Operation and Service Manual

QCM100
Quartz Crystal Microbalance Analog Controller

QCM25
Crystal Oscillator

SRS Stanford Research Systems

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Certification

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

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.

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.

Safety and Preparation for Use

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.

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.

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.

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.

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.

Line Fuse

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

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.

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.

Serviceable Parts

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

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Chapter 4 QCM Circuit Description

Chapter 5 Parts List
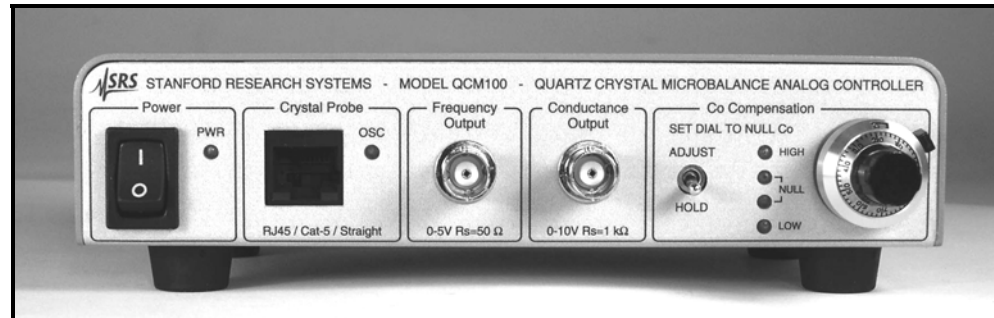
Front Panel Overview

Figure 1. Front Panel of QCM100 Analog Controller

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.

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.

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 Ω.

The BNC shield is electrically connected to chassis ground.

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 KΩ.

The BNC shield is electrically connected to chassis ground.

C$_o$ Compensation:

A switch is available to set the controller into the Adjust Mode for nulling C$_o$.

A ten-turn DIAL, controls the bias voltage (Varactor bias) required by the QCM25 Crystal Oscillator to null C$_o$.

Four LEDs (HIGH/NULL/LOW) provide visual feedback while nulling C$_o$.

Set the C$_o$ Compensation switch back to HOLD after nulling C$_o$.

Back Panel Overview

Figure 2. Back Panel of QCM100 Analog Controller.

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.

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)

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 Through) cable is used to electrically connect the two boxes. A cable up to 25 feet in length may be used.

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

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.

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/holder)

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.

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 Ω
Connector	BNC

Conductance Output (Vc)

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

In This Chapter

Unpacking

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.

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.

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 QCM crystals.

Optional Equipment

- Replacement Crystals (SRS Part# O100RX1)

- Replacement ITO Crystals (SRS Part# O100RX2)

- Flow Cell (SRS Part# O100FC.)

- Crystal Cleaning Basket (SRS Part# O100CCB)

- Replacement Crystal Holder (O100RH)
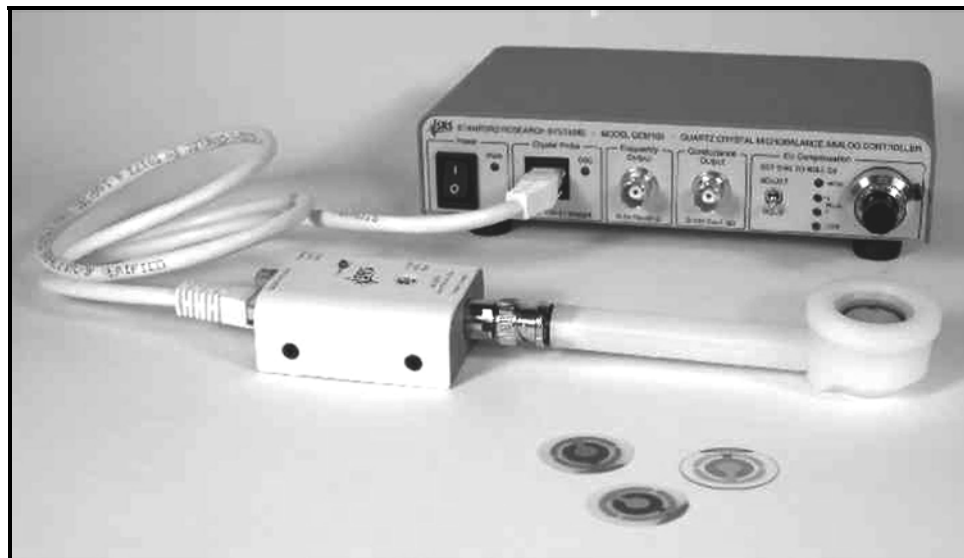
Quick Start Instructions

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 8.0 (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 (i.e. at "true" series resonance), perform a Capacitance Cancellation procedure as described in Chapter 2. Consult Chapter 3 for additional tips on QCM operation in liquids.

11. For operation with a *flow cell* (see Figure 14), pay special attention when filling the flow chamber for the first time that no air bubbles get trapped in the measurement volume. Consult Chapter 3 for some useful tips on QCM operation in liquid flow cells, including bubble elimination techniques. Temperature stabilization to better than +/-0.1°C is essential for high accuracy measurements in aqueous solutions due to the high temperature coefficient of viscosity.

12. 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 (Consult Chapter 2 for additional details). Temperature stabilization is essential in these experiments as well for high accuracy measurements.
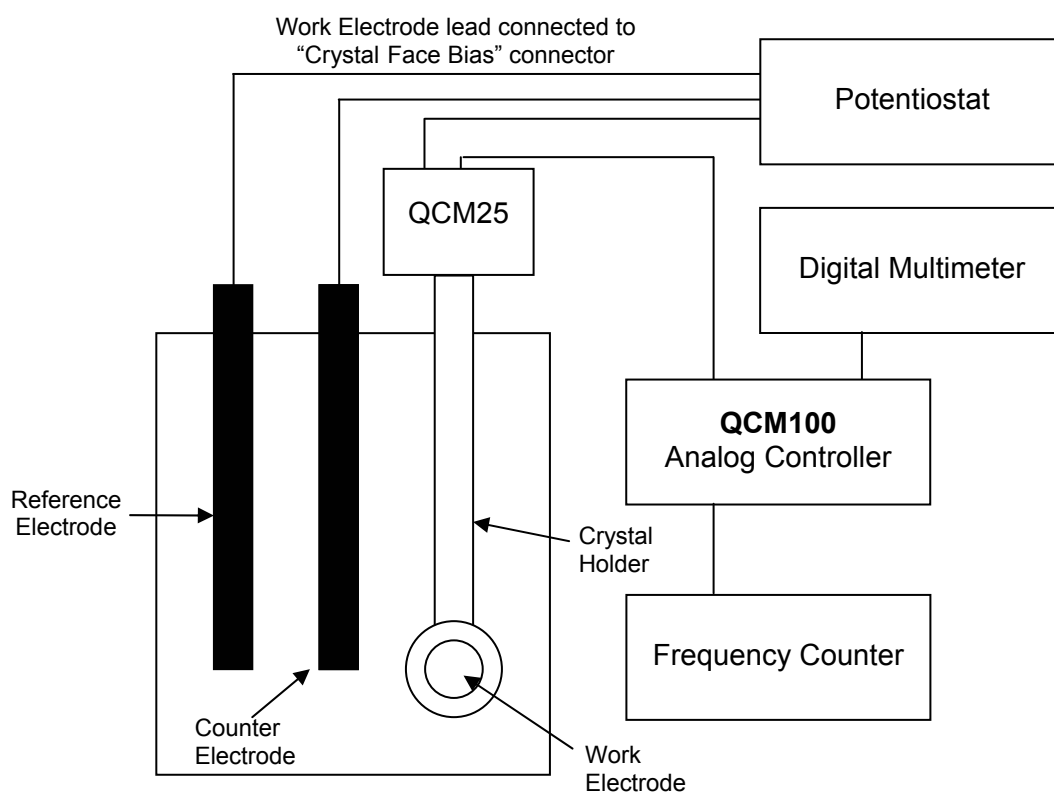
Figure 2. Basic Electrochemical Quartz Crystal Microbalance (EQCM) setup.

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.
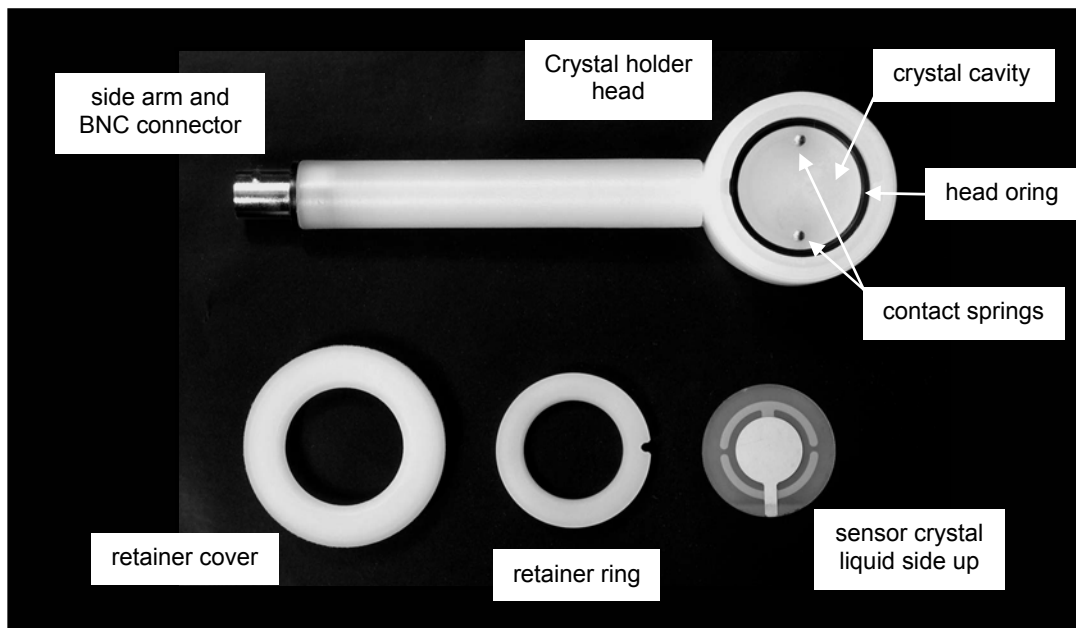
Figure 3. Crystal Holder components.

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.
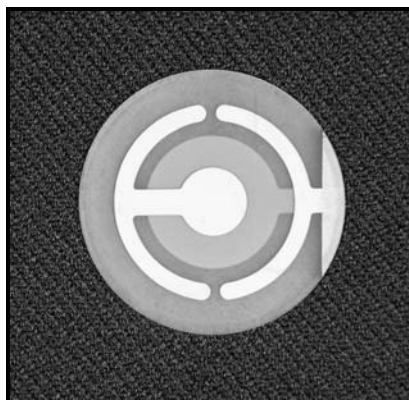
Fig 4. Contact Surface of QCM crystal

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.
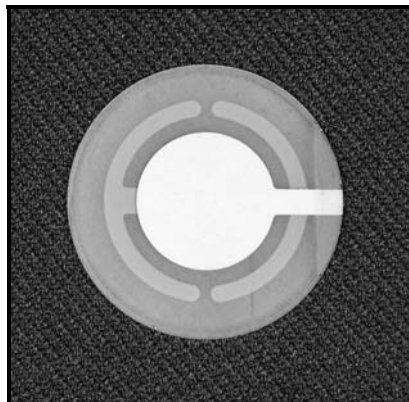
Figure 5. Liquid surface of QCM crystal

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 that they travel freely (i.e. their motion is not restricted.) They should drop 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 protrude above the surface of the oring, by an amount equal or larger than the thickness of the sensor crystal.

5. Inspect the sensor crystal at this time and clean it 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.
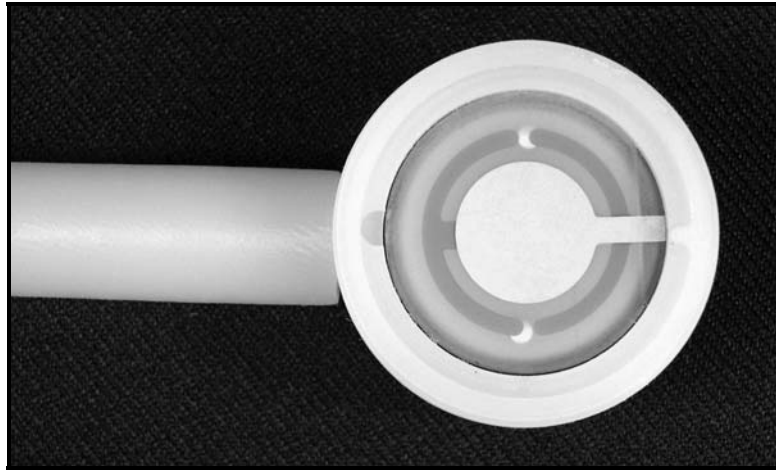
Figure 6. QCM Crystal in Crystal Holder cavity with wrap around electrode pointing towards reference pin.

7. Turn the crystal 90º clockwise before laying it centered onto the head oring. Turning the crystal as instructed 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 electrode orientation.

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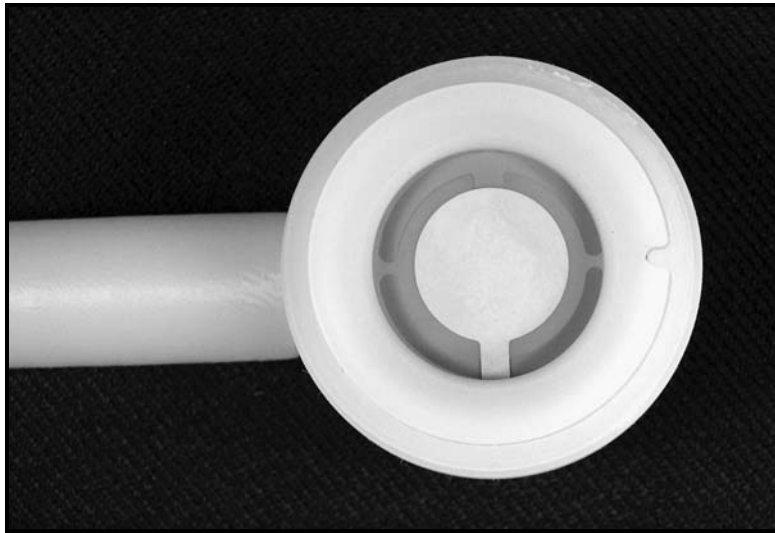
Figure 8. Retainer ring in place.

9. Attach 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.
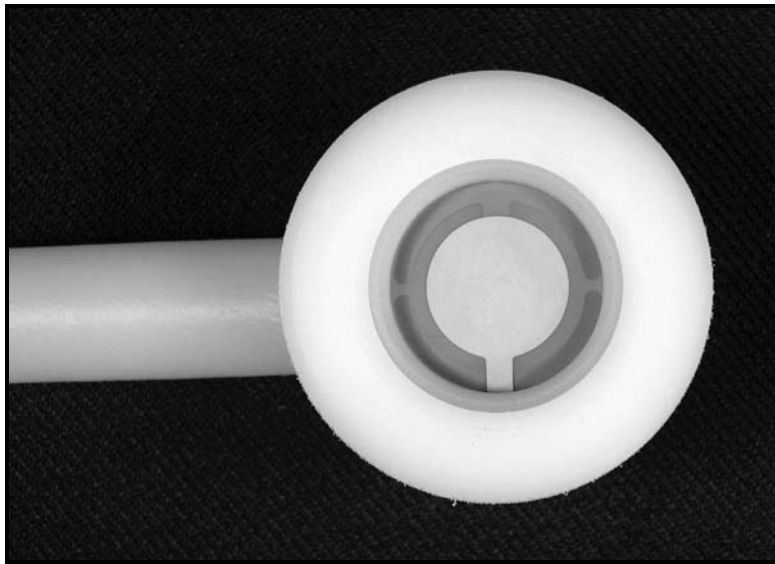
Fig 9. Retainer cover in place.

10. Tighten the 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.

Flow Cell

The Flow Cell Adapter (SRS Part# O100FC) attaches to the crystal holder to create a small volume Stagnation Point Flow Cell.

Figure 12. The axial flow cell adapter mounted on a crystal holder.

Use the Axial Flow Cell Adapter for adsorption/desorption studies when: (1) well defined flow conditions are needed, (2) high sensitivity is required, (3) small rinse volume is desirable and (4) flow-induced surface shear forces need to be minimized.
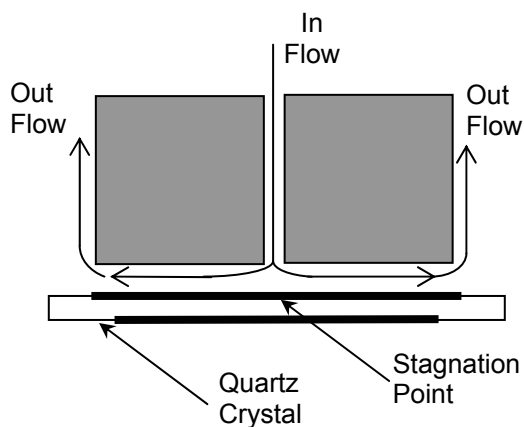
Figure 13. Schematic representation of the liquid flow pattern in the Axial Flow Cell

A cross sectional view of the Axial Flow Cell, including a schematic representation of the stagnation point flow, is shown in figure 13. In the axial flow cell the sample flows

radially from the input port at the center of the cell to the exit channel at the circumference of the cell, in a volume of about 150μl. The sample solution is perpendicularly injected towards the flat surface of the QCM crystal. The stagnation point is located at the center of the crystal electrode overlapping the highest sensitivity area of the flat QCM oscillator.

The hydrodynamics associated with stagnation point flow are well understood. At the stagnation point there is zero hydrodynamic flow- i.e. without surface shear forces. While the injected solution flows about the stagnation point, any exchange with the surface of the crystal is diffusion limited. Thus the rate of adsorption of the sample molecules (or particles) to the crystal surface is diffusion limited as well. The hydrodynamics and deposition of molecules in stagnation point flow conditions have been investigated by Dabros and Van deVen and the user is referred to their publications for details:

> Dabros T., van de Ven T. G. M., "A direct method for studying particle deposition onto solid surfaces." Colloid and Polymer Science 261 (1983) 694-707

> Dabros, T., and T. G. M. Van de Ven, "Deposition of latex particles on glass surfaces in an impinging jet". Physicochem. Hydrodynamics 8 (1987)161-172.

The stagnation point flow cell was specifically designed for the study of adsorption kinetics of particles, micelles and chemical and biological molecules at solid-liquid interfaces under well-controlled hydrodynamic conditions. Examples of surface-volume processes that have been studied with the aid of stagnation flow cells include: DNA-protein interactions, protein adsorption, cell adhesion, biofouling, biocompatibility, polymer degradation and hydration, biofilm formation, self-assembled monolayers, etc.

Installation
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 ($\approx$ 0.15 mL). The flow cell is made of chemically resistant Kynar® and includes two inlet and outlet ports with 0.040" ID thru hole and fitted with barbed hose adapters for 0.062" ID tubing. Simply slide your tube over the barbed stems to create a reliable, low pressure connection to a syringe, siphon system or peristaltic pump. Consult Chapter 3 for additional tips on the operation of lquid flow cells.

Tip. For flowing QCM setups requiring connection to a flow injection or sequential injection analysis system it is common practice to interface the capillary tubing to the flow cell using a short section of 1/16" ID PHARMED® tubing (for example, part # 1557 from www.upchurch.com).

Eliminating gas bubbles trapped inside the crystal chamber is essential for accurate measurements. Please consult the "Bubbles and Liquid Flow Cells" section in Chapter 3 for some useful bubble elimination tricks.

Operation
Two modes of operation are common for QCM flow cells:

Batch Mode: The crystal is exposed to a sequence of sample/solvent batches through a series of load / rinse exchanges. Syringes and the siphon principle are commonly used to manually inject new solutions into the crystal chamber

Flow Mode: A constant flow of solution/solvent runs over the crystal in an open- or closed-flow configuration.

In open-flow systems the Syphon principle is recommended to implement the lowest noise flow setup. Syringe pumps and 6 port injection valves are commonly used to expose the crystal to a sequence of analytes (see Figure 14). Most standard Flow Injection Analysis (FIA) and Sequential Injection Analysis (SIA) equipment is compatible with QCM flow cell operation.

Peristaltic pumps are often applied to closed-flow systems but they always add noise to the frequency signal due to pressure transients and coupled vibrations (pulse-dampening modules are always recommended).

In all cases, the flow rate must be kept under 5mL/min to avoid excessive stress on the sensor and to avoid leaks of liquid over the oring.
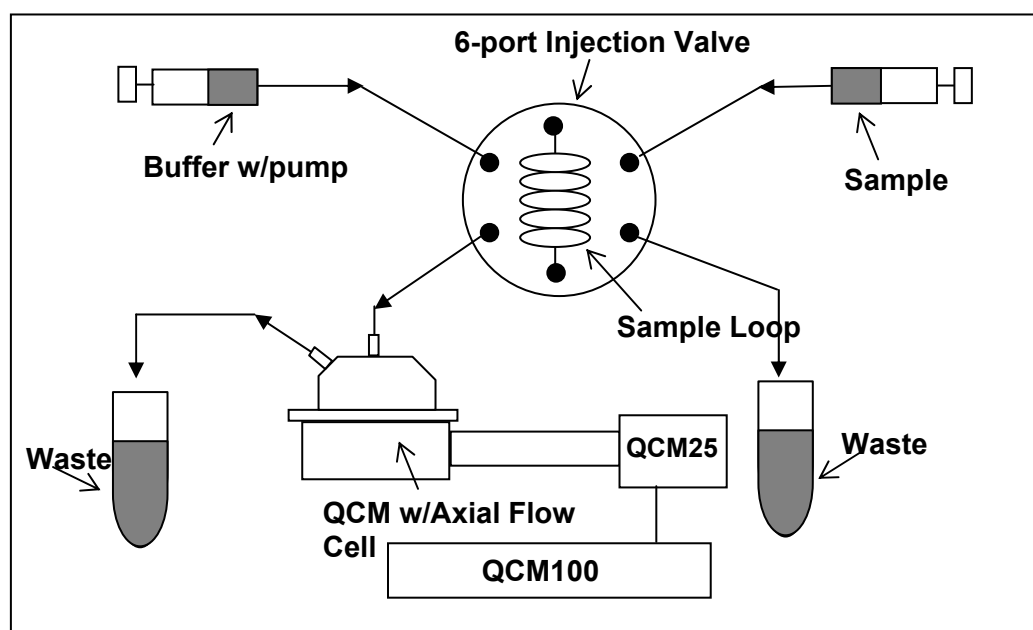
Figure 14. A Flow Injection Analysis-QCM system consisting of syringe pump for buffer solution, 6-port injection valve for analyte injection and Axial Flow Cell for QCM Flow Chamber.

Specifications:

Flow Volume (crystal chamber) ≈ 0.15 mL

Materials:

Cell   Kynar®
Inlet-Outlet Tubes   Tefzel ®
Oring   Viton®

In/Out Ports	Barbed hose adapters for 1/16" ID tubing, w/0.040" ID thru-hole.
	(Model P-663 from www.upchurch.com)
Recommended flow rate	<0.2 mL/min
Maximum flow rate	5 mL/min

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

In This Chapter

Background

Sauerbrey[1] 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:

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

where

Δf = the observed frequency change in Hz,

Δm = the change in mass per unit area in g/cm^2,

C_f = the sensitivity factor for the crystal (56.6 Hz μg^{-1} 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 [2]. 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 QCM 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[3] 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.

C_0

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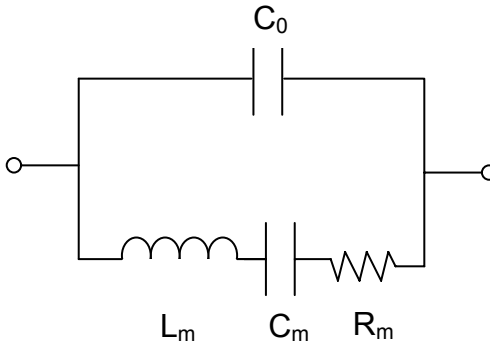
Figure 1. Butterworth-van Dyke model of Quartz Crystal Resonator.

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 Ω (for a dry crystal), R_m = 400 Ω (for a crystal with one face in water), or R_m = 3500 Ω (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[4], 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 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.
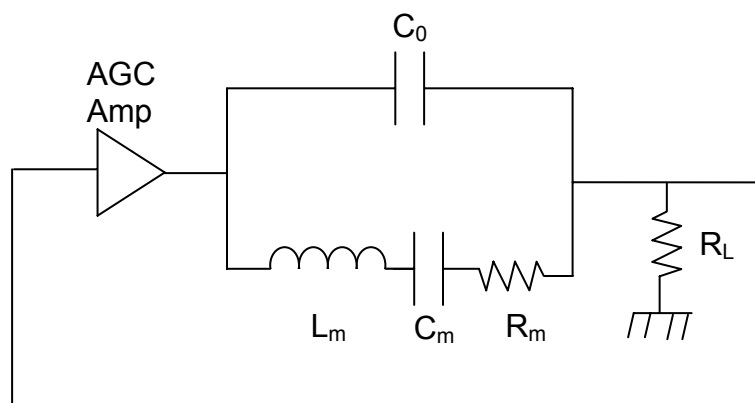
Figure 2. Oscillator Circuit consisting of AGC Amplifier, Quartz Resonator and Load Resistor.

Placing the crystal in an oscillator circuit provides a simple way to measure its motional parameters[5]. 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° (or an integral multiple of 360°) provided there is sufficient gain (the Barkhausen condition). Absent C_o, 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_o cannot be ignored in QCM applications. In the circuit shown in Figure 2, C_o 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_o, and the circuit will not oscillate at all.
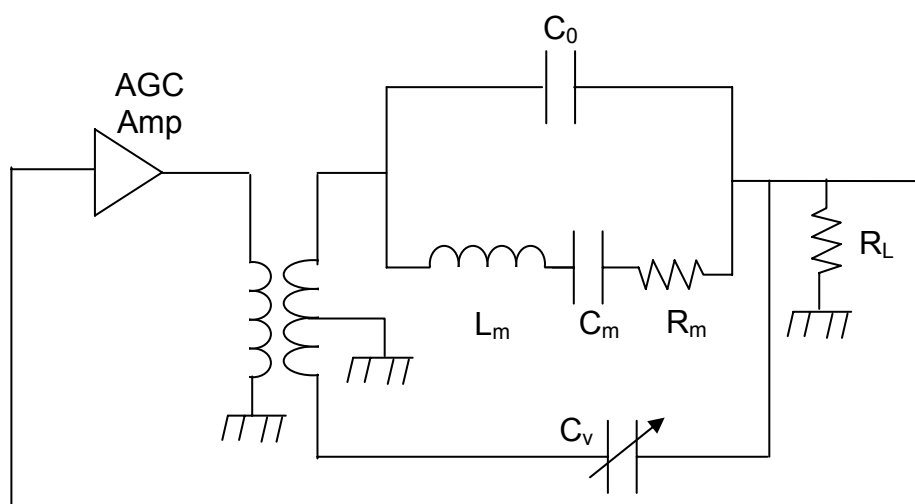
Figure 3. Oscillator Circuit with Varactor Nulling of C_0.

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.*
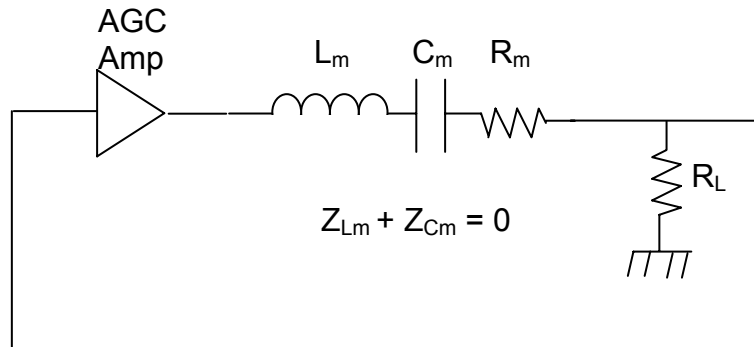
Figure 4. Oscillator Circuit Model with C_0 cancelled by C_v.

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[6], 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 reproducibly of C_v is good enough (±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 8.0, which will provide 9.0 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 the ten-turn dial set to 8.0 (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 around 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 V_{pp} square wave into 50 Ω provided by the QCM100 Frequency Output. Counters are relatively simple to set-up and read via their computer interfaces.

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±0.01 MHz
Waveform (into 50 Ω)	2.4 V square wave
Stability (second to second)	0.002 Hz
Stability (minute to minute)	0.10 Hz
Temperature coefficient (static)	8 Hz/ºC
Frequency/mass coefficient	0.057 Hz/(ng/cm^2)

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 4×10^{-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 ±1 cycle per gate interval.

Virtually all frequency counters can measure the frequency of the 2.4 V_{pp} square wave in 50 Ω 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 360º. Referring to Figure 5, important sources of phase shift within the network include:

1. 180º from the inverting amplifier A_1

2. 180º + [37 μº/Hz deviation from 5 MHz] from the low pass filter

3. 0º + [0.20º/pF ($R_m = 40\ \Omega$) or 0.81º/pF ($R_m = 375\ \Omega$)] from uncompensated C_o

4. 0º + [0.20º/Hz ($R_m = 40\ \Omega$) or 0.04º/Hz ($R_m = 375\ \Omega$) 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 μº/Hz deviation x 500 Hz = 0.0185º when operated 500 Hz from 5 MHz. This will cause a dry crystal to run 0.0185º/(0.20º/Hz) = 0.092 Hz off series resonance, or a wet crystal to run 0.0185º/(0.04º/Hz) = 0.462 Hz off series resonance. Since the $d\phi/df$ of the low pass filter is 1000x 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 ±0.01 pF. The corresponding phase error for a wet crystal is ±0.01 pF x 0.81º/pF = ± 0.0081º, which gives rise to a frequency reproducibility of ±0.0081º/(0.04º/Hz) = ±0.20 Hz for a wet crystal. This error is virtually insignificant.

In water, the dominant 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/ºC. The importance of temperature stabilization in liquid experiments is evident from the following table. With proper temperature stabilization (and/or compensation) it is possible to perform QCM measurements in water with detection limits well below 0.1Hz rms.

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

Source of Error	Typical magnitude of Error for wet crystal
Phase shift in low pass filter	0.65 Hz (<0.1%)
Reproducibility of Co null	<0.20 Hz
Temperature dependence of viscosity (static)	≈0.8 Hz / 0.1ºC

Resistance Measurement

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

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

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

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

Resistance Calculation
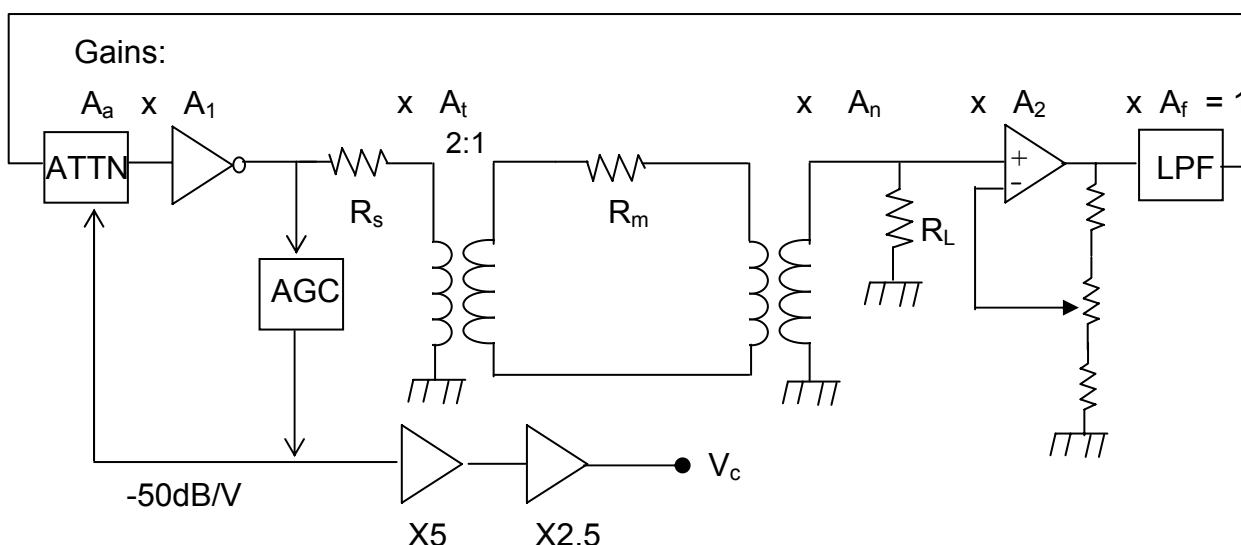
Figure 5. QCM Gain Model

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°, 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° of phase shift. The low pass filter is adjusted to provide 180º 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 V_{pp}. The attenuator is controlled by this voltage, between 0 and 1 Vdc, providing an attenuation of 50 dB/volt so that $A_a = 10^{-Vagc \cdot 50 / 20}$. The AGC voltage is amplified by 5x in the QCM25 Crystal Oscillator, and by 2.5 x 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, $A_a = 10^{-Vc/5}$.

2. A fixed gain amplifier with gain $A_1 = 45$ dB + 20 log (250/200) = 46.94 dB (or 222 x.) 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 Ω. This source resistance consists of two series 50 Ω resistors, one of which is inside the amplifier A_1. This source impedance is reduced by a factor of 4 x, to 25 Ω, 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 x, the transformer also increases the load impedance seen at the input of the transformer by 4 x, so that when $R_m = 0$ Ω, the load will be 200 Ω.

5. R_m, the motional resistance of the crystal at series resonance. R_m can vary from about 10-40 Ω for a dry crystal, to about 375 Ω for a crystal in water, to about 5 kΩ 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 Ω. 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 x. 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 5th order Bessel low pass filter with $f_c = 3.7$ MHz, adjusted so as to provide 180º of phase shift at 5 MHz. The phase shift of this filter, together with the 180º phase shift of the inverting amplifier A_1, provides the 360º 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 $A_f = -7.8$ dB (or 0.407x).

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 Ω 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.

Motional Resistance vs. Conductance Voltage
Rm = (10,000 x 10^(-Vc/5) - 75) Ohms
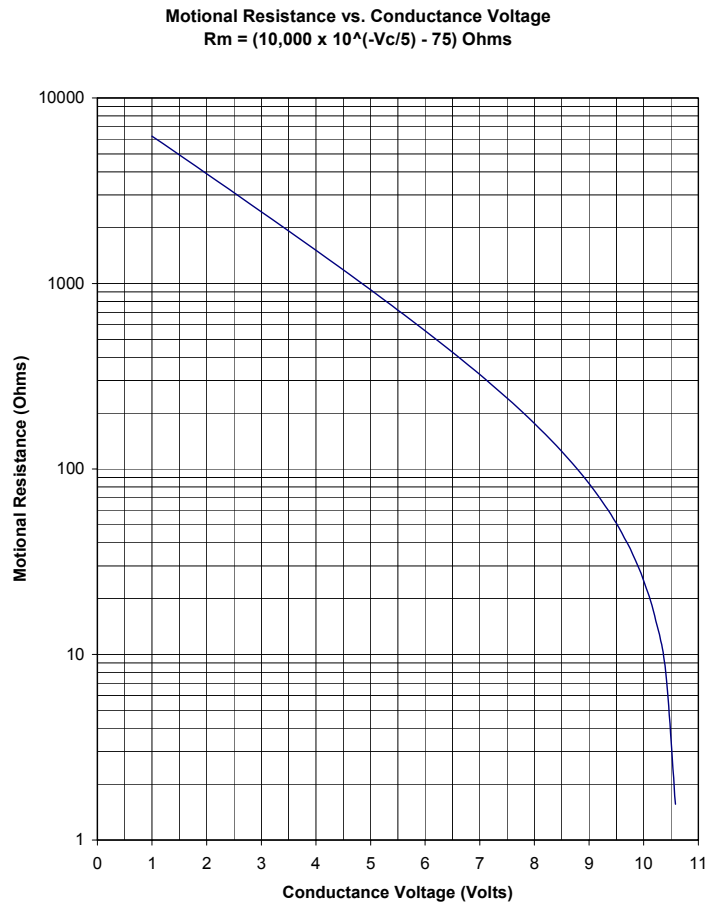
Figure 6. Motional series resonance resistance vs. conductance voltage

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 $R_m < 2\ k\Omega$), 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 $4\ \Omega/°C$ change 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):

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

$$dR_m / dV_c \quad = 10{,}000 \cdot 10^{-Vc/5} \cdot \ln(10) \cdot (-1/5)$$

$$= -2{,}000 \cdot \ln(10) \cdot 10^{-Vc/5}$$

$$\approx -4605 \cdot 10^{-Vc/5}$$

$$\approx -0.4605 \cdot (R_m + 75)$$

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

$$\Delta R_m/R_m \quad = \Delta V_c \cdot [dR_m / dV_c] / R_m$$

$$= \Delta V_c \cdot [-0.4605 \cdot (R_m + 75)] / R_m$$

$$= \pm 28\ ppm$$

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.*

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 18 pF capacitor. Two resistor values are used: 25 Ω and 925 Ω. The equation for R_m may be inverted to determine the calibration value for V_c. (Motional resistance, R_m, in Ω and conductance voltage output, V_c, in volts.)

$$R_m = 10{,}000 \times 10^{-Vc/5} - 75$$

$$V_c = 5 \log [\ 10{,}000 / (R_m + 75)\ ]$$

The low pass filter is adjusted so that the QCM25 Crystal Oscillator oscillates at 5 MHz with the 25 Ω resistor in place of the crystal. The varactor dial is adjusted so that the Crystal Controller oscillates at 5 MHz with the 925 Ω resistor in place of the crystal. Calibration potentiometers in the QCM25 Crystal Oscillator are adjusted so that (P1 pot) $V_c = 10.000\ \pm 0.005$ Vdc with a calibration resistor of 25 Ω, and (P2 pot) $V_c = 5.000\ \pm 0.005$ Vdc with a calibration resistor of 925 Ω. Iterate P1 and P2 adjustments as necessary.

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 an important area of application for this technology.

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).

$$C_f = 2 \cdot n \cdot f_o^2 / (\rho_q \cdot \mu_q)^{1/2} \qquad \text{(eqn. 3)}$$

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,

ρ_q = density of quartz = 2.648 g cm^{-3},

μ_q = shear modulus of quartz = 2.947$\cdot$10^{11} g$\cdot$cm$^{-1}\cdot$s^{-2}.

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.

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

where

ρ_f = density of film material in g/cm^3,

Δm = change in mass per unit area in g/cm^2 (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[9]. As the thickness of the film increases, the Sauerbrey equation must be extended to incorporate the elasticity of the deposit. Lu and Lewis[10] gave a simple equation (eqn. 5) for the calculation of the dependence of Δf on Δm, which is currently applied by most QCM users to calculate rigid thin-film thicknesses in gas phase depositions.

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

where,

Δm = change in mass per unit area in g/cm^2,

N_q = Frequency Constant for AT-cut quartz crystal = 1.668×10^{13} Hz Å,

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

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 = $[(\rho_q \cdot \mu_q)\, /\, (\rho_f \cdot \mu_f)]^{1/2}$,

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

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

μ_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[11] 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 fairly recently, it was believed that excessive viscous loading would prohibit use of the QCM in liquids. In fact, operation in liquids is indeed possible[12], and the response of the QCM is still extremely sensitive to mass changes at the crystal-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[13], and later by Kanazawa and Gordon[14].

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:

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

where

f_u = frequency of oscillation of unloaded crystal,

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

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

ρ_L = density of the liquid in contact with the electrode,

η_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.

Δf and ΔR 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[15].

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

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

Where

ΔR = change in series resonance resistance in Ω,

n = number of sides in contact with liquid,

ω_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[17] (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 kΩ (it will support crystal operation in highly viscous solutions up to 88% (w/w) glycerol in water). Transformer isolation of the oscillator circuit provides compatibility with virtually any potentiostat.

As an example, eqn. 6 predicts a decrease in f_0 of 715 Hz on transfer from vacuum to pure water[18] 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[19], making the QCM an excellent tool for the evaluation of fluid properties. Application examples include in situ monitoring of lubricant and petroleum properties[20]. The tight correspondence between theory (eqns. 6 & 7) and experiment is clearly illustrated by Figure 7.
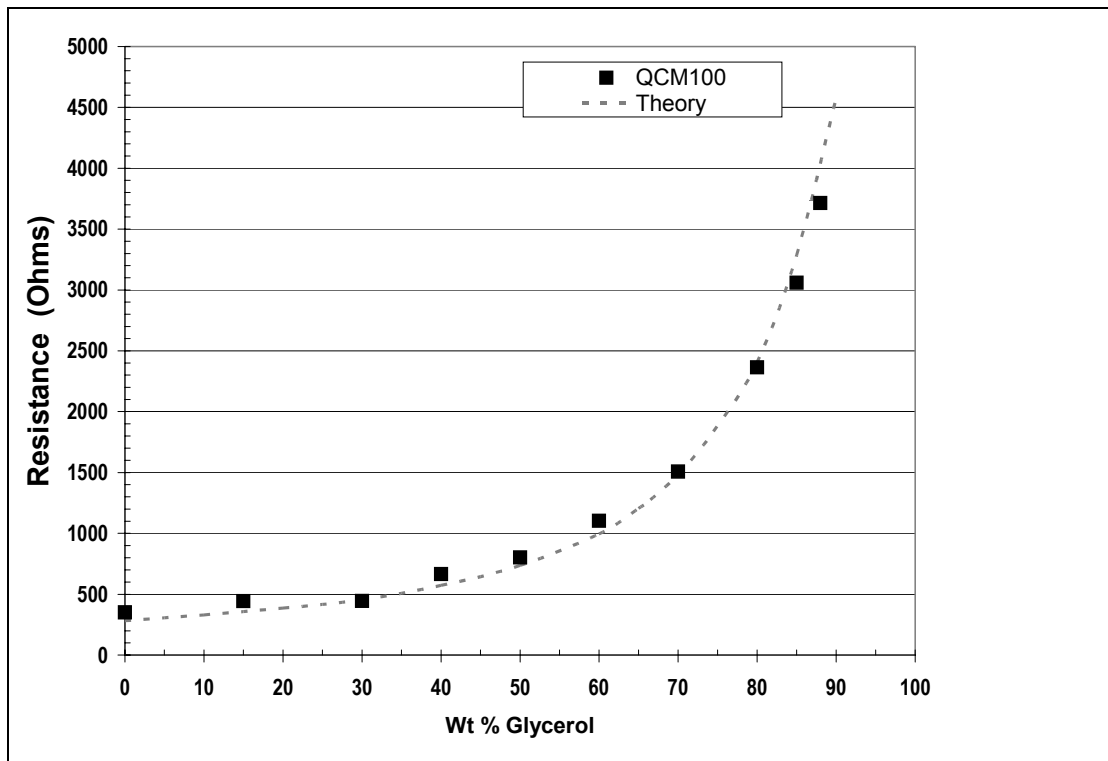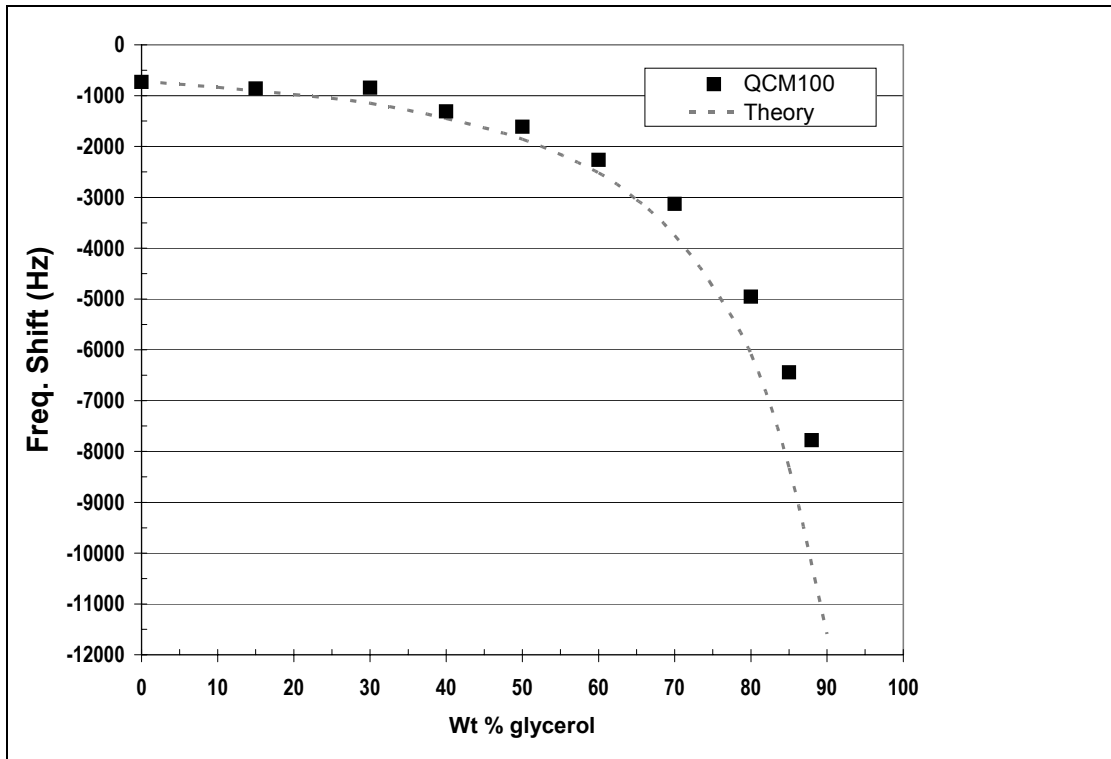
Figure 7. Frequency Shift (Hz) and ResitanceShift(Ohms) versus glycerol weight percentage (in water) as predicted by theory and as measured with QCM100 and a 5 MHz polished crystal.

Immersion Test

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.

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 ≈715 Hz, and an increase in series resonance resistance of ≈ 380 Ω, is expected when switching from air to complete immersion in water at 20°C.

Glycerol/H$_2$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 20ºC. 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 ±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[21], corrosion, oxide formation, dissolution studies[22], adsorption/desorption of surfactants[23] and changes in conductive polymer films during redox processes[24].

The basic principles and applications of the QCM to electrochemical processes have been extensively reviewed in the electrochemical literature[25] 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.

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.
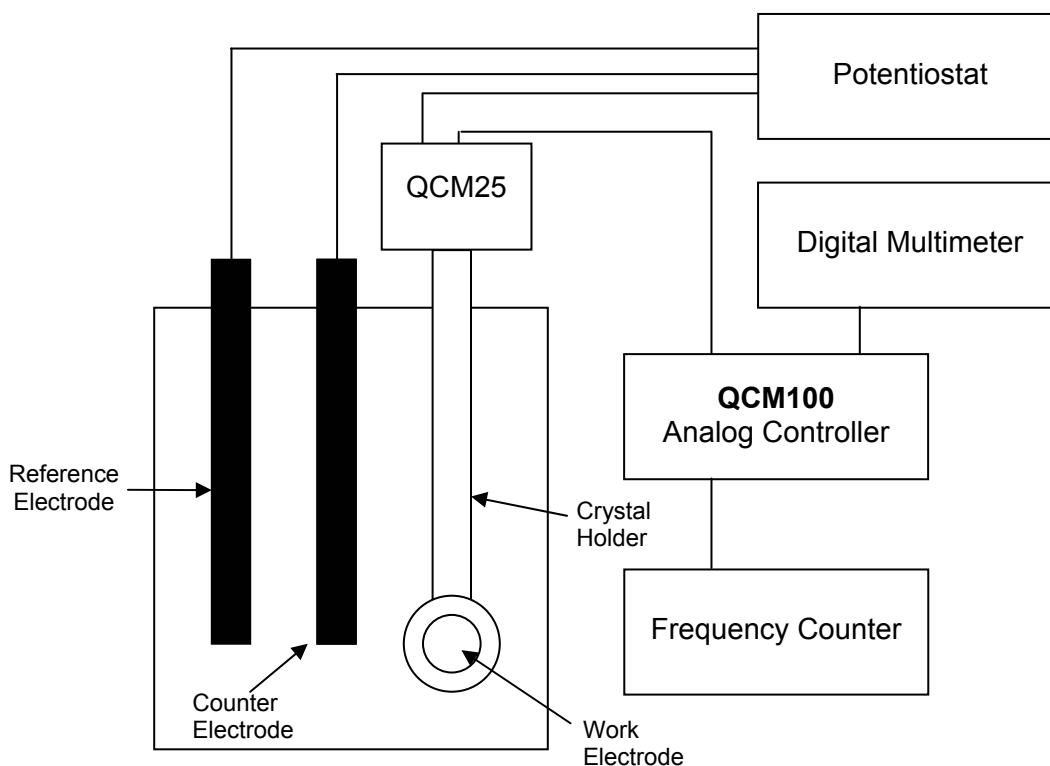
Figure 8. Schematic of EQCM apparatus

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's front face (i.e. liquid surface) 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 $CuSO_4$ in 0.1 M H_2SO_4, using a 1 inch diameter, Au coated, quartz crystal mounted in a standard Crystal Holder as the working electrode. (Note: cathodic current is treated as positive)
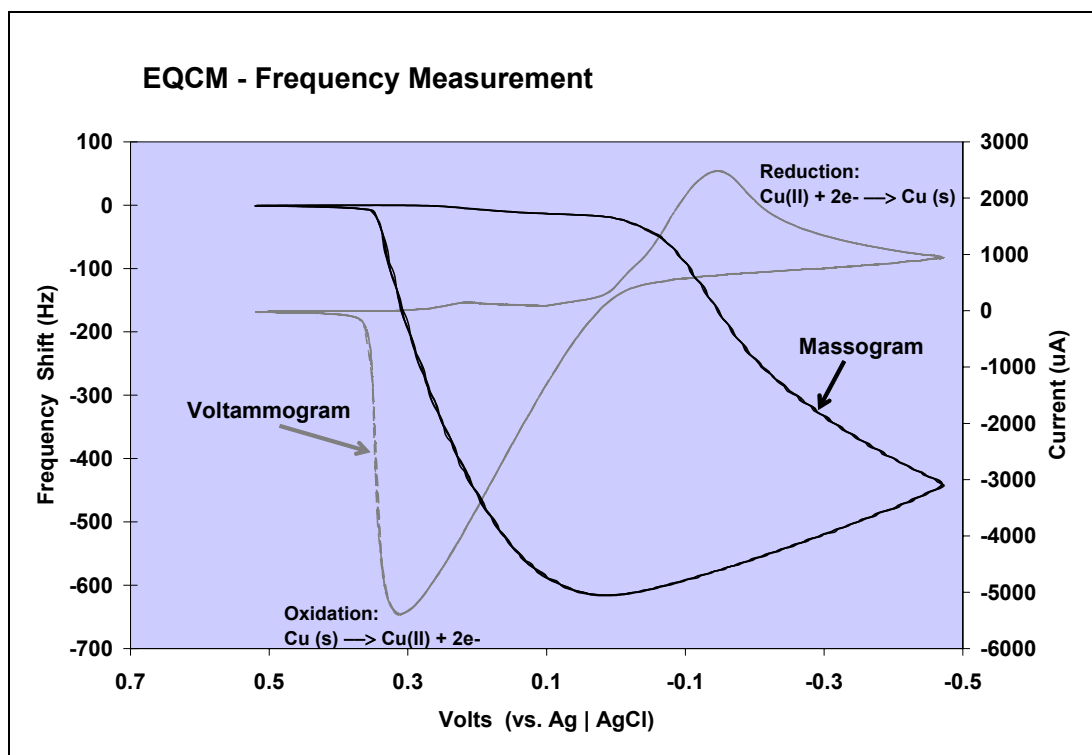
Figure 9. Cyclic voltammogram and massogram data for Cu deposition on a Au electrode. The frequency–potential diagram shows a frequency decrease in perfect sync with the deposition of Cu metal (reduction) on the crystal's surface.

The mass sensing capabilities of the QCM100 are complemented by its ability to simultaneously detect subtle changes in the viscous loading of the QCM crystal during redox processes. Figure 10 is a graphical representation of the changes in series resonance resistance that take place at the QCM sensor (i.e. working electrode) during a cyclic voltammetric scan of a 50mM solution of $K_3Fe(CN)_6$ in 1M Na_2SO4 (50mV/sec scan rate). As the potential of the electrode becomes less positive, $Fe(CN)_6^{3-}$ is depleted and replaced by a layer of $Fe(CN)_6^{4-}$ adjacent to the sensor crystal. Since solutions of $Fe(CN)_6^{4-}$ are more viscous than $Fe(CN)_6^{3-}$ the resistance readings increase at more negative voltages as the more viscous reduced product exerts additional loading on the crystal. The resistance change corresponding to the conversion of $Fe(CN)_6^{3-}$ to $Fe(CN)_6^{4-}$ is 4 Ohms, in complete agreement with a 0.9% estimated relative change in $(\rho\eta)^{1/2}$ calculated from previously reported calibration curves [26].
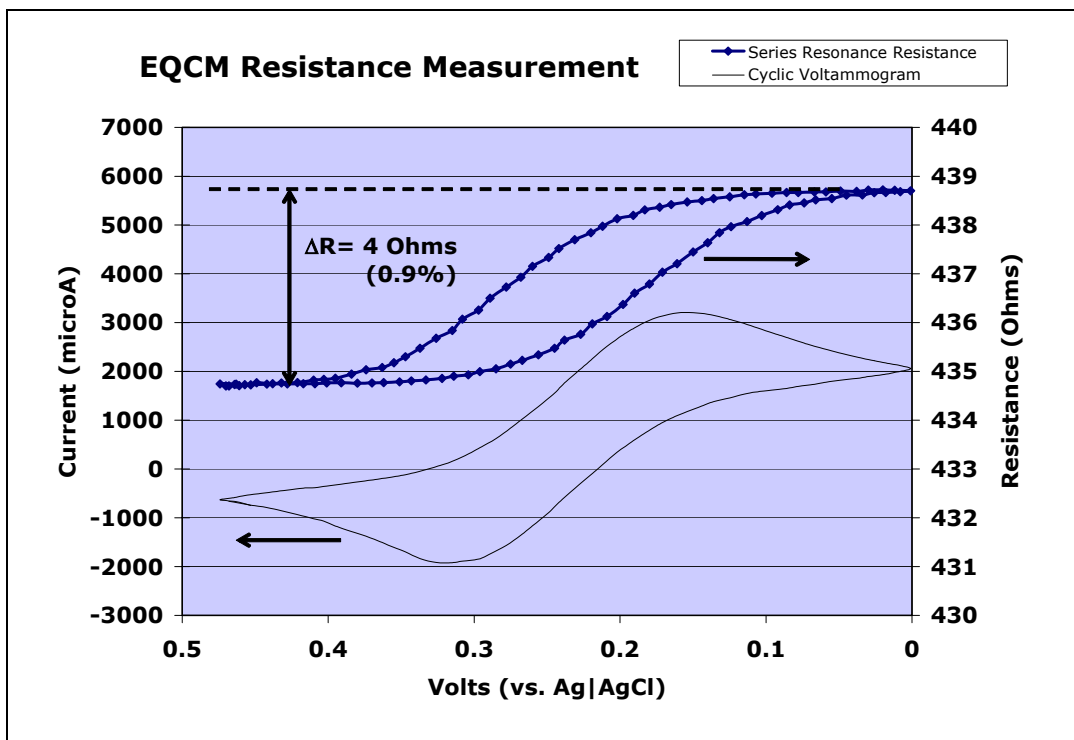
Figure 10. Changes in series resonance resistance at the QCM sensor during the electrochemical oxidation/reduction of $Fe(CN)_6^{3-}$/$Fe(CN)_6^{4-}$. The resistance–potential diagram shows a resistance increase in perfect sync with thegeneration of a viscous layer of $Fe(CN)_6^{4-}$ (reduction) adjacent to the QCM electrode.

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[27]. 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 Δf as is given by equation 8:

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

where

Δf = 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 cm^2,

F = Faraday's constant = 9.648×10^4 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 µg in C_f to g in M_w.)

A plot of Δf 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 $AgNO_3$ in 0.5 M HNO_3 is subjected to a reducing potential and Ag is deposited with a fixed cathodic current density of 50-500 µA/cm^2. The cathodic current is integrated to obtain the charge as a function of time. Excellent linearity is generally observed in Δf vs Q plots for depositions within 1 µg/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[28], and users are referred to the publications list at the end of this chapter for details.

Polymer Modified Electrodes

The EQCM has been extensively used to study polymer modified electrodes, particularly as a gravimetric tool to follow redox processes[29]. 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[30]. 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!

0.1M Pyrrole in 0.1M HCLO$_4$
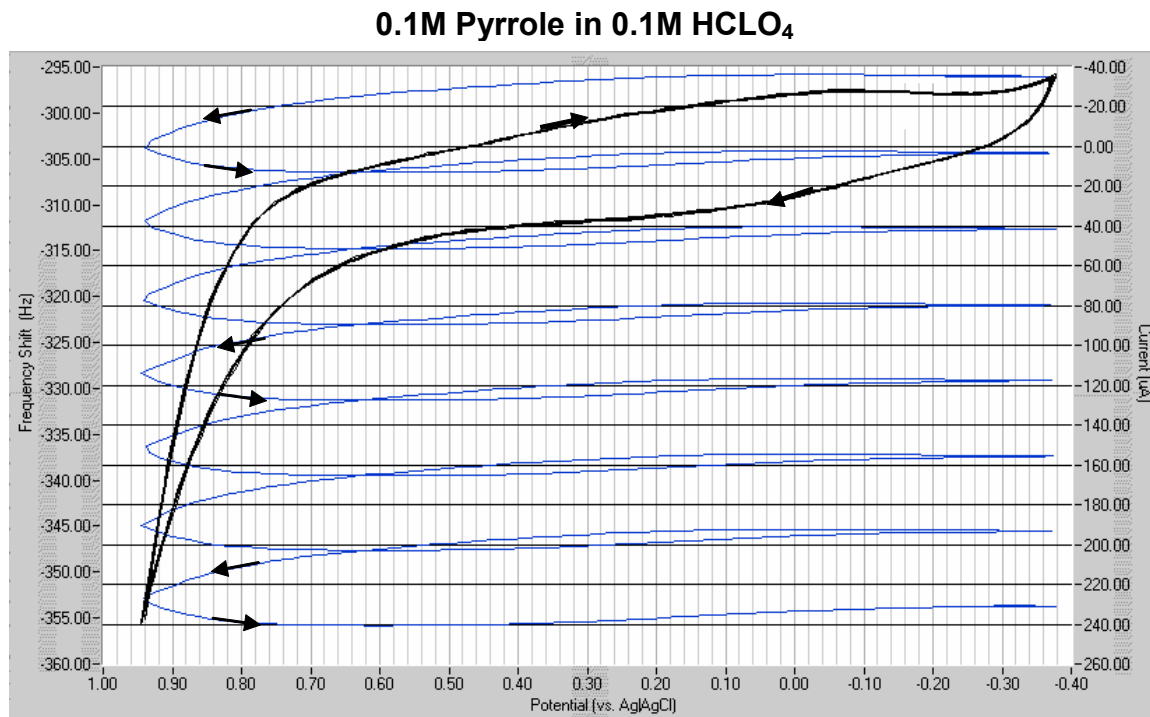
Figure 11. Voltammogram and massogram data for the oxidation of pyrrole to form a polypyrrole film on a gold coated QCM Sensor Crystal. Seven cycles of voltammetry, between - 0.4 and 0.95 V were conducted in this experiment. Pyrrole monomer can be oxidized to its radical at 0.65 V. As this happens, a 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[31]. Some theoretical models[32], based on the simultaneous measurement of Δf and ΔR, 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[33].

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[34].*

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 specificity into the device. This usually involves the addition of a sensitive layer on the surface of the crystal[35].

Organic polymers comprise the most common type of coating used with QCM chemical sensors due to their capability to reversibly sorb vapors and liquids[36]. 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[37], as well as for the investigation and/or monitoring of biochemically significant processes.
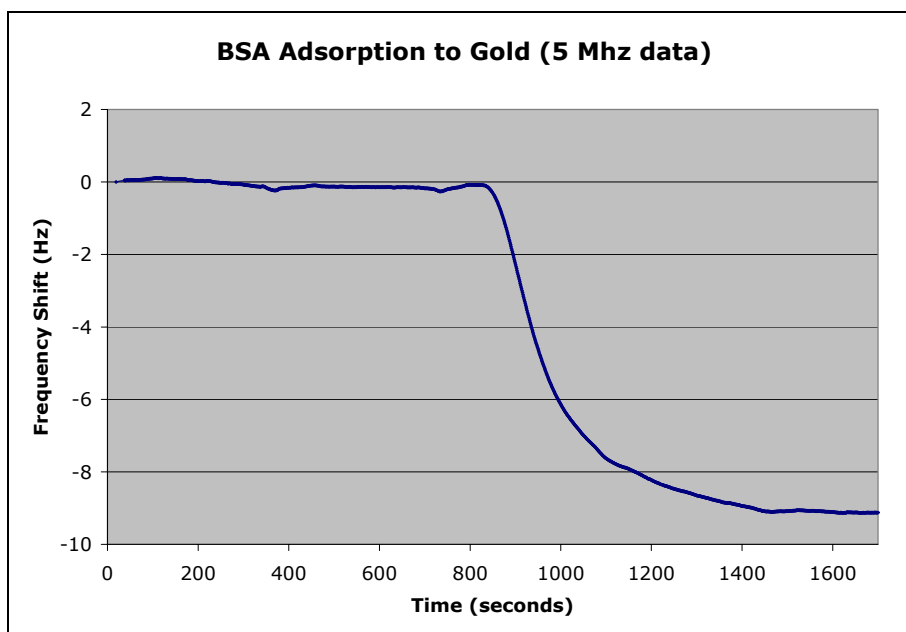
Figure 12. A 10μg/ml solution of BSA in 2mM NaCl is flowed over a polished Au/Cr QCM crystal in an axial flow cell at a rate of 50μL/min. Due to the non-specific adsorption of the protein, the frequency of oscillation decreases –9Hz over a period of 5 minutes. The sensitivity of the QCM100 for the detection of microgram quantities of proteins is clearly demonstrated by this very straightforward experiment.

An example of a complex and dynamic biochemical process which has been successfully studied with quartz crystal microbalances is the adsorption of proteins to solid surfaces [38]. Figure 12 is the result of a QCM experiment following the adsorption kinetics of bovine

serum albumin (BSA) from an aqueous saline solution on to a polished unmodified gold surface (i.e. physical adsorption). The adsorbed mass is small compared to the mass of the quartz crystal, evenly distributed and rigidly attached to the gold surface resulting in a frequency decrease of -9Hz proportional to the mass of protein adsorbed on the polished gold electrode. The sensitivity of the QCM100 for the detection of microgram quantities of proteins is clearly demonstrated by this very simple experiment.

Sensitive, selective detection of biochemically active compounds can be achieved by employing antigen-antibody[39], 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[40]. QCM studies have provided detailed information about the functionalized surfaces developed for a range of biochip and biosensor applications.

Antigen-Antibody Interaction (Bare Gold, 5 MHz)

Step 1. Antigen non-specific adsorption to bare gold.
Mouse Gamma Globulin
400 microg/mL

Step 2. Blocking of remaining non-specific sites.
Ovalbumin
1 mg/mL

Step 3. Antigen-Antibody specific binding.
Goat anti-mouse IgG
40 microg/mL
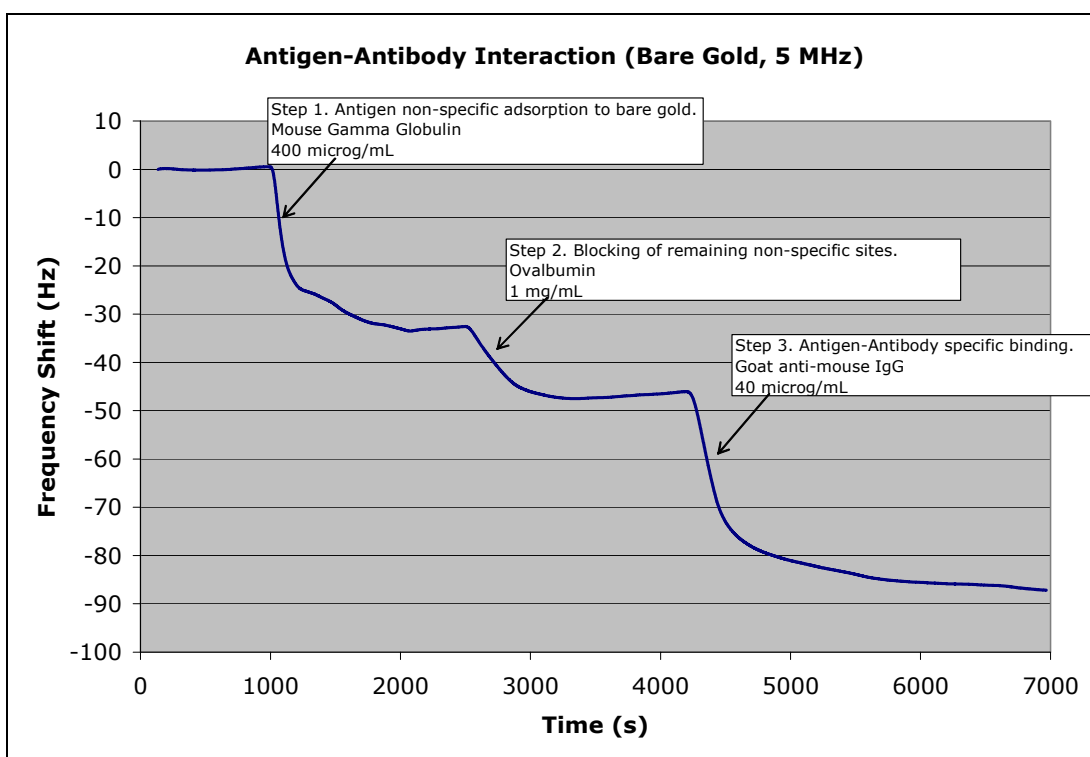
Figure 13. Antigen-antibody reaction monitored with a QCM100 system. This example shows the immobilization of mouse gamma globulin antigen on a bare gold surface (Step 1) and the subsequent binding of an antibody directed against the gamma globulin (Step 3). Since the gold surface is not completely covered by antigen in Step 1, a blocking solution of concentrated ovalbumin is used in Step 2 to block all uncovered sites.

Figure 13 is an example of an application of the QCM100 system as a protein biosensor and a demonstration of the sensitivity of the technology towards protein-protein interactions. The entire experiment took place on a polished Au/Cr QCM crystal housed within an axial flow cell connected to a standard flow injection analysis system consisting of a single syringe pump and a 6-port injection valve. Typical flow rates were 50 μL/min, temperature stability was +/-0.1°C at 27°C and the buffer solution was PBS pH7.5. Antigen (mouse gamma globulin) was first introduced into the cell (Step 1) resulting in a –35Hz frequency step caused by the non-specific metal-protein binding interactions between the protein and the bare gold surface (i.e. physical adsorption). The

remaining non-specific binding sites were then blocked with excess ovalbumin (Step 2) resulting in the second (and smaller) frequency step. Finally (Step 3), antibody (goat anti mouse IgG) was flowed over the immobilized protein layer and the specific interaction between antigen and antibody proteins resulted in the final –40Hz frequency step. The real advantage of the QCM technology in this application is that it is ***label free - the sample flowed over the immobilized surface layer does not need to be modified or labeled in any way***. Thus it is much more physiologically relevant because labeling something with a fluorescent probe (i.e. ELISA) often changes its properties. The ability to see changes in the QCM signal after every individual step provides an additional advantage over standard immunoassays such as ELISA, where no user feedback is available until the entire process is completed.

TIP
Using a QCM biosensor you cannot only tell whether something binds to a given protein immobilized on the crystal, but you can also tell how tightly it binds[41]- this is very useful additional information.

QCM Systems are applied routinely by biologists, immunologists and biochemists to obtain information about processes such as: (1) protein adsorption/desorption[42], (2) cell adhesion[43], (3) Protein-protein interaction, (4) Degradation of polymers, (5) biofouling and biofilm formation, (6) drug analysis[44], (7) self-assembled monolayers[45] and (8) DNA biosensors[46]. For more detailed information please consult the references listed at the end of this chapter.

Self-Assembled Monolayers

A self-assembled monolayer (SAM) is defined as a two-dimensional film, one molecule thick, covalently assembled at an interface. The classical example of a SAM is the reaction of alkanethiols with a gold surface.

Since sulfur donor atoms strongly coordinate on metal substrates (Au, Ag, Pt, etc), sulfur-containing molecules such as disulfides (R-SS-R), sulfides (R-S-R) and thiols[47] (RSH) can form various functionalized SAMs with highly organized and compact construction. For example, when a clean gold surface is immersed in an alkanethiol solution, the following self-assembly chemisorption reaction takes place:

$$\text{Au} + \text{RSH} \leftrightarrow \text{Au–SR} + 1/2\ \text{H}_2\uparrow$$

This reaction self terminates at one monolayer, when all accessible gold sites are consumed. The Langmuir adsorption model has been applied successfully to model the adsorption /desorption kinetics of these processeses.

The self-assembly of alkanethiol monolayers onto gold has been studied extensively due to the potential application of these interfaces to (1) chemical and biological sensing, (2) nano-and micro-device manufacturing and (3) surface modification.

A significant amount of work has been dedicated to understanding the steady-state properties of SAMs once they have formed. However, more recently it has become clear that alkanethiol SAMs are highly dynamic structures, and a lot of renewed effort has been dedicated to the understanding of the mechanism of monolayer formation[48].

The QCM100 system provides a unique opportunity to monitor, in-situ and in real-time, the rate of adsorption of alkanethiols onto gold - the change (i.e. decrease) in frequency resulting from the adsorption of alkanethiol molecules onto the gold electrode of a QCM crystal allows direct measurement of the rate of formation of SAMs.

Tip
Silanes are another common material used in SAMs[49]. Silanization has also been studied with QCMs using crystals with electrodes custom coated with thin layers of Si(111).

Several examples of direct measurement of adsorption kinetics of alkanethiolate SAMs on QCM crystals, from both gas and liquid phase, are included in the references list at the end of this chapter.
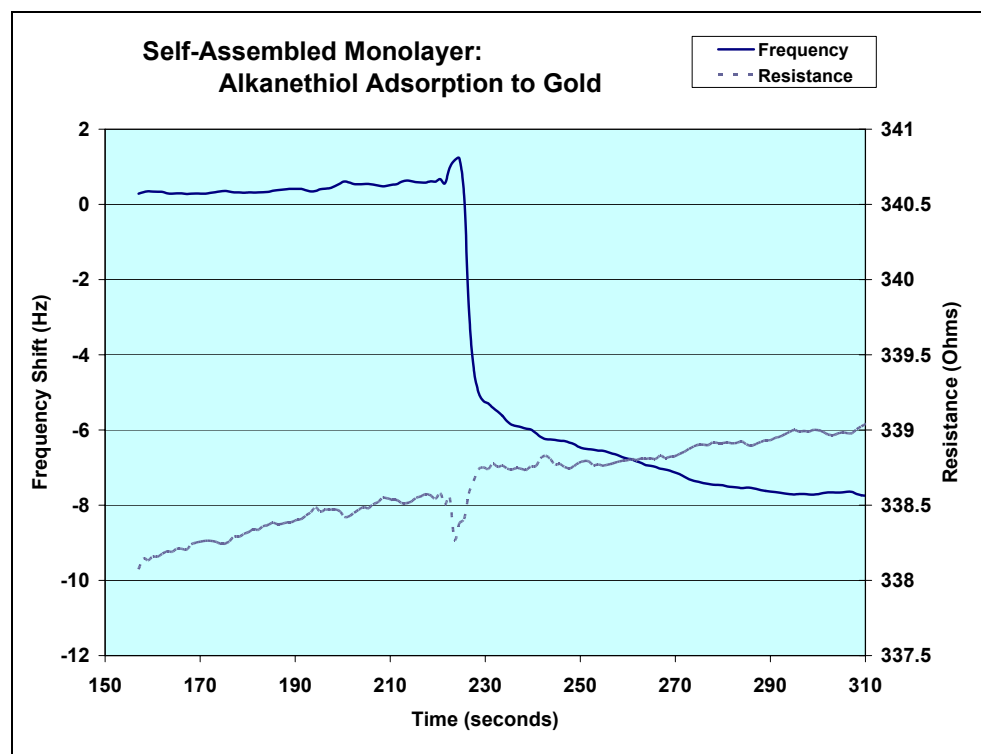
Figure 14. Raw QCM "Δf vs time" and "Resistance vs time" data for adsorption of $5 \cdot 10^{-5}$M 16-mercaptohexadecanoic acid from ethanol to bare gold.

Figure 14 is a graphical representation of the chemical adsorption kinetics of 16-mercaptohexadecanoic acid on to bare gold measured, in real time, with a QCM100 quartz crystal microbalance. In this simple experiment, a polished Au/Cr crystal (mounted on a standard holder) was immersed in 200 mL of ethanol housed inside a temperature stabilized 500mL beaker. The reaction was triggered by rapidly injecting 1mL of 10^{-2}M solution of 16-mercaptohexadecanoic acid, providing a diluted $5 \cdot 10^{-5}$M solution of alkanethiol to react with the bare gold.. A short transient in the frequency and resistance indicates the point of insertion of the thiol and is due to a slight temperature difference between the solvent and the sample solution. The fast drop in frequency following the injection is due to the fast formation of thiol-gold bonds, followed by a slower annealing process. The absence of a sharp positive step in the resistance verifies that the fast frequency drop is not due to a change in the viscosity of the solution. The results are in excellent agreement with the observations of Blanchard's group [50]

corresponding to the adsorption/desorption kinetics of thiols from hexane and under very similar experimental conditions.

Besides good mechanical and chemical properties, an additional advantage of SAMs is that they make it possible to tailor probe surfaces at the molecular level for the immobilization of specific biomolecules such as proteins[51] or DNA[52]. Several studies have reported significant improvement in detection limits when SAM immobilization is used to design immunosensor QCM probes[53].

Dissipation Technique

An alternative method[54] 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[55] have shown that as long as the effect of the parasitic capacitance (C_0) is properly cancelled (i.e. as easily accomplished with the QCM100), the results provided by the Dissipation Technique should be in good agreement with the measurements provided by the QCM100 System.

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[6] For example, from the Conductance Output of the QCM100.

[7] Conductance is the inverse of resistance: Conductance = 1/Resistance or Resistance = 1/Conductance. The units of resistance are Ohms [Ω = V/A] and the units of conductance are Siemens (S = A/V).

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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.

In This Chapter

Introduction

The standard sensor crystal used by the QCM100 System consists of a thin disk of 5 MHz, AT-cut, α-quartz with circular electrodes patterned on both sides.
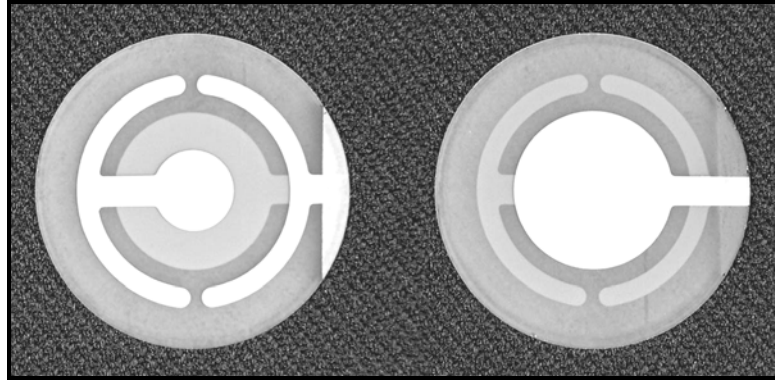
Figure 1. Standard 1 inch QCM sensor crystal. The crystal on the left shows the contact surface, while the one on the right shows the liquid surface.

Standard sensor crystals are 1 inch in diameter and are available with a variety of electrode materials.

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.

Table I: Standard 1 inch QCM Sensor Crystals					
SRS Part# (Qty 10 ea.)	**Frequency (MHz)**	**Material**	**Diam (inch)**	**Finish**	**Maxtek Part#**
O100RX1	5.0	Chrome/Gold	1.0	Polished	149211-1
O100RX2	5.0	Indium Tin Oxide	1.0	Transparent	N. A.
O100RX3	5.0	Titanium/Gold	1.0	Polished	149238-1
O100RX4	5.0	Titanium/Platinum	1.0	Polished	149240-1

Principle of Operation

AT-cut quartz crystals are most commonly used as QCM sensors because of their superior mechanical and piezoelectric properties[1], 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[2],

- a contacting Newtonian fluid[3],

- a viscoelastic layer of finite thickness[4].

Frequency

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

Operation at 5 MHz is regarded as optimal for laboratory use since it provides (1) acceptable (submonolayer) sensitivity, (2) robustness (331 µm crystal thickness), and (3) stable oscillation in most viscous media.

Geometry

Figure 1 shows a top and bottom view of a standard 1inch 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 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[5] or ≈ 0.40 cm^2.

All standard 1 inch QCM sensor crystals are planar, with both faces parallel to within 1 µm. Crystal thickness is 331 µm 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[6].

Surface Finish

Electrode surface roughness can cause large apparent mass loadings due to the liquid that is trapped within pores at the crystal surface[7]. 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 QCM100 1 inch sensor crystals are available in two finishes - unpolished ($\approx$ 3 μm average surface roughness, typical) or polished (optically clear, $\approx$ 50 Å average surface roughness, typical).

Rough surfaces are popular because they are less expensive and provide enhanced surface area. 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[8].

Tip
For liquid-phase applications, optically polished crystals are required[9] if crystal-to-crystal reproducibility is to be expected.

A water Immersion Test (refer to Chapter 2) usually provides a quick-and-easy way to test the quality of a crystal finish for liquid-QCM applications.

Electrode Materials

Gold electrodes (100-1000 nm thick) are the most commonly used in QCM applications 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 is recommended as a substitute 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).

A zinc layer, sandwiched between the adhesion layer and the electrode pad on the front or deposition side of the crystal has a relatively low bulk modulus, and has been shown to absorb stress imposed by the deposited materials. The buffer layer prolongs useful crystal life, particularly when depositing dielectric materials. The crystal should have a modest surface roughness as keying-in structure. The buffer layer can be a zinc layer of 600 nm

sandwiched between a titanium or chromium adhesion layer of 10 to 16 nm and a gold, silver, or aluminum outer electrode layer of about 200 nm[10].

For applications requiring transparent electrodes, tin-doped indium oxide (ITO) electrodes are recommended. ITO is routinely used to make transparent conductive coatings which are applied in a wide variety of applications. Transparent electrodes are often used in cell adhesion studies when visualization of the sample cells is required during the experiments. ITO coated QCM crystals can be special-ordered directly from Stanford Research Systems or through your local SRS representative.

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[11]. 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 573ºC, above which α-quartz looses 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^2 range with a wide dynamic range extending into the 100 μg/cm^2 range.

Sauerbrey[12] 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

Δf = the observed frequency change in Hz,

Δm = the change in mass per unit area, in g/cm^2,

C_f = the sensitivity factor for the crystal (56.6 Hz μg^{-1}cm^2 for a 5 MHz crystal at room temperature).

The minimum detectable mass change is typically a few ng/cm^2 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 0.18 ng/cm^2 should be expected from a QCM system with a 0.01 Hz frequency measurement resolution. As a comparison, consider that a monolayer of a 20Kda protein (100% coverage) adsorbed on a QCM crystal amounts to roughly 10Hz frequency shift, or 180 ng/cm2.

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, rigid, thin-film deposits originating from a low pressure (i.e. vacuum) gas environment[13]. 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 presented simple ways to calibrate the mass sensitivity of QCMs for electrochemical applications[14] and for vacuum thin-film deposition processes[15] and some useful calibration guidelines were also included in Chapter 2 of this manual.

There is ample evidence supporting a Gaussian mass sensitivity distribution for AT-cut crystals[16], 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. In order to assure reproducibility of results, it is very important to assure uniform coverage of the electrodes during measurements.

There are also situations in which the QCM does not act as a microbalance at all, but responds instead to properties such as viscosity[17] and/or elasticity[18] of the liquid or film in contact with its surface.

Maximum Loads

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

The maximum load on a crystal is limited by two factors: (1) total damping or (2) lost sensitivity. For highly viscous or solid materials, the damping of the crystal increases with increasing layer thickness. At a certain thickness (usually a couple of micrometers) the damping becomes so high that the crystal can no longer be driven, i.e. the measurement fails due to lack of oscillation. More elastic materials do not couple completely to the crystal's oscillation. With increasing layer thickness the outermost parts of the attached layer will couple weakly and at a certain thickness (usually a few micrometers) it is lost completely. Oscillation is still detected, and a frequency is still measured, but the equipment can only sense the part of the layer in the vicinity of the crystal[19].

Useful Life

Sensor crystals are often reusable several times. However, reusing a crystal requires careful handling and cleaning procedures that do not harm the quartz material, its electrode pads and its coatings. Many practitioners, consider their QCM crystals expendable, and always discard them at the end of their measurements[20].

Traces of consumption and wear can often be detected visually:

- Edges of the sensor crystal might become cracked and the coating start to show scratches and holes.

- In electrochemistry experiments it is not unusual to observe changes in the adhesion layer of the liquid surface electrode which ultimately result in peeling of the metal pad). A common problem is loss of the Cr adhesion layer in Au/Cr electrodes. Tip: these changes are visible from the contact side of the crystal.

- The liquid surface electrode might become irreversibly discolored or stained from chemical reaction with the analytes, buffers or solvent.

When a crystal is close to being consumed, the measurement signal will become noisy, possibly even shaky. 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[21]. When this occurs, the circuit may occasionally resonate at one of the anharmonic frequencies. The oscillation may switch to an anharmonic mode, or it may alternate between the fundamental and anharmonic frequencies, a condition known as mode hopping. 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[22] are often recommended instead. Crystals exposed to etching solutions (i.e. Piranha solution) usually need to be replaced after two to three experiments.

Film stress can be particularly damaging. Stress can bend the crystal and induce a frequency change not related to mass. It can cause the electrode to tear from the quartz and, in the worst case, it can even cause the quartz itself to fracture [23].

Temperature effects

The intrinsic dependence of the resonant frequency of a quartz crystal on temperature is well known and generally quite small [24]. In fact, the AT-cut quartz crystals commonly used in QCM experiments owe their popularity to their near zero temperature coefficient

at room temperature. As a result, the intrinsic temperature dependence of the QCM sensor crystals is negligible at or around room temperature ($\approx$ 1-3 Hz/°C) and is generally ignored for monolayer adsorption/desorption processes in the gas phase.

A thermal effect less often discussed in connection with quartz crystal oscillators is based on the fact that dynamic changes in temperature around a crystal unit can produce thermal gradients which induce frequency transients dependent on the rate of temperature change[25] around the sensor. The static frequency vs. temperature characteristic is modified by this thermal-transient effect resulting from the thermal-gradient-induced stresses[26]. Proper thermal compensation requires consideration of both static and dynamic (i.e. rate-of-change) frequency-temperature behavior of the QCM crystals.

Larger changes in frequency with temperature should be expected 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 Hz/ °C (and 4Ω/°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°C, and preferably better. 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 liquid 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[27] - the dependence of resonator frequency at a specific temperature on its prior temperature history. For example, it is often observed that the "frequency vs Temperature" curve obtained going from T1 to T2 will not coincide with the one obtained immediately after going from T2 to T1. The causes of hysteresis and retrace are not well understood; the experimental evidence to date is inconclusive. The mechanisms that can cause these effects include strain changes, changes in the quartz, contamination redistribution in the crystal enclosure, and apparent hysteresis or retrace due to thermal gradients.

In electrochemical experiments temperature control is often required to control reaction rates and is typically achieved with temperature controlled baths and jacketed cells.

Tight temperature control is necessary for QCM measurements involving protein adsorption, protein-protein interaction, immunosensor development, self-asembled monolayers, Langmuir films and DNA hybridization studies. Temperature stabilization better than +/-0.05°C is generally required to eliminate temperature related transients and drifts in lengthy measurements. This level of temperature control is particularly important if small series resonance resistance changes need to be detected and measured.

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. The table below summarizes some of the most relevant static temperature coefficients for 5MHz QCM crystals around room temperature.

Tip

Whenever practical, the use of flow cells is recommend for both gas and liquid studies to minimize temperature transient effects. Temperature stabilization better than +/-0.05°C is generally required to eliminate temperature related transients and drifts in lengthy measurements.

The table below compiles some very important temperature coefficients:

Temperature coefficient in air	+/- 1-3 Hz/°C
Temperature coefficient in water	8Hz/°C
	- 4Ω/°C

Crystal Handling

Note

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

- Keep the crystals in a clean and dry place. When not in use store them in their original box and wrapper.

- Avoid touching the metal electrodes of the crystal.

- Rinse only with deionized water, or another appropriate residue-free solvent, before drying the crystal.

- Always use a flow of dry, oil-free, inert gas (e.g., nitrogen) to blow-dry the crystal. It is better to blow the liquid off the crystal than to let it evaporate on the electrodes.

- Do not handle the sensor crystal using bare fingers. Hold the sensor crystal with tweezers and only from its outer edge (i.e. outside the electrode area) to prevent scratches. The tweezers should have smooth gripping surfaces and preferably be made out of soft plastic material.

- Before starting a surface cleaning confirm that the crystal material will not be damaged by the cleaning solutions. Perform a test run on a discarded or practice crystal whenever possible.

Cleaning

The surface properties of the sensor crystal determine the interaction of sample material with the surface. Therefore, the development of proper protocols for surface preparation and cleaning are required to obtain reproducible measurements. This section provides the basic information you need to develop a cleaning protocol suitable for 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 the measurements. The counter electrode and electrical contacts for the electrodes are on the Contact Surface of the crystal in the leak-poof 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 all exposed quartz surfaces***.

Tip

A Crystal Cleaning Basket (SRS Part# O100CCB described at the end of this chapter) is available directly from Stanford Research Systems. This accessory makes cleaning and

surface modification treatment of the standard 1" QCM crystals very safe and easy. The cleaning basket holds four crystals, is made entirely of Teflon ® and it is specifically designed for immersion into a 100mL beaker.

Several cleaning procedures are described below which can be used as guidelines to develop your own. Proper crystal handling practices must be used throughout any cleaning process.

General Purpose

For general purpose applications such as electrochemistry, liquid and 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.

Hydrocarbon contaminants

UV/ozone treatment[28], CO_2 snow cleaning[29] and plasma cleaning[30] are some low cost and very efficient methods used for cleaning hydrocarbon impurities adsorbed from the ambient air. Neither method affects the quartz/gold surfaces. They are both often applied to components used in high vacuum environments.

Biomaterials
(lipids, proteins and similar biomolecules)

Step 1. Treat the crystal in a UV/ozone or plasma cleaning chamber for 10 minutes

Step 2. Immerse the crystal 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[31].

Step 3. Immediately rinse with deionized water and dry with nitrogen gas.

Step 4. Treat the crystal again with UV/ozone for 10 minutes immediately before measurement (this removes any remaining surface contaminants.)

Lipid vesicles

Step 1. Treat the crystal in a UV/ozone or plasma cleaning chamber for 10 minutes

Step 2. Immerse the crystal into water with 2% of sodium dodecyl sulfate (SDS) at room temperature for 30 minutes[32].

Step 3. Immediately rinse with deionized water and blow dry with nitrogen gas.

Step 4. Treat the crystal again with UV/ozone for 10 minutes immediately before measurement (this removes any remaining surface contaminants.)

Self-assembled Monolayers

It is common practice to wash crystals with piranha solution at the end of a QCM immunoassay. Piranha solution is also often used to precondition the crystals for a SAM deposition.

Step 1. Treat the crystal(s) with piranha solution for three minutes.

Steps 2 and 3. Repeat treatment 2 more times with fresh piranha solution.

Step 4. Rinse liberally with deionized water and dry in a gentle flow of nitrogen gas.

<u>**Piranha Solution**</u>: Piranha solutions are used to remove organic residues from substrates, particularly in microfabrication labs. The traditional piranha solution is a 3:1 mixture of sulfuric acid and 30% hydrogen peroxide. The solution may be mixed before application or prepared on the sample, applying the sulfuric acid first, followed by the peroxide.

Warnings

- *Piranha solutions are extremely reactive and may result in explosion or skin burns if not handled with extreme caution*.
    - **Prepare the smallest possible volume**. Tip: Some QCM users mix the cleaning solution on the crystal surface, pipetting the proper ratio of sulfuric acid and hydrogen peroxide directly on the liquid surface electrode of the quartz resonator.
    - **Do not expose the crystal holder to Piranha solution**. Wash separately.
    - Wear gloves, goggles and a lab coat.
    - Work in a fume hood.
    - The mixture of hydrogen peroxide and sulfuric acid is very exothermic. Do not touch the glassware after mixing- HOT! (up to 120°C)
    - Use heat resistant glassware. This mixture can get really hot and shutter non-thermal graded glass!
    - Rinse thoroughly.
    - Keep the etching solution away from organic solvents.
    - Treat with very healthy respect
    - Properly clean and dispose of all chemicals.
    - Consider safer alternatives compatible with your application.
    - If not sure how to proceed, STOP and seek help from an experienced chemist!
- Prolonged exposure to Piranha solution damages QCM crystals. The failure mechanism is believed to involve chemical degradation of the Cr bonding layer located between the quartz and the gold electrode. Typically, a QCM crystal can be exposed to Piranha solution a maximum of three times before noticeable degradation of performance occurs. The first signs of crystal degradation are reduced stability in the frequency baseline[33].

Polystyrene removal

Step 1. Immerse the crystal into a 1:1 solution of hexane and deionized water and treat it in an ultrasonic bath for 1 minute.

Step 2. Rinse thoroughly with deionized water and blow dry with nitrogen gas.

Crystal rinsing

Rinse sensor crystals with deonized 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 underneath to prevent transferring contaminants from the tweezers onto the crystal. This is generally most critical in biological applications.

2. Blow the remaining liquid off the crystal with a gentle flow of nitrogen gas.

3. Use a clean, lint-free cloth to wick off any liquid remaining on the edge of the crystal.

Surface Modifications

The biggest drawback of the QCM sensor 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 chance of experiencing interferences. This issue has been 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 (i.e. a coating) applied to the surface of the crystal[34].

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.

In biosensor research, the chemical stability of the sensor substrate often limits the quality of the data generated. The continuous oxidation of metal electrodes can make it very difficult to reach a drift-free signal baseline in aqueous media. Polyimide, polystyrene and PVC are amongst the polymeric materials recommended to protect QCM devices.

Tip

A Crystal Cleaning Basket (SRS Part# O100CCB described at the end of this chapter) is available directly from Stanford Research Systems. This accessory makes cleaning and surface modification treatment of the standard 1" QCM crystals very safe and easy. The cleaning basket holds four crystals, is made entirely of Teflon ® and it is specifically designed for immersion into a 100mL beaker.

Several examples of surface modification techniques are described below. While not exhaustive, they may serve as useful guidelines while developing your own protocols.

Sputtering or evaporation

Thin films (i.e. nm thickness) of metals or metal oxides are commonly deposited by sputtering or evaporation. To obtain reproducible results careful attention must be paid to cleanliness, 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.

Spin-coating

Spin-coating[35] is a technique by which very thin polymeric films (nm to   m thickness) are deposited onto a solid substrate[36].

To fabricate thin polymer films, the polymer material is first dissolved in a volatile solvent. If a drop of solution is placed on a substrate, it can flow to form a metastable, continuous film or form a droplet on the surface, depending on the "wettability" of the substrate. By spinning the substrate, the droplet is forced to spread out while the solvent evaporates. If deposition conditions such as choice of solvent, solution concentration and

spin-speed are chosen carefully, a thin film of uniform thickness is deposited on the substrate.

Polystyrene is a common material spin-coated onto QCM sensor crystals. Toulene is the solvent of choice. UV/Ozone treatment can be used to tailor the hydrophobicity of organic polymeric coatings[37].

Compact and easy-to-use laboratory spin-coaters, compatible with QCM crystals, are commercially available. Consult the factory for recommendations.

Langmuir-Blodgett films

Langmuir-Blodgett films (LBFs) are artificial structures prepared by sequential transfer of monomolecular layers (one molecule thick), performed on a liquid surface (usually H_2O), onto a solid substrate (such as a glass slide or a silicon wafer). LBFs are very thin and very well ordered. This technology is attractive to researchers because of its ability to produce thin films (1) whose thicknesses can be precisely varied and (2) which can be modified to produce smart sensing devices.[38].

Self-assembled monolayers (SAM)

Self -assembled monolayer (SAM) techniques offer a new strategy for the immoblization of antibodies, antigens and DNA on the surface of quartz crystal electrodes[39].

SAMs can be deposited on gold or silver electrodes by *thiolization*. Since sulfur donor atoms strongly coordinate on metal substrates (Au, Ag, Pt, etc), sulfur containing molecules such as disulfides (R-SS-R), sulfides (R-S-R) and thiols[40] can form various functionalized SAMs with highly organized and compact construction. Besides good mechanical and chemical properties, an additional advantage of SAMs is that they make it possible to tailor electrode surfaces at the molecular level for the immobilization of specific biomolecules such as proteins or DNA[41].

Tip
Thiolization agents specifically designed for SAM immobilization of proteins and DNA on metallic surfaces have recently become commercially available. Consult the factory for up-to-date recommendations.

A silane layer (silanization) is another common material used for SAMs[42]. However, since the coating can react irreversibly with the quartz material, the QCM crystal cannot be used repeatedly in this application.

SAMs vs. Polymer films: Most conventional methods used for the development of QCM immunosensors have relied heavily on polymeric coatings deposited on the electrodes and capable of forming hydrophobic or covalent bonds with antibodies. Polymeric films suffer of several disadvantages: (1) polymer films attach to the electrode surface through weak hydrophobic bonds which can be easily broken by mechanical interaction, washing, and even changes in pH, (2) swelling of the polymer films in aqueous solution can lead to reduced sensitivity and reproducibility of the immunosensor.

Electroless Deposition Pre-treatment

QCMs are used to measure (1) plating rates and thicknesses in both electrolytic and electroless baths, (2) plating efficiencies in electrolytic baths and (3) etching rates in chemical etching processes. It is important to assure that the Sensor Crystal is properly preconditioned during the electroless[43] deposition of metals. Plating initiation must be complete, and the crystal must be in close proximity to 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 prescribed in some cases. It is recommended not to expose the entire Crystal Holder to catalysis during pre-treatment, to avoid excessive metallization of the holder during deposition.

Crystal Holder

Description

The standard Crystal Holder, bundled with the QCM100 system, is specifically designed to provide users with a rugged, compact and easy-to-use sensor crystal housing for QCM experiments in air or liquids.
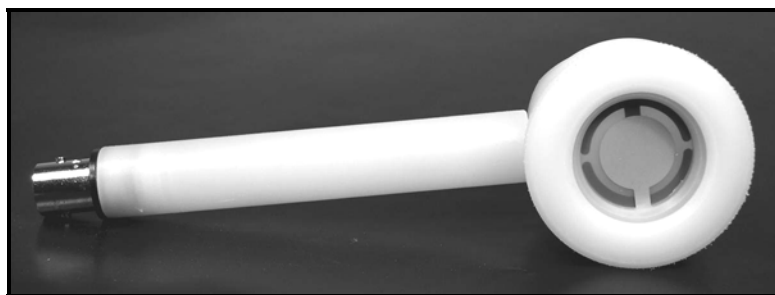
Figure 2. The Crystal Holder with a 1 inch sensor crystal mounted.

Its main features include:

- rugged design[44]

- 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[45] (for compatibility with electrochemical QCM measurements)

- chemical resistance: Kynar[®46] material with Viton O-rings

- broad temperature range: -25ºC to 110ºC

- 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 adapters available (SRS Part# O100FC and O100AFC)

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.

Head Cleaning

It is not uncommon for crystals to break or for oring seals to leak during normal operation. If chemical leakage into the crystal cavity is suspected, it is very important to act fast and rinse the cavity, the POGO® contacts and the POGO® contact sockets to remove any traces of solution that might lead to damage of the holder.

Start by removing the crystal from the Crystal Holder and exposing the POGO® pins. Putting your thumbnail (or the flat head of a jeweler screwdriver) under the POGO® head pull firmly up to remove each contact pin from its socket. Rinse the pins and the sockets with deionized water to remove all traces of chemicals. Repalce the POGO® pins with new ones if necessary.

Keep in mind that 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 specially true in electrochemical applications where oxidizing acids are often components of the liquid solution in contact with the crystal.

Crystal Cleaning Basket

A Crystal Cleaning Basket (SRS Part# O100CCB) is available directly from Stanford Research Systems. This accessory makes cleaning and surface modification treatment of the standard 1" QCM crystals very safe and easy. The cleaning basket is shown in Figure 3, it holds four crystals, is made entirely of Teflon ® and it is specifically designed for immersion into a 100mL beaker.
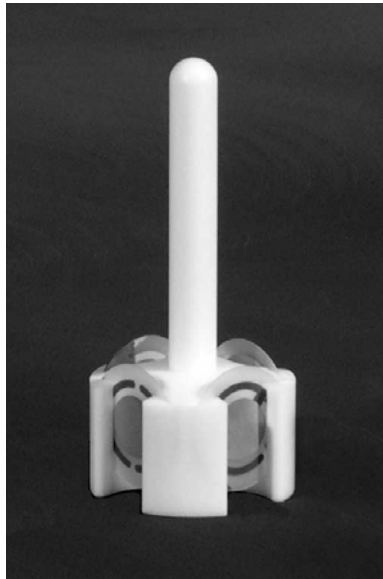
Figure 3. Crystal Cleaning Basket – SRS Part# O100CCB. The entire basket is made out of Teflon and is shown here holding its maximum load of 4 crystals (not included).

Tips for Operation in Liquids

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

For reproducible measurements, keep the following tips in mind.

Check for Chemical Compatibility

Before starting an experiment check for chemical compatibility between sample solutions, solvents, holder, flow cell, orings and crystals. For example, avoid contact between Viton® orings and DMSO solvent. If necessary consider replacing incompatible components with alternative materials.

Check the POGO contacts regularly

It is good practice to check the POGO contacts regularly for signs of corrosion and wear. Replace the pins with new ones if necessary (see "Head Cleaning" above).

Degas the sample liquid.

Whenever possible, sample liquids should be degassed to avoid the growth of air bubbles on the surface of immersed crystals.

Presoak the crystal in the sample liquid.

To minimize long-term (i.e. hours long) signal drift it is best to immerse the quartz crystal, premounted on its holder, in the sample solution several hours before measurements are started.

Temperature-independent frequency drifts as large as 10 Hz, and resistance drifts as large 2 ohms, are to be expected over a 24hr period even in the purest deionized water bath. Long term drifts have many different origins including chemical interaction between the liquid and the electrodes, swelling of the orings, diffusion of liquid into the quartz, changes in coatings, etc.

In flowing systems, expose the crystal to the carrier solution for as long as practically possible prior to sample injection.

Wait for the temperature to stabilize.

To avoid the generation of air bubbles and reduce temperature related signal changes, the sample liquid should be at approximately the same temperature as the sensor/holder and the entire experimental setup should be temperature stabilized.

 The generation of air bubbles is facilitated when the temperature of the liquid is lower than that of the holder/flow cell. Avoid temperature differences greater than 2°C between the sample liquid and the crystal holder.

Keep in mind that frequency readings are not just affected by the static temperature, but also by the rate of change of temperature around the sensor. This is very important during the implementation of temperature compensation or stabilization schemes. For example, PI, PID and Fuzzy Logic stabilized temperature controllers are recommended instead of On-Off controllers for temperature stabilization.

To ensure signal stability for flowrates greater than ≈0.2 mL/min use external temperature stabilization (as necessary) to make sure that the sample liquid is temperature equilibrated prior to flowing into a flow chamber. Immersing the flow cell/crystal holder in a water bath and running the sample fluid through the same bath (i.e. heating loop) prior to entering the QCM chamber is a simple way to assure temperature equalization between the holder and its liquid sample solutions.

Prepare your solutions carefully

To avoid unwanted effects due to changes in the properties of the carrier/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 each measurement series.

Avoid mechanical vibrations

Keep the sensor away from mechanical equipment containing motors or similar vibrating parts. Fasten all dangling cables that might transfer vibrations to the crystal holder/flow cell.

Avoid transients

Avoid sudden mechanical stresses such as knocking on the crystal holder, pulling on cables, sudden shifts in the experimental setup, etc.

Avoid sudden temperature changes. In AT-cut quartz crystals, frequency fluctuations depend not only on the T but also on the rate of change of T.

Avoid sudden pressure changes such as pressure transients in gas flow systems or flowrate changes in liquid flow injection systems. Whenever possible replace peristaltic pumps with Syphon setups or syringe pumps.

Relax mechanical stress

It is often a good practice to tap on the holder/flow cell before starting a new set of measurements. Gentle tapping helps to dislodge trapped bubbles and relaxes mechanical stresses at the oring seats resulting in reduced drift problems.

Wait for the signal to stabilize after liquid exchange

In flowing setups it is important to keep in mind that detectable signal transients are to be expected after sudden changes in flow rates and after liquid exchanges (i.e. new sample injections). Flow transients can last less several seconds and can seriously compromise your long-term measurements if bubbles are introduced into the flow stream, or large temperature differences between the liquid and the holder are established.

Use small and constant flow rates

During liquid flow experiments, flowrates should be kept small and constant to eliminate signal transients due to pressure and temperature fluctuations. Recommended flow rates should be below 0.2 mL/min to assure minimal transients and flow-induced noise in the frequency measurements.

Rely on gravity, the Syphon principle or syringe pumps to flow liquids through a cell in Open-Flow Systems whenever possible. If necessary, use Flow Injection Analysis (FIA) compatible pumps and high-quality injection ports to flow sample and carriers over the

crystal. Syringe based injection analysis systems often produce cleaner baselines because of the absence of noise transients induced by peristaltic pumps.

Persitaltic pumps are suitable for flow measurements in closed systems but they always add noise to the signal. A capillary tube located between the chamber outlet and the pump is often recommended to reduce noise caused by pressure fluctuations induced by the pump. Pulse-dampening modules, located between the pump and the crystal, are often used in Flow Injection Analysis setups[47] although noise reduction is not always as good as expected.

In order to avoid excessive stress to the crystal and leaks over the oring selas, flowrates should not exceed 5mL/min under any circumstances. External temperature (i.e. heating loop) stabilization of the liquid samples is recommended for flow rates above 0.2 mL/min.

Do not tighten the crystal retainer during experiments
Tightening of the crystal retainer will exert additional stress on the crystal and change its frequency of oscillation. Tighten the retainer at the beginning of an experiment and do not touch it again until all measurements are finished. Orings often swell when coming in contact with liquids and that can contribute additional drift in the frequency when immersing a crystal holder in a new liquid.

Dry QCM crystals carefully
A common trick used to eliminate residual water from QCM crystals that need to be immersed in dry organic solvents is to rinse the cleaned/dried QCM crystals with tetrahydrofurane (THF) before immersion followed by drying in a flow of dry nitrogen.

Tips for Operation in Gases

To minimize errors in QCM measurements, all gas-phase experiments (i.e. gas sensor development) should be designed carefully. Changes in temperature, flow-rates and gas pressure will adversely affect QCM measurements.

For reproducible measurements, keep the following tips in mind.

Check for Chemical Compatibility
Before starting an experiment check for chemical compatibility between the sample gases, holder, flow cell, orings and crystals. If necessary consider replacing components with alternative materials..

Operate in a flowing gas configuration
In order to avoid frequency transients due to sudden air movements around the crystal, operate the QCM sensor in a flowing gas configuration. Frequency transients as large as 10 Hz can be registered by simply walking past a QCM crystal fully exposed to air.

Operation within a flow cell also facilitates achieving proper temperature equalization between the crystal and the gas sample.

Wait for the temperature to stabilize

In order to avoid frequency transients due to temperature changes it is best to temperature stabilize the flow cell/crystal holder and eliminate temperature differences between the gas samples and the holder. Immersion in a temperature-stabilized water bath often does the job, and allows to set up a preheating loop to equalize the gas temperature with the sensor. Keep in mind that changes in frequency are not only related to static changes in temperature around the crystal, but also to the rate of change of temperature with time.

Use small and constant flow rates
During flow experiments, flowrates should be kept small and constant to eliminate signal transients due to pressure and temperature fluctuations.

Control humidity if necessary
Adjustment of the humidity is often a requirement for accurate gas phase measurements. It is generally recommended to adjust/control the humidity of the gas before flowing into the measurement chamber. A common procedure consists of exposing the gas to saturated salt solutions with well known humidity values [48].

Bubbles and Liquid Flow Cells

Eliminating gas bubbles trapped inside flow cell chambers is essential for accurate long-term QCM measurements. The highest risk of bubble formation is when liquid enters an empty chamber. Bubbles can also form spontaneously if liquids are not previously degassed and the chamber temperature is greater ($\Delta T > 2°C$) than the liquid temperature.

This section describes some simple tricks known to effectively prevent and remove bubble trapping in flowing QCM systems and also presents some of the common indicators used to detect the presence of bubbles in liquid flow chambers.

Eliminating dissolved gases from all sample solutions is the most basic precaution recommended for the minimization of bubble trapping. Commercially available online degassing stages and bubble traps are recommended for flow injection analysis setups.

When filling an empty chamber with a syringe pump for the first time the following procedure generally works very well to displace all trapped bubbles: Connect a >3mL syringe, loaded with the solution you wish to inject into the QCM chamber, to the inlet port of the flow cell. Connect the outlet port to the body of a 3mL syringe with its plunger removed and mounted vertically to act as a waste collector. Push about 1-2mL of solution through the chamber into the waste container. Press the syringe back and forth a few times until no more bubbles are seen to evolve into the waste container. The number of bubbles will decrease after each back and forth action until no more bubbles are visible. Flow reversals are very efficient at displacing bubbles out of the chamber.

For Syphon systems (see Figure 4) a similar method can be employed to remove bubbles from a freshly filled chamber: In this case the sample reservoir, with the sample solution, is connected to the inlet port and a 3-5 mL syringe, loaded with >2 mL of the same sample, is connected to the output port. Pull the syringe plunger up to (1) force liquid into the chamber and (2) eliminate the bubbles formed from the fresh syringe connection. Press the syringe back and forth a few times until no more bubbles evolve into the sample reservoir. Stop the flow at the inlet and disconnect the syringe when no more bubbles are seen.

It is generally preferable to position the output port above the inlet port in flowing systems. Fewer bubbles are generally trapped if the chamber is filled slowly from the bottom up, with the output port being the last section of the internal chamber to come in contact with liquid.
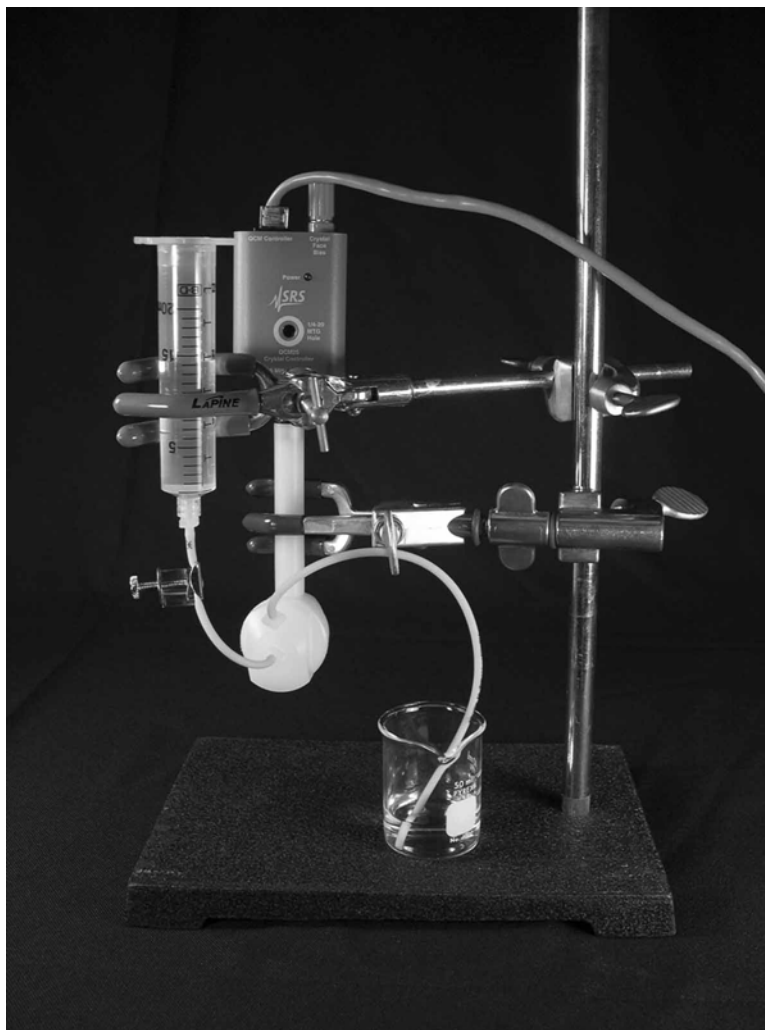
Figure 4. Simple Syphon setup with axial flow cell, syringe-body sample reservoir and flow clamp.

The presence or relocation of bubbles on the surface of a crystal is generally detected by paying careful attention to the frequency and resistance readings from the sensor. Bubbles displace liquid from the surface of the QCM crystal resulting in increased frequency and reduced resistance readings. Tapping gently on a flow cell with a hard object can change the number or location of bubbles- if a sharp and opposite sudden shift in frequency and resistance readings is observed, the presence of trapped bubbles must be suspected.

It is sometimes possible to infer the presence of bubbles if the frequency and resistance of the crystal are premeasured by direct immersion of the holder/crystal into the same

sample solution used in the flow setup. Resistance values significantly smaller than the immersion results should prompt the presence of trapped bubbles within the flow chamber.

Temperature stabilization usually requires immersion of the flow cell into a constant temperature liquid bath. In many cases the liquid bath is operated above room temperature. If the flowrates are high (i.e. greater than 0.2mL/min) or the temperature of the bath is far away from the temperature of the sample liquid (i.e. $\Delta T > +2°C$), external thermal equilibration of the sample fluid is recommended. A common trick is to add a temperature equalization loop, immersed in the liquid bath, between the sample container and the flow cell to provide complete equalization.

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[46] Kynar® polyvinilidene 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.atofinachemicals.com.

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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.

In This Chapter

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 Ω output resistance of U1 plus R12 (49.9 Ω) plus the crystal's resistance (0-4 kΩ) and terminated into R17 (49.9 Ω). 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 Vpp provided that the crystal's series resistance is less than 4 kΩ. Dry crystals have about 10 Ω of resistance at series resonance while crystals with one face in water have about 400 Ω 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 3.5x-5.2x 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_{cond} vs. $R_{crystal}$ characteristic.

The output of U4 drives a 5th 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, Vc, at pin 5. The gain is equal to (45-50xVc) (dB), where Vc is between 0 and 1 Vdc. Increasing Vc decreases the amplifier gain. The SLD output current on pin 6 will ramp Vc 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 5x, 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_{cond} vs. $R_{crystal}$ 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 2.5x before being output on the front panel V_{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 Ω) 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 Ω) which drive the output BNC via the balun, T1. The output has a 50 Ω 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 1x. (The gain of 1x is with respect to the AGC voltage in the QCM25. One needs to be aware that the QCM25 has a source resistance of 2x1 kΩ 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 $V_{cond} > 2.0$, which corresponds to crystal with a resistance of less than 4 kΩ.

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_{cond} BNC output is driven by the second filter via a 1 kΩ resistor. Together, these filters provide a gain of 2.5x for the AGC signal from the QCM25. The gain is adjusted at the factory by setting P1.

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 though 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 ±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 ±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 ±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**x** the varactor hold voltage. The resistive divider, R20-R23, provides 1.00**x** and 0.95**x** the varactor hold voltage. When in the HOLD mode, the multiplexer sends the 1.00**x** tap to the varactor via the output filter/buffer, U8B. When in the ADJUST mode, the multiplexer switches between the 1.05**x** and 0.95**x** taps at 75 Hz. This 75 Hz offset square wave is filtered by the output filter/buffer to produce an offset and 90° 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 100x 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 1x and 100x 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 16x 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.

Chapter 5

QCM Parts List

QCM100 Parts List

REF.	SRS PART	VALUE	DESCRIPTION
C 1	5-00318-569	2.2U/T35	Cap, Tantalum, SMT (all case sizes)
C 2	5-00318-569	2.2U/T35	Cap, Tantalum, SMT (all case sizes)
C 3	5-00318-569	2.2U/T35	Cap, Tantalum, SMT (all case sizes)
C 4	5-00299-568	.1U	Cap, Ceramic 50V SMT (1206) +/-10% X7R
C 5	5-00372-552	56P	Capacitor, Chip (SMT1206), 50V, 5%, NPO
C 6	5-00363-552	10P	Capacitor, Chip (SMT1206), 50V, 5%, NPO
C 7	5-00299-568	.1U	Cap, Ceramic 50V SMT (1206) +/-10% X7R
C 8	5-00299-568	.1U	Cap, Ceramic 50V SMT (1206) +/-10% X7R
C 9	5-00299-568	.1U	Cap, Ceramic 50V SMT (1206) +/-10% X7R
C 10	5-00299-568	.1U	Cap, Ceramic 50V SMT (1206) +/-10% X7R
C 11	5-00299-568	.1U	Cap, Ceramic 50V SMT (1206) +/-10% X7R
C 12	5-00052-512	.01U	Cap, Stacked Metal Film 50V 5% -40/+85c
C 13	5-00052-512	.01U	Cap, Stacked Metal Film 50V 5% -40/+85c
C 14	5-00056-512	.1U	Cap, Stacked Metal Film 50V 5% -40/+85c
C 15	5-00056-512	.1U	Cap, Stacked Metal Film 50V 5% -40/+85c
C 16	5-00299-568	.1U	Cap, Ceramic 50V SMT (1206) +/-10% X7R
C 17	5-00299-568	.1U	Cap, Ceramic 50V SMT (1206) +/-10% X7R
C 18	5-00299-568	.1U	Cap, Ceramic 50V SMT (1206) +/-10% X7R
C 19	5-00299-568	.1U	Cap, Ceramic 50V SMT (1206) +/-10% X7R
C 20	5-00052-512	.01U	Cap, Stacked Metal Film 50V 5% -40/+85c
C 21	5-00052-512	.01U	Cap, Stacked Metal Film 50V 5% -40/+85c
C 22	5-00052-512	.01U	Cap, Stacked Metal Film 50V 5% -40/+85c
C 23	5-00052-512	.01U	Cap, Stacked Metal Film 50V 5% -40/+85c
C 24	5-00060-512	1.0U	Cap, Stacked Metal Film 50V 5% -40/+85c
C 25	5-00299-568	.1U	Cap, Ceramic 50V SMT (1206) +/-10% X7R
C 26	5-00375-552	100P	Capacitor, Chip (SMT1206), 50V, 5%, NPO
C 27	5-00299-568	.1U	Cap, Ceramic 50V SMT (1206) +/-10% X7R
C 28	5-00299-568	.1U	Cap, Ceramic 50V SMT (1206) +/-10% X7R
D 1	3-00010-303	GREEN	LED, T1 Package
D 2	3-00010-303	GREEN	LED, T1 Package
D 3	3-00011-303	RED	LED, T1 Package
D 4	3-00011-303	RED	LED, T1 Package

D 5	3-00011-303	RED	LED, T1 Package
D 6	3-00011-303	RED	LED, T1 Package
J 1	1-00505-100	RJ45, MODULAR	Connector, Misc.
J 2	1-00003-120	BNC	Connector, BNC
J 3	1-00003-120	BNC	Connector, BNC
L 1	6-00236-631	FR47	Ferrite bead, SMT
L 2	6-00236-631	FR47	Ferrite bead, SMT
P 1	4-00370-441	500	Pot, Multi-Turn Trim, 3/8" Square Top Ad
P 2	4-00019-443	20K	Pot, 10-Turn Panel
PC1	7-01422-701	QCM100	Printed Circuit Board
Q 1	3-00580-360	MMBT3906LT1	Integrated Circuit (Surface Mount Pkg)
R 1	4-01213-462	10.0K	Thin Film, 1%, 50 ppm, MELF Resistor
R 2	4-01280-462	49.9K	Thin Film, 1%, 50 ppm, MELF Resistor
R 3	4-01471-461	470	Thick Film, 5%, 200 ppm, Chip Resistor
R 4	4-01503-461	10K	Thick Film, 5%, 200 ppm, Chip Resistor
R 5	4-01503-461	10K	Thick Film, 5%, 200 ppm, Chip Resistor
R 6	4-01503-461	10K	Thick Film, 5%, 200 ppm, Chip Resistor
R 7	4-01503-461	10K	Thick Film, 5%, 200 ppm, Chip Resistor
R 8	4-01503-461	10K	Thick Film, 5%, 200 ppm, Chip Resistor
R 9	4-01503-461	10K	Thick Film, 5%, 200 ppm, Chip Resistor
R 10	4-01575-461	10M	Thick Film, 5%, 200 ppm, Chip Resistor
R 11	4-01338-462	200K	Thin Film, 1%, 50 ppm, MELF Resistor
R 12	4-01455-461	100	Thick Film, 5%, 200 ppm, Chip Resistor
R 13	4-01447-461	47	Thick Film, 5%, 200 ppm, Chip Resistor
R 14	4-01447-461	47	Thick Film, 5%, 200 ppm, Chip Resistor
R 15	4-01455-461	100	Thick Film, 5%, 200 ppm, Chip Resistor
R 16	4-01455-461	100	Thick Film, 5%, 200 ppm, Chip Resistor
R 17	4-01146-462	2.00K	Thin Film, 1%, 50 ppm, MELF Resistor
R 18	4-01209-462	9.09K	Thin Film, 1%, 50 ppm, MELF Resistor
R 19	4-01242-462	20.0K	Thin Film, 1%, 50 ppm, MELF Resistor
R 20	4-01088-462	499	Thin Film, 1%, 50 ppm, MELF Resistor
R 21	4-01088-462	499	Thin Film, 1%, 50 ppm, MELF Resistor
R 22	4-01227-462	14.0K	Thin Film, 1%, 50 ppm, MELF Resistor
R 23	4-01213-462	10.0K	Thin Film, 1%, 50 ppm, MELF Resistor
R 24	4-01338-462	200K	Thin Film, 1%, 50 ppm, MELF Resistor
R 25	4-01338-462	200K	Thin Film, 1%, 50 ppm, MELF Resistor
R 26	4-01213-462	10.0K	Thin Film, 1%, 50 ppm, MELF Resistor
R 27	4-01191-462	5.90K	Thin Film, 1%, 50 ppm, MELF Resistor
R 28	4-01455-461	100	Thick Film, 5%, 200 ppm, Chip Resistor
R 29	4-01447-461	47	Thick Film, 5%, 200 ppm, Chip Resistor
R 30	4-01447-461	47	Thick Film, 5%, 200 ppm, Chip Resistor
R 31	4-01117-462	1.00K	Thin Film, 1%, 50 ppm, MELF Resistor
R 32	4-01117-462	1.00K	Thin Film, 1%, 50 ppm, MELF Resistor

R 33	4-01146-462	2.00K	Thin Film, 1%, 50 ppm, MELF Resistor
R 34	4-01146-462	2.00K	Thin Film, 1%, 50 ppm, MELF Resistor
R 35	4-01527-461	100K	Thick Film, 5%, 200 ppm, Chip Resistor
R 36	4-01199-462	7.15K	Thin Film, 1%, 50 ppm, MELF Resistor
R 37	4-01479-461	1.0K	Thick Film, 5%, 200 ppm, Chip Resistor
R 38	4-01338-462	200K	Thin Film, 1%, 50 ppm, MELF Resistor
R 39	4-01338-462	200K	Thin Film, 1%, 50 ppm, MELF Resistor
R 40	4-01213-462	10.0K	Thin Film, 1%, 50 ppm, MELF Resistor
R 41	4-01191-462	5.90K	Thin Film, 1%, 50 ppm, MELF Resistor
R 42	4-01660-462	2.00M	Thin Film, 1%, 50 ppm, MELF Resistor
R 43	4-01660-462	2.00M	Thin Film, 1%, 50 ppm, MELF Resistor
R 44	4-01215-462	10.5K	Thin Film, 1%, 50 ppm, MELF Resistor
R 50	4-01191-462	5.90K	Thin Film, 1%, 50 ppm, MELF Resistor
R 51	4-01479-461	1.0K	Thick Film, 5%, 200 ppm, Chip Resistor
R 52	4-01242-462	20.0K	Thin Film, 1%, 50 ppm, MELF Resistor
R 53	4-01242-462	20.0K	Thin Film, 1%, 50 ppm, MELF Resistor
R 54	4-01660-462	2.00M	Thin Film, 1%, 50 ppm, MELF Resistor
R 55	4-01338-462	200K	Thin Film, 1%, 50 ppm, MELF Resistor
R 56	4-01527-461	100K	Thick Film, 5%, 200 ppm, Chip Resistor
R 57	4-01213-462	10.0K	Thin Film, 1%, 50 ppm, MELF Resistor
R 58	4-01213-462	10.0K	Thin Film, 1%, 50 ppm, MELF Resistor
R 59	4-01471-461	470	Thick Film, 5%, 200 ppm, Chip Resistor
R 60	4-01338-462	200K	Thin Film, 1%, 50 ppm, MELF Resistor
R 61	4-01184-462	4.99K	Thin Film, 1%, 50 ppm, MELF Resistor
R 62	4-01213-462	10.0K	Thin Film, 1%, 50 ppm, MELF Resistor
R 63	4-01213-462	10.0K	Thin Film, 1%, 50 ppm, MELF Resistor
R 64	4-01660-462	2.00M	Thin Film, 1%, 50 ppm, MELF Resistor
R 65	4-01660-462	2.00M	Thin Film, 1%, 50 ppm, MELF Resistor
R 66	4-01213-462	10.0K	Thin Film, 1%, 50 ppm, MELF Resistor
R 67	4-01191-462	5.90K	Thin Film, 1%, 50 ppm, MELF Resistor
R 68	4-01519-461	47K	Thick Film, 5%, 200 ppm, Chip Resistor
R 69	4-01479-461	1.0K	Thick Film, 5%, 200 ppm, Chip Resistor
R 70	4-01527-461	100K	Thick Film, 5%, 200 ppm, Chip Resistor
R 71	4-01479-461	1.0K	Thick Film, 5%, 200 ppm, Chip Resistor
R 72	4-01431-461	10	Thick Film, 5%, 200 ppm, Chip Resistor
R 73	4-01431-461	10	Thick Film, 5%, 200 ppm, Chip Resistor
R 74	4-01479-461	1.0K	Thick Film, 5%, 200 ppm, Chip Resistor
R 75	4-01527-461	100K	Thick Film, 5%, 200 ppm, Chip Resistor
R 76	4-01479-461	1.0K	Thick Film, 5%, 200 ppm, Chip Resistor
R 77	4-01479-461	1.0K	Thick Film, 5%, 200 ppm, Chip Resistor
R 78	4-01479-461	1.0K	Thick Film, 5%, 200 ppm, Chip Resistor
SW1	2-00025-217	SPDT	Switch, On-None-On, Toggle, Right Angle
T 1	6-00622-610	ADT1-6T	Transformer

U 1	3-00346-329	7812	Voltage Reg., TO-220 (TAB) Package
U 2	3-00112-329	7805	Voltage Reg., TO-220 (TAB) Package
U 3	3-00581-360	AD822	Integrated Circuit (Surface Mount Pkg)
U 4	3-00684-360	CD4060BCM	Integrated Circuit (Surface Mount Pkg)
U 5	3-00375-360	DS8921AM	Integrated Circuit (Surface Mount Pkg)
U 6	3-00749-360	74HC541	Integrated Circuit (Surface Mount Pkg)
U 7	3-01469-360	MAX6250BCSA	Integrated Circuit (Surface Mount Pkg)
U 8	3-00581-360	AD822	Integrated Circuit (Surface Mount Pkg)
U 9	3-01445-360	LMC6082IM	Integrated Circuit (Surface Mount Pkg)
U 10	3-01445-360	LMC6082IM	Integrated Circuit (Surface Mount Pkg)
U 11	3-01370-360	OPA277UA	Integrated Circuit (Surface Mount Pkg)
U 12	3-00372-360	LM13700M	Integrated Circuit (Surface Mount Pkg)
U 13	3-01445-360	LMC6082IM	Integrated Circuit (Surface Mount Pkg)
U 14	3-00752-360	4052	Integrated Circuit (Surface Mount Pkg)
U 15	3-00728-360	LM393	Integrated Circuit (Surface Mount Pkg)
U 16	3-00728-360	LM393	Integrated Circuit (Surface Mount Pkg)
Y 1	6-00958-620	76.8KHZ	Crystal
Z 0	0-00002-008	2607	Dial
Z 0	0-00009-000	FOOT	Hardware, Misc.
Z 0	0-00025-005	3/8"	Lugs
Z 0	0-00043-011	4-40 KEP	Nut, Kep
Z 0	0-00098-042	#6 LOCK	Washer, lock
Z 0	0-00141-032	2-520194-2	Termination
Z 0	0-00185-021	6-32X3/8PP	Screw, Panhead Phillips
Z 0	0-00187-021	4-40X1/4PP	Screw, Panhead Phillips
Z 0	0-00197-002	3ED8	Power Entry Hardware
Z 0	0-00222-021	6-32X1/4PP	Screw, Panhead Phillips
Z 0	0-00240-026	4-40X3/8PF	Screw, Black, All Types
Z 0	0-00252-057	GROMMET DG532	Grommet
Z 0	0-00295-050	3" RED	Wire #18 UL1007 Stripped 3/8x3/8 No Tin
Z 0	0-00296-050	3" BLACK	Wire #18 UL1007 Stripped 3/8x3/8 No Tin
Z 0	0-00297-026	6-32 X 3/16"	Screw, Black, All Types
Z 0	0-00330-050	5-1/2" #18	Wire #18 UL1007 Stripped 3/8x3/8 No Tin
Z 0	0-00434-054	2" #26 WHITE	Wire #26 UL1061
Z 0	0-00517-000	BINDING POST	Hardware, Misc.
Z 0	0-00901-005	0.250"	Lugs
Z 0	0-00907-020	6-32X1/4 PF UC	Screw, Flathead Phillips
Z 0	2-00049-211	SPST ON-NONE-OF	Switch, Rocker
Z 0	6-00965-615	15V-15W-1A	Power Supply
Z 0	7-01419-720	QCM100	Fabricated Part
Z 0	7-01420-720	QCM100	Fabricated Part
Z 0	7-01421-720	QCM100	Fabricated Part
Z 0	7-01423-709	QCM100	Lexan Overlay

Z 0   9-00267-917   GENERIC   Product Labels

QCM25 Parts List

REF.	SRS PART	VALUE	DESCRIPTION
C 1	5-00318-569	2.2U/T35	Cap, Tantalum, SMT (all case sizes)
C 2	5-00299-568	.1U	Cap, Ceramic 50V SMT (1206) +/-10% X7R
C 3	5-00299-568	.1U	Cap, Ceramic 50V SMT (1206) +/-10% X7R
C 4	5-00299-568	.1U	Cap, Ceramic 50V SMT (1206) +/-10% X7R
C 5	5-00299-568	.1U	Cap, Ceramic 50V SMT (1206) +/-10% X7R
C 6	5-00298-568	.01U	Cap, Ceramic 50V SMT (1206) +/-10% X7R
C 7	5-00299-568	.1U	Cap, Ceramic 50V SMT (1206) +/-10% X7R
C 8	5-00299-568	.1U	Cap, Ceramic 50V SMT (1206) +/-10% X7R
C 9	5-00299-568	.1U	Cap, Ceramic 50V SMT (1206) +/-10% X7R
C 10	5-00387-552	1000P	Capacitor, Chip (SMT1206), 50V, 5%, NPO
C 11	5-00299-568	.1U	Cap, Ceramic 50V SMT (1206) +/-10% X7R
C 12	5-00387-552	1000P	Capacitor, Chip (SMT1206), 50V, 5%, NPO
C 13	5-00387-552	1000P	Capacitor, Chip (SMT1206), 50V, 5%, NPO
C 14	5-00299-568	.1U	Cap, Ceramic 50V SMT (1206) +/-10% X7R
C 15	5-00299-568	.1U	Cap, Ceramic 50V SMT (1206) +/-10% X7R
C 16	5-00299-568	.1U	Cap, Ceramic 50V SMT (1206) +/-10% X7R
C 17	5-00299-568	.1U	Cap, Ceramic 50V SMT (1206) +/-10% X7R
C 18	5-00299-568	.1U	Cap, Ceramic 50V SMT (1206) +/-10% X7R
C 19	5-00364-552	12P	Capacitor, Chip (SMT1206), 50V, 5%, NPO
C 20	5-00372-552	56P	Capacitor, Chip (SMT1206), 50V, 5%, NPO
C 21	5-00372-552	56P	Capacitor, Chip (SMT1206), 50V, 5%, NPO
C 22	5-00380-552	270P	Capacitor, Chip (SMT1206), 50V, 5%, NPO
C 23	5-00376-552	120P	Capacitor, Chip (SMT1206), 50V, 5%, NPO
C 24	5-00384-552	560P	Capacitor, Chip (SMT1206), 50V, 5%, NPO
D 1	3-00010-303	GREEN	LED, T1 Package
D 2	3-00803-360	MMBV609	Integrated Circuit (Surface Mount Pkg)
J 1	1-00505-100	RJ45, MODULAR	Connector, Misc.
L 1	6-00236-631	FR47	Ferrite bead, SMT
L 2	6-00013-606	2.2UH - 5PH	Inductor, Variable
L 3	6-00171-606	4.7UH-5PH	Inductor, Variable
P 1	4-00486-441	50	Pot, Multi-Turn Trim, 3/8" Square Top Ad
P 2	4-00486-441	50	Pot, Multi-Turn Trim, 3/8" Square Top Ad
PC1	7-01426-701	QCM25	Printed Circuit Board
R 1	4-01471-461	470	Thick Film, 5%, 200 ppm, Chip Resistor
R 2	4-01431-461	10	Thick Film, 5%, 200 ppm, Chip Resistor
R 3	4-01431-461	10	Thick Film, 5%, 200 ppm, Chip Resistor
R 5	4-01447-461	47	Thick Film, 5%, 200 ppm, Chip Resistor

R 6	4-01447-461	47	Thick Film, 5%, 200 ppm, Chip Resistor
R 7	4-01175-462	4.02K	Thin Film, 1%, 50 ppm, MELF Resistor
R 8	4-01117-462	1.00K	Thin Film, 1%, 50 ppm, MELF Resistor
R 9	4-00217-408	1.000K	Resistor, Metal Film, 1/8W, 0.1%, 25ppm
R 10	4-00217-408	1.000K	Resistor, Metal Film, 1/8W, 0.1%, 25ppm
R 11	4-01463-461	220	Thick Film, 5%, 200 ppm, Chip Resistor
R 12	4-00992-462	49.9	Thin Film, 1%, 50 ppm, MELF Resistor
R 13	4-01447-461	47	Thick Film, 5%, 200 ppm, Chip Resistor
R 14	4-01527-461	100K	Thick Film, 5%, 200 ppm, Chip Resistor
R 15	4-01527-461	100K	Thick Film, 5%, 200 ppm, Chip Resistor
R 16	4-01447-461	47	Thick Film, 5%, 200 ppm, Chip Resistor
R 17	4-00992-462	49.9	Thin Film, 1%, 50 ppm, MELF Resistor
R 18	4-01184-462	4.99K	Thin Film, 1%, 50 ppm, MELF Resistor
R 19	4-01184-462	4.99K	Thin Film, 1%, 50 ppm, MELF Resistor
R 20	4-01431-461	10	Thick Film, 5%, 200 ppm, Chip Resistor
R 21	4-01076-462	374	Thin Film, 1%, 50 ppm, MELF Resistor
R 22	4-01021-462	100	Thin Film, 1%, 50 ppm, MELF Resistor
R 23	4-01021-462	100	Thin Film, 1%, 50 ppm, MELF Resistor
T 1	6-00622-610	ADT1-6T	Transformer
T 2	6-00622-610	ADT1-6T	Transformer
U 1	3-00369-340	AD8367ARU	Integrated Circuit (Thru-hole Pkg)
U 2	3-00375-360	DS8921AM	Integrated Circuit (Surface Mount Pkg)
U 3	3-00686-360	OPA337UA	Integrated Circuit (Surface Mount Pkg)
U 4	3-00898-360	AD8009	Integrated Circuit (Surface Mount Pkg)
Z 0	0-00025-005	3/8"	Lugs
Z 0	0-00150-026	4-40X1/4PF	Screw, Black, All Types
Z 0	0-00241-021	4-40X3/16PP	Screw, Panhead Phillips
Z 0	0-00276-102	PCB POST, RED	Binding Post
Z 0	0-00277-053	4" #24 BLK	Wire #24 UL1007 Strip 1/4x1/4 Tin
Z 0	0-00386-003	BNC BUSHING	Insulators
Z 0	0-00696-043	3/8X5/8 .032THK	Washer, nylon
Z 0	1-00388-120	MALE BNC 4979	Connector, BNC
Z 0	7-01412-720	EQCM	Fabricated Part
Z 0	7-01413-720	EQCM	Fabricated Part
Z 0	9-00267-917	GENERIC	Product Labels