\Delta\omega}{\omega_0^2 C_1} = -\frac{\Delta f}{\pi f_0^2 C_1}$$

and

$$R_2 = \Delta R$$

the final equations to convert actual measurements (changes in resistance and frequency) to the required mechanical impedance are obtained:

$$\begin{aligned} \Delta R &= Z_m 2ze \times \operatorname{Re}(Z_s) \\ \Delta X &= Z_m 2ze \times \operatorname{Im}(Z_s) = -\frac{\Delta f}{\pi f_0^2 C_1} \end{aligned}$$

### 8.4.3 Mechanical Impedances of Various Loads

#### A) Rigid layer

With a relatively thin and rigid layer on the surface of the crystal, the surface mechanical impedance is given by the equation

$$Z_s = j\omega\rho_s$$

Where  $\rho_s$  is the mass per area of the layer.

As the impedance has only an imaginary component just acoustic energy is stored and no power dissipates.

#### B) Newtonian fluid

With a Newtonian fluid the surface mechanical impedance is given by the equation

$$Z_s = (1 + j) \times \sqrt{\frac{\omega\rho_1\eta_1}{2}}$$

Where

$$\begin{aligned} \rho_1 &= \text{fluid density} \\ \eta_1 &= \text{fluid viscosity} \end{aligned}$$

For a Newtonian fluid the dissipated power and energy stored components are equivalent.

#### C) Maxwellian fluid

A Maxwellian fluid is a type of non-Newtonian fluid that considers the finite reorientation time of molecules under shear stress. The fluid exhibits a first-order relaxation process.

$$\eta(\omega) = \frac{\eta_0}{1 + j\omega\tau}$$

Where

$\eta_0$  = Low-frequency shear viscosity

$\tau$  = Relaxation time

Thus the surface mechanical impedance is given by the equation

$$Z_s = \sqrt{\frac{j\omega\rho_l\eta_0}{1 + j\omega\tau}}$$

## D) Viscoelastic layer

With a viscoelastic film of finite thickness the surface mechanical impedance is given by the equation

$$Z_s = \sqrt{G\rho_f} \tanh(\gamma h_f)$$

Where

$G$  = Complex shear modulus

$G = G' + jG''$

$G'$  = Storage modulus

$G''$  = Loss modulus

$\rho_f$  = Film density

$\gamma$  = Complex wave propagation constant

$$\gamma = \sqrt{\frac{j\omega\rho_f}{G}}$$

$h_f$  = Film thickness

### 8.4.4 Multiple Layer Combinations

Usually surface loads on the TSM resonator consist of multiple combinations of mass layers, liquids and viscoelastic layers. In such a case, when more than one layer is present on top of the quartz interface, the impedances for all the layers have to be considered and calculated to obtain the total mechanical impedance. In an ideal situation (for example an ideal mass layer on the crystal surface between the crystal and a Newtonian fluid) the displacement is constant and the impedances are additive. Thus in the example mentioned the mechanical impedance would be:

$$Z_s = j\omega\rho_s + (1 + j) \times \sqrt{\frac{\omega\rho_l\eta_1}{2}}$$

This equation is the one used when fitting with the **RF+L** model. Use it to either study viscosity changes in liquids or rigid films in liquids.

In real life this is seldom true and multiple layers do not add algebraically. Rather, they combine in nonlinear fashions; the simplest (and most common) of which is the case of a finite viscoelastic layer with a Newtonian fluid on top. Due to the phase shift across the viscoelastic layer, the total impedance is not equal to the sum of the characteristic impedances of the individual layers. Instead the surface mechanical impedance is represented by

$$Z_s = Z_s^{film} \left[ \frac{Z_s^{fluid} \cosh(\gamma h_f) + Z_s^{film} \sinh(\gamma h_f)}{Z_s^{film} \cosh(\gamma h_f) + Z_s^{fluid} \sinh(\gamma h_f)} \right]$$

To generalise the above equation, here is the formula for the characteristic impedance of the  $n^{th}$  viscoelastic layer.

$$Z_c^{(n)} = Z_c^{(n)} \left[ \frac{Z_c^{(n+1)} \cosh(\gamma^{(n)} h_f^{(n)}) + Z_c^{(n)} \sinh(\gamma^{(n)} h_f^{(n)})}{Z_c^{(n)} \cosh(\gamma^{(n)} h_f^{(n)}) + Z_c^{(n+1)} \sinh(\gamma^{(n)} h_f^{(n)})} \right]$$

The key to calculating impedances is that the outermost layer of a composite resonator is stress free ( $Z_c^{(n+1)} = 0$ ) or in contact with a semi-infinite fluid. Then the surface mechanical impedance can be calculated by working down to the resonator/film interface. With an increasing number of parameters characterising or extracting the density, thickness and shear moduli would be difficult.

When fitting with the **RF+VF+L** model there are two different ways to handle viscoelastic properties:

- **Use Viscosity** (standard): This model uses the equation  $G = \eta + j\omega\mu$ , where  $\eta$  is the elasticity ( $G'$ ) and  $\mu$  is the viscosity. This is the normal method to examine viscoelasticity.
- **Use  $G''$** : This model assumes that  $G = G' + jG''$ , where  $G''$  is held constant over the measurement frequency range. This may not be valid assumption but sometimes it can be considered to be a constant.

### 8.4.5 Optimising Impedance with Harmonics

In most cases with multiple layers there are several unknown parameters. As each harmonic by definition has a distinct frequency different from the others, the harmonics also have individual wavelength, attenuation, reflection, phase shift, etc. This means that there are as many equations as there are harmonic frequencies recorded.



The task then is to alter the values of the unknown parameters so as to minimize the difference between the measured impedance and the calculated impedance (from the model described above) for all harmonics simultaneously. For this purpose the Levenberg-Marquardt algorithm is used. In practice the steps are the following.

- Obtain measured changes in resistance and frequency for each harmonic. ( $R$  and  $f$ )
- Calculate recession from frequency. ( $X$ )
- An error term is calculated for each harmonic ( $i$ ) from the differences between the measured and calculated components. The equation used is

$$\text{error}_i = \left[ \left( \Delta R_N - \text{zm2ze} \times \text{Re}(Z_s) \right)^2 + \left( \Delta X_N - \text{zm2ze} \times \text{Im}(Z_s) \right)^2 \right] / N$$

The division by  $N$  (the number of the harmonic {1,3,5,7,9,11}) is done to receive approximately equal weight for each harmonic during calculations.

- The Levenberg-Marquardt algorithm tries to minimise all error terms by varying selected parameters. The parameters that can be varied are those that the mechanical impedance is a function of, namely thickness, density, viscosity and elasticity.

The questions that remain for the user are

- Precisely which multiple layer combination is to be used for the model. Currently two models are available, rigid film and liquid (**RF+L**) or rigid film, viscoelastic film and liquid (**RF+VF+L**).
- Which values to fit. The variables selected for fitting will use the given value as the first term in the modeling, and the Levenberg-Marquardt algorithm might find a local minimum for one set of parameters and not the actual minimum.
- Which harmonics to include. In many cases the more equations the better the answer will be, but the fundamental frequency has a tendency to show curious phenomena not necessarily useful for the experiment and so should sometimes be left out. Check the **View Fit** screens for different combinations, keeping in mind that three harmonics are needed to run the analysis algorithm.

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2. **Modeling the Responses of Thickness-Shear Mode Resonators under Various Loading Conditions**, Helen L. Bandey, Stephen J. Martin, Richard W. Cernosek, and A. Robert Hillman. *Anal. Chem.* 1999, 71, 2205-2214

## 9. Technical Specifications and Features

- Impedance analysis
- Gas and liquid phase measurements
- High resolution and sensitivity (RMS values of noise level in air and liquid is 0.05 Hz and 0.21 Hz, respectively)
- Direct measurements at air/water interfaces
- Continuous flow measurements
- Crystals easily mounted in measuring chamber or crystal holder
- Flexible choice of surfaces
- Not fixed to any resonant frequency, crystals in the range 3-55 MHz can be used
- Multi-frequency (quick jumps between overtones) and temperature controlled measurements
- Mass and viscoelastic parameters simultaneously
- Real time measurements
- Easy to use Windows based software
- Straightforward operation
- Mass sensitivity (5 MHz crystal)
  - o  $\sim 1 \text{ ng/cm}^2$  in air/gas
  - o  $\sim 5 \text{ ng/cm}^2$  in liquid
- D-factor sensitivity
  - o  $\sim 2 \times 10^{-8}$  in air
  - o  $\sim 3 \times 10^{-8}$  in liquid
- Max film thickness  $\sim 5 \text{ mm}$
- Active sensor area  $\sim 20 \text{ mm}^2$
- Frequency range 3-55 MHz (can measure up to the 11th overtone of a 5 MHz crystal)

## 10. Chemical Compatibility of Viton

Chemical compound	Compatibility
Acetaldehyde	D- Severe Effect
Acetate LMW	N/A
Acetic acid <5%	N/A
Acetic acid >5%	N/A
Acetic anhydride	D- Severe Effect
Acetone	D- Severe Effect
Acetonitrile	D- Severe Effect
Acetyl bromide	N/A
Acetyl chloride	A- Excellent
Air	A- Excellent
Aliphatic hydrocarbons	N/A
Aluminum chloride	A- Excellent
Aluminum sulfate	A- Excellent
Alums	N/A
Ammonia, gas and liquid	D- Severe Effect
Ammonium acetate	N/A
Ammonium carbonate	N/A
Ammonium chloride	A- Excellent
Ammonium hydroxide	A- Excellent
Ammonium nitrate	N/A
Ammonium phosphate	N/A
Ammonium sulfate	A- Excellent
Amyl acetate	D- Severe Effect
Amyl alcohol	A- Excellent
Amyl chloride	N/A
Aniline	N/A
Aniline hydrochloride	D- Severe Effect
Aqua regia (80% HCl, 20% H)	N/A
Aromatic hydrocarbons	N/A
Arsenic salts	N/A
Barium salts	N/A
Benzaldehyde	D- Severe Effect
Benzenesulfonic acid	A- Excellent
Bleaching liquors	A- Excellent

Boric acid	A- Excellent
Bromine	A- Excellent
Butane	A- Excellent
Butanol (butyl alcohol)	A- Excellent
Butyl acetate	D- Severe Effect
Butyric acid	N/A
Calcium oxide	N/A
Calcium salts	N/A
Carbon bisulfide	N/A
Carbon dioxide	A- Excellent
Carbon tetrachloride	A- Excellent
Chlorine, dry	A- Excellent
Chlorine, wet	B- Good
Chloroacetic acid	D- Severe Effect
Chlorobenzene	A- Excellent
Chlorobromomethane	A- Excellent
Chloroform	A- Excellent
Chlorosulfonic acid	D- Severe Effect
Chromic acid, 30%	A- Excellent
Chromium salts	N/A
Copper salts	N/A
Cresol	A- Excellent
Cyclohexane	A- Excellent
Cyclohexanone	D- Severe Effect
Diacetone alcohol	N/A
Dimethyl formamide	D- Severe Effect
Essential oils	N/A
Ethanol (ethyl alcohol)	A- Excellent
Ether	N/A
Ethyl acetate	D- Severe Effect
Ethyl bromide	N/A
Ethyl chloride	A- Excellent
Ethylamine	N/A
Ethylene chlorohydrin	A- Excellent
Ethylene dichloride	B- Good
Ethylene glycol	A- Excellent
Ethylene oxide	D- Severe Effect
Fatty acids	A- Excellent

Ferric chloride	B- Good
Ferric sulfate	A- Excellent
Ferrous chloride	N/A
Ferrous sulfate	N/A
Fluoboric acid	N/A
Fluoroborate salts	N/A
Fluosilicic acid	N/A
Formaldehyde	D- Severe Effect
Formic acid	D- Severe Effect
FREON® TMS	N/A
Gasoline, high-aromatic	A- Excellent
Gasoline, nonaromatic	A- Excellent
Glucose	A- Excellent
Glue, P.V.A.	A- Excellent
Glycerin	A- Excellent
Hydriodic acid	N/A
Hydrobromic acid, 30%	A- Excellent
Hydrochloric acid (conc)	B- Good
Hydrochloric acid (dil)	A- Excellent
Hydrochloric acid (med)	B- Good
Hydrocyanic acid	A- Excellent
Hydrocyanic acid, gas, 10%	A- Excellent
Hydrofluoric acid, 50%	A- Excellent
Hydrofluoric acid, 75%	B- Good
Hydrogen peroxide (dil)	A- Excellent
Hydrogen peroxide, 90%	N/A
Hypochlorous acid	A- Excellent
Iodine solutions	N/A
Iodoform	N/A
Kerosene	A- Excellent
Ketones	N/A
Lacquer solvents	D- Severe Effect
Lactic acid	A- Excellent
Lead acetate	N/A
Linseed oil	A- Excellent
Lithium hydroxide	N/A
Magnesium chloride	A- Excellent
Magnesium sulfate	A- Excellent



Malic acid	A- Excellent
Manganese salts	N/A
Mercury salts	N/A
Methane	A- Excellent
Methanol (methyl alcohol)	D- Severe Effect
Methyl chloride	A- Excellent
Methyl ethyl ketone (MEK)	D- Severe Effect
Mixed acid (40% H <sub>2</sub> SO <sub>4</sub> , 15% HNO <sub>3</sub> )	N/A
Molybdenum disulfide	N/A
Monoethanolamine	D- Severe Effect
Naphtha	A- Excellent
Natural gas	N/A
Nickel salts	N/A
Nitric acid (conc)	N/A
Nitric acid (dil)	A- Excellent
Nitric acid (med)	A- Excellent
Nitrobenzene	N/A
Nitrogen oxides	N/A
Nitrous acid	N/A
Oils, animal	N/A
Oils, mineral	A- Excellent
Oils, vegetable	N/A
Oleic acid	B- Good
Oxalic acid, cold	A- Excellent
Oxygen, gas	N/A
Palmitic acid	A- Excellent
Perchloric acid	A- Excellent
Perchloroethylene	A- Excellent
Phenol (carbolic acid)	N/A
Phosphoric acid, 50%	A- Excellent
Phthalic acid	N/A
Plating solutions	A- Excellent
Polyglycol	N/A
Potassium carbonate	N/A
Potassium chlorate	N/A
Potassium hydroxide (conc)	B- Good
Potassium hydroxide (med)	B- Good
Potassium iodide	N/A

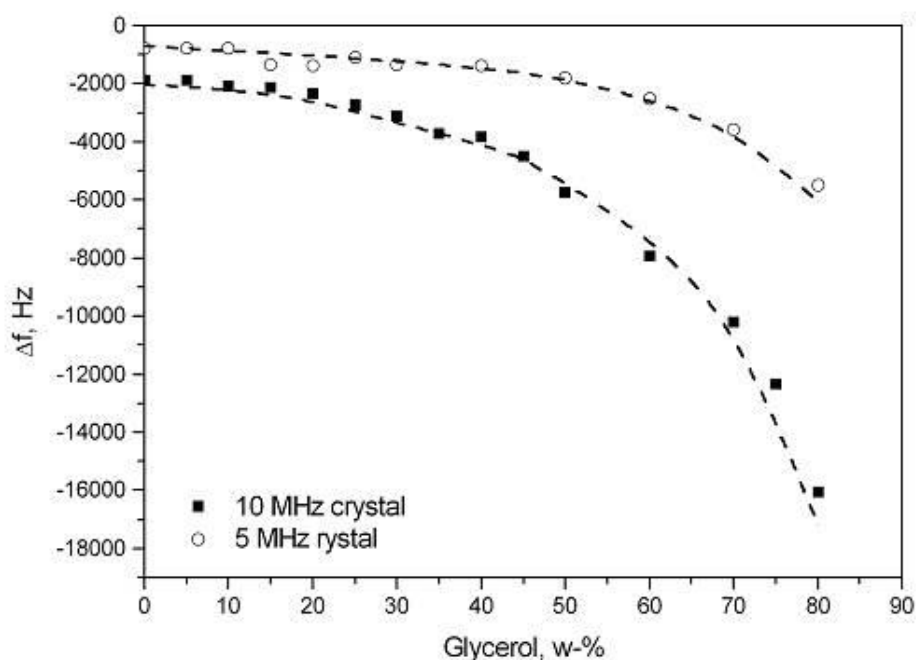
Propanol (propyl alcohol)	B- Good
Pyridine	D- Severe Effect
Silicone fluids	N/A
Silicone oils	A- Excellent
Silver nitrate	A- Excellent
Soap solutions	A- Excellent
Sodium bicarbonate	A- Excellent
Sodium bisulfate	N/A
Sodium bisulfite	A- Excellent
Sodium borate	A- Excellent
Sodium carbonate	B- Good
Sodium chlorate	N/A
Sodium chloride	A- Excellent
Sodium ferrocyanide	N/A
Sodium hydrosulfite	N/A
Sodium hydroxide (conc)	B- Good
Sodium hydroxide (dil)	B- Good
Sodium hydroxide, 25%	B- Good
Sodium hypochlorite, <5%	A- Excellent
Sodium hypochlorite, >5%	B- Good
Sodium nitrate	N/A
Sodium silicate	A- Excellent
Sodium sulfide	N/A
Sodium sulfite	N/A
Steam, up to 40 psi	B- Good
Stearic acid	N/A
Styrene	A- Excellent
Sulfuric acid (conc)	A- Excellent
Sulfuric acid (dil)	A- Excellent
Sulfuric acid (med)	A- Excellent
Sulfurous acid	A- Excellent
Tannic acid	N/A
Tanning liquors	N/A
Tartaric acid	A- Excellent
Tin salts	N/A
Toluene (toluol)	A- Excellent
Trichloroacetic acid	C- Fair
Trichloroethylene	A- Excellent

Trisodium phosphate	A- Excellent
Turpentine	A- Excellent
Urea	N/A
Uric acid	N/A
Water, fresh	A- Excellent
Water, salt	A- Excellent
Xylene	A- Excellent
Zinc chloride	A- Excellent

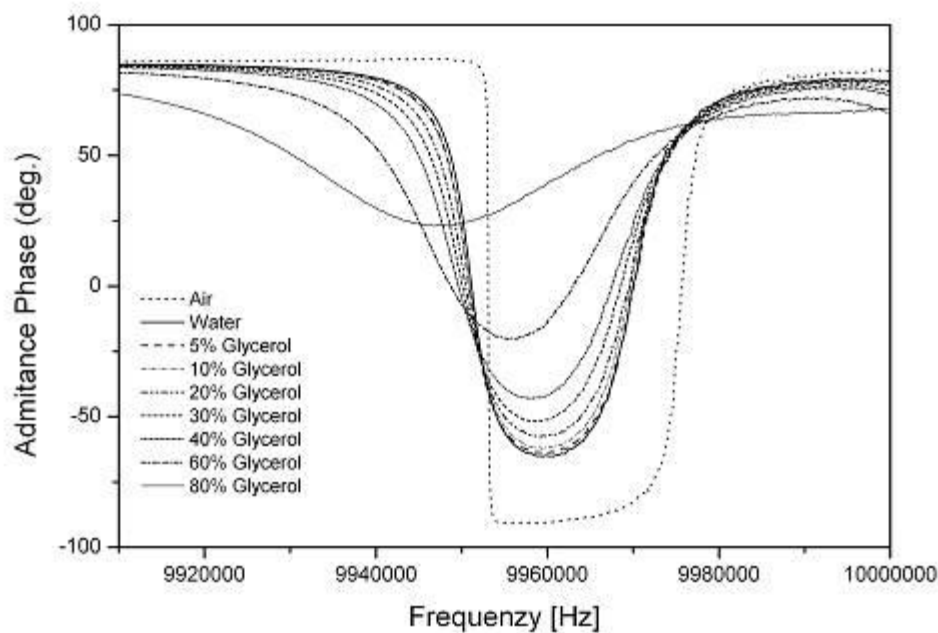
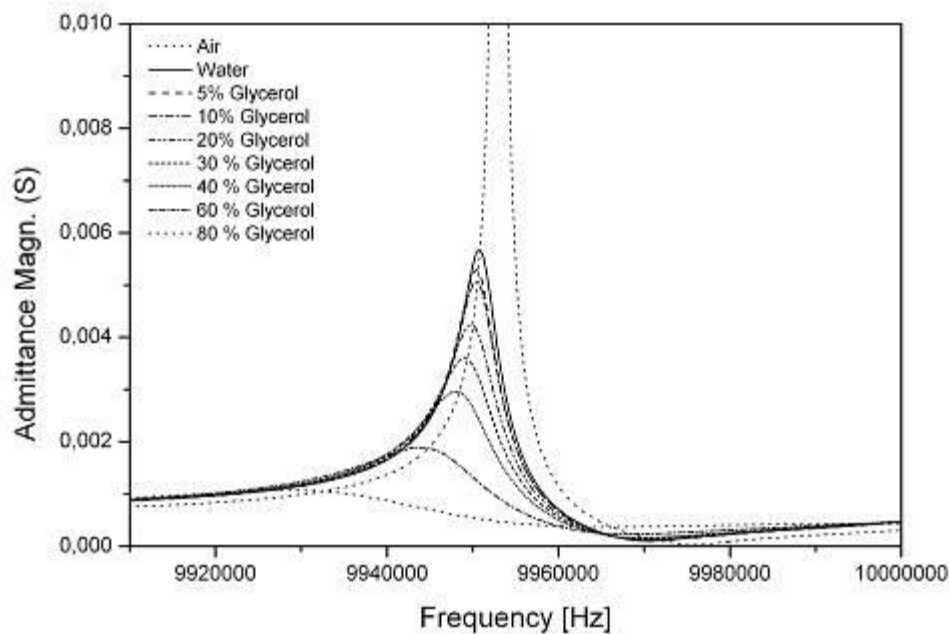
# 11. Example Measurements Made with the QCM-Z500

## 11.1 Solutions of Different W-% of Glycerol

As the QCM-Z500 uses impedance analysis it is highly suitable for operation under heavy viscous loading. The standard measuring chamber supports operation in either gas or liquid environments, and provides single-electrode exposure to liquids (a prerequisite for compatibility with electrochemical QCM measurements). Figure 11.1 shows the frequency change of polished, gold coated 5 and 10 MHz crystals in contact with different glycerol solutions measured with the QCM-Z500. The tight correspondence between theory and experimental results is clearly illustrated. Figures 11.3 and 11.4 on the other hand show the admittance phase and admittance magnitude of a polished, gold coated 10 MHz crystal from which the data in figure 11.1 was calculated. The results prove that the QCM-Z500 is an excellent tool for the evaluation of fluid properties.



**Figure 11.1:** Change in frequency against glycerol weight percentage (in water) as measured with the QCM-Z500 (circles and squares) and predicted by theory (dashed lines) for two different quartz crystals with different fundamental resonance frequency.



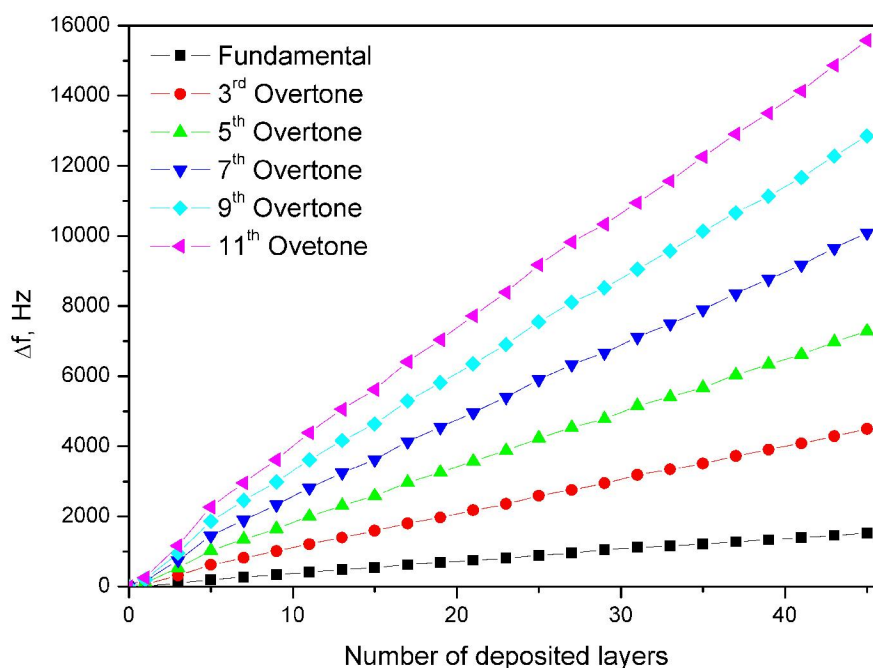
**Figures 11.2 and 11.3:** *Admittance Magnitude and Admittance Phase of a polished, gold coated 10 MHz crystal in contact with different glycerol solutions measured with the QCM-Z500.*

## 11.2 Rigid Film Deposition

Anything that has a mass can generate a response from a QCM sensor. The universal response of the device is the reason for the wide range of

application of the technology. The use of the QCM technique as a thickness monitoring device in different metal evaporation and sputtering applications is widely known. In the same way the QCM can be used to monitor the deposition of precisely defined rigid layers such as for example Langmuir-Blodgett films.

Figure 11.4 below shows the ex situ frequency change measured in air with the QCM-Z500 instrument after depositing stearic acid monolayers on both sides of a 5 MHz quartz crystal. The frequency change of the same crystal was measured after each deposition process by placing the same crystal into the standard QCM-Z500 measuring chamber and recording the frequency of the crystal in air. The monolayers were deposited on the quartz crystal with a KSV Minitrough 2 film balance from a  $\text{MnCl}_2$  subphase at a constant surface pressure of 30 mN/m.

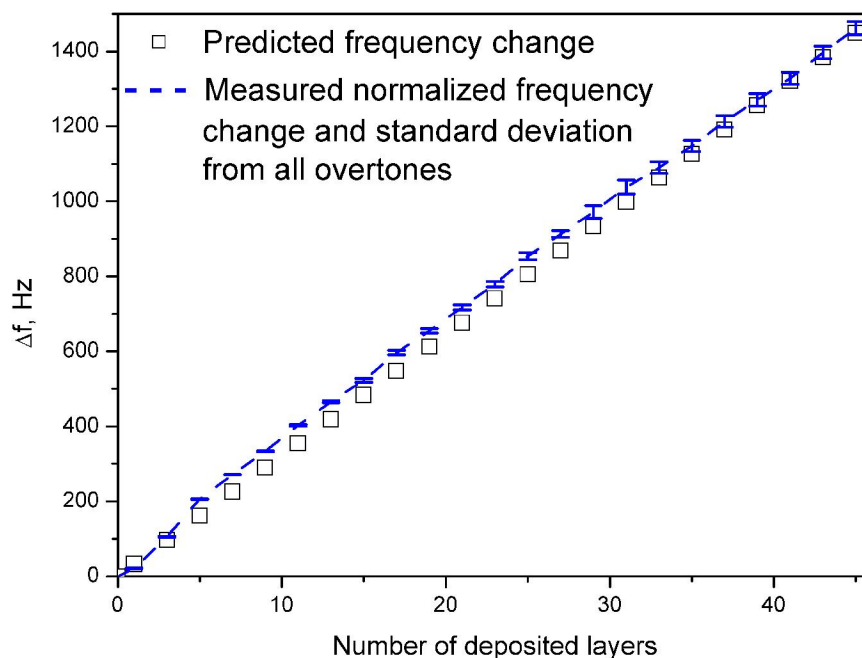


**Figure 11.4:** Frequency change at different overtones measured ex situ in air induced by deposition of Stearic acid monolayers on the quartz crystal.

By taking the area per stearic acid molecule measured from the Langmuir compression isotherm ( $20 \text{ \AA}^2/\text{molecule}$ ), the active electrode area on the quartz crystal ( $19.63 \text{ mm}^2$ ) and the average molecular weight ( $343.5 \text{ g/mol}$  for the stearic acid–manganese complex when 50 % of the stearic acid monolayer is undissociated as in this case), the Sauerbrey equation predicts that 1 stearic acid monolayer deposited on both sides of the quartz crystal should induce a 32.2 Hz change in frequency. Figure 11.5 below shows how well the predicted and the measured frequency change correlate with each other. The measured frequency change is plotted as the blue dotted line as an



average of the normalized frequencies of all the overtones shown in figure 8.4 and the predicted frequency change is shown as open squares.



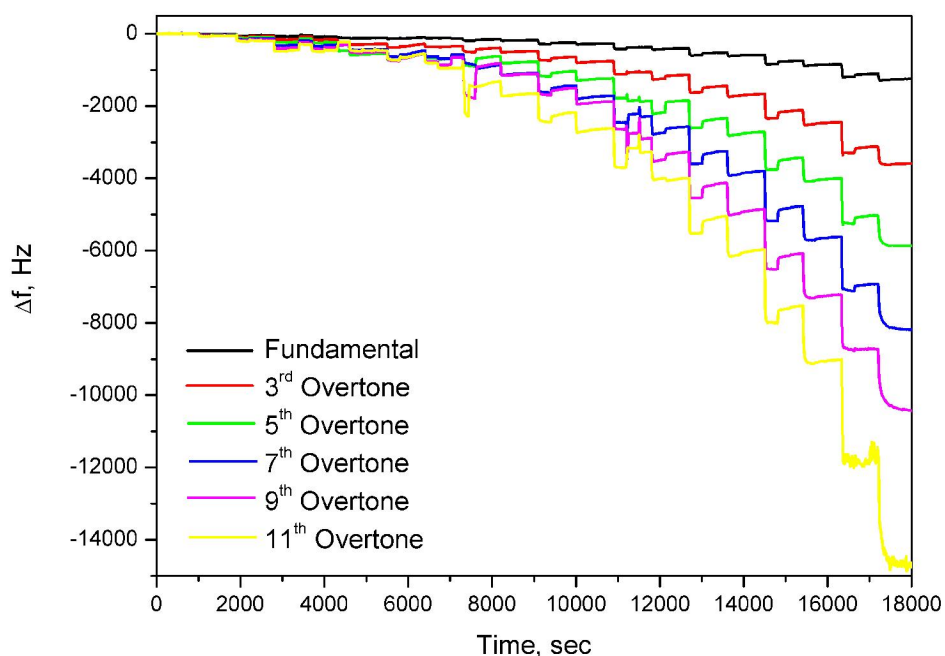
**Figure 11.5:** The predicted and measured frequency change as a function of number of deposited monolayers on the quartz crystal. The standard deviation for the average between the different overtones is also shown.

### 11.3 Alternate Adsorption of Oppositely Charged Macromolecules

The assembly of ultrathin films containing biological macromolecules, polymers, nanoparticles and other compounds has attracted a lot of interest during the last 3 decades due to their potential applications. The methods usually used for preparing these ultrathin films are spin coating, solution casting, thermal deposition, self-assembly or the Langmuir-Blodgett technique. However, during the last decade a new way of preparing ultrathin films has been extensively studied, and that is layer-by-layer assembly of polyions. This technique makes use of the alternate adsorption of oppositely charged linear or branched macromolecules (for example negatively and positively charged polymers, nanoparticles and proteins). The technique is very simple and provides the means to form ultrathin films of various substances.

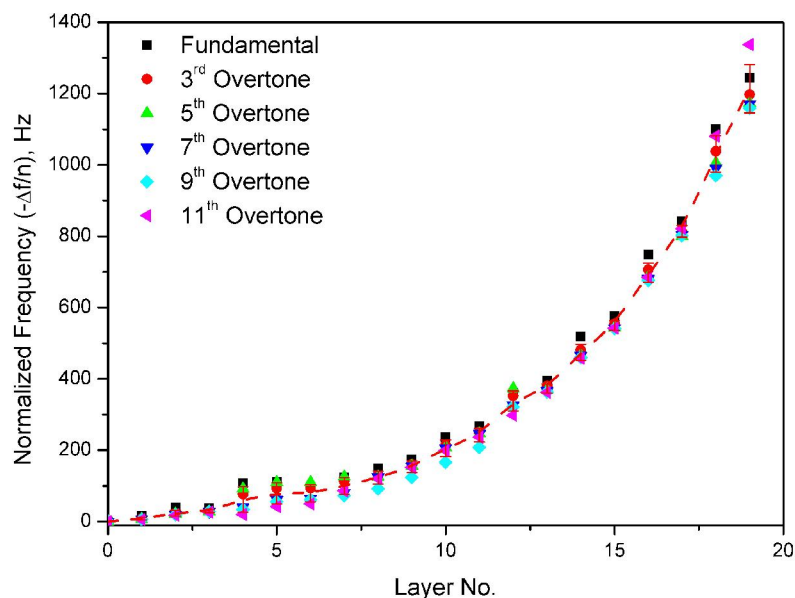
Figure 11.6 shows an example of an in situ layer-by-layer assembly build-up of oppositely charged macromolecules studied with the QCM-Z500. The polyelectrolytes used in the study shown in figure 11.7 were hyaluronic acid and chitosan dissolved in a solution containing 0.15 M NaCl with a pH of 4.5.

It is worthwhile to notice that it was possible to measure up to the 11th overtone of a 5 MHz crystal, which is enabled by the propriety design of the flow through measuring cell and the use of impedance analysis of the crystal.



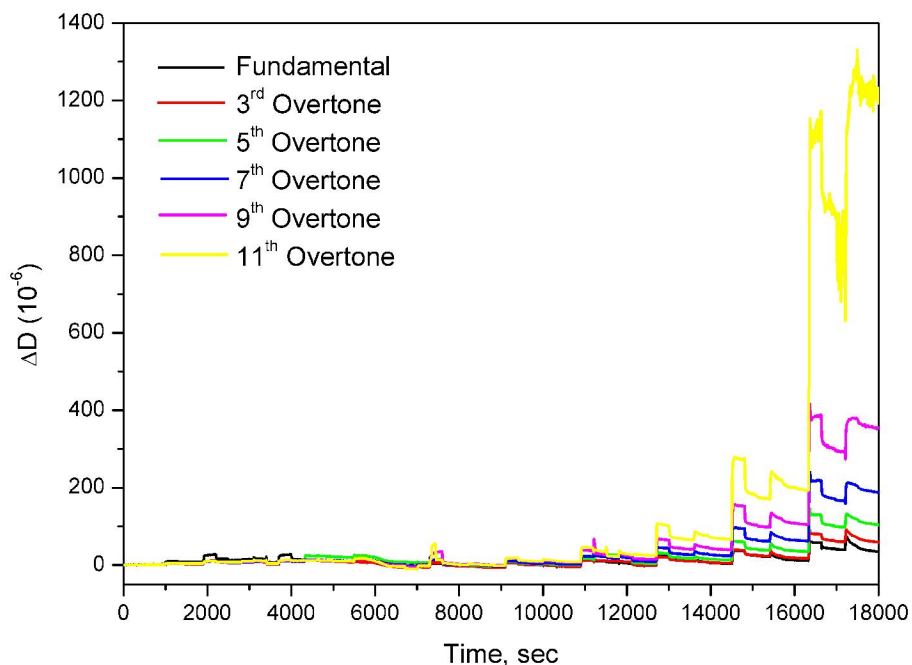
**Figure 11.6:** Frequency change at multiple overtones of a 5 MHz crystal induced by alternate adsorption of 9 (HA/CHI) double layers plus a last deposition of a HA layer i.e. in total 19 layers.

Figure 11.7 shows the normalized frequencies calculated from all overtones in figure 11.6. It can clearly be seen that the data correlates well with each other, and as there is no large dependence of  $-\Delta f/n$  with the overtones ( $n$ ) the Sauerbrey relation should hold to a good approximation. This exponential character of the HA/CHI buildup process has also been demonstrated in literature, for example Langmuir, Vol. 20, No. 2, 2004 p. 448. However, in that study the frequency changes for the complete buildup process of 20 layers was only reported for the fundamental and 5th overtone frequencies. One reason for this could be that they did not use the impedance analysis technique as was used for the measurement in figure 11.6. above, which also serves as a good example of the power of using the impedance analysis for QCM measurements as it enables the measurements on very highly dampened systems.



**Figure 11.7:** Normalized frequencies calculated from all overtones in figure 11.6 for the buildup process of HA/CHI multilayers.

Although the results in figure 11.7 demonstrate the validity of Sauerbrey relation, looking at the dissipation changes for the same buildup process actually indicates that the layers deposited after the 7<sup>th</sup> (HA/CHI) bilayer are not so well connected to the surface of the quartz crystal as one would expect from figure 11.7. This is shown in figure 11.8 below. One explanation for this could be that before the 7<sup>th</sup> (HA/CHI) bilayer the buildup process of the multilayer is happening in small patches rather than in an homogeneous film, while after the 7<sup>th</sup> (HA/CHI) bilayer the multilayer forms a homogenous film leading to a situation where the outer layers of the multilayer are not so well coupled to the quartz surface.

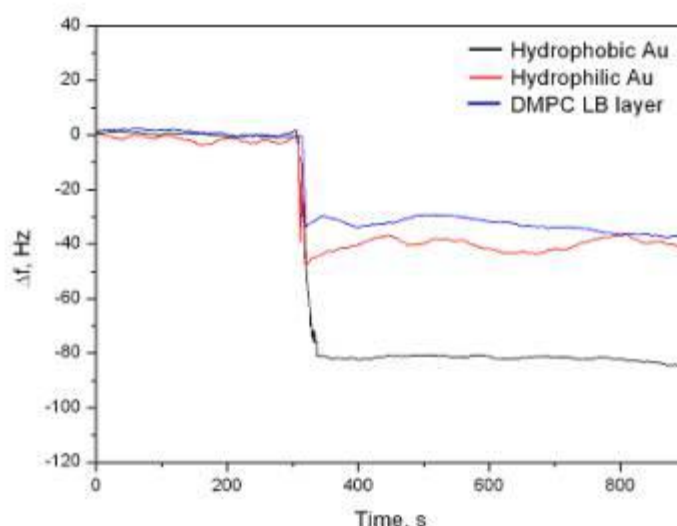


**Figure 11.8:** Dissipation changes at multiple overtones of a 5 MHz crystal induced by alternate adsorption of HA and CHI.

## 11.4 Protein Adsorption

Anything that has a mass can generate a response from a QCM sensor. The universal response of the device is the reason for the wide range of application of the technology. The use of QCM has dramatically increased in recent years in the field of biotechnology. The QCM is routinely used to obtain information about for example protein adsorption / desorption, cell adhesion, protein-protein interaction, degradation of polymers, biofouling and biofilm formation, drug analysis and DNA Biosensors.

Figure 11.9 show measurements adsorption of the protein Human Serum Albumin (HSA) to 5 MHz quartz crystals treated to have different properties. Measurements were performed with the QCM-Z500 standard measuring chamber. The frequency changes of 83, 39 and 36 Hz for the Hydrophobic Au, Hydrophilic Au and LB layer surfaces, respectively, are in good agreement with a protein adsorption study to differently treated silica made with an in situ ellipsometer (reference 17). The table below shows the comparison between the results with the QCM-Z500 and the ellipsometer study. The tight correspondence between the results is clearly illustrated.



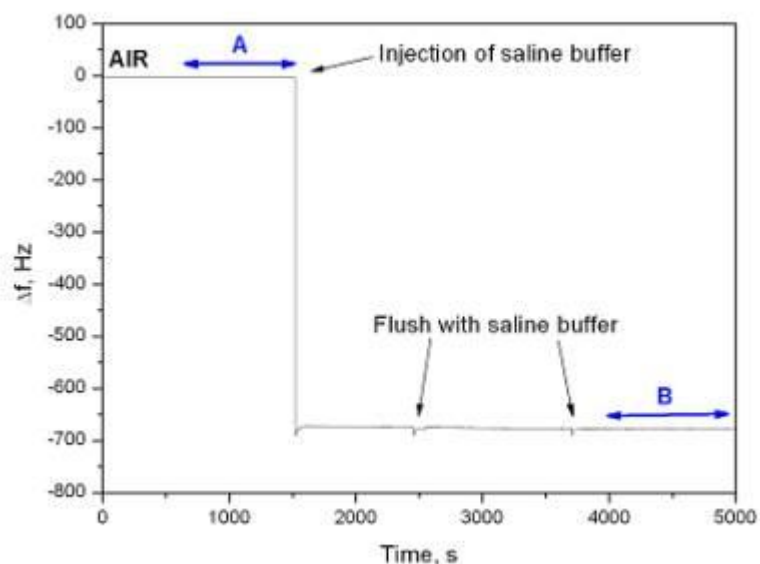
**Figure 11.9:** Frequency changes during adsorption of HSA to 5 MHz crystals with different properties.

*Adsorbed amounts of HSA at different surfaces.*

Surface	Adsorbed amounts of HSA determined with QCM-Z500	Adsorbed amounts of HSA from reference 17
Hydrofobic	0.73 mg/m <sup>2</sup>	0.80 mg/m <sup>2</sup>
Hydrofilic	0.34 mg/m <sup>2</sup>	0.35 mg/m <sup>2</sup>
PC LB layer	0.32 mg/m <sup>2</sup>	0.30 mg/m <sup>2</sup>

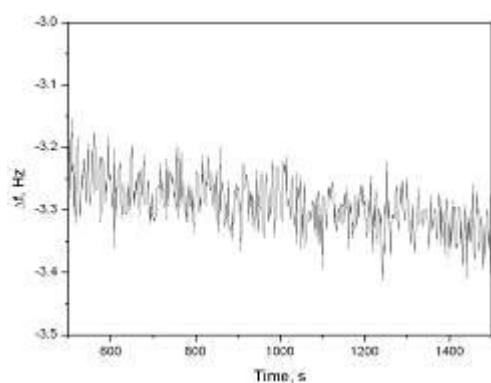
## 11.5 Signal to Noise Ratio Example

The mounting of the quartz crystal into the measuring chamber is a very critical issue for not damping the quartz crystal too much, which on the other hand can affect the noise level and consequently the sensitivity during the measurement. Due to KSV Instruments' proprietary electronic design, measuring chamber design and software algorithms the noise level of the QCM-Z500 instrument is equal or even better than with the "pinging principle" used by some other manufacturers, this even at the maximum acquisition speed. This is illustrated by the measurement below. The frequency of the crystal was first monitored in air, after which a buffer solution was introduced into the measuring chamber.

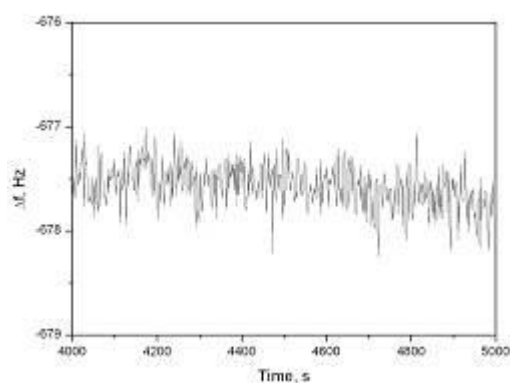


**Figure 11.10:** Monitoring frequency changes with the QCM-Z500 of a 5 MHz crystal before and after introducing a buffer solution into the measuring chamber.

The sections marked A and B in figure 11.10 were chosen to be expanded for looking at the noise level. One can clearly see that the noise level is very low for both air (see figure 11.11 A) and the buffer solution (see figure 11.11 B). The calculated RMS values of the noise level for air and the buffer solution are 0.05 Hz and 0.21 Hz, respectively.



**Figure 11.11 A**



**Figure 11.11 B**



## 12. Electrochemical chamber QCM

### 12.1 Overview

The electrochemical chamber QCM (EQCM) is a modification to the parallel flow measurement chamber that enables the insitu study of electrochemical polymerization reactions. In particular it allows the observation of change in mass against change in ionic charge.

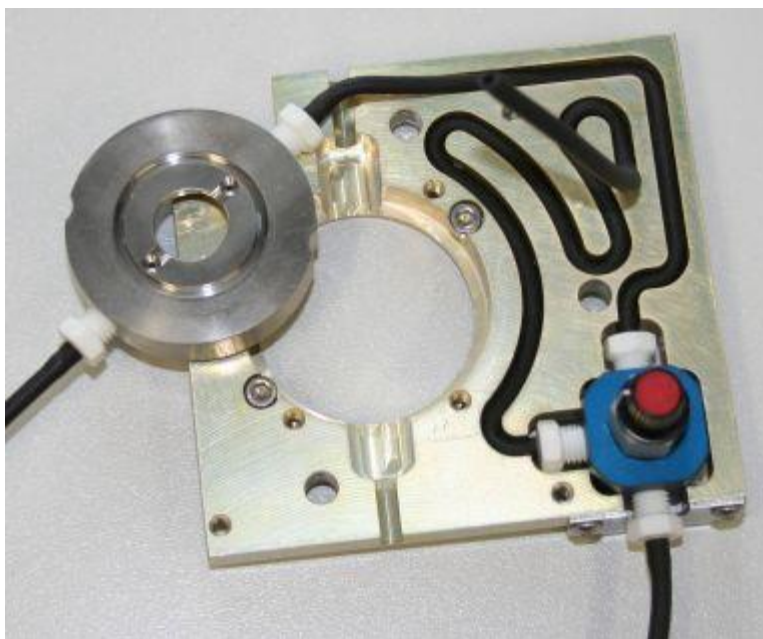
### 12.2 Converting to the EQCM

Lift the top module separate from the bottom module and remove the crystal holder, crystal and o-ring according to the instructions in section **4.4.1 Disassembling the Parallel Flow Chamber**. Open the black glass holder by turning it anticlockwise and gently remove the round glass window and the large o-ring. Remove the four locking screws.



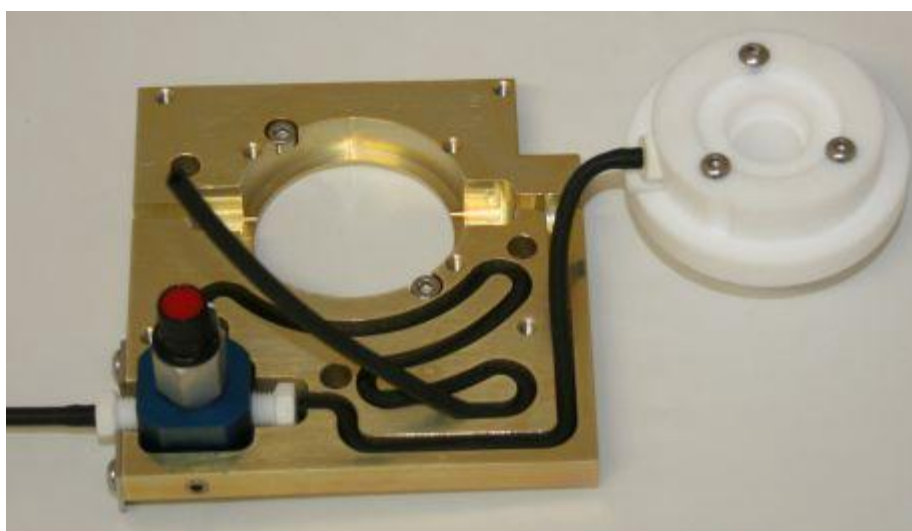
**Figure 12.1:** The top module with crystal holder, crystal, glass holder, glass window, both o-rings and the first screw removed.

The aluminum chamber support stage can now be removed from the top cover. Lift the metal chamber up from its slot.



**Figure 12.2:** *The chamber support stage with the metal chamber lifted up.*

Hold the chamber inlet tube in place and turn the metal chamber clockwise to detach it. Attach the bottom part of the EQCM chamber to the chamber inlet tube.



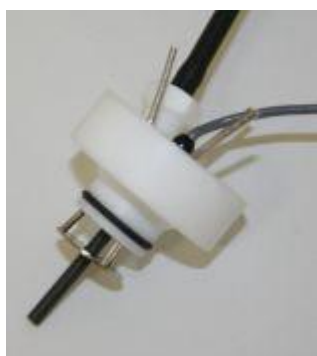
**Figure 12.3:** *The EQCM chamber attached to the chamber inlet tube.*

Place the chamber into its slot and place the top module cover onto the chamber support stage. Attach the lock screws and the black glass holder.



**Figure 12.4:** *The bottom part of the EQCM chamber attached to the top module.*

Note that the EQCM does not use the glass window or the large o-ring that the parallel chamber does. Also note that the chamber outlet is from the top part of the EQCM chamber, and not from the top module.



**Figures 12.5 and 12.6:** *The top part of the EQCM chamber and the entire EQCM chamber attached to the top module.*

## 12.3 EQCM Measurement

### 12.3.1 Preparation

The crystal is placed inside the chamber in the same way as with the parallel flow chamber. Lift the top module and remove the white crystal holder to get to the crystal, see section **4.4.1 Disassembling the Parallel Flow Chamber** for details. When the crystal has been cleaned and placed inside the crystal chamber reattach the top module to the bottom module with the locking screw.

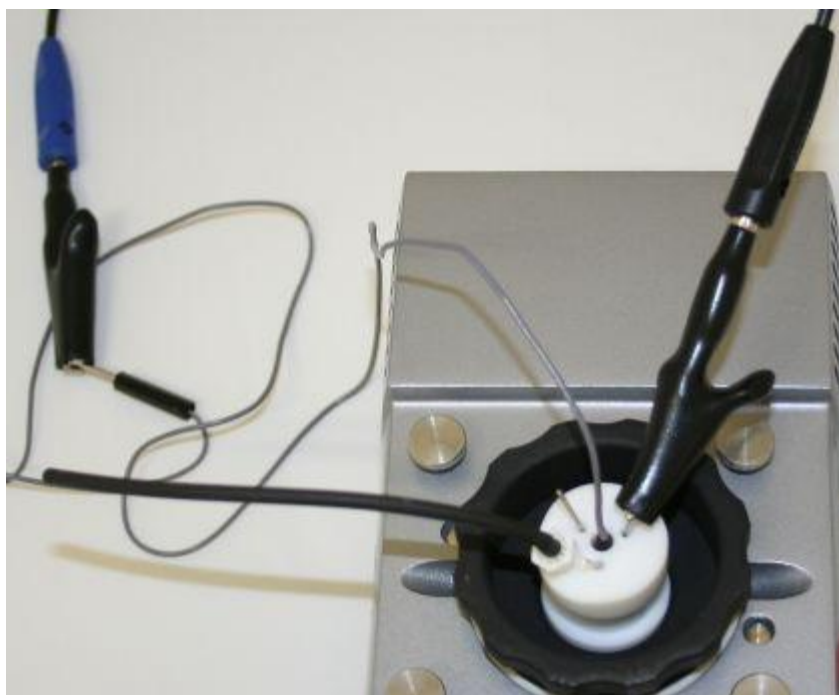
Push the reference electrode gently through the top part of the electrochemical chamber. The platinum counter electrode is fixed to the top part and does not need to be attached separately. Push the top part gently in to the middle of the bottom part of the electrochemical chamber.

Connecting the potentiostat to the QCM chamber depends on the experiment setup. This example is for a 3-electrode system. The counter electrode (CE) is connected to one of the platinum electrode poles. It does not matter which pole is used.



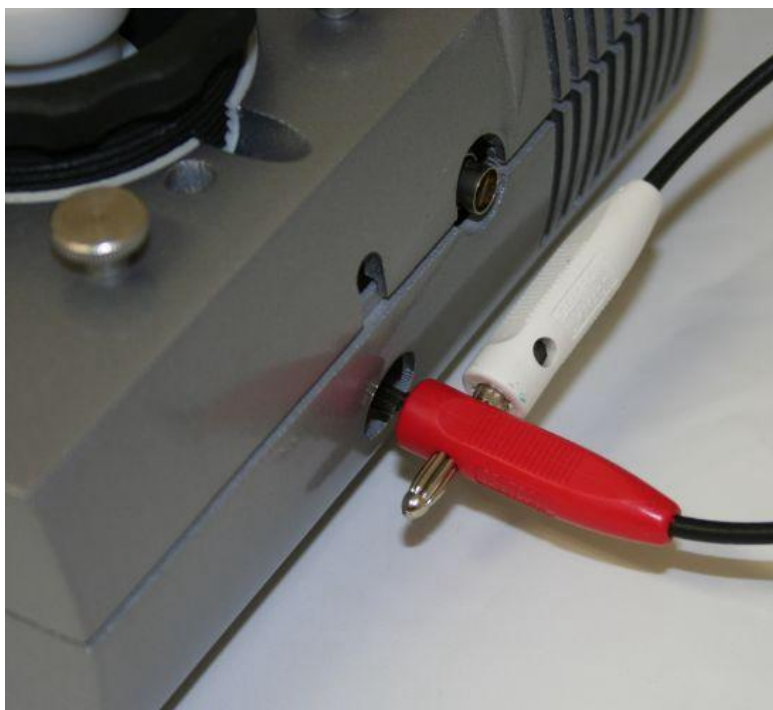
**Figure 12.7:** *The counter electrode connected to a platinum electrode.*

The reference electrode (RE) is connected to the end of the electrode wire.



**Figure 12.8:** *The reference electrode connected to the end of the electrode wire.*

The working electrode (WE) and the sense electrode (S) are connected straight to the bottom module.

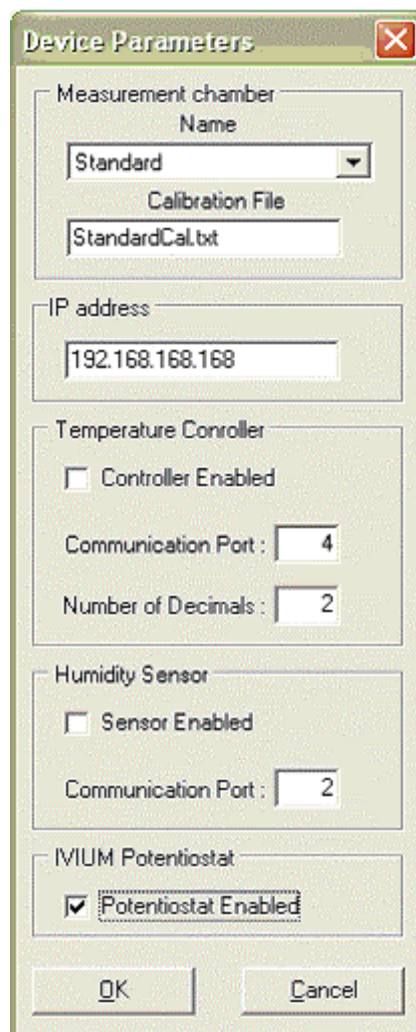


**Figure 12.9:** *The working electrode and the sense electrode connected to the bottom module.*

### 12.3.2 Measurement



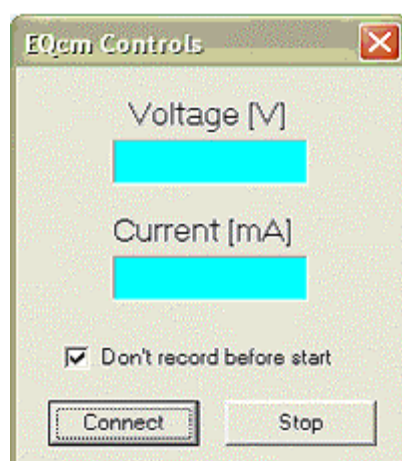
Start the QCM software. Select **Device Parameters** from the **Edit** menu. Activate the potentiostat by checking **Potentiostat Enabled** and press **OK** button.



**Figure 12.10:** *Activating the potentiostat from the Device Parameters window.*

Open the Ivium software and press the Connect button in the left upper corner. The Ivium software has to be connected to the potentiostat before the QCM control is connected. Once the Ivium software is connected, open the Potentiostat Controls window in the KSV QCM software, and press the **Connect** button. When the **Don't record before start** option is checked the QCM software does not record data points before measurement is started from the potentiostat software. The **Voltage** and **Current** fields are blank unless a measurement from the potentiostat is running. An error announcement will appear while pressing the **Connect** button if the Ivium software is not connected to the potentiostat. If no announcements appear the QCM measurement can be stated.





**Figure 12.11:** *The EQCM can be activated by pressing the Connect button.*

## 13. - Contact Information

If any problems arise please feel free to contact a local distributor or KSV Instruments directly.

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