

**QCM100  
Quartz Crystal  
Microbalance  
and  
Analog Controller**



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## **Certification**

Stanford Research Systems certifies that this product met its published specifications at the time of shipment.

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## **Warranty**

This Stanford Research Systems product is warranted against defects in materials and workmanship for a period of one (1) year from the date of shipment.

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## **Service**

For warranty service or repair, this product must be returned to a Stanford Research Systems authorized service facility. Contact Stanford Research Systems or an authorized representative before returning this product for repair.

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# Safety and Preparation for Use

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## Line Voltage

The QCM100 Analog Controller operates from a 90-132 or 175-264 V AC power source having a line frequency between 47 and 63 Hz. Power consumption is 20 VA total.

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## Power Entry Module

A power entry module, labeled A. C. POWER on the back plane of the QCM100 box provides connection to the power source and to a protective ground.

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## Power Cord

The QCM100 package includes a detachable, three-wire power cord for connection to the power source and protective ground.

The exposed metal parts of the box are connected to the power ground to protect against electrical shock. Always use an outlet which has a properly connected protective ground. Consult with an electrician if necessary.

Keep all electrical wiring in your experimental setup neatly organized and in good working condition. Inspect all HV wires periodically for problems as part of your safety checkups.

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## Grounding

A chassis grounding lug is available in the back plane of the QCM100 box, next to the power entry module. Connect a heavy duty ground wire, #12AWG or larger, from the CHASSIS GROUND lug directly to a facility earth ground to provide additional protection against electrical shock.

Both front panel BNC shields are connected to the chassis ground and the AC power source ground via the power cord. Do not apply any voltage to the shield.

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## GFCI (Ground Fault Circuit Interrupter)

GFCI protected outlets are often available in production and laboratory environments, particularly in proximity to water sources. GFCI's are generally regarded as an important defense against electrocution. However, the use of GFCI in conjunction with the QCM100 must not be regarded as a substitute for proper grounding and careful system design. GFCI's must also be tested regularly to verify their functionality. Always consult an electrician when in doubt.

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## Line Fuse

The LINE FUSE is internal to the instrument and may not be serviced by the user.

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## **Operate Only With Covers In Place**

To avoid personal injury, do not remove the product covers or panels. Do not operate the product without all covers and panels in place.

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## **Liquid Contact**

With the exception of the Crystal Holder, this product is intended for use only in a clean dry laboratory environment. Operation in other environments may cause damage to the product and reduce the effectiveness of the safety features. To reduce the risk of fire or electrocution do not expose this product to rain or excessive moisture. Be careful not to spill liquid of any kind onto or into the product.

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## **Serviceable Parts**

The QCM100 Analog Controller does not include any user serviceable parts inside. Refer service to a qualified technician.

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## Front Panel Overview

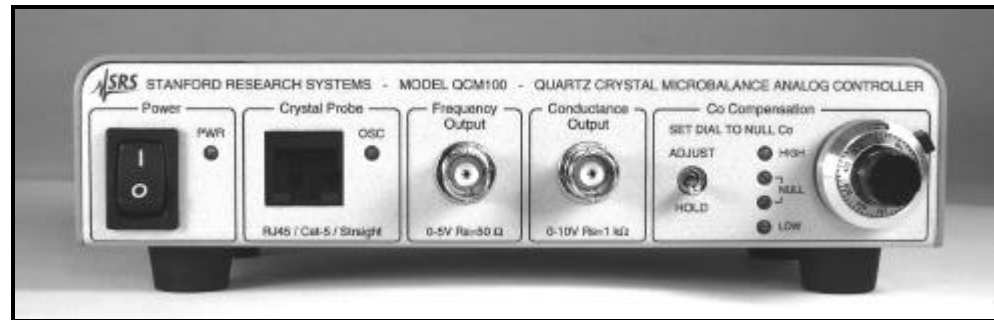


Figure 1. Front Panel of QCM100 Analog Controller

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### Power Switch (w/ green PWR LED).

The QCM100 Analog Controller is turned on by flipping the power switch.

A green PWR LED lights up to indicate the presence of electrical power.

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### Crystal Probe Connector (w/ green OSC LED)

The Crystal Probe connector is an RJ-45 connector used to connect the QCM100 Analog Controller to the QCM25 Crystal Oscillator (QCM Controller connector).

A 3 foot long Cat-5 (Straight) cable is used to electrically connect the two boxes.

A green OSC LED lights to indicate the presence of an oscillating crystal in the circuit and the Conductance Output is  $>2$  V.

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### Frequency Output Connector

The Frequency Output connector is a BNC connector. The frequency signal has TTL (square wave) levels and a source resistance of  $50 \Omega$ .

The BNC shield is electrically connected to chassis ground.

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### Conductance Output Connector

The Conductance Output connector is a BNC connector. The conductance signal ( $V_c$ ) is related to the series resonance resistance of the QCM crystal by:

$$R = 10,000 \times (10^{-V_c/5}) - 75 \Omega$$

Voltage levels span between 0 and 10.625 VDC and source impedance is  $1 \text{ K}\Omega$ .

The BNC shield is electrically connected to chassis ground.

## **C<sub>o</sub> Compensation:**

A switch is available to set the controller into the Adjust Mode for nulling C<sub>o</sub>.

A ten-turn DIAL, controls the bias voltage (Varactor bias) required by the QCM25 Crystal Oscillator to null C<sub>o</sub>.

Five LEDs (HIGH/NULL/LOW) provide visual feedback while nulling C<sub>o</sub>.

Set the C<sub>o</sub> Compensation switch back to HOLD after nulling C<sub>o</sub>.



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## Back Panel Overview



*Figure 2. Back Panel of QCM100 Analog Controller.*

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### Power Entry Module.

The Power Entry Module is used to connect the QCM100 Analog Controller to a power source through the power cord provided with the instrument. The center pin is connected to the QCM100 chassis so that the entire box can be grounded.

The source voltage requirements are: 90-132 or 175-264 VAC, 47-63 Hz (20 VA TOTAL).

Connect the QCM100 to a properly grounded outlet. Consult an electrician if necessary.

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### Chassis Ground

Use this grounding lug to connect the QCM100 chassis directly to facility ground.

## QCM25 Crystal Oscillator Overview



Figure 3. QCM25 Crystal Controller (top view)

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### QCM Controller Connector

The QCM Controller connector is a RJ-45 connector used to electrically connect the QCM25 Crystal Oscillator to the QCM100 Analog Controller (Crystal Probe connector).

A 3 foot long Cat-5 (Straight) cable is used to electrically connect the two boxes.

A green Power LED lights up to indicate the presence of electrical power in the QCM25 box.

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### Crystal Face Bias

The Crystal Face Bias connector provides a direct electrical connection to the QCM crystal's liquid face electrode (i.e. outer electrode in contact with the solution).

Use this connector to electrically connect the QCM crystal's liquid face to the Work Electrode lead of a Potentiostat while using the QCM crystal in an electrochemical setup.

Transformer isolation between the crystal electrodes and the oscillator circuit makes the QCM100 System ideal for electrochemical research and compatible with virtually all potentiostats.

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## 5 MHz Crystal

Use this BNC connector to electrically connect the QCM25 Crystal Oscillator to a Crystal Holder (or directly to your custom 5MHz QCM crystal)

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## 1/4-20 MTG Hole

Use this threaded hole to mount the QCM25 Crystal Oscillator in your experimental setup, using a 1/4-20 threaded fastener.

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## Power LED

This LED lights up to indicate power is available to the QCM25 electronics. This requires connection to a powered QCM100 Analog Controller.

# Specifications

## Frequency Output

Frequency	5 MHz (nominal)
Level	TTL (square wave)
Source Impedance	50 $\Omega$
Connector	BNC

## Conductance Output (Vc)

Resistance Calculation	$R = 10,000 \times (10^{-V_c/5}) - 75 \Omega$
Resistance Range	0 to 5000 $\Omega$
Voltage Level	0 to 10.625 VDC, log scale
Impedance	1 K $\Omega$
Connector	BNC

## Capacitance Cancellation

Range	10 to 40 pF (20 pF nominal)
Achievable Cancellation	0.01 pF

## Quartz Crystals

Frequency	5 MHz, AT-cut, plano-plano
Diameter	1 inch
Electrodes	Chromium/gold, titanium/gold, titanium/platinum (polished/unpolished)

## Crystal Holder

Material	Kynar
O-ring	Viton
Connector	BNC

## Chapter 1

# Getting Started

This chapter provides instructions for (1) unpacking, (2) checking and (3) connecting the QCM100 Analog Controller to its accessories and to your experiment.

Quick Start instructions are also provided to perform QCM measurements.

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# Unpacking

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## Before You Open the Box

Read the entire Safety and Preparation for Use section of this manual before starting any installation procedure.

Read and follow all installation and operation instructions in this manual to ensure that the performance of this instrument is not compromised.

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## Checklist

- Open the box(es) and inspect all components of the QCM100 System.
- Report any damage to Stanford Research Systems immediately.
- Compare the contents of the shipping boxes against your original order and the checklist below. Report any discrepancies to Stanford Research Systems immediately.

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## Standard Equipment Supplies

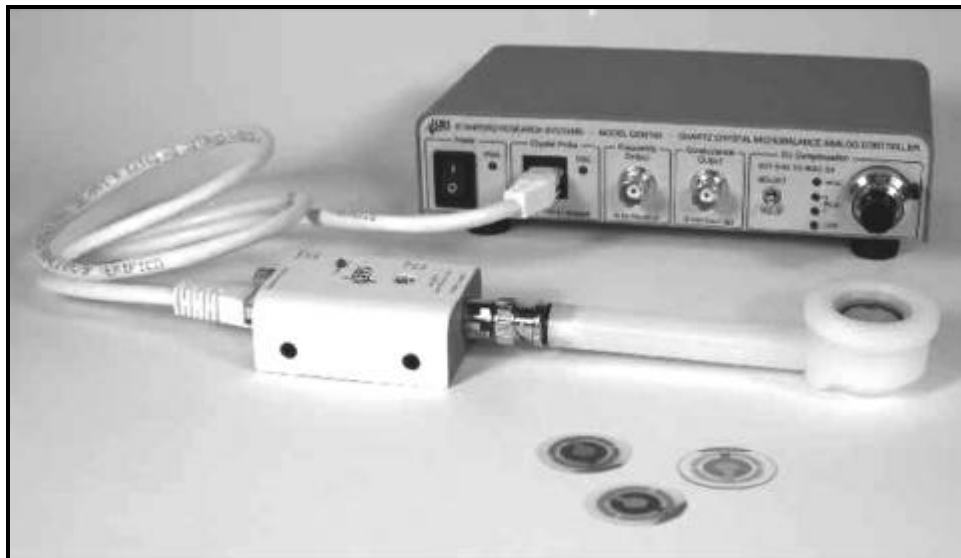
- QCM100 Quartz Crystal Microbalance Analog Controller
- QCM25 Crystal Oscillator
- Operation and Service Manual
- Power cord
- Cat-5 Cable (3 foot long)
- Crystal Holder
- Three (3) chromium/gold , unpolished QCM crystals.

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## Optional Equipment

- Replacement Crystals
- Flow Cell

## Quick Start Instructions



*Figure 1. Basic QCM Setup.*

1. With the power switch in the Off position, connect the QCM100 Analog Controller to a grounded outlet using the power cord.
2. Connect the QCM100 Analog Controller to the QCM25 Crystal Oscillator using the Cat-5 cable (3 feet long with RJ-45 end connectors).
3. Mount a fresh QCM crystal in the Crystal Holder. See separate instructions in the next section.
4. Connect the Crystal Holder to the 5 MHz Crystal BNC connector of the QCM25 Crystal Oscillator.
5. Connect the frequency output signal of the QCM100 to your frequency counter. See Chapter 2 for more information about selecting a frequency counter.
6. Connect the Conductance Output to a digital voltmeter or analog-to-digital converter.
7. Set the  $C_o$  Compensation switch to Hold and the ten-turn dial to 5.0 (Dry Operation Setting).
8. Turn the Power switch on and check that the Power LEDs in the QCM100 and QCM25 boxes light up. The OSC LED of the QCM100 lights up as soon as oscillation is established in the dry crystal. A frequency very close to 5 MHz (nominal dry frequency) should be displayed by the frequency counter at this time, and the Conductance Output voltage should be close to 10.0 VDC.
9. The QCM System is ready for mass and viscosity measurements.



10. For operation under liquid immersion, record the “dry” frequency and conductance readings and immerse the entire crystal in the liquid solution of interest. For accurate measurements, perform a Capacitance Cancellation procedure as described in Chapter 2.
11. For operation in an electrochemical setup, using the liquid face of the QCM crystal as the working electrode surface, connect the “Work Electrode” lead of the potentiostat to the Crystal Face Bias connector of the QCM25 oscillator.

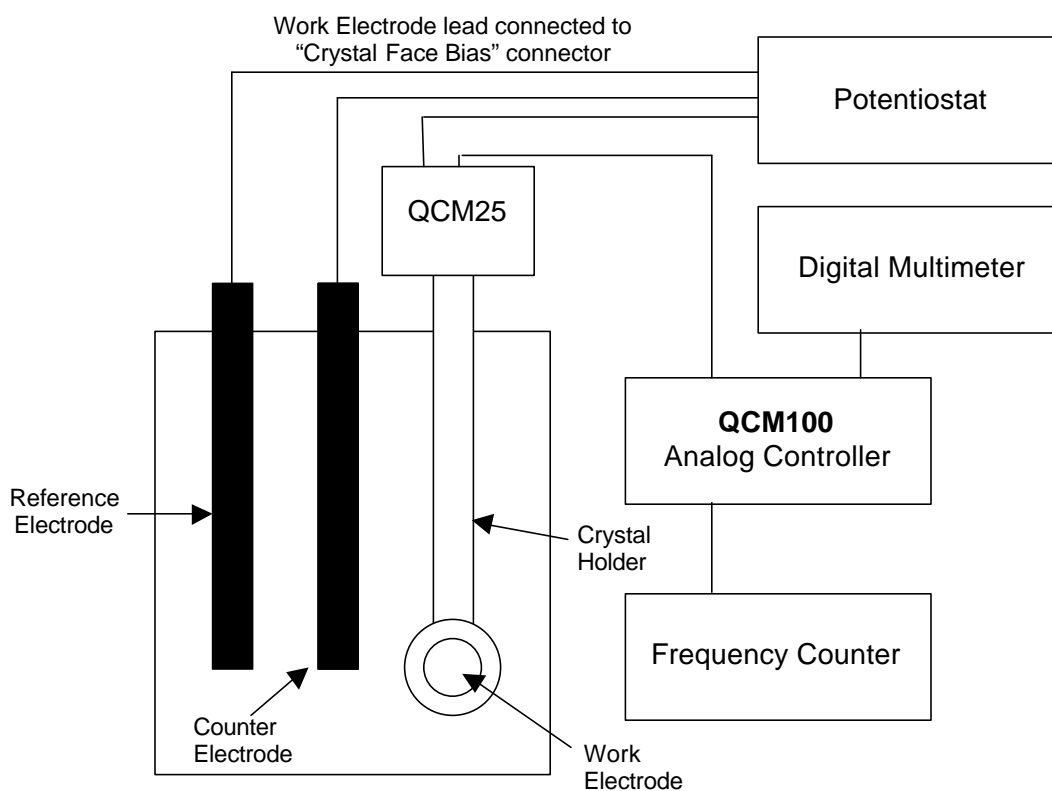


Figure 2. Basic Electrochemical Quartz Crystal Microbalance (EQCM) setup.

## Crystal Installation

This section describes the procedure required to replace/install the QCM crystal of the Crystal Holder.

Figure 3 shows the basic components of the Crystal Holder, including a standard 1 inch sensor crystal.

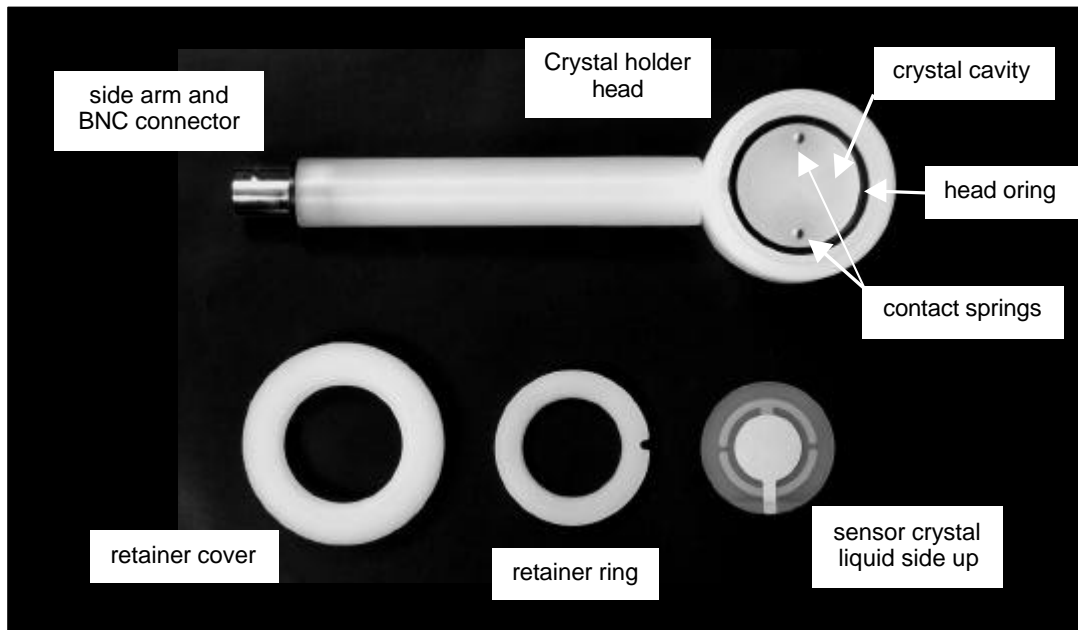


Figure 3. Crystal Holder components.

The standard 1 inch diameter sensor crystal has two sides that must be clearly identified before this procedure is started:

### Contact Surface

The contact surface has two separate circuits and the smaller electrode pad.

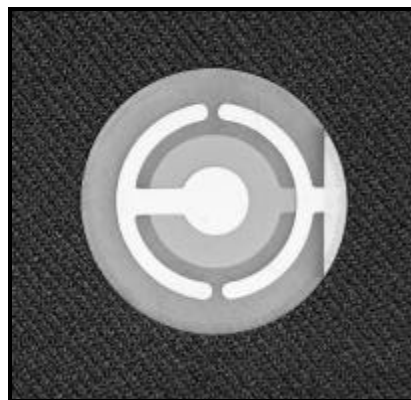
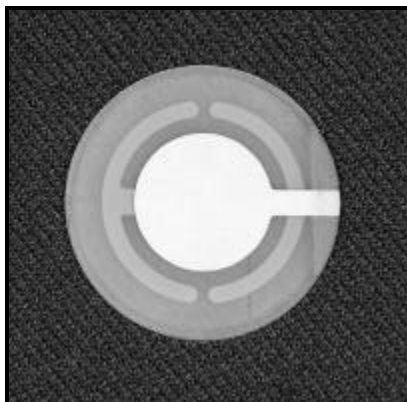


Fig 4. Contact Surface of QCM crystal

## Liquid Surface

The liquid surface has the larger electrode pad, which connects through a wrap around pad to one of the circuits on the Contact Surface. This is the outside (i.e. modified) surface, in direct contact with the gas or liquid during QCM experiments.

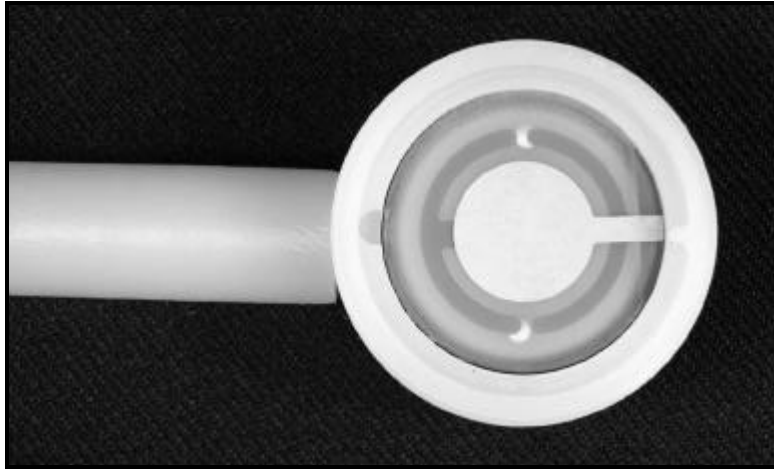


*Figure 5. Liquid surface of QCM crystal*

In order to insert a new crystal into the holder, the following steps must be followed:

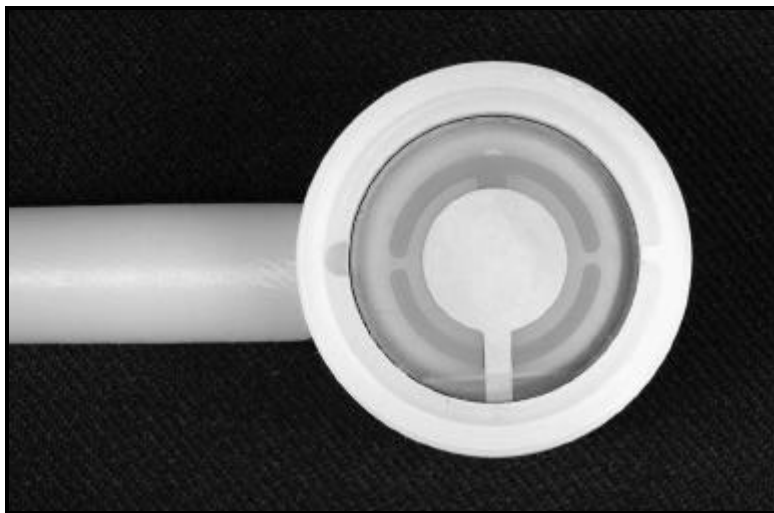
1. Place the Crystal Holder's head on a flat surface, with its crystal cavity pointing up. The crystal cavity contains two spring-loaded contacts (POGO® pins), which connect the two Contact Surface circuits of the crystal to the BNC connector on the opposite end of the probe.
2. Inspect the head oring to make sure it is free of defects, clean and properly seated in its dovetail groove. The oring should be free of low spots and show sufficient height above the center ring when viewed from the side with the naked eye.
3. Make sure the crystal cavity is clean and dry. Dry if necessary.
4. Test the travel of the POGO® contacts. Gently depress the POGO® pins (a thin wooden applicator does a good job). Make sure they move freely and that travel is not restricted. They should depress to a level well below the surface of the probe oring (by an amount at least equal to the thickness of the crystal). When fully extended, they should rise above the surface of the oring, by an amount equal or larger than the crystal thickness.
5. Inspect the sensor crystal at this time and clean if necessary.

6. Hold the crystal, Contact Surface down, above the Crystal Holder's head and point the wrap-around electrode towards the reference pin (at end of probe). See Figure 6 below.



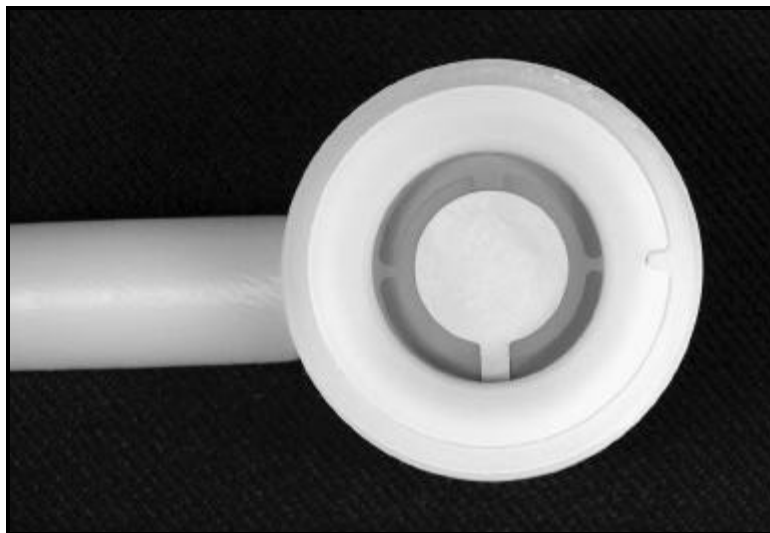
*Figure 6. QCM Crystal in Crystal Holder cavity with wrap around electrode pointing towards reference pin.*

7. Turn the crystal 90° clockwise before laying it centered onto the head oring. Turning the crystal as indicated assures a fresh contact surface develops between the crystal electrodes and the POGO pins. The crystal should end up as shown in Figure 7 below.



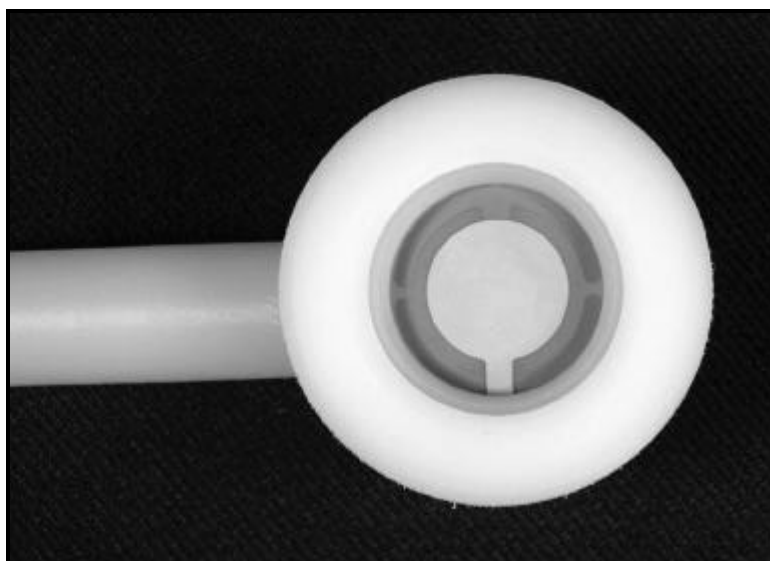
*Figure 7. Crystal in place with correct orientation.*

- Place the retainer ring (or Flow Cell) over the crystal, with its notch mating with the reference pin as shown in Figure 8 below.



*Figure 8. Retainer ring in place.*

- Mount the retainer cover and thread the first quarter turn. Inspect the retainer ring to make sure the alignment notch remained mated with the reference pin.



*Fig 9. Retainer cover in place.*

- Tighten retainer cover the rest of the way – finger tight is OK.

11. Connect the Crystal Holder to the QCM25 Crystal Oscillator as shown in Figure 10.



*Figure 10. The QCM Probe consisting of a Crystal Holder and QCM25 Crystal Oscillator.*

## Chapter 2

# Theory, Operation and Calibration

This chapter provides a brief introduction to the measurement techniques and calibration procedures available to QCM100 users and describes the most popular theoretical models used to interpret the results.

The procedure for capacitance compensation is also described in detail

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## Background

Sauerbrey<sup>1</sup> was the first to recognize the potential usefulness of the Quartz Crystal Microbalance (QCM) technology and demonstrate the extremely sensitive nature of these piezoelectric devices towards mass changes at the surface of QCM electrodes. The results of his work are embodied in the Sauerbrey equation, which relates the mass change per unit area at the QCM electrode surface to the observed change in oscillation frequency of the crystal:

$$\Delta f = - C_f \cdot \Delta m \quad (\text{eqn. 1})$$

where

$\Delta f$  = the observed frequency change in Hz,

$\Delta m$  = the change in mass per unit area in  $\text{g}/\text{cm}^2$ ,

$C_f$  = the sensitivity factor for the crystal ( $56.6 \text{ Hz } \mu\text{g}^{-1} \text{ cm}^2$  for a 5 MHz AT-cut quartz crystal at room temperature).

The Sauerbrey equation relies on a linear sensitivity factor,  $C_f$ , which is a fundamental property of the QCM crystal. Thus, *in theory*, the QCM mass sensor does not require calibration. However, it must be kept in mind, that the Sauerbrey equation is only strictly applicable to uniform, rigid, thin-film deposits<sup>2</sup>. Vacuum and gas phase thin-film depositions which fail to fulfill any of these conditions actually exhibit more complicated frequency-mass correlations and often require some calibration to yield accurate results.

For many years, QCMs were just regarded as gas-phase mass detectors, however, recently their application has been extended since scientists realized that they can be operated in contact with liquids and viscoelastic deposits. In this case, both frequency and series resonance resistance of the quartz oscillator are important to completely characterize the material in contact with the crystal electrode. The development of QCM systems for use in fluids opened a new world of applications, including electrochemistry and micro-rheology. More recent developments have focused on tailoring electrode surface chemistry (i.e. specialized polymer coatings) so that these devices can be applied as discriminating mass detectors for (1) specific gas detection, (2) environmental monitoring, (3) biosensing and (4) basic surface-molecule interaction studies.

The purpose of this chapter is to provide a brief introduction to the different measurement and calibration techniques available to QCM100 users, and to briefly describe the most popular theoretical models used to interpret the results. A complete coverage of these subjects is obviously beyond the scope of this manual. However, many articles have been published on the operation and calibration of QCMs in applications ranging from vacuum thin-film deposition to electrochemical experiments, and QCM users are referred to the publications list at the end of this chapter for more detailed information.

## The QCM Oscillator

The Butterworth van Dyke (BVD) electrical model<sup>3</sup> for a quartz crystal resonator is shown in Figure 1. This model is often used to represent the electrical behavior of a crystal resonator near series resonance. The model has also been useful in predicting the frequency shifts and losses of an AT-cut quartz crystal in QCM applications.

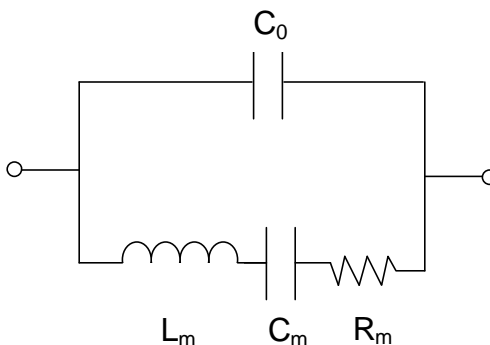


Figure 1. Butterworth-van Dyke model of Quartz Crystal Resonator.

The BVD electrical model consists of two arms. The motional arm has three series components modified by the mass and viscous loading of the crystal:

- 1)  $R_m$  (resistor) corresponds to the dissipation of the oscillation energy from mounting structures and from the medium in contact with the crystal (i.e. losses induced by a viscous solution).
- 2)  $C_m$  (capacitor) corresponds to the stored energy in the oscillation and is related to the elasticity of the quartz and the surrounding medium.
- 3)  $L_m$  (inductor) corresponds to the inertial component of the oscillation, which is related to the mass displaced during the vibration.

Typical values for a 1" diameter, 5 MHz crystal used in the QCM100 System are  $C_m = 33$  fF,  $L_m = 30$  mH, and  $R_m = 10 \Omega$  (for a dry crystal),  $R_m = 400 \Omega$  (for a crystal with one face in water), or  $R_m = 3500 \Omega$  (for a crystal with one face in 88% glycerol).

The motional arm is shunted by the parasitic capacitance,  $C_o$ , which represents the sum of the static capacitances of the crystal's electrodes, holder, and connector capacitance. In the QCM100 System<sup>4</sup>,  $C_o$  is about 20 pF, a value which has been kept small by placing the electronics directly on the Crystal Holder, thereby eliminating any cable capacitance.

In a QCM application the motional inductance,  $L_m$ , is increased when mass is added to the crystal electrode - the frequency shift of the series resonance is a sensitive indicator of the added mass. Films of less than  $1 \text{ ng/cm}^2$  can easily be resolved by the QCM. The motional resistance,  $R_m$ , can also provide important information about a process since soft films and viscous liquids will increase motional losses and increase the value of  $R_m$ .

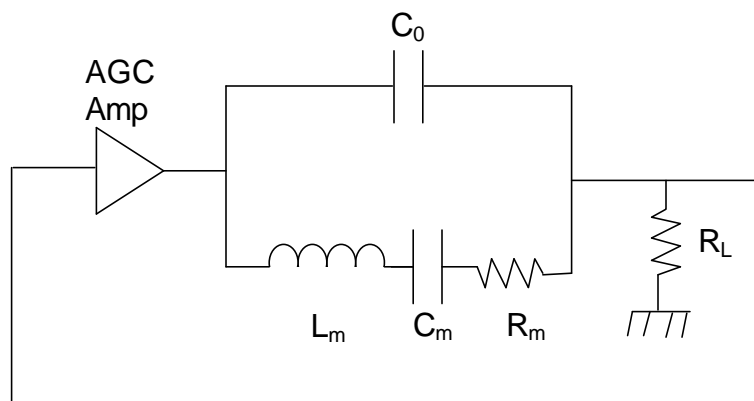


Figure 2. Oscillator Circuit consisting of AGC Amplifier, Quartz Resonator and Load Resistor.

Placing the crystal in an oscillator circuit provides a simple way to measure its motional parameters<sup>5</sup>. Figure 2 shows the BVD crystal model, driven by an automatic gain control amplifier (AGC), and terminated into a load resistor,  $R_L$ . By returning the voltage on  $R_L$  to the input of the AGC amplifier, the circuit will oscillate at a frequency for which the phase shift around the loop is  $0^\circ$  (or an integral multiple of  $360^\circ$ ) provided there is sufficient gain (the Barkhausen condition). Absent  $C_0$ , it is easy to see that the phase condition is satisfied at the series resonance of  $C_m$  and  $L_m$  ( $f_{SR} = [1/[2\pi(L_m C_m)^{1/2}]$ ). At series resonance, the reactance of  $C_m$  and  $L_m$  cancel, leaving only  $R_m$ . In this case, an amplifier gain of  $A_v = (R_m + R_L)/R_L$  will provide a loop gain of 1 to sustain oscillation.

Unfortunately,  $C_0$  cannot be ignored in QCM applications. In the circuit shown in Figure 2,  $C_0$  injects a leading current into  $R_L$  which must be canceled by a lagging current via the motional arm, in order to achieve the zero phase condition. This requires the circuit run above series resonance, where the net reactance of  $C_m$  and  $L_m$  is inductive. In fact, if  $R_m$  is large enough, it is possible that the motional arm will not be able to contribute enough lagging current to cancel the leading current via  $C_0$ , and the circuit will not oscillate at all.

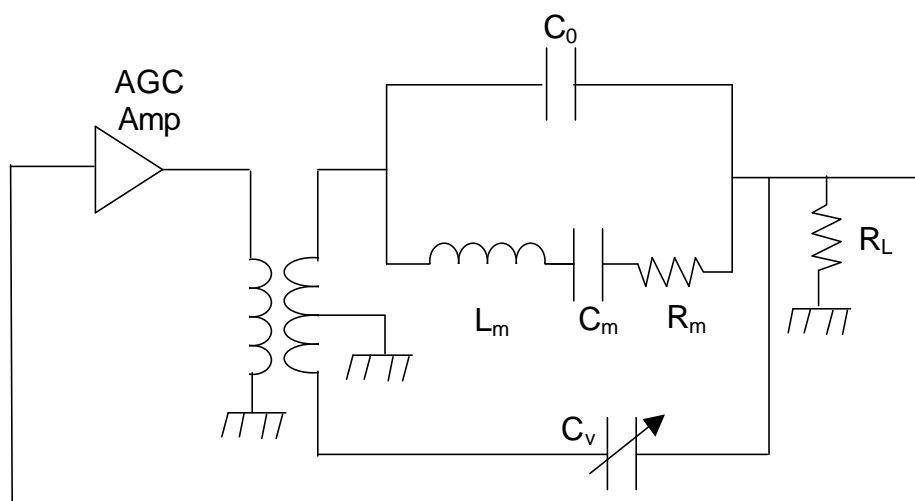


Figure 3. Oscillator Circuit with Varactor Nulling of  $C_0$ .

A method to cancel  $C_o$  is shown in Figure 3. In this circuit the AGC amplifier drives a transformer with two secondary windings. One secondary drives the crystal and load as before, while the other secondary inverts the voltage. The inverted voltage source injects a current via an adjustable capacitor,  $C_v$ , to cancel the current injected via  $C_o$ . Exact cancellation is achieved when the adjustable capacitor is made equal to  $C_o$ . *In the SRS QCM25 Crystal Oscillator,  $C_v$  is a varactor, which is made equal to  $C_o$  by finding the bias setting which minimizes the gain required to sustain oscillation.*

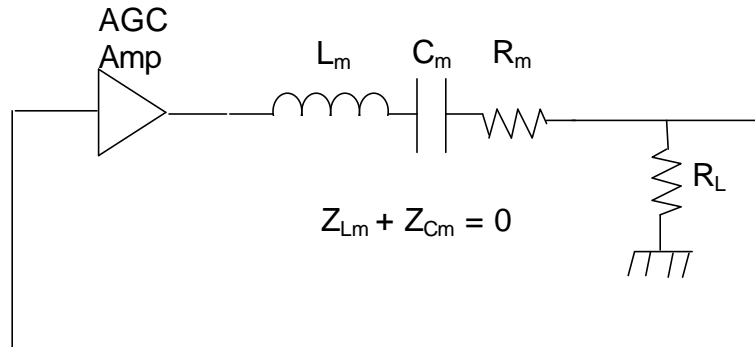


Figure 4. Oscillator Circuit Model with  $C_o$  cancelled by  $C_v$ .

With  $C_o$  canceled the circuit simplifies to that shown in Figure 4. For this circuit, the zero phase condition is achieved at series resonance where the reactance of  $C_m$  and  $L_m$  cancel. At series resonance  $R_m$  and  $R_L$  form a resistive attenuator requiring an AGC gain of  $A_v = (R_m + R_L)/R_L$  to sustain oscillation. By knowing the AGC gain<sup>6</sup>,  $A_v$ , required to sustain oscillation, we can determine  $R_m = R_L \cdot (A_v - 1)$ .

## Capacitance Cancellation

The QCM100 System incorporates a method of nulling  $C_o$  capacitance insuring that the frequency and resistance values measured correspond to the true series resonant parameters of the quartz oscillator.

The front panel of the QCM100 Analog Controller includes (1) a ten-turn DIAL to control the bias voltage required by the varactor  $C_v$ , and (2) a switch to set the controller into the Adjust Mode for nulling  $C_o$ .

There are two ways to operate the QCM100 Analog Controller to null  $C_o$ .

1. The unit-to-unit variations in  $C_o$  are small enough and the reproducibility of  $C_v$  is good enough ( $\pm 2$  pF) that most users can just set the varactor bias to a fixed value and forget about the whole issue. Set the ten-turn dial to 5.0, which will provide 6.0 volts of reverse bias to the varactor, making  $C_v$  about 18 pF. This method is recommended for “dry” applications where  $R_m$  is low. This is not recommended for “sticky” applications (such as solutions of glycerol) where  $R_m$  can be very high.
2. Null  $C_o$  with the conductance lock-in peak detection circuit. In the Adjust Mode, the unit will modulate the varactor bias with a 75 Hz sine wave and indicate if the  $C_o$  compensation is High, Low or Nulled. Start with ten-turn dial set to 5.0 (the LED should indicate that the crystal is oscillating) and switch to Adjust Mode. Reduce the setting on the dial if the High LED is on, increase the setting if the Low LED is on, and lock the dial at the middle of the range for which both Null LEDs glow with equal intensity. Return the switch to the HOLD Mode setting when done.

### As A General Rule:

- Capacitance cancellation is essential for accurate measurements of liquids and lossy (i.e. soft) films.
- Capacitance cancellation should be checked and readjusted every time the environment of the crystal is changed. For example, when transitioning from air to a liquid phase.
- The cancellation adjustment must be performed with the Crystal Holder and crystal in the actual measurement environment.
- The switch must be in HOLD position during actual QCM measurements.

## Frequency Measurement

The QCM100 provides a Frequency output port (BNC).

Virtually any commercially available frequency counter can measure the frequency of the 2.4 Vpp square wave into 50  $\Omega$  provided by the QCM100 Frequency Output. Counters are relatively simple to set-up and read via their computer interfaces.

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### Frequency Counter Selection Criteria

The selection criteria for a frequency counter for QCM application include resolution, speed, time-base stability, computer interfaces and software drivers. Careful selection is required, otherwise the frequency counter may degrade the quality of mass measurements.

The table below lists the typical characteristics of the frequency signal from the QCM100 Analog Controller for a crystal in water.

Description	Typical Value
Frequency	5 $\pm$ 0.01 MHz
Waveform (into 50 $\Omega$ )	2.4 V square wave
Stability (second to second)	0.002 Hz
Stability (minute to minute)	0.10 Hz
Temperature coefficient	8 Hz/ $^{\circ}$ C
Frequency/mass coefficient	0.057 Hz/(ng/cm <sup>2</sup> )

Many of the frequency counter's characteristics are determined by its time-base. If the time-base changes frequency by 10 ppm the reported values will also change by 10 ppm. While the accuracy of the counter's time-base is not particularly important, the stability of the time-base is critically important as variations in the time-base will be indistinguishable from changes in accumulated mass on the surface of the crystal. Often manufacturers will specify accuracy and aging but do not specify short-term stability. In virtually all counters, the short-term stability will improve if they are allowed to warm-up for an extended period of time. To avoid degrading frequency measurements, the time-base should have a 1 second stability of better than .002 Hz/5 MHz or  $4\times 10^{-10}$ .

The speed/resolution of a counter is also important. The accumulated mass can change rapidly in a typical QCM measurement and it is desirable to make frequency measurements with a resolution of  $1:10^{10}$  in a one second interval to not significantly degrade the mass resolution of, or add noise to, the measurement. Simply counting cycles of the frequency output over a one second interval can not provide resolution better than  $1:5\times 10^6$ , and so a more elaborate counter architecture is required. A "reciprocal-interpolating" counter can provide a much better frequency resolution than  $\pm 1$  cycle per gate interval.

Virtually all frequency counters can measure the frequency of the 2.4 Vpp square wave in 50  $\Omega$  provided by the QCM100 Frequency Output.

Counters are available with RS-232 and/or IEEE-488 interfaces to facilitate computer data acquisition. The speed of the interface is not very critical, as typically only one reading is taken each second. Counters are relatively simple to set-up and read via their computer interfaces. Software drivers for National Instruments LabView products, or other data acquisition programs, are often available.

Frequency counters used at SRS for QCM measurements are listed below:

Manufacturer	Model	Digits/Second
Stanford Research Systems	SR620	10
Agilent	53131	10
Agilent	53132	12

## Errors In The Measurement Of Frequency

The QCM25 Crystal Oscillator will oscillate at the frequency such that the phase shift around the entire loop is  $360^\circ$ . Referring to Figure 5, important sources of phase shift within the network include:

1.  $180^\circ$  from the inverting amplifier  $A_1$
2.  $180^\circ + [37 \mu^\circ/\text{Hz deviation from 5 MHz}]$  from the low pass filter
3.  $0^\circ + [0.20^\circ/\text{pF} (R_m = 40 \Omega) \text{ or } 0.81^\circ/\text{pF} (R_m = 375 \Omega)]$  from uncompensated  $C_o$
4.  $0^\circ + [0.20^\circ/\text{Hz} (R_m = 40 \Omega) \text{ or } 0.04^\circ/\text{Hz} (R_m = 375 \Omega) \text{ deviation from series resonance}]$  from the crystal in the  $R_s / R_m / R_L$  network.

If an extraneous phase shift (2) or (3) is present, the oscillator will operate away from series resonance allowing the crystal network (4) to cancel the extraneous phase shift. The small value of the extraneous phase shifts, together with the large  $d\phi/df$  of the crystal network, keeps these frequency errors small.

The QCM25 Crystal Oscillator is intended to operate only with 5 MHz crystals. Typical accuracy of the crystal frequency is 100 ppm, or 500 Hz. The low pass filter will add an additional phase shift of  $37 \mu^\circ/\text{Hz deviation} \times 500 \text{ Hz} = 0.0185^\circ$  when operated 500 Hz from 5 MHz. This will cause a dry crystal to run  $0.0185^\circ/(0.20^\circ/\text{Hz}) = 0.092 \text{ Hz}$  off series resonance, or a wet crystal to run  $0.0185^\circ/(0.04^\circ/\text{Hz}) = 0.462 \text{ Hz}$  off series resonance. Since the  $d\phi/df$  of the low pass filter is  $1000\times$  smaller than the  $d\phi/df$  of a wet crystal, the low pass filter does not contribute a significant error to the measurement of the series resonant frequency.

By modulating the varactor capacitance which nulls  $C_o$ , and using synchronous detection to locate the minimum gain operating point, the QCM100 allows the user to reproducibly null  $C_o$  to  $\pm 0.01 \text{ pF}$ . The corresponding phase error for a wet crystal is  $\pm 0.01 \text{ pF} \times 0.81^\circ/\text{pF} = \pm 0.0081^\circ$ , which gives rise to a frequency reproducibility of  $\pm 0.0081^\circ/(0.04^\circ/\text{Hz}) = \pm 0.20 \text{ Hz}$  for a wet crystal. This error is virtually insignificant.

In water, the dominate source of frequency drift comes from the temperature dependence of the viscosity of the liquid. The series resonant frequency of a 5 MHz AT-cut crystal in water will increase by about 8 Hz/°C.

Summary of sources of frequency error (in Water,  $\Delta f = 700$  Hz)

<b>Source of Error</b>	<b>Typical magnitude of Error for wet crystal</b>
Phase shift in low pass filter	0.65 Hz (<0.1%)
Reproducibility of Co null	<0.20 Hz
Temperature dependence of viscosity	$\approx 0.8$ Hz/0.1°C



## Resistance Measurement

The QCM100 Analog Controller provides a Conductance<sup>7</sup> Voltage output (BNC port), that is related to the crystal's motional series resonance resistance:

$$R_m = 10,000 \times 10^{-V_c/5} - 75 \quad (\text{equation 2})$$

Where  $R_m$  is the motional series resonance resistance in  $\Omega$  and  $V_c$  is the conductance voltage output in V.

A high-precision digital voltmeter<sup>8</sup>, with at least 6 digits of resolution and computer interface is recommended for this measurement.

## Resistance Calculation

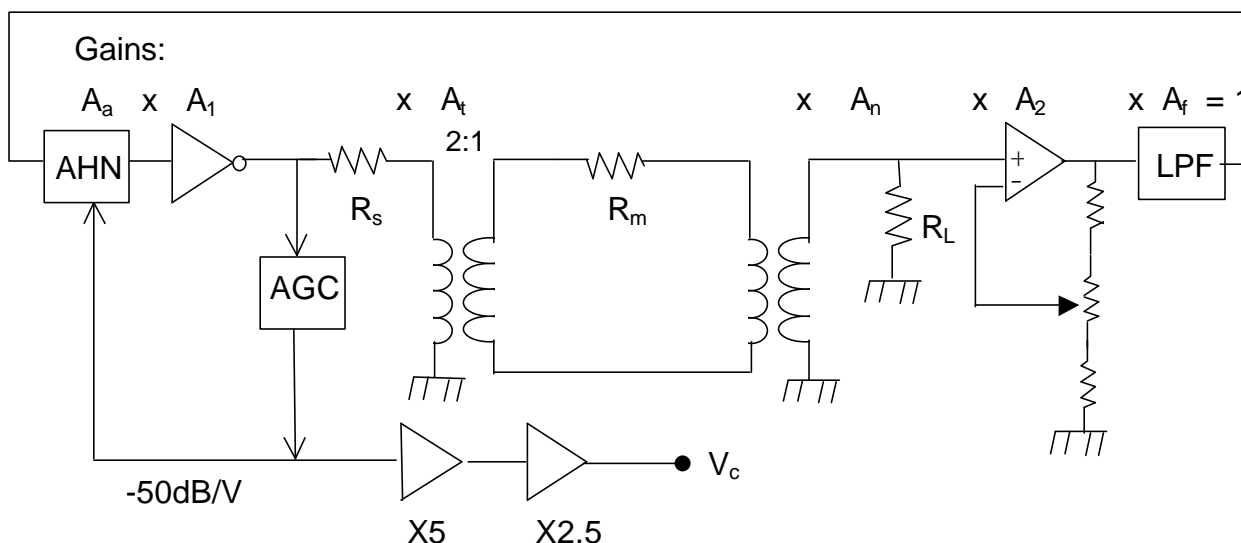


Figure 5. QCM Gain Model

A gain model of the QCM25 Crystal Oscillator is shown in Figure 5. At series resonance the reactance of the crystal's motional inductance and motional capacitance cancel and so the crystal may be represented by just  $R_m$ , the motional resistance of the crystal. (It is also assumed that the static capacitance,  $C_o$ , has been nulled as previously described.) The circuit will oscillate at the frequency for which the net phase shift around the loop is  $360^\circ$ , provided there is sufficient gain to overcome the circuit losses.

Two network elements in the model provide a phase shift. The inverting amplifier provides  $180^\circ$  of phase shift. The low pass filter is adjusted to provide  $180^\circ$  of phase shift at 5 MHz. Hence the circuit will oscillate at the frequency for which the crystal is resistive, i.e. at series resonance.

The loop gain is the product of the gain (or attenuation) of each of the network elements. If the loop gain is exactly one, then the oscillation amplitude will be maintained at a fixed level. An AGC circuit controls the loop gain via a voltage controlled variable attenuator.

From left to right, the circuit consists of the following:

1. A voltage controlled variable attenuator with attenuation of  $A_a$ . An automatic gain control circuit generates a voltage to maintain the oscillation amplitude at a fixed level of 1 Vpp. The attenuator is controlled by this voltage, between 0 and 1 Vdc, providing an attenuation of 50 dB/volt so that  $A_a = 10^{-V_{agc} \cdot 50 / 20}$ . The AGC voltage is amplified by 5× in the QCM25 Crystal Oscillator, and by 2.5× in the QCM100 Analog Controller, before being output via the Conductance BNC on the front panel of the QCM100. Hence, referenced to the voltage  $V_c$  at the QCM100 Conductance output BNC,  $A_a = 10^{-V_c / 5}$ .
2. A fixed gain amplifier with gain  $A_1 = 45 \text{ dB} + 20 \log (250/200) = 46.94 \text{ dB}$  (or 222×.) This inverting amplifier has a bandwidth of 500 MHz, and so introduces very little extraneous phase shift.
3. A source resistance,  $R_s$ , of 100  $\Omega$ . This source resistance consists of two series 50  $\Omega$  resistors, one of which is inside the amplifier  $A_1$ . This source impedance is reduced by a factor of 4×, to 25  $\Omega$ , by the 2:1 transformer which follows.
4. An isolation transformer with a 2:1 turns ratio, hence an attenuation of  $A_t = 0.5$ . This transformer allows galvanic isolation of the crystal from the oscillator circuit which is important in electrochemistry applications. In addition to reducing the source impedance by 4×, the transformer also increases the load impedance seen at the input of the transformer by 4×, so that when  $R_m = 0 \Omega$ , the load will be 200  $\Omega$ .
5.  $R_m$ , the motional resistance of the crystal at series resonance.  $R_m$  can vary from about 10-40  $\Omega$  for a dry crystal, to about 375  $\Omega$  for a crystal in water, to about 5 k $\Omega$  for a crystal in 90% (w/w) glycerol/water solution.
6. A second isolation transformer with a turns ratio of 1:1. This transformer allows galvanic isolation of the crystal from the oscillator circuit.
7. A load resistance,  $R_L$ , of 50  $\Omega$ . The network of  $R_s$ ,  $R_m$ , and  $R_L$  provide a network attenuation,  $A_n$ , which depends on the crystal's motional resistance.

$$A_n = R_L / ( R_s/4 + R_m + R_L )$$

8. An RF amplifier with an adjustable gain,  $A_2$ , of about 4.43×. The gain of this amplifier,  $A_2$ , is set during calibration to compensate for gain variations of all the other circuit elements.
9. A low pass filter. This filter is a 5<sup>th</sup> order Bessel low pass filter with  $f_c = 3.7 \text{ MHz}$ , adjusted so as to provide 180° of phase shift at 5 MHz. The phase shift of this filter, together with the 180° phase shift of the inverting amplifier  $A_1$ , provides the 360° of phase shift necessary for oscillation. The low pass filter is required to suppress spurious oscillations which would occur due to the high bandwidth of the loop amplifiers. The low pass filter attenuates a signal at 5 MHz by about  $A_f = -7.8 \text{ dB}$  (or 0.407×).

The motional resistance of the crystal at series resonance can now be computed. The product of the gain (or attenuation) of all of the elements around the loop is exactly one when the circuit is oscillating at constant amplitude. Hence,

$$A_a \cdot A_1 \cdot A_t \cdot A_n \cdot A_2 \cdot A_f = 1$$

Rearranging and substituting the equation for  $A_n$ ,

$$1 / A_n = (R_s/4 + R_m + R_L) / R_L = A_a \cdot (A_1 \cdot A_t \cdot A_2 \cdot A_f)$$

Solving for  $R_m$ ,

$$R_m = R_L \cdot A_a \cdot (A_1 \cdot A_t \cdot A_2 \cdot A_f) - R_L - R_s / 4$$

From the characteristics of the voltage variable attenuator described above,  $A_a = 10^{-V_c/5}$ , where  $V_c$  is the voltage at the Conductance output BNC on the QCM100.  $A_2$  is adjusted during factory calibration so that the product of the gains  $(A_1 \cdot A_t \cdot A_2 \cdot A_f) = 200$ . So we have,

$$R_m = 10,000 \cdot 10^{-V_c/5} - 75$$

Where  $R_m$  is the motional series resonance resistance in  $\Omega$  and  $V_c$  is the conductance voltage output in V.

The motional resistance of the crystal at series resonance,  $R_m$ , can be computed from the above equation. Figure 6 below graphs  $R_m$  vs  $V_c$ .

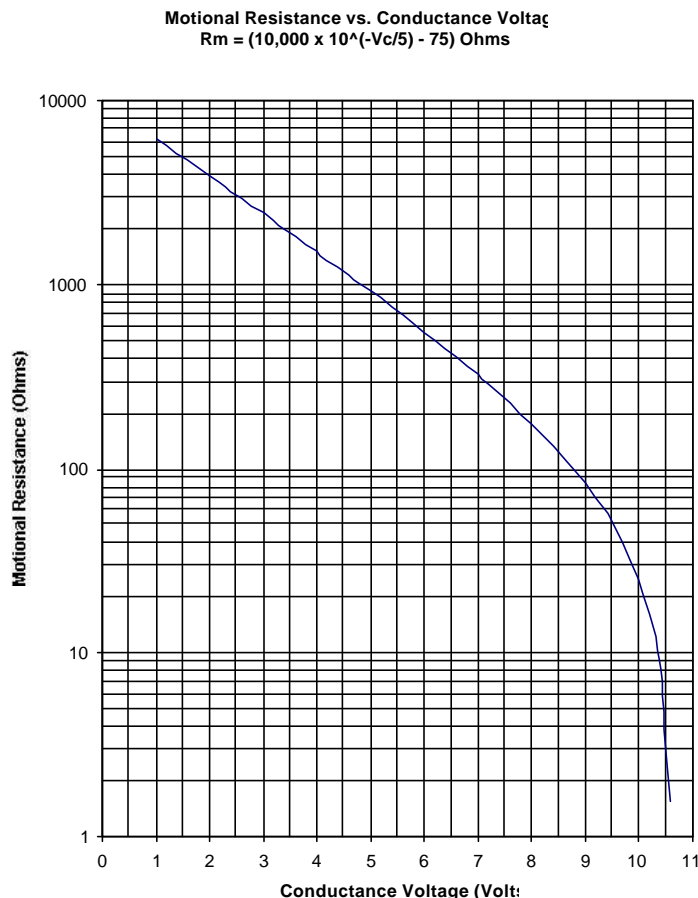


Figure 6. Motional series resonance resistance vs. conductance voltage

## Errors In The Measurement Of $R_m$

Errors in the measurement of  $R_m$  will be less than  $3 \Omega + 3\%$  of  $R_m$  (for  $R_m < 2 \text{ k}\Omega$ ), and are dominated by the departure of the voltage controlled attenuator from its nominal (voltage - gain) characteristic.

Keep in mind that the resistance measurement in liquids and soft films is also affected by temperature, mostly through the temperature coefficient of the viscosity. For example, a  $4 \Omega/^\circ\text{C}$  drift in resistance is to be expected in water around room temperature.

## Noise In The Measurement Of $R_m$

$V_c$  varies logarithmically with  $R_m$  over most of the range of interest. There is an important advantage in this: the fractional resolution of the resistance is nearly independent of the resistance and so allows detailed and low-noise measurement of the viscous losses. To estimate the noise in resistance measurements, we can take the derivative of the equation for the motional resistance (units are Ohms and Ohms/Volt):

$$R_m = 10,000 \cdot 10^{-V_c/5} - 75$$

$$\begin{aligned}
 dR_m / dV_c &= 10,000 \cdot 10^{-V_c/5} \cdot \ln(10) \cdot (-1/5) \\
 &= -2,000 \cdot \ln(10) \cdot 10^{-V_c/5} \\
 &= -4605 \cdot 10^{-V_c/5} \\
 &= -0.4605 \cdot (R_m + 75)
 \end{aligned}$$

Noise on the  $V_c$  signal,  $\Delta V_c$ , is typically  $\pm 50 \mu\text{V}$  (with one second averaging).  $R_m$  for a 5 MHz crystal in water is about  $375 \Omega$ . The fractional noise in the resistance measurement is then:

$$\begin{aligned}
 \Delta R_m / R_m &= \Delta V_c \cdot [dR_m / dV_c] / R_m \\
 &= \Delta V_c \cdot [-0.4605 \cdot (R_m + 75)] / R_m \\
 &= \pm 28 \text{ ppm}
 \end{aligned}$$

This low noise floor for fractional resistance measurements allows very small changes in dissipation losses to be measured. This is also the reason why a high precision voltmeter (i.e. with at least six digits of resolution) is recommended for these measurements.

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## Calibration of $R_m$

Resistance measurements for the QCM25 Crystal Oscillator/QCM100 are calibrated by replacing the crystal with a precision resistor in parallel with a 15 pF capacitor. Two resistor values are used:  $51.10 \Omega$  and  $1.000 \text{ k}\Omega$ . The equation for  $R_m$  may be inverted to determine the calibration value for  $V_c$ . (Motional resistance,  $R_m$ , in  $\Omega$  and conductance voltage output,  $V_c$ , in volts.)

$$\begin{aligned}
 R_m &= 10,000 \cdot 10^{V_c/5} - 75 \\
 V_c &= 5 \log [ 10,000 / (R_m + 75) ]
 \end{aligned}$$

The low pass filter is adjusted so that the QCM25 Crystal Oscillator oscillates at 5 MHz with the  $51.10 \Omega$  resistor in place of the crystal. The varactor dial is adjusted so that the Crystal Controller oscillates at 5 MHz with the  $1.000 \text{ k}\Omega$  resistor in place of the crystal. Calibration potentiometers in the QCM25 Crystal Oscillator are adjusted so that  $V_c = 9.496 \text{ Vdc}$  with a calibration resistor of  $51.10 \Omega$ , and  $V_c = 4.843 \text{ Vdc}$  with a calibration resistor of  $1.000 \text{ k}\Omega$ .

## Gas-Phase Measurements

The first use of QCMs was as mass sensors and thickness monitors in gas phase, thin-film depositions. To this date, this continues to be one of the most important areas of application for this technology.

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### Sauerbrey Equation

Sauerbrey's equation (eqn. 1) is often used to calculate mass loadings and thin-film thicknesses in vacuum depositions. The basic assumption is that the incremental change in mass from the foreign film is treated as though it were really an extension of the thickness of the underlying quartz. The foreign film is considered rigid and so thin that it does not experience any shear forces during vibration. As a result, the sensitivity factor,  $C_f$ , is a fundamental property of the quartz crystal and does not consider any of the properties of the foreign film (i.e. it is only dependent on the acousto-elastic properties of quartz).

$$C_f = 2nf_o^2/(\rho_q \cdot \mu_q)^{1/2} \quad (\text{eqn. 3})$$

where

$n$  = number of the harmonic at which the crystal is driven,

$f_o$  = the resonant frequency of the fundamental mode of the crystal in Hz,

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

$\mu_q$  = shear modulus of quartz = 2.947·10<sup>11</sup> gcm<sup>-1</sup>·s<sup>-2</sup>.

The dependence of the frequency change on the mass coverage per unit area, emphasizes the fact that, within certain limits, the sensitivity factor is independent of the electrode geometry. Thus, in theory, the QCM mass sensor does not require calibration for this application. This ability to calculate mass loading from first principles is obviously a very attractive feature of these devices.

Film thickness is often the parameter of interest in gas-phase thin-film depositions. If the mass coverage is believed to be uniform, the thickness of the film is easily calculated by dividing the mass per unit area provided by Sauerbrey's equation by the material's density.

$$T_f = \Delta m / \rho_f \quad (\text{eqn. 4})$$

where

$\rho_f$  = density of film material in g/cm<sup>3</sup>,

$\Delta m$  = change in mass per unit area in g/cm<sup>2</sup> (calculated from Sauerbrey's equation),

$T_f$  = thickness of the film in cm.

## Z-match Method

It is generally accepted that when the mass loading from the deposit causes a change in frequency of less than 2% of the frequency of the unloaded crystal, Sauerbrey's equation can be used to obtain accurate results in thin-film thickness calculations<sup>9</sup>. As the thickness of the film increases, the Sauerbrey equation must be extended to incorporate the elasticity of the deposit. Lu and Lewis<sup>10</sup> give a simple equation (eqn. 5) for the calculation of the dependence of  $\Delta f$  on  $\Delta m$ , which is currently applied by most QCM users to calculate rigid thin-film thicknesses in gas phase depositions.

$$\Delta m = [ (N_q \cdot \rho_q) / (\pi \cdot Z \cdot f_L) ] \cdot \tan^{-1} [ Z \cdot \tan[\pi \cdot (f_U - f_L) / f_U] ] \quad (\text{eqn. 5})$$

where,

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

$N_q$  = Frequency Constant for AT-cut quartz crystal =  $1.668 \times 10^{13} \text{ Hz } \text{\AA}$ ,

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

$f_U$  = frequency of unloaded crystal (prior to deposition) in Hz,

$f_L$  = frequency of loaded crystal in Hz,

$Z$  = Z-Factor of film material =  $[(\rho_f \cdot \mu_f) / (\rho_q \cdot \mu_q)]^{1/2}$ ,

$\rho_f$  = density of film material in  $\text{g} \cdot \text{cm}^{-3}$ ,

$\mu_q$  = shear modulus of quartz =  $2.947 \times 10^{11} \text{ g} \cdot \text{cm}^{-1} \cdot \text{s}^{-2}$ ,

$\mu_f$  = shear modulus of film material.

This analysis of frequency changes, including the acoustic impedances of the quartz and film, is often called the "Z-match" method. The accuracy of the mass load and film-thickness calculation is often limited by how well the Z-Factor and density of the material are known. Density and Z-Factor values are typically very close to bulk values. The bulk density and shear modulus values for common film materials can be found in many material reference handbooks.

The Lu and Lewis equation is generally considered to be a good match to the experimental results<sup>11</sup> for frequency changes up to 40% (relative to the unloaded crystal). Keep also in mind that the Z-match equation strictly applies to "rigid" deposits. Films which behave viscoelastically, such as some organic polymer films with large thickness or viscosity, will exhibit significant deviations from both equations 1 and 5.

Crystal failures are also often seen before a 40% shift in frequency is reached. Common problems are (1) shorts in the crystal electrodes due to excessive buildup, (2) mode hopping to other (anharmonic) resonant frequencies due to the buildup of composite resonant modes, (3) deviations from theory due to fringing electrode fields developed between the electrodes and the film, (4) unexpected shifts in fundamental frequency due to stress build up on the crystal surface, (5) splitting of source material resulting in non-uniform films, etc.

## Liquid Contact Measurements

Until recently, it was believed that excessive viscous loading would prohibit use of the QCM in liquids. In fact, operation in liquids is indeed possible<sup>12</sup>, and the response of the QCM is still extremely sensitive to mass changes at the solid-solution interface. For many years, QCMs have been used in direct contact with liquids and/or viscoelastic films to assess changes in mass and viscoelastic properties during chemical and electrochemical surface processes.

When the QCM comes in contact with a solution, there is a decrease in frequency that is dependent upon the viscosity and the density of the solution. A quantitative understanding of the resonator behavior is a prerequisite for proper interpretation of experimental results under total liquid immersion. This problem was first treated by Glassford<sup>13</sup>, and later by Kanazawa and Gordon<sup>14</sup>.

Kanazawa's treatment of the influence of the solution properties on the crystal (eqn. 6) permits the prediction of the change in resonance frequency which accompanies immersion of the crystal into a viscous medium:

$$\Delta f = -f_u^{3/2} \cdot [(\rho_L \cdot \eta_L) / (\pi \cdot \rho_q \cdot \mu_q)]^{1/2} \quad (\text{eqn. 6})$$

where

$f_u$  = frequency of oscillation of unloaded crystal,

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

$\mu_q$  = shear modulus of quartz = 2.947 × 10<sup>11</sup> g cm<sup>-1</sup> · s<sup>-2</sup>,

$\rho_L$  = density of the liquid in contact with the electrode,

$\eta_L$  = viscosity of the liquid in contact with the electrode.

Viscous coupling of the liquid medium to the oscillating crystal surface results not only in a decrease in the series resonant frequency but also in damping of the resonant oscillation - the viscous loss is manifested as an increase in series resonance resistance,  $R$ , of the QCM resonator. Thus,  $R$  serves as an excellent independent measure of viscous loading by the medium (liquid or soft-film) at the crystal's surface.

$\Delta f$  and  $\Delta R$  measurements are both routinely used as independent indicators of mass loading and viscosity at the crystal-liquid interface of the QCM resonator during chemical and electrochemical depositions in solution<sup>15</sup>.

In a separate study<sup>16</sup>, a Butterworth-Van Dyke equivalent circuit model (Figure 1) was applied to derive a linear relationship between the change in series resonance resistance,  $\Delta R$ , of the quartz oscillator and  $(\rho_L \cdot \eta_L)^{1/2}$  under liquid loading:

$$\Delta R = [n \cdot \omega_s \cdot L_u / \pi] \cdot [(2\omega_s \cdot \rho_L \cdot \eta_L) / (\rho_q \cdot \mu_q)]^{1/2} \quad (\text{eqn. 7})$$

Where

$\Delta R$  = change in series resonance resistance in  $\Omega$ ,



$n$  = number of sides in contact with liquid,

$\omega_s$  = angular frequency at series resonance ( $2\pi f_s$ ),

$L_u$  = inductance for the unperturbed (dry) resonator, usually in mH.

The QCM100 System was specifically designed for operation under heavy viscous loading. The standard Crystal Holder supports operation in gas and liquid environments, and provides single-electrode exposure to liquids<sup>17</sup> (i.e.  $n = 1$  in eqn. 7) as required for compatibility with electrochemical QCM measurements. The Crystal Oscillator provides both frequency and resistance change signals and will maintain oscillation up to a series resonance resistance of about 5 k $\Omega$  (it will support crystal operation in highly viscous solutions up to 88% (w/w) glycerol in water).

As an example, eqn. 6 predicts a decrease in  $f_0$  of 715 Hz on transfer from vacuum to pure water<sup>18</sup> at 20°C, in agreement with the results observed with a QCM100 using 1 inch diameter, polished, gold coated, 5 MHz crystals, mounted on a standard Crystal Holder. Excellent agreement between the frequency and resistance equations and the experimental results has been proved<sup>19</sup>, making the QCM an excellent tool for the evaluation of fluid properties. Application examples include in situ monitoring of lubricant and petroleum properties<sup>20</sup>. The tight correspondence between theory (eqns. 6 & 7) and experiment is clearly illustrated by Figure 7.

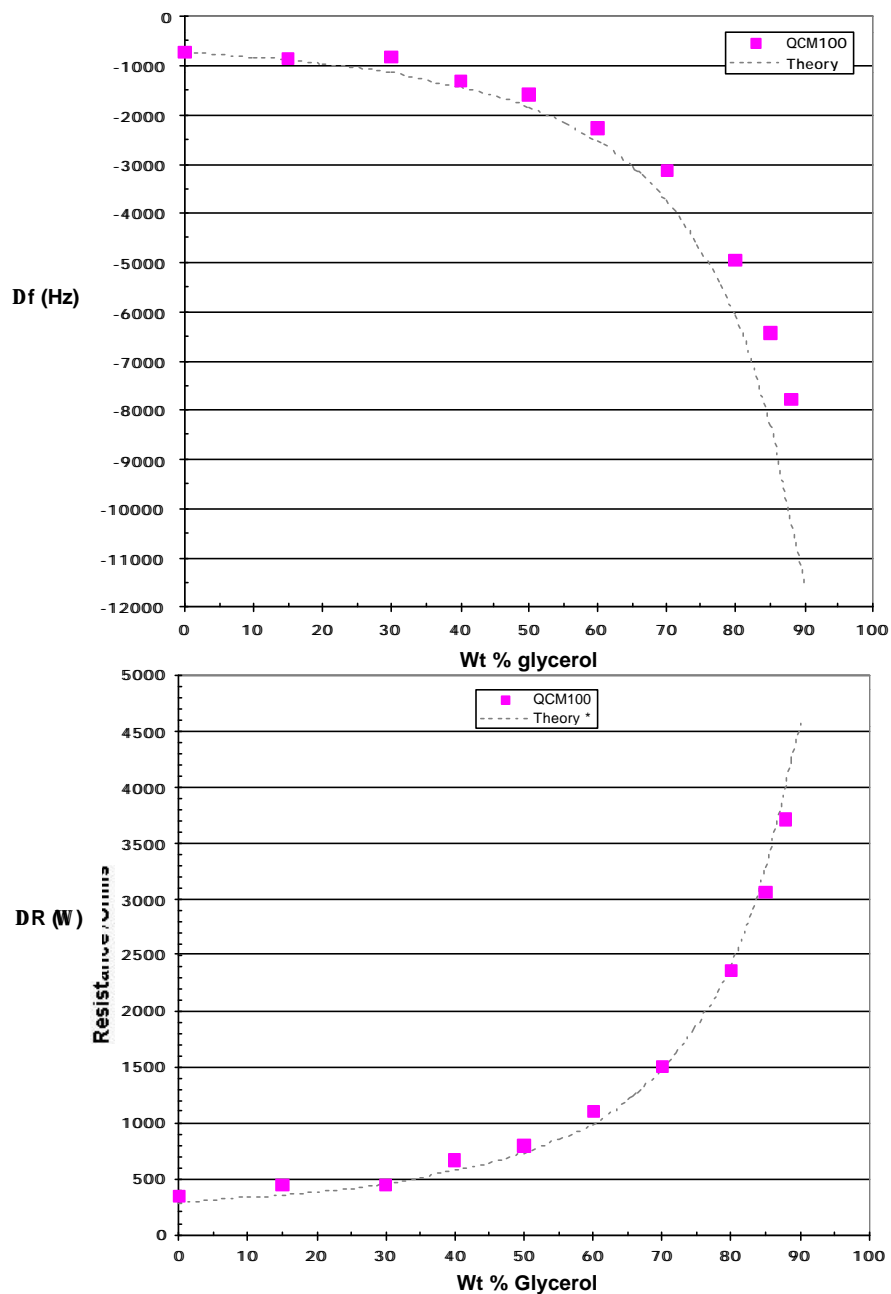


Figure 7. *Df* and *DR* versus glycerol weight percentage (in water) as predicted by theory and as measured with QCM100 and a 5 MHz polished crystal.

## Dissipation Technique

An alternative method<sup>21</sup> for studying the properties of the loaded QCM Sensor, called the “Dissipation Technique” has been used in gaseous as well as in liquid environments. In this case, the crystal is driven at its resonant frequency by an oscillator that can be intermittently disconnected causing the crystal oscillation amplitude to decay exponentially. From the recorded decay curve the absolute Q-factor (inversely proportional to R) and the frequency of the oscillator are simultaneously obtained. Independent studies<sup>22</sup> have shown that as long as the effect of the parasitic capacitance ( $C_0$ ) is properly cancelled, the results provided by the Dissipation Technique should be in good agreement with the measurements provided by the QCM100 System.

## Temperature

The intrinsic dependence of the resonant frequency of a quartz crystal on temperature is well known and generally quite small. In fact, the AT-cut quartz crystal commonly used in QCM experiments owe their popularity to their near zero coefficient at room temperature. As a result, the intrinsic temperature dependence of the QCM sensor crystals is negligible near room temperature ( $\approx 1-3 \text{ Hz/}^\circ\text{C}$ ) and is generally ignored for monolayer adsorption/desorption processes in the gas phase.

Much larger changes in frequency with temperature are observed when QCM crystals are immersed in liquids. This is due to the coupling of the shear mode oscillation with the temperature dependent viscosity and density of the fluid. The temperature coefficient due to this effect is  $\approx 8 \text{ Hz/}^\circ\text{C}$  for water. As a result, for experiments in liquid phase in which the frequency is to be monitored at length, the temperature must be controlled to at least  $0.1^\circ\text{C}$ , and preferably better. In electrochemical experiments this is often achieved with temperature controlled baths and jacketed cells. If temperature control is not possible or practical, it is always good practice to wait at least 30 minutes before performing any accurate measurements after the crystal comes in contact with a new medium and measure the temperature of the solution around the crystal during the experiments to perform temperature compensation. It is also common practice to soak the mounted crystal(s) in the solution overnight before performing any experiments to assure more stable readings.

Careful control of the temperature is required in high accuracy measurements to avoid frequency hysteresis effects - the dependence of resonator frequency at a specific temperature on the prior temperature history of the resonator. For example, it is often observed that the frequency vs temperature curve obtained going from  $T_1$  to  $T_2$  will not coincide with the one obtained immediately after going from  $T_2$  to  $T_1$ . This effect must be carefully considered during accurate determinations.

Each individual QCM user must determine the effect of temperature on the experiments being performed and either control the temperature accordingly, or measure the temperature and compensate for it.

## Electrode Polishing

Electrode surface roughness can cause large apparent mass loadings due to the liquid that is trapped within pores at the crystal surface<sup>23</sup>. As a general rule, optically polished crystals (50 Å average surface roughness) are required to obtain good agreement between theory and experiment during liquid immersion experiments. The water immersion checkup test (below) provides a quick-and-easy way to test the crystal finish for liquid-QCM applications.

## System Checkup

A comparison against the theoretical predictions of equations 6 and 7 is usually a good starting point when testing a new experimental liquid-QCM100 setup. Two common “checkup” procedures are described.

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### Water Immersion

For a gold coated, 5 MHz, *polished* crystal, and assuming that the electrode capacitance has been properly cancelled, a decrease in frequency of  $\approx 715$  Hz, and an increase in series resonance resistance of  $\approx 380$   $\Omega$ , is expected when switching from air to complete immersion in water at 20°C.

---

### Glycerol/H<sub>2</sub>O Immersion

Figure 7 shows resistance and frequency change values expected for a polished 5 MHz crystal immersed in a series of viscous glycerol/water solutions at 20°C. Operation at increasing glycerol concentrations is an excellent test of a QCM experimental setup, and should provide predictable results up to more than 88% glycerol.

In both procedures, an agreement between measured and expected values within  $\pm 25\%$  is generally considered acceptable for glycerol concentrations up to 70%.

Frequency shifts are much larger (at least a factor of two) and unpredictable for unpolished crystals so they are not recommended for system checkup.

## Electrochemical Quartz Crystal Microbalance

In most electrochemical experiments, mass changes occur as material is deposited or lost from the “working” electrode. It is of interest to monitor those changes simultaneously with the electrochemical response, and the QCM is the standard means of doing so. As a gravimetric probe, the QCM has been used in many types of electrochemical studies, including: underpotential deposition of metals<sup>24</sup>, corrosion, oxide formation, dissolution studies<sup>25</sup>, adsorption/desorption of surfactants<sup>26</sup> and changes in conductive polymer films during redox processes<sup>27</sup>.

The basic principles and applications of the QCM to electrochemical processes have been extensively reviewed in the electrochemical literature<sup>28</sup> and will only be discussed briefly in this manual. Please refer to the publications list at the end of this chapter for more detailed information.

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### Electrochemical Apparatus

A schematic diagram of the apparatus for electrochemical quartz crystal microbalance (EQCM) experiments is given in Figure 8. In this example, a 1 inch diameter, polished QCM crystal is mounted on a Crystal Holder with only one electrode exposed to the conductive solution. The Crystal Holder is connected to a QCM25 Crystal Oscillator, and the liquid-contact electrode is connected to the “working electrode” lead of the potentiostat (through the “Crystal Face Bias” connector of the QCM25 Crystal Oscillator). A QCM100 Analog Controller provides independent frequency and conductance outputs which are read and displayed by a frequency counter and a digital multimeter (or A/D converter), respectively.

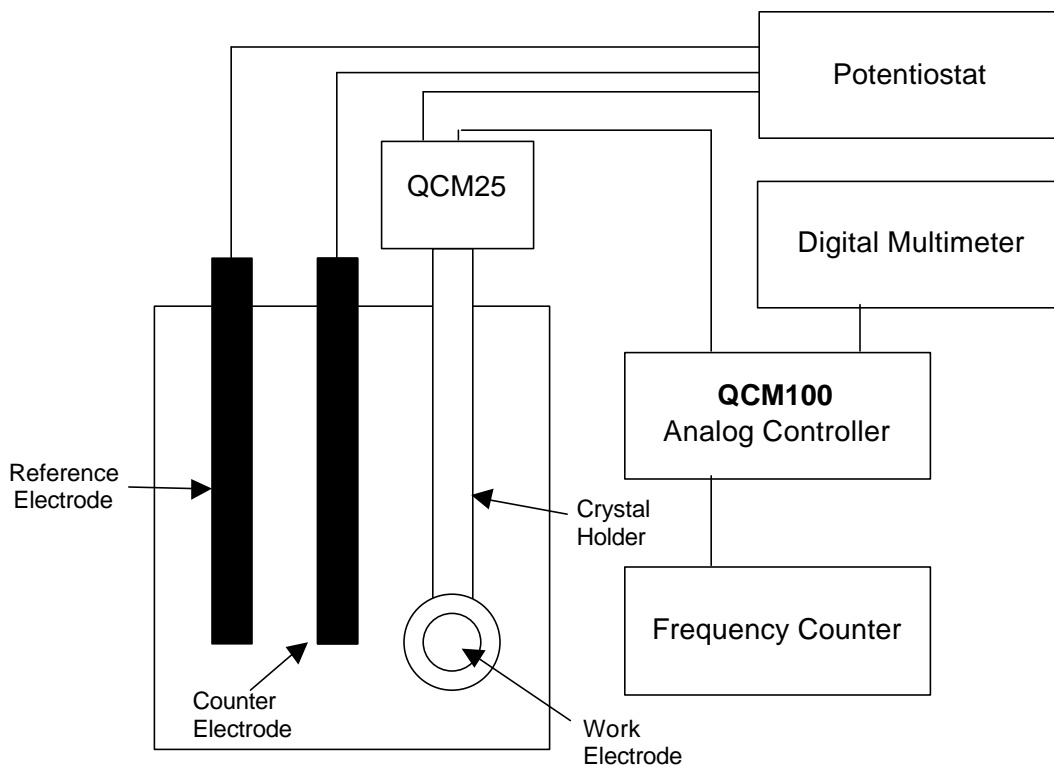


Figure 8. Schematic of EQCM apparatus

A PC (not shown) is often interfaced to the potentiostat, frequency counter and DMM, and integrates the QCM and electrochemical data into a single software package.

### Note

The QCM25 Crystal Oscillator provides transformer isolation of the crystal front face electrode. This allows direct electrical connection of the quartz crystal face to the “working electrode” pin of any standard potentiostat/galvanostat.

With the instrument in Figure 8, a typical cyclic voltammetric-EQCM experiment would involve the application of the electrochemical waveform to the working electrode and the simultaneous measurement of the current flowing through the electrochemical cell and the oscillation frequency and series resonance resistance of the crystal.

Figure 9 is an example of a typical voltammogram-massogram plot obtained from a 10 mM solution of  $\text{CuSO}_4$  in 0.1 M  $\text{H}_2\text{SO}_4$ , using a 1 inch diameter, Au coated, quartz crystal mounted in a standard Crystal Holder as the working electrode.

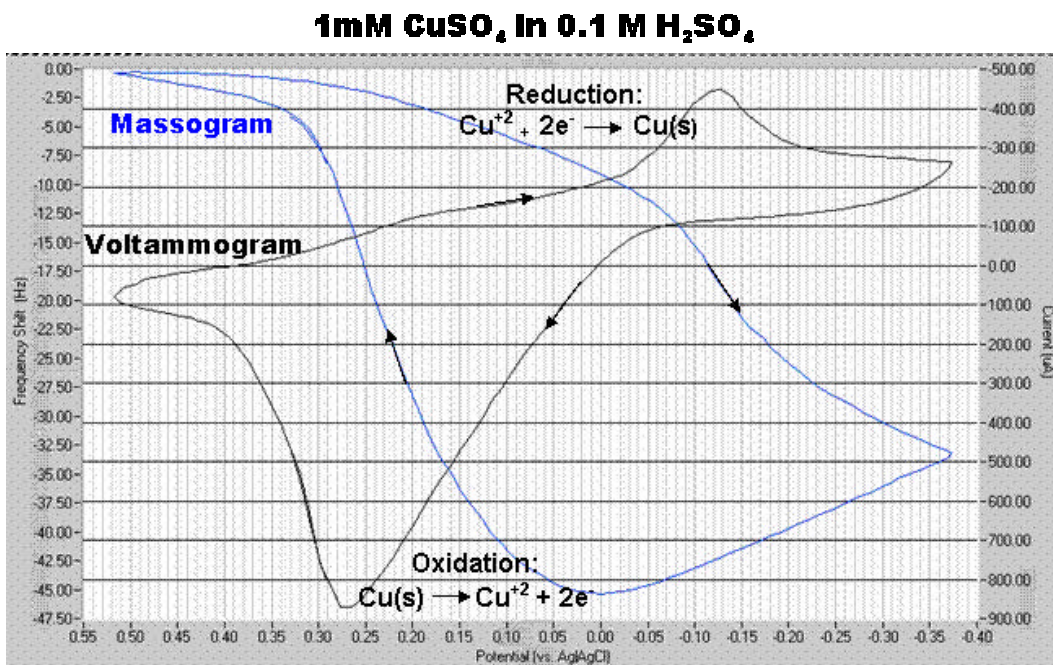


Figure 9. Cyclic voltammogram and massogram data for Cu deposition on a Au electrode. The frequency–potential diagram shows a frequency decrease in perfect sync with the deposition of Cu metal on the crystal's surface.

## Calibration

It has been amply demonstrated in the literature that when experiments involve only relative frequency shifts which are measured in a fixed solution, the offset caused by the viscous loading of the liquid, has negligible effect on the accuracy of the Sauerbrey equation for the determination of small mass changes in rigid deposits<sup>29</sup>. Quantitative interpretation of the EQCM data in those cases is based on the combination of the Sauerbrey equation (eqn. 1) and Faraday's law. The former relates change in frequency to change in mass for *thin, rigid deposits*, whereas the latter relates charge passed in an electrochemical experiment to the number of moles of material electrolyzed. Therefore, frequency changes can be related to the total charge passed.

An example would be the electrodeposition of Ag on a Pt electrode QCM crystal. The charge,  $Q$ , is an integral measure of the total number of electrons delivered at the interface during the reduction process. To the extent, that each electron supplied results in the deposition of one atom of Ag, there should be a linear relationship between  $Q$  and  $\Delta f$  as is given by equation 8:

$$\Delta f = 10^6 \cdot M_w \cdot C_f \cdot Q / (n \cdot F \cdot A) \quad (\text{eqn. 8})$$

where

$\Delta f$  = frequency change in Hz,

$M_w$  = apparent molar mass of the depositing species in grams/mole,

$C_f$  = Sauerbrey's sensitivity factor for the crystal used (see eqn. 1),

$Q$  = integrated charge during the reduction in Coulombs,

$A$  = active deposition area of the working (liquid contact) electrode in  $\text{cm}^2$ ,

$F$  = Faraday's constant =  $9.648 \times 10^4$  Coulomb/mole,

$n$  = number of electrons transferred to induce deposition (i.e.  $n = 1$  for Ag deposition).

(The factor of  $10^6$  provides for the unit conversion from mg in  $C_f$  to g in  $M_w$ .)

A plot of  $\Delta f$  vs  $Q$  will deliver the apparent mass per electron of the deposited species, when  $n$  is taken into account. This is often used to elucidate the mass changes that accompany redox processes, and hence is very useful for characterizing the mechanisms of electron-transfer reactions.

However, before any calculations can be performed based on eqn. 8, the EQCM must be calibrated in order to properly derive (1) the proportionality constant,  $C_f$ , of the Sauerbrey equation in solution and (2) to account for the effective area of the working electrode. This is generally done using a well behaved electrochemical reaction - typically electrodeposition of silver, copper or lead on a Au or Pt electrode.

The EQCM calibration method favored by Stanford Research Systems for its QCM100 System is based on the galvanostatic deposition of Ag. A 50 mM solution of  $\text{AgNO}_3$  in 0.5 M  $\text{HNO}_3$  is subjected to a reducing potential and Ag is deposited with a fixed cathodic current density of 50-500  $\mu\text{A}/\text{cm}^2$ . The cathodic current is integrated to obtain the charge as a function of time. Excellent linearity is generally observed in  $\Delta f$  vs  $Q$  plots for depositions within 1  $\mu\text{g}/\text{cm}^2$ , providing a very reliable way to calibrate the proportionality constant of eqn. 8.

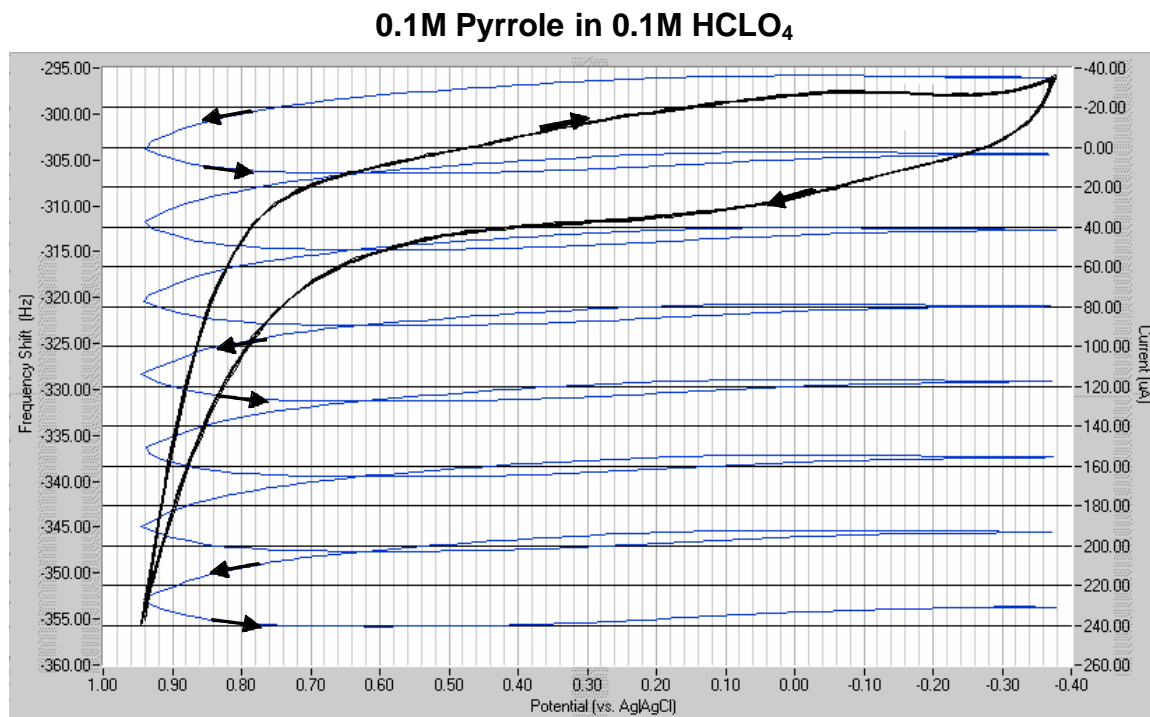
Several calibration procedures are also described in the electrochemistry literature<sup>30</sup>, and users are referred to the publications list at the end of this chapter for details.

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## Polymer Modified Electrodes

The EQCM has been extensively used to study polymer modified electrodes, particularly as a gravimetric tool to follow redox processes<sup>31</sup>. However, for the linear frequency-to-mass relationship (described by eqn. 8) to hold true, the polymer overlayer must exhibit no changes in rigidity during the electrochemical process. Otherwise, the viscoelastic changes will also contribute to the frequency change, leading to an erroneous interpretation of the mass changes<sup>32</sup>. As a consequence, it is essential to determine whether or not viscoelastic properties of the polymer film influence the frequency measurement during polymer film experiments!





*Figure 10. Voltammogram and massogram data for the oxidation of pyrrole to form a polypyrrole film on a gold coated QCM Sensor Crystal. Seven cycles of voltammetry, between - 0.4 and 0.95 V were conducted in this experiment. Pyrrole monomer can be oxidized to its radical at 0.65 V. As this happens, a thin polypyrrole film is formed on the crystal surface, resulting in a decrease in the fundamental frequency of oscillation of the crystal. The continuous growth of the film is evidenced by the irreversible decrease in frequency during the scans.*

A straightforward way to detect changes in film viscoelastic properties of redox films is to simultaneously monitor the series resonance resistance,  $R$ , of the quartz oscillator during the electrochemical experiment<sup>33</sup>. Some theoretical models<sup>34</sup>, based on the simultaneous measurement of  $\Delta f$  and  $\Delta R$ , have been discussed in the literature for the extension of EQCM gravimetric measurements to non-rigid films. The viscoelastic analysis of polymeric thin films in EQCM systems, is complex because the shear wave exists simultaneously in the quartz crystal, the viscoelastic film and the adjacent solution, so reflection of the shear wave must be taken into account. However, solution of this problem would be worthwhile, specially if the material properties of the film could be derived. This would allow correlation of the electrochemical behavior of the film with its material properties<sup>35</sup>.

The unique property of the QCM technique is its ability to determine the mass of very thin layers while simultaneously giving information about their viscoelastic properties. The ability to measure both mass and structural changes means it is possible to detect phase-transitions, cross-linking and swelling in polymeric thin films<sup>36</sup>.

## Chemical and Biological Sensors

Anything that has 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. However, the downside of such universal sensitivity is that you always have a great danger of interference. For analytical purposes, it is imperative to find ways of getting the QCM sensor to respond only to what you are interested in, i.e. build sensitivity into the device. This usually involves the addition of a sensitive layer on the surface of the crystal<sup>37</sup>.

Organic polymers comprise the most common type of coating used with QCM sensors due to their capability to reversibly sorb vapors and liquids<sup>38</sup>. In much of the work published on the use of polymer coatings for vapor sensing, the acoustic properties of the polymer material have been neglected. The relative importance of the mass-loading and viscoelastic contributions of the film to the observed QCM response is a subject that has yet to be resolved.

In no area have the QCM applications seen such dramatic increase in recent years as in the field of biochemical analysis. QCM devices are routinely used as biochemical and immunological probes<sup>39</sup>, as well as for the investigation and/or monitoring of biochemically significant processes. Sensitive, selective detection of biochemically active compounds can be achieved by employing antigen-antibody<sup>40</sup>, enzyme substrates and other receptor-protein pairs. The potential analytical uses of these materials has been reviewed, particularly with respect to the development of biochemical sensors<sup>41</sup>. QCM studies have provided detailed information about the functionalized surfaces developed for a range of biochip and biosensor applications.

QCM Systems are applied routinely by biologists and biochemists to obtain information about processes such as: (1) protein adsorption/desorption<sup>42</sup>, (2) cell adhesion<sup>43</sup>, (3) Protein-protein interaction, (4) Degradation of polymers, (5) biofouling and biofilm formation, (6) drug analysis<sup>44</sup> and (7) DNA Biosensors<sup>45</sup>.

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<sup>18</sup> For pure water, at 20°C,  $\rho_L = 0.9982 \text{ g cm}^{-3}$ , and  $\eta_L = 1.002 \cdot 10^{-2} \text{ g cm}^{-1} \text{ s}^{-1}$ .

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## Chapter 3

# Sensor Crystals and Holders

This chapter describes the basic features and functionality of the QCM Sensor Crystals and Holder, including recommended practices for (1) cleaning, (2) handling, (3) surface modification, (4) probe mounting, (5) electrical connection and (6) general maintenance.

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## Introduction

The standard sensor crystal used by the QCM100 System consists of a thin disk of 5 MHz, AT-cut,  $\alpha$ -quartz with circular electrodes patterned on both sides.

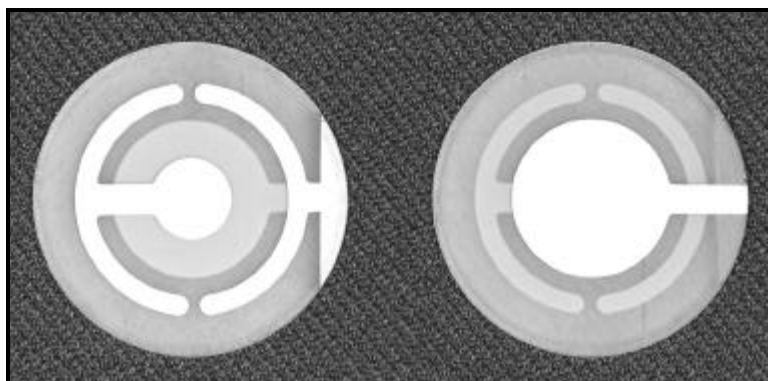


Figure 1. Standard 1 inch QCM sensor crystal. The crystal on the left shows the contact surface, while the one on the right shows the liquid surface.

Standard sensor crystals are 1 inch in diameter and are available with a variety of electrode materials and either a polished or unpolished finish.

Stanford Research Systems also provides a rugged and easy to operate Crystal Holder compatible with both gas and liquid QCM experiments. Crystal Holders must be electrically connected to a Crystal Oscillator, Model QCM25, for operation with a QCM100 Analog Controller.

## Sensor Crystals

QCM Sensor Crystals are available directly from Stanford Research Systems in a variety of electrode materials and surface finishes.

Table I: Standard 1 inch QCM Sensor Crystals					
SRS Part#	Frequency (MHz)	Material	Diam (inch)	Finish	Maxtek Part#
6-00613	5.0	Chrome/Gold	1.0	Polished	149211-1
6-00614	5.0	Chrome/Gold	1.0	Unpolished	149211-2
6-00615	5.0	Titanium/Gold	1.0	Polished	149238-1
6-00616	5.0	Titanium/Gold	1.0	Unpolished	149238-2
6-00617	5.0	Titanium/Platinum	1.0	Polished	149240-1
6-00618	5.0	Titanium/Platinum	1.0	Unpolished	N. A.

# Principle of Operation

AT-cut quartz crystals are most commonly used as QCM sensors because of their superior mechanical and piezoelectric properties<sup>1</sup>, and because they can be cut to give nearly zero temperature coefficients at room temperature.

Due to the piezoelectric properties and crystalline orientation of AT-cut quartz, the application of a voltage between the sensor crystal electrodes results in the production of internal mechanical stress. An oscillating electric field of the proper frequency applied across the disk induces a pure shear mode oscillation that propagates through the crystal. The designation of the oscillation as a pure shear mode indicates that the motion of the disk surface is perfectly parallel to the disk's face.

For shear mode oscillation there are several frequencies that correspond to resonant conditions. For all resonant modes, displacement maxima occur at the crystal faces, making the device sensitive to surface perturbations. The perturbations to be considered include surface loading by

- a thin-film mass layer<sup>2</sup>,
- a contacting Newtonian fluid<sup>3</sup>,
- a viscoelastic layer of finite thickness<sup>4</sup>.

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## Frequency

The nominal frequency of oscillation of all standard QCM Sensor Crystals is 5 MHz (fundamental mode). The unperturbed crystals will normally be within  $\pm 1,000$  ppm of their nominal frequency.

Operation at 5 MHz is regarded as the best for laboratory use and assures (1) acceptable (submonolayer) sensitivity, (2) robustness (331  $\mu\text{m}$  crystal thickness), (3) stable oscillation in most viscous media.

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## Geometry

Figure 1 shows a top and bottom view of a standard 1 inch diameter QCM Sensor Crystal, with what is called a “wrap-around” electrode configuration. A conductive metallic pad is used to allow connection to the front electrode (liquid surface) from the back of the crystal (electrical contact surface). This is required for mounting of the crystal into its Crystal Holder and for proper operation in conductive liquids.

The exposed area of the front electrode in contact with the liquid is  $1.37 \text{ cm}^2$ , however, the active electrode oscillation (i.e. displacement area) is mostly restricted to the area of overlap between the two circular pad electrodes<sup>5</sup> or  $0.40 \text{ cm}^2$ .

All standard QCM sensor crystals are planar, with both faces parallel to within  $1 \mu\text{m}$ . Crystal thickness is  $331 \mu\text{m}$  as required for fundamental oscillation at 5 MHz.

The large diameter of the crystal (1 inch), and the relatively much smaller oscillation area, assures good separation between the active electrode pads and the mounting structure of the holder and minimizes the coupling of other resonant modes to the thickness shear oscillation<sup>6</sup>.

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## Surface Finish

The sensor crystal surface is available in two finishes - unpolished ( $3\ \mu\text{m}$  average surface roughness) or polished (optically clear,  $50\ \text{\AA}$  average surface roughness).

Rough surfaces are most common because they are less expensive. However, they suffer from a quantitatively unpredictable dependence of the oscillation frequency in a liquid due to trapping of fluid in the pores and pits on the surface<sup>7</sup>.

### Note

For liquid-phase applications, optically polished crystals are required<sup>8</sup> if crystal-to-crystal reproducibility is to be expected.

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## Electrode Materials

Gold electrodes (100-1000 nm thick) are the most commonly used in QCM application because of the ease with which gold is evaporated. However, other metals such as Pt, Cu, Al and Ni have also been used.

A thin (2-20 nm) adhesion layer of either Cr, Ti or Si is often deposited directly on the quartz to aid in the adhesion of the metal electrode. Chromium is recommended for polished blank surfaces and also for crystals operated in a harsh environment. However, Cr can be a problem in some electrochemical applications - spurious electrochemical responses can sometimes result if diffusion of the adhesion material to the electrode surface occurs. In that case Titanium should be utilized as the alternative adhesive layer. If Ti is still a problem, Palladium can be utilized as a barrier metal between the Cr or Ti and the primary metallization (consult Stanford Research Systems for availability of alternative electrode materials).

In principle, any type of material that can be deposited onto the surface of the underlying metal electrode can be used on the sensor crystals<sup>9</sup>. The only limitation on the use of such materials is that their deposition must be carried out in such a way that the temperature of the quartz crystal does not exceed  $573^\circ\text{C}$ , above which  $\alpha$ -quartz loses its piezoelectric activity. Quartz blanks are available directly from Stanford Research Systems, contact the factory or your local representative for details. Strict attention to cleanliness is required while performing a custom electrode deposition.

It is important to keep in mind that mass changes at the QCM active electrode surface influence the frequency because these electrodes are part of the composite resonator composed of (1) the quartz crystal, (2) its metal electrodes, (3) any film deposited on the electrodes and (4) any liquid adjacent to the electrode surface which experiences shear forces. For this reason, when electrodes become delaminated (due to poor adhesion of the underlayer or stress caused by the deposit), discontinuous changes in frequency occur which render the crystal useless.

## Mass Sensitivity

The quartz crystal microbalance is an extremely sensitive sensor capable of measuring mass changes in the nanogram/cm<sup>2</sup> range with a wide dynamic range extending into the 100 µg/cm<sup>2</sup> range.

Sauerbrey<sup>10</sup> was the first to recognize the potential usefulness of the technology and demonstrate the extremely sensitive nature of these piezoelectric devices towards mass changes at the surface of the QCM electrodes. The results of his work are embodied in the Sauerbrey equation, which relates the mass change per unit area at the QCM electrode surface to the observed change in oscillation frequency of the crystal:

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

where

$\Delta f$  = the observed frequency change in Hz,

$\Delta m$  = the change in mass per unit area, in g/cm<sup>2</sup>,

$C_f$  = the sensitivity factor for the crystal (56.6 Hz µg<sup>-1</sup>cm<sup>2</sup> for a 5 MHz crystal at room temperature).

The minimum detectable mass change is typically a few ng/cm<sup>2</sup> and limited by the noise specifications of the crystal oscillator and the resolution of the frequency counter used to measure frequency shifts. For example, based on Sauerbrey's equation, a minimum detectable mass specification of 0.018 ng/cm<sup>2</sup> should be expected from a QCM system with a 0.001 Hz frequency measurement resolution.

The Sauerbrey equation relies on a sensitivity factor,  $C_f$ , which is a fundamental property of the QCM crystal. Thus, *in theory*, the QCM mass sensor does not require calibration. This ability to calculate the mass sensitivity from first principles is obviously a very attractive feature of these devices. However, it is very important to notice, that the Sauerbrey equation is only strictly applicable to uniform, thin-film deposits originating from a low pressure (i.e. vacuum) gas environment<sup>11</sup>. Thick deposits and operation in liquid environments or in contact with viscoelastic films, relies on the use of more complex equations relating the frequency shifts to mass loading, and often requires calibration of the setup for accurate results. Several articles have been published on simple ways to calibrate the mass sensitivity of QCMs for electrochemical applications<sup>12</sup> and for vacuum thin-film deposition processes<sup>13</sup> and some useful calibration guidelines are also described in the previous chapter of this manual.

There is ample evidence supporting a Gaussian mass sensitivity for AT-cut crystals<sup>14</sup>, with the maximum sensitivity at the center of the electrode and zero sensitivity at the edges for harmonically driven plane crystals. The mass sensitivity distribution has also been shown to become slightly more confined to the electrode region as the mass loading is increased.

There are also situations in which the QCM does not act as a microbalance at all, but responds instead to properties such as viscosity<sup>15</sup> and/or elasticity<sup>16</sup> of the liquid or film in contact with its surface.

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## Maximum Loads

In general terms, the sensor crystal can be coated with almost any material as long as it can be applied in a sufficiently thin and well attached layer. The layer thickness may vary from a few Angstroms to a few micrometers. The maximum layer thickness depends on the viscoelastic properties of the applied material.

Basically, the crystal load is limited by two factors - (1) total damping and (2) lost sensitivity. For highly viscous or solid materials, the damping of the crystal will increase with increasing layer thickness. At a certain thickness (usually a couple of micrometers) the damping becomes too high and the crystal cannot be driven anymore, i.e. the measurement fails due to lack of oscillation. More elastic materials will not couple completely to the crystal's oscillation. With increasing layer thickness the outermost parts of the attached layer will couple weaker and at a certain thickness (usually a few micrometers) the coupling is lost completely. In this case, a measurement can still be performed but the equipment will only sense the part of the layer in the vicinity of the crystal<sup>17</sup>.

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## Useful Life

A sensor crystal can be reused up to 20 times on average, or until the frequency drops below 60% of its uncoated value. However, reusing the crystal requires careful handling and cleaning procedures that do not harm the crystal or its coating. In most QCM experiments, the crystals are considered expendable, especially if low-cost, unpolished crystals are involved<sup>18</sup>.

Traces of consumption and wear can often be seen visually. Edges of the sensor crystal might become cracked and the coating start to show scratches and holes. When the crystal is close to being consumed, the measurement signal will become noisy, possibly even shaky. It might even be difficult to obtain a stable baseline. Spurious signals might become evident in electrochemical QCM experiments.

As the sensor crystal is coated, the series resonance resistance increases, indicating a loss of crystal  $Q$ <sup>19</sup>. When this occurs, the circuit may occasionally resonate at one of the anharmonic frequencies. The oscillation may continue to oscillate at the anharmonic, or it may alternate between the fundamental and anharmonic modes, a condition known as mode hopping. This is a potentially dangerous scenario, since it might lead to early termination of a deposition or film-growth process. Notice that there is no outward evidence of mode hopping except for a discontinuity in the film thickness. Also, even though the film thickness changes dramatically, the mass sensitivity and rate of growth change by only a few percent.

Some experiments can cause irreversible changes on the crystal surface. For example, the use of silver depositions on gold electrodes for calibration of electrochemical QCMs is not always recommended because silver is hard to remove reversibly from gold electrodes. Copper or lead<sup>20</sup> are often recommended instead.

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

## Temperature effects

The intrinsic dependence of the resonant frequency of a quartz crystal on temperature is well known and generally quite small. In fact, the AT-cut quartz crystal commonly used in QCM experiments owe their popularity to their near zero coefficient at room temperature. As a result, the intrinsic temperature dependence of the QCM sensor crystals is negligible at or around room temperature ( $\approx 1\text{-}3\text{ Hz/}^\circ\text{C}$ ) and is generally ignored for monolayer adsorption/desorption processes in the gas phase.

Much larger changes in frequency with temperature are observed when QCM crystals are immersed in liquids. This is due to the coupling of the shear mode oscillation with the temperature dependent viscosity and density of the fluid. The temperature coefficient due to this effect is  $\approx 8\text{ Hz/}^\circ\text{C}$  for water. As a result, for experiments in liquid phase in which the frequency is to be monitored at length, the temperature must be controlled to at least  $0.1^\circ\text{C}$ , and preferably better. In electrochemical experiments this is often achieved with temperature controlled baths and jacketed cells. If temperature control is not possible or practical, it is always good practice to wait at least 30 minutes before performing any accurate measurements after the crystal comes in contact with a new medium and measure the temperature of the solution around the crystal during the experiments to perform temperature compensation.

Careful control of the temperature is required in high accuracy measurements to avoid frequency hysteresis effects - the dependence of resonator frequency at a specific temperature on the prior temperature history of the resonator. For example, it is often observed that the frequency vs temperature curve obtained going from  $T_1$  to  $T_2$  will not coincide with the one obtained immediately after going from  $T_2$  to  $T_1$ . This effect must be carefully considered during accurate determinations.

Each individual QCM user must determine the effect of temperature on the experiments being performed and either control the temperature accordingly, or measure the temperature and compensate for it.



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## Crystal Handling

### Note

Please read the following instructions about general handling of sensor crystals.

- Keep the crystals in a clean environment. When not in use, store them in their original box and wrapper.
- Avoid scratching the center part of the crystal.
- Always rinse with deionized water, or another appropriate pure liquid, before drying the crystal.
- Always use a flow of dry, oil-free, non-reactive gas (e.g. nitrogen) to blow-dry the crystal. It is better to chase liquid off the crystal than to evaporate it on the crystal.
- Hold the sensor crystal with a pair of tweezers. Using bare fingers will contaminate the crystal. Hold it on the outer edge outside the electrode area to prevent scratches. The tweezers should be blunt ended with smooth gripping surfaces and preferably made of soft plastic material.
- Before starting a surface cleaning, ensure that the crystal material will not be damaged by the chemicals. Perform a test run on a discarded or practice crystal whenever possible.

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## Cleaning

The surface properties of the sensor crystal determine the interaction of sample material with the surface. Therefore, the development of proper procedures for cleaning and surface preparation are required to obtain reproducible measurements. This section provides the basic information you need to develop a cleaning procedure suited to your sample/surface system.

Figure 1 shows a standard 1 inch diameter, gold-coated, sensor crystal. When mounted on a Crystal Holder, it is the Liquid Surface that will be in contact with the sample (gas or liquid) during QCM measurements. The counter electrode and electrical contacts for the electrodes are on the Contact Surface of the crystal in the leak-proof crystal chamber.

The most appropriate cleaning method depends on the sample system, the interaction of the sample with the crystal surface, and the properties of the Sensor Crystal itself.

### Note

Before starting a surface cleaning, ensure that the crystal material will not be damaged by the chemicals. Perform a practice test on a discarded crystal whenever possible. ***Avoid basic (high pH) cleaners since they will etch the quartz surface.***

Several proven cleaning procedures follow. Proper crystal handling procedures must be used throughout any cleaning process.

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### General Purpose

For general purpose applications such as electrochemistry and liquid or viscoelastic film studies, it is usually sufficient to sonicate the crystals in a solution of non-basic detergent in deionized water. Immediately rinse liberally with deionized water and dry in a gentle flow of nitrogen gas.

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### Hydrocarbon contaminants

UV/ozone treatment<sup>21</sup> is a powerful tool for removing hydrocarbon impurities which have been adsorbed from the ambient air. This method does not affect the quartz surface, it is low cost and is very efficient. It is often used for crystals used in high vacuum environments.

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### Biomaterials (lipids, proteins and similar biomolecules)

Start by treating the crystal in a UV/ozone chamber for 10 minutes, then immerse it into a 1:1:5 solution of hydrogen peroxide (30%), ammonia (25%) and deionized water heated to a temperature of about 75°C for 5 minutes<sup>22</sup>. Immediately rinse liberally with deionized water and dry in a gentle flow of nitrogen gas. Immediately before measurement, treat the crystal with UV/ozone for 10 minutes.

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### Lipid vesicles on SiO<sub>2</sub> surfaces

Treat the crystal in a UV/ozone chamber for 10 minutes, then immerse it into water with 2% of sodium dodecyl sulfate (SDS) at room temperature for 30 minutes<sup>23</sup>. Rinse generously with deionized water and blow dry with nitrogen gas. Immediately before measurement, treat the crystal with UV/ozone for 10 minutes.

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### Polystyrene removal

To clean polystyrene (PS) off a crystal, immerse the crystal into a 1:1 solution of hexane and deionized water and treat it in an ultrasonic bath for 1 minute. Rinse thoroughly with deionized water and blow dry with nitrogen gas.

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### Crystal rinsing

Rinse sensor crystals with deionized or distilled water or another appropriate pure liquid. In order to prevent recontamination follow these two steps:

1. Hold the crystal with a pair of tweezers from below to prevent washing contaminants from the tweezers onto the crystal. This is generally most critical in biological applications.
2. Chase the liquid off the crystal with a flow of nitrogen gas. Liquid remaining on the edge of the crystal can be wicked off with a clean, lint-free cloth.

## Surface Modifications

The biggest drawback of the QCM is that it is inherently non-specific - *anything that has mass can generate a response from the device*. The danger of this universal response is that you have a greater danger of interference. This issue is being addressed in various ways so that the device will only respond to the analyte of interest. Those “ways” usually involve a chemically or biologically sensitive layer applied to the surface of the crystal<sup>24</sup>.

Often, the hardest part of the problem is deciding what kind of chemically sensitive material you are going to put on top of the crystal so that it responds specifically to what you are trying to measure.

The surface of the sensor crystal can be custom modified by evaporation, spin-coating, and chemical treatment. Several examples of surface modification follow. While not exhaustive, they may serve as a useful starting point when developing your own procedures.

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### Sputtering or evaporation

Thin films (in the nm range) of metals or metal oxides can be applied by sputtering or evaporation. To ensure reproducible results careful attention to cleanliness must be paid, both in the vacuum chamber and in the preparation of the crystals prior to coating. It is generally realized by individual researchers that, unless highly specialized coatings are required, it is a lot more convenient and cost-effective to have a specialized commercial source deposit the electrodes on crystal blanks.

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### Spin-coating

Thin films (nm to microns) of polymers and other materials can be applied by spin coating<sup>25</sup>. Polystyrene is a common material spin-coated on QCM sensor crystals. UV/Ozone treatment can be used to change the hydrophobicity of organic polymeric coatings<sup>26</sup>.

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### Self-assembled monolayers (SAM)

Self-assembling monolayers can be laid down on gold or silver by thiolization<sup>27</sup> or on SiO<sub>2</sub> by silanization<sup>28</sup> to control surface properties.

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### Electroless Deposition Pre-treatment

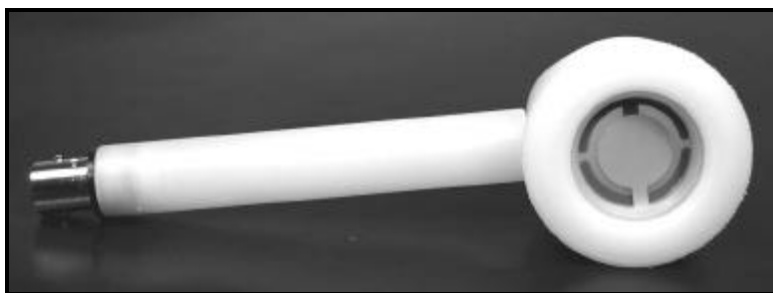
QCMs are used to measure plating rate and thickness in both electrolytic and electroless baths, plating efficiency of electrolytic baths and etching rate in chemical etching processes. It is important to assure that the Sensor Crystal is prepared for the task at hand during electroless<sup>29</sup> depositions of metals. Plating initiation must be complete, and the crystal must be in close approximation of the action taking place in the rest of the tank. Preplating is recommended if adhesion problems are observed with untreated crystals. Pre-treatment with catalyst may be required in some cases. It is usually best not to expose the entire Crystal Holder to catalysis during pre-treatment, to avoid excessive metallization of the holder during deposition.

## Crystal Holder

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### Description

The standard Crystal Holder, included with the QCM100, is specifically designed to provide users with a rugged, compact and easy-to-use sensor crystal housing for QCM experiments in air or liquids.



*Figure 2. The Crystal Holder with a 1 inch sensor crystal mounted.*

Its main features include:

- rugged design<sup>30</sup>
- compatibility with all standard, 1 inch diameter, QCM sensor crystals
- compatible with Crystal Oscillator, SRS Model QCM25
- liquid and gas compatibility (leak-proof design)
- single-electrode exposure to liquids<sup>31</sup> (for compatibility with electrochemical QCM measurements)
- chemical resistance: Kynar<sup>®32</sup> material with Viton orings
- broad temperature range: -25°C to 110°C
- easy crystal replacement (a simple, hand-removable retainer cover permits easy crystal replacement without tools)
- standard female BNC connector for easy electrical connection
- flow cell adapter available (Option 01)

Several methods for mounting sensor crystals have been described in the scientific QCM literature. The mounting fixture requires serious consideration because of possible influences of stress on the absolute frequency of oscillation and because simple and rapid exchange of crystals is required when the thin-film electrodes become damaged or used up.

For electrochemical applications in solution, it must be feasible to expose only one side of the QCM disk to the liquid bath (This is necessary to prevent the two QCM electrodes from being capacitively shunted by the solution, which can cause cessation of the oscillation) The Crystal Holder was specifically designed to address all the above issues

while at the same time providing optimal crystal performance when connected to a QCM25 Crystal Oscillator and a QCM100 Analog Controller.

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## Head Cleaning

It is not uncommon for crystals to break and for chemicals to enter the crystal cavity. In either case, it is very important to act fast and rinse the crystal cavity, the POGO contacts and the POGO contact sockets to remove any traces of solution that might lead to corrosion.

Even though the POGO contacts and sockets are gold coated, unrinsed chemicals can still lead to corrosion and permanent damage to the holder. This is especially true in electrochemical experiments where oxidizing acids are often part of the liquid solution.

Start by removing the crystal from the Crystal Holder and exposing the POGO pins. Putting your thumbnail under the POGO head pull firmly with your fingers to remove each contact pin from its socket. Rinse the pins and the sockets with deionized water to remove all traces of chemicals.

## Tips for Operation in Liquids

To minimize measurement errors in liquid phase QCM experiments, the sample liquid should be prepared carefully. Changes in temperature or the properties of the solvent as well as air bubbles will affect the sensor signal.

For reproducible measurements, keep the following tips in mind.

### **Degas the sample liquid**

The sample liquid should be degassed prior to measurement to avoid the formation of air bubbles on the surface of the crystal.

### **Soak the crystal in the sample liquid overnight**

To minimize random fluctuations, it is best to immerse the crystal, mounted in its holder, in the sample solution several hours before the experiment is started.

### **Wait for the temperature to stabilize**

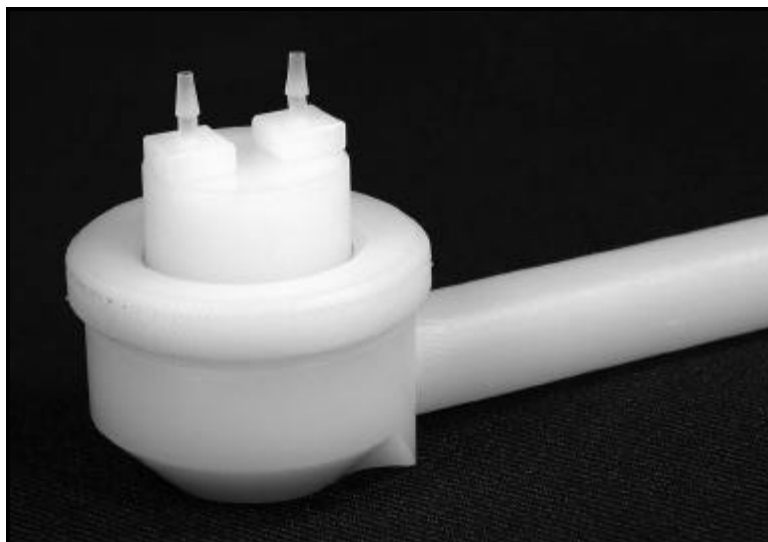
To avoid the formation of air bubbles and reduce temperature related artifacts, the sample liquid should have approximately the same temperature as the measurement chamber's working temperature ( $\pm 2^\circ\text{C}$ ). Wait at least one hour for the temperature to stabilize, before performing any accurate measurements, after a crystal is immersed in a liquid.

### **Prepare your solutions carefully**

To avoid unwanted effects due to changes in the properties of the buffer liquid or solvent, solutions should be prepared carefully. Whenever possible, use purified samples at high concentration and dilute them in the appropriate buffer or solvent just before measurement. Use solvents or buffers from the same stock during one measurement.

## Flow Cell Adapter

The Flow Cell Adapter easily attaches to the Crystal Holder to create a low volume flow cell. The flow cell is made from chemically resistant Kynar<sup>®</sup> and has two inlet and outlet ports (Tefzel<sup>®</sup>) compatible with 0.062" ID tubing. An oring provides a chemically resistant seal between the cell and the face of the sensor crystal.



*Figure 3. The Flow Cell mounted on a Crystal Holder.*

The flow cell is used in place of the Crystal Retainer Ring of the Crystal Holder. Once installed, the cell creates a flow chamber of small volume.

Cell Material:	Kynar <sup>®</sup>
Inlet & Outlet tubes:	Tefzel <sup>®</sup>
O-ring:	Viton

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- <sup>30</sup> The CH105-K Crystal Holder is also compatible with Maxtek's 1 inch diameter crystals and is also a replacement for its crystal holders model CHC-100, CHT-100 and CHK-100.
- <sup>31</sup> Operation in liquids requires that the crystal be mounted in a holder such that only the front surface of the crystal is in contact with the fluid, while at the same time providing an electrical connection to both electrodes.
- <sup>32</sup> Kynar<sup>®</sup> polyvinylidene fluoride, a homopolymer of 1,1-di-fluoro-ethene, is a tough thermoplastic that offers unique properties including: high chemical inertness, low permeability to gases and liquids, resistance to radiation and excellent mechanical strength and toughness. For detailed material information consult: [www.atofinchemicals.com](http://www.atofinchemicals.com).

## Chapter 4

# QCM Circuit Description

The Quartz Crystal Microbalance consists of two circuits - the QCM25 Crystal Oscillator located in a small enclosure that attaches directly to the crystal holder, and the QCM100 Analog Controller. The QCM25 attaches to the QCM100 via a Cat-5 cable wired straight-through to RJ-45 connectors.

This section describes the circuitry of both the QCM25 and the QCM100.

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## Introduction

The Quartz Crystal Microbalance consists of two circuits - the QCM25 Crystal Oscillator located in a small enclosure that attaches directly to the crystal holder, and the QCM100 Analog Controller. The QCM25 attaches to the QCM100 via a Cat-5 cable wired straight-through to RJ-45 connectors. This cable can be up to 25 feet in length.

The QCM25 consists of transformer isolated and gain controlled RF amplifiers which maintain the 5 MHz oscillation of the crystal in the holder. The QCM25 is powered from the QCM100, which also provides the varactor bias to the QCM25 to null the effect of the crystal's static and holder capacitance, allowing the crystal to run at the series resonance frequency. The 5 MHz signal from the QCM25 is sent differentially to the QCM100 via one twisted pair in the Cat-5 cable, allowing measurement of the crystal's series resonant frequency. An analog voltage, which is proportional to the RF gain in dB required to sustain the crystal's oscillation, is also passed to the QCM100, allowing measurement of the crystal's motional resistance.

## QCM25 Circuit Description

The heart of the QCM25 is U1, an AD8367 RF amplifier with 500 MHz bandwidth and up to 45 dB of voltage-controlled gain. The integrated circuit also has a square-law detector (SLD) and automatic gain control (AGC) amplifier which measures and controls the amplitude of its output. The oscillation of the 5 MHz crystal is sustained by the gain provided by this integrated circuit. The gain required to sustain the oscillation is a measure of the losses in the crystal.

The RF output of U1 is applied via the transformer T1 to the resistor network formed from the series combination of the 50  $\Omega$  output resistance of U1 plus R12 (49.9  $\Omega$ ) plus the crystal's resistance (0-4 k $\Omega$ ) and terminated into R17 (49.9  $\Omega$ ). The attenuation of this network is the smallest at the series resonant frequency of the crystal. The AGC amplifier has sufficient gain to maintain the amplitude of the output of U1 at 1 V<sub>pp</sub> provided that the crystal's series resistance is less than 4 k $\Omega$ . Dry crystals have about 10  $\Omega$  of resistance at series resonance while crystals with one face in water have about 400  $\Omega$  of resistance at series resonance.

At series resonance, the crystal impedance is resistive. In addition there is about 15 pF of capacitance in parallel with this resistance due to the crystal's electrodes and holder. The current which passes through this capacitance is canceled by an equal and opposite current which passes through the varactor diode, D2. The QCM100 provides a bias to the varactor diode so that the varactor capacitance is equal to the electrode plus holder capacitance. The varactor is driven by the inverted version of the 5 MHz signal from the center-tapped secondary of transformer T1.

The output from the crystal network is amplified by U4, an AD8009 RF operational amplifier. The gain of U4 can be adjusted between 3.5 $\times$ -5.2 $\times$  with the potentiometer P2. The pot is adjusted during factory calibration to calibrate the offset on the AGC voltage. The slope and offset of the AGC voltage is adjusted to assure compliance to the  $V_{\text{cond}}$  vs.  $R_{\text{crystal}}$  characteristic.

The output of U4 drives a 5<sup>th</sup> order Bessel low-pass filter. The filter serves two purposes. The first is to attenuate very high frequency signals so that the loop will only oscillate at the crystal's fundamental mode. The second is to provide 180° of phase shift at 5 MHz. The filter's phase shift, together with the 180° of phase shift from the inverting amplifier U1, gives the 360° of phase shift required to sustain oscillation. The filter is adjusted during factory calibration so that the loop oscillates at 5 MHz when the crystal is replaced by a 50 Ω resistor.

The gain of U1 is controlled by the voltage,  $V_c$ , at pin 5. The gain is equal to  $(45-50 \times V_c)$  (dB), where  $V_c$  is between 0 and 1 Vdc. Increasing  $V_c$  decreases the amplifier gain. The SLD output current on pin 6 will ramp  $V_c$  up (to decrease the gain) if the detected signal at the amplifier output, pin 10, is greater than 1 Vpp. The SDL output sinks a current to increase the amplifier gain if the detected amplifier output is less than 1 Vpp. In this way, U1 adjusts the loop gain to maintain the oscillation at constant amplitude. R11 and C4 determine the AGC loop characteristics and have been selected to provide a critically damped response.

The AGC voltage is buffered and amplified by U3, an OPA337 operational amplifier. The gain, which is about 5×, is adjusted during factory calibration to calibrate the slope of the AGC curve. The slope and offset of the AGC voltage is adjusted to assure compliance to the  $V_{\text{cond}}$  vs.  $R_{\text{crystal}}$  characteristic. The amplified AGC voltage and ground reference are sent to the QCM100 via two 1.000 kΩ resistors over a twisted pair. The signal is received in the QCM100 by a differential amplifier to remove common mode signals. The AGC signal is filtered and amplified by 2.5× before being output on the front panel  $V_{\text{cond}}$  BNC.

The 5 MHz signal on the primary of T1 is converted to a TTL signal by U2, a DS8921A RS-485 transceiver. The 5 MHz TTL signal is converted by U2 into a differential RS-485 signal which drives one pair of the Cat-5 cable connected to the QCM100. This pair is terminated into 100 Ω and converted to TTL in the QCM100.

The front face of the crystal is connected to the shield of the BNC connector which is connected to the binding post connector on the QCM25. The back face of the crystal is connected to the front face via the RF transformers, and so both faces of the crystal are at the same dc potential. Both faces are electrically isolated at dc from all circuits in the QCM25 and the QCM100 allowing the user to make unburdened measurements of dc currents on and off the front face of the crystal as might occur in electrochemistry measurements.

The QCM25 chassis ground is ac coupled to the circuit ground via the series combination of C9 (0.1 μF) and R5 (47 Ω). The front face of the crystal (and so the bias point binding post) are ac coupled to the circuit ground via the series combination of C10 (1000 pF) and R6 (47 Ω).

## QCM100 Circuit Description

The QCM100 Analog Controller is used with the QCM25 Oscillator to provide power, varactor bias, and conversion of the differential 5 MHz and AGC signals from the QCM25 into single-ended signals available to the user on the QCM100 front panel BNCs.

The QCM100 is powered by a universal input +15VDC/1A power supply. The line input should be between 90 and 264 VAC, 47 to 63 Hz, allowing worldwide operation from line power. The +15 VDC from the switching power supply is re-regulated to +12 VDC and +5 VDC by linear regulators. The +12 VDC power supply is used for analog circuits in the QCM100 and the +5 VDC supply is used to power the 5 MHz TTL output buffer in the QCM100 and to power the QCM25 oscillator via the Cat-5 cable.

The differential RS-485 5 MHz signal from the QCM25 is terminated into R12 (100  $\Omega$ ) and converted to a single-ended TTL signal by U5, a DS8921A RS-485 transceiver. The 5 MHz TTL signal drives all eight inputs of U6, a 74HC541 octal buffer. The outputs of the octal buffer are combined via R15 & R16 (each 100  $\Omega$ ) which drive the output BNC via the balun, T1. The output has a 50  $\Omega$  output impedance and the balun ensures that the shield current returns to the source, which reduces the opportunity for the 5 MHz spreading everywhere.

The differential AGC signal is ac terminated by R29/R30 and C16/17 and is applied to the differential amplifier U9A, creating a single-ended voltage with a gain of 1 $\times$ . (The gain of 1 $\times$  is with respect to the AGC voltage in the QCM25. One needs to be aware that the QCM25 has a source resistance of 2 $\times$ 1 k $\Omega$  for the differential AGC signal to compute the gain correctly.) U9B functions as a comparator which turns the OSC LED “on” when the AGC voltage exceeds about 0.8 VDC, or  $V_{\text{cond}} > 2.0$ , which corresponds to crystal with a resistance of less than 4 k $\Omega$ .

The single-ended AGC voltage is further amplified and filtered by two low-pass Butterworth filters. Both filters have two poles. The first, U10B, is set to 80 Hz and the second, U10A, is set to 8 Hz. The  $V_{\text{cond}}$  BNC output is driven by the second filter via a 1 k $\Omega$  resistor. Together, these filters provide a gain of 2.5 $\times$  for the AGC signal from the QCM25. The gain is adjusted at the factory by setting P1.

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### Capacitive Nulling By The QCM100

The rest of the circuits on the QCM100 schematic are used to determine and set the correct bias for the varactor in the QCM25. As previously discussed, a varactor is used in the QCM25 circuit which cancels the current that flows through the crystal's electrode and holder capacitance. By canceling this current, the capacitances are effectively eliminated from the oscillator circuit, allowing the crystal to oscillate at its series resonance frequency. The varactor capacitance is controlled by the ten-turn potentiometer on the front panel of the QCM100. Cancellation is achieved when the varactor capacitance is equal to the crystal's electrode and holder capacitance. Increasing the dial setting increases the reverse bias on the varactor which decreases the varactor capacitance. The dial should be set to the position which minimizes the gain required to sustain oscillation; it is at this point where the capacitive currents cancel.

The gain required to sustain oscillation can be inferred from the AGC voltage - the higher the AGC voltage, the lower the gain required to sustain oscillation. This can be done manually (by finding the dial setting for which the AGC voltage is at a maximum) or by modulating the varactor voltage and detecting the minimum gain setting using synchronous detection. The second method is much faster and more accurate and is used by the QCM100.

When the ADJUST/HOLD switch on the front panel of the QCM100 is placed in the ADJUST position, the varactor voltage will be modulated by  $\pm 5\%$  around the dial set point. The modulation frequency is 75 Hz and the waveform is sinusoidal. If the dial is set below the optimum set point then increasing the varactor bias will increase the AGC voltage. If the dial is set above the optimum set point then increasing the varactor bias will decrease the AGC voltage. If the varactor voltage is modulated, then the AGC will also be modulated. The AGC modulation will be in-phase with the varactor modulation if the dial is below the optimum set point and the AGC modulation will be out of phase with the varactor modulation if the dial is above the optimum set point. The AGC modulation will go to zero when the dial is set to the optimum set point.

The QCM100 uses a synchronous detector (i.e. lock-in amplifier) to measure the AGC modulation. The user need only adjust the dial to null the detected AGC voltage as indicated by four front panel LEDs. If the HIGH LED is “on” the dial should be moved to a lower setting. . If the LOW LED is “on” the dial should be moved to a higher setting. Both NULL LEDs will be “on” when the dial is in the optimum position. The reproducibility of this procedure is typically  $\pm 0.01$  pF.

Nulling the crystal capacitance is only important if the motional loss (i.e. crystal resistance) is high. The variation of AGC voltage will be very small when the crystal losses are low, and so it may not be possible to use this method in low loss situations.

Dry crystals will oscillate very near their series resonance frequency even when the capacitance has not been nulled. Wet crystals, or any situation for which the crystal's motional losses are high, will require capacitive cancellation in order to oscillate at series resonance, or in some cases, to oscillate at all.

The 75 Hz modulation frequency is provided by U4, a CD4060 oscillator with a 14-stage binary divider. A 76.8 kHz crystal is used in the oscillator circuit. The oscillator frequency is divided by  $2^{10}$ , providing a 75 Hz square wave. The 75 Hz square wave is level shifted by R9/R10 to produce a square wave between +6 and +12 VDC. That square wave is used to switch a dual 1:4 analog multiplexer, U14. The analog multiplexer is used to generate the  $\pm 5\%$  modulated varactor voltage and to synchronously detect a 75 Hz signal on the amplified AGC voltage.

U7, a MAX6250, provides +5.00 VDC used as the varactor reference voltage. The front panel 10-turn potentiometer, P2, divides the reference voltage, which is amplified and buffered by U8A. The output of U8A is  $1.05\times$  the varactor hold voltage. The resistive divider, R20-R23, provides  $1.00\times$  and  $0.95\times$  the varactor hold voltage. When in the HOLD mode, the multiplexer sends the  $1.00\times$  tap to the varactor via the output filter/buffer, U8B. When in the ADJUST mode, the multiplexer switches between the  $1.05\times$  and  $0.95\times$  taps at 75 Hz. This 75 Hz offset square wave is filtered by the output filter/buffer to produce an offset and  $90^\circ$  phase-shifted sine wave to modulate the varactor voltage.



The AGC voltage from the differential amplifier U9A, is filtered and 90° phase-shifted by the two-pole Butterworth filter U10B. The AC component of this signal is amplified by 100× by U11, an OPA277 low-offset voltage operational amplifier. The output of U11 is further amplified by a voltage controlled gain amplifier consisting of U12, an LM13700 dual operational transconductance amplifier, and U13B.

The gain of the voltage controlled amplifier, U12, is controlled by the AGC voltage. The gain increases exponentially with the AGC voltage, varying between 1× and 100× as the AGC voltage goes from 0 VDC to 10 VDC. As mentioned previously, there is little modulation of the AGC voltage when the crystal losses are low (i.e., when the AGC voltage is high.) The purpose of this gain control is to increase the gain for the AGC modulation when the crystal losses are low, so that the apparent sensitivity of the front panel dial is more nearly constant over a wide variety of crystal resistances.

The gain of U12 is proportional to its bias current. In this circuit, the lower half of U12 is used as the amplifier channel. The top half of U12, together with the Darlington pairs (that are normally used as output buffers), are used to generate an amplifier bias current which varies exponentially with the AGC voltage.

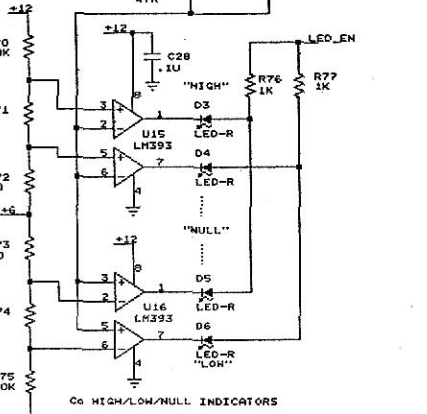
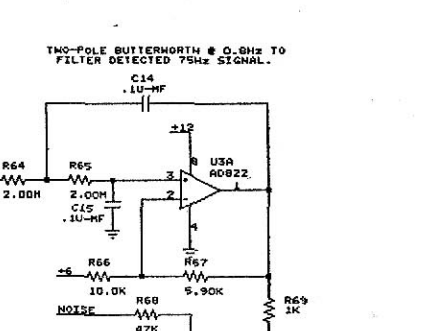
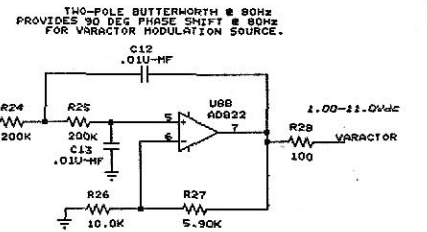
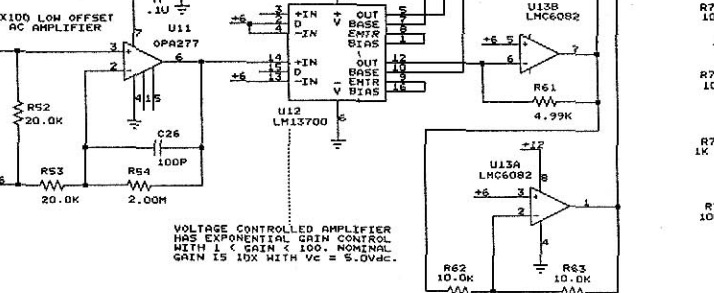
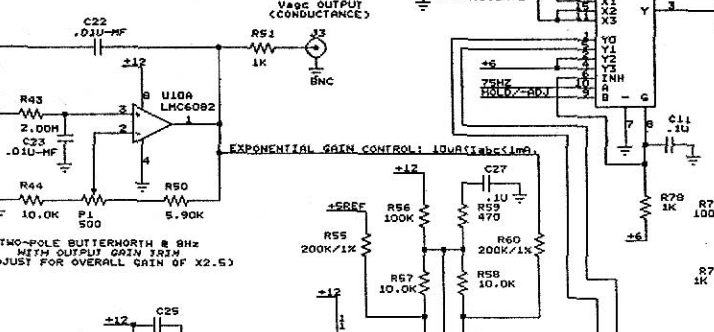
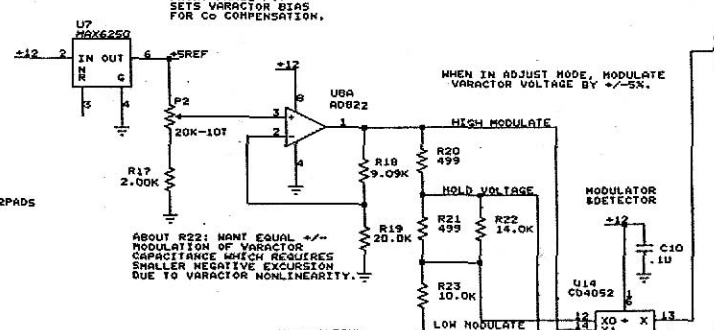
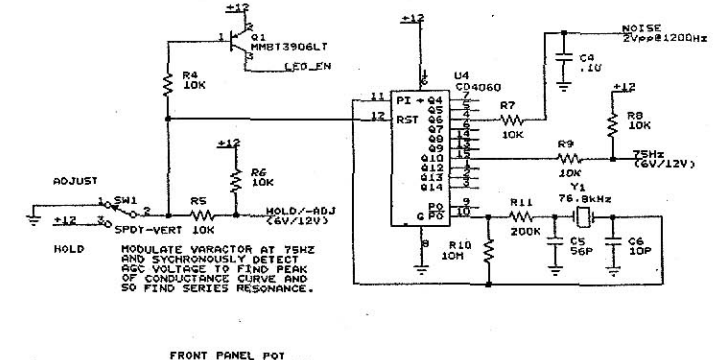
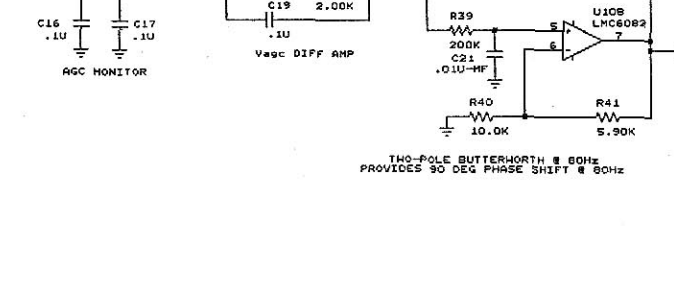
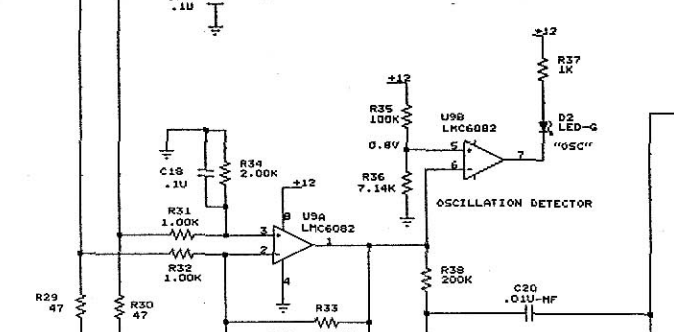
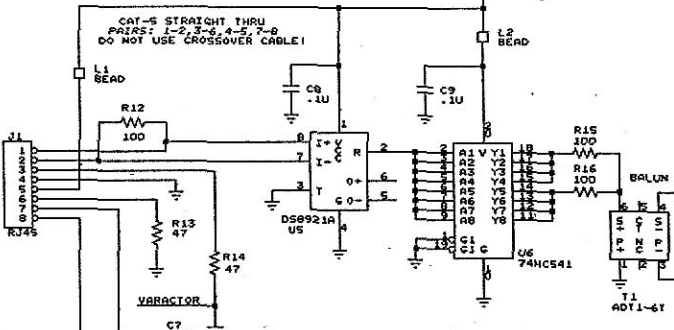
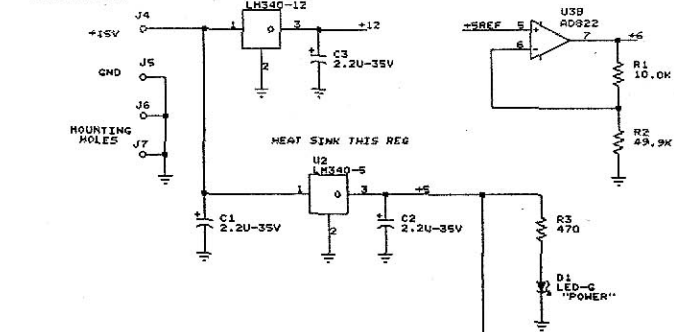
The output of the transconductance amplifier, pin 12 on U12, is a current. This current is converted to a voltage by U13B, which is arranged as a transimpedance amplifier. U13A inverts the output of U13B, and the multiplexer switches between the signal and its inverse at 75 Hz to synchronously detect the modulation on the AGC signal. The detected signal is filtered by U3A, a two-pole Butterworth filter with a low-pass set to 0.8 Hz.

The detected signal will be a positive if the dial setting is too high, and will be negative if the dial setting is too low. The quad comparators, U15 and U16, activate front panel LEDs to indicate to the user how to adjust the dial: If the HIGH LED is “on” the dial should be set lower and if the LOW LED is “on” the dial should be set higher. The NULL LEDs indicate that the dial is set correctly. A sawtooth waveform at 16× the modulation frequency is added to the detected signal via R68 in order to “blur” the comparator response. Even with this blurring, the sensitivity and reproducibility is remarkable: the crystal’s electrode and holder capacitance can be nulled with a resolution of about 0.01 pF.

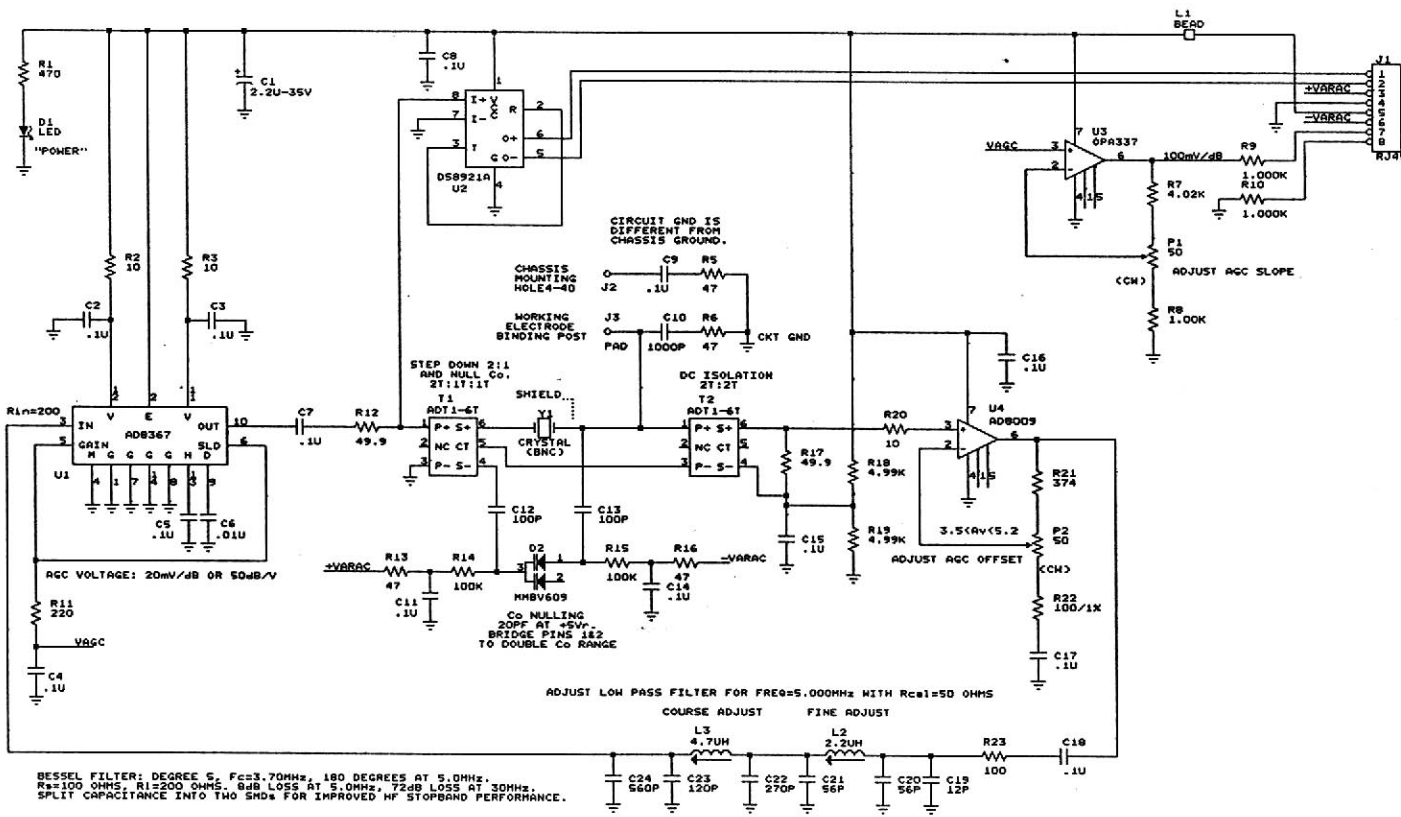
The 75 Hz modulation on the varactor voltage will also modulate the frequency of the 5 MHz signal which is used to detect mass accumulation on the crystal face. Most users will want to turn this modulation off while making mass measurements. However, the effect of this modulation, and frequency modulations caused by the line frequency, will be virtually eliminated if gate times for the frequency measurement are an integral multiple of 0.2 S so that there are an integral number of modulation cycles during each measurement.



+15V FROM PHIHONG  
PSA15LN2-150



STANFORD RESEARCH SYSTEMS			
Title	QCN100 ANALOG CONTROLLER		
Size/Document Number	QCN100_C		
Date	December 19, 2002	Sheet	1 of 1



CAT-5 STRAIGHT THRU  
PAIRS: 1-2,3-6,4-5,7-8

BESSEL FILTER: DEGREE 5,  $F_c=3.70\text{MHz}$ , 180 DEGREES AT 5.0MHz.  
 $R=100\ \Omega$ ,  $R1=200\ \Omega$ ,  $R_{db}\ \text{LOSS AT } 5.0\text{MHz}$ ,  $72\text{dB LOSS AT } 20\text{MHz}$   
 SPLIT CAPACITANCE INTO TWO ENDS FOR IMPROVED HF STOPBAND PERFORMANCE.

2.2U: TOKO 332PN-T1016Z  
 4.7U: TOKO 332PN-T1020Z (SRS 6-171)

RESISTANCE CALIBRATION:  $R_m = (10,000 \times 10^{-(V_{cond}/5)} - 75)\ \Omega$   
 OR,  $V_{cond} = 5 \times \text{LOG} (10,000 / (R_m + 75))\ \text{VOLTS}$   
 ADJUST P1 & P2 SO THAT AT THE OUTPUT OF THE QCM100:  
 WITH  $R_{cal}=51.50\ \Omega$ ,  $V_{cond} = 9.496\text{V}$   
 WITH  $R_{cal}=1.00K\ \Omega$ ,  $V_{cond} = 4.843\text{V}$   
 (NOTE: THERE IS A GAIN OF 2.5X FOR THE AGC SIGNAL IN THE QCM CONTROLLER.)

STANFORD RESEARCH SYSTEMS 1290 REAHWOOD SUNNYVALE, CA 94089	
Title	QUARTZ CRYSTAL MICROBALANCE (QCM25)
Size	Document Number
C	QCM_C
Date:	December 19, 2002 Sheet 1 of 1