QCM100- Quartz Crystal Microbalance Theory 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 results.

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:

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

where,

Δf - the observed frequency change, in Hz,
Δm - the change in mass per unit area, in g/cm^2, and
C_f - the sensitivity factor for the crystal used (i.e. 56.6 Hz μg^{-1} cm^2 for a 5MHz 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, more 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 (3) basic surface-molecule interaction studies.

The purpose of this chapter is to provide a brief introduction to the different measurement and calibration techniques available to QCM100 users, and to briefly describe the most popular theoretical models used to interpret the results. A complete coverage of these subjects is obviously beyond the scope of this note. 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.
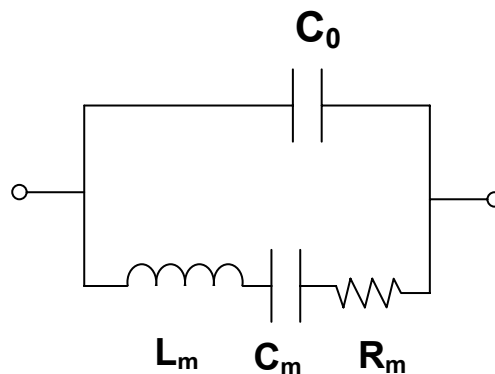
$$C_0$$

$$L_m \quad C_m \quad R_m$$

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, and (3) L_m (inductor) corresponds to the inertial component of the oscillation, which is related to the mass displaced during the vibration. Typical values of these parameters for a 1" diameter, 5MHz, crystal used in the QCM100 system are C_m=33fF, L_m=30mH, and R_m=10Ω (for a dry crystal),

R_m=400Ω (for a crystal with one face in water), or R_m=3500Ω (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 20pF, 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 and films of less than 1ng/cm^2 can be easily 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 so increase the value of R_m.
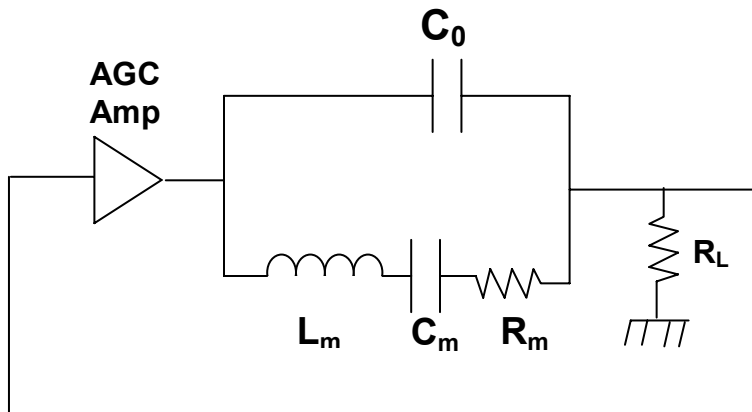

Figure 2. Oscillator Circuit consisting of AGC Amplifier, Quartz Resonator and Load Resistor.

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 (i.e. $f_{SR} = [\ 1 / [2 \cdot \Pi \cdot (L_m \cdot C_m)^{1/2}\ ])$. 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.
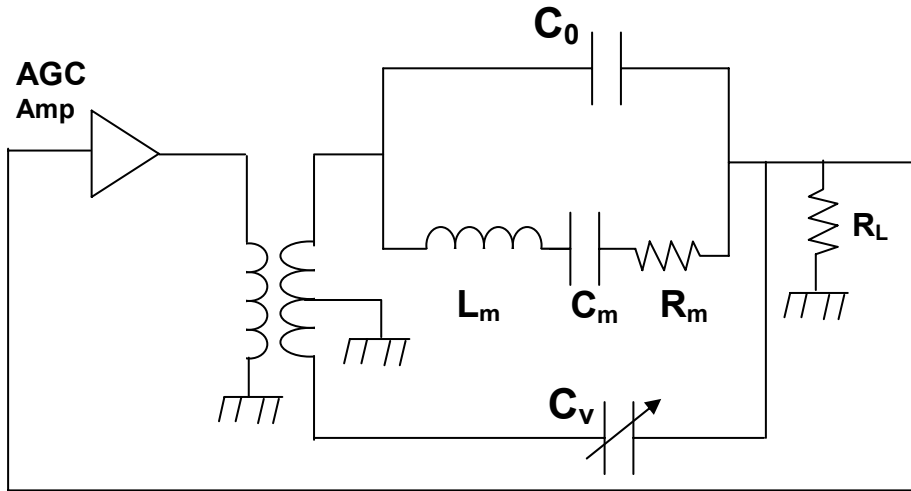

Figure 3. Oscillator Circuit with Varactor Nulling of C_0.

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 Controller, 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.***
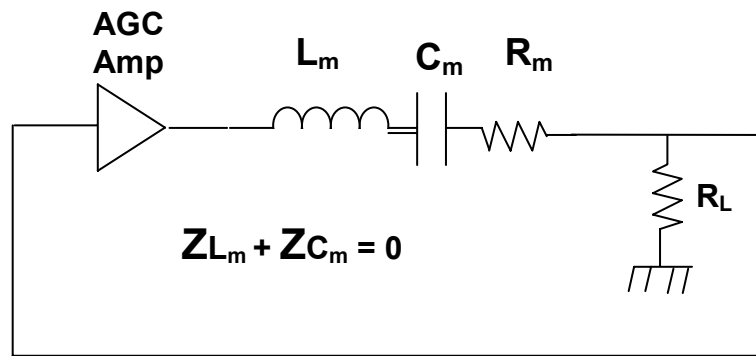

Figure 4. Oscillator Circuit Model with C_0 cancelled by C_v.

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 (Cv), 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 and so oscillate at series resonance.

1. The unit-to-unit variations in C_o are small enough and the reproducibly of C_v is good enough (±2pF) that most users can just set the varactor bias to a fixed value and forget about the whole issue. Set the ten-turn dial to 5.0, which will provide 6.0 volts of reverse bias to the varactor, making Cv about 18pF. This method is recommended for "dry" applications where R_m is low, and 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 75Hz sine wave and indicate if the C_o compensation is High, Low or Nulled. Start with ten-turn dial set to 5.0 (the LED should indicate that the crystal is oscillating) and switch to **Adjust Mode**. Reduce the setting on the dial if the High LED is "on", increase the setting if the Low LED is "on", and lock the dial at the middle of range of values 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 everytime the environment of the crystal is changed. For example, when transitioning from air to a liquid phase.
♦ The cancellation adjustment must be performed with the crystal holder and crystal in the actual measurement environment.

Frequency Measurement

The QCM100 provides a Frequency output port (BNC).

Virtually any commercially available frequency counter can measure the frequency of the 2.4Vpp square wave in 50Ω 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 controller for a crystal in water.

Item	Description	Typical Value
1	Frequency	5 ±0.01 MHz
2	Waveform (into 50Ω)	2.4V square wave
3	Stability (second to second)	0.002 Hz
4	Stability (minute to minute)	0.10 Hz
5	Temperature coefficient	8 Hz / °C
6	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 10ppm the reported values will also change by 10ppm. 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 .002Hz / 5MHz or $1:4 \cdot 10^{-10}$.

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 so as not to 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 $1: 5 \cdot 10^6$, 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 2.4Vpp square wave in 50Ω provided by the QCM100 Frequency Output.

Counters are available with either RS-232 or IEEE-488 (or both) to facilitate interfacing the counter to a computer for 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 Lab View products, or other data acquisition programs, are often available.

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

Manufacturer	Model	Digits/Second	Base Price (10/2002)
Stanford Research Systems	SR620	10	$4,950
Agilent	53131	10	$1,862
Agilent	53132	12	$2,888

Errors in the measurement of frequency

The QCM25 Crystal Controller will oscillate at the frequency such that the phase shift around the entire loop is 360º. Important sources of phase shift within the network include:

1. 180º from the inverting amplifier, A_1.
2. 180º + [37μº / Hz deviation from 5MHz] from the low pass filter
3. 0º + [0.20º/pF (R_m = 40Ω) or 0.81º/pF (R_m =375Ω)] from uncompensated C_o
4. 0º + [0.20º/Hz (R_m =40Ω) or 0.04º/Hz(R_m =375Ω) 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 above) to cancel the extraneous phase shift. The small value of the extraneous phase shifts, together with the large dϕ/df of the crystal network, keeps these frequency errors small.

The QCM25 Crystal Controller is intended to operate only with 5MHz crystals. Typical accuracy of the crystal frequency is 100ppm, or 500Hz. The low pass filter will add an additional phase shift of 37μº / Hz deviation x 500Hz = 0.0185º when operated 500Hz from 5MHz, which will cause a dry crystal to run 0.0185º / 0.20º/Hz = 0.092Hz off series resonance, or a wet crystal to run 0.0185º /

0.04º/Hz = 0.462Hz off series resonance. Since the dφ/df of the low pass filter is 1000x smaller than the dφ/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 ±0.01pF. The corresponding phase error for a wet crystal is ±0.01pF × 0.81º/pF = ± 0.0081º, which gives rise to a frequency reproducibility of ± 0.0081º / 0.04º/Hz = ±0.20Hz for a wet crystal. This error is virtually insignificant.

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

Summary of sources of frequency error (in Water, Δf=700Hz)

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	≈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:

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

Where,

R_m - motional series resonance resistance, in Ω
V_c - 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

Gains:

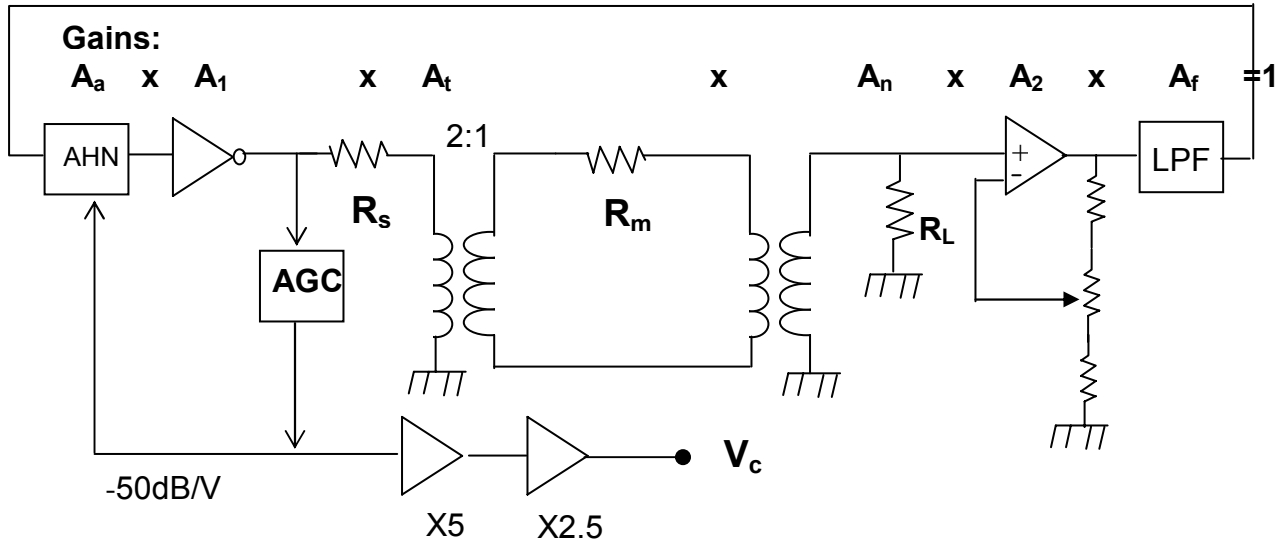$A_a \times A_1 \times A_t \times A_n \times A_2 \times A_f = 1$

Figure 5. QCM Gain Model

A gain model of the QCM25 Crystal Controller 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°, providing 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 5MHz. 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 $1V_{pp}$. The attenuator is controlled by this voltage, between 0 and $1V_{dc}$, providing an attenuation of 50dB/volt, so that $A_a = 10^{-Vagc \cdot 50 / 20}$. The AGC voltage is amplified by 5x in the QCM25 Crystal Controller, and by 2.5x 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, $A_a = 10^{-Vc/5}$.

Stanford Research Systems   *(408)744-9040*

2. A fixed gain amplifier with gain A_1 = 45dB + 20 log (250/200) = 46.94dB (or -222x.) This inverting amplifier has a bandwidth of 500MHz, and so introduces very little extraneous phase shift.

3. A source resistance, R_s, of 100Ω. This source resistance consists of two series 50Ω resistors, one of which is inside the amplifier A_1. This source impedance is reduced by a factor of 4x, to 25Ω, by the 2:1 transformer which follows.

4. An isolation transformer with a 2:1 turns ratio, hence an attenuation of A_t = 0.5x. 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 4x, the transformer also increases the load impedance seen at the input of the transformer by 4x, so that when R_m=0Ω, the load will be 200Ω.

5. R_m, the motional resistance of the crystal at series resonance. R_m can vary from about 10-40Ω for a dry crystal, to about 375Ω for a crystal in water, to about 5kΩ 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 50Ω. 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 4.43x. 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 = 3.7MHz, adjusted so as to provide 180º of phase shift at 5MHz. 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 5MHz by about A_f = -7.8dB (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, $A_a = 10^{-Vc/5}$, 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,

---

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

Where,

Rm- motional series resonance resistance, in Ω
Vc- 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:
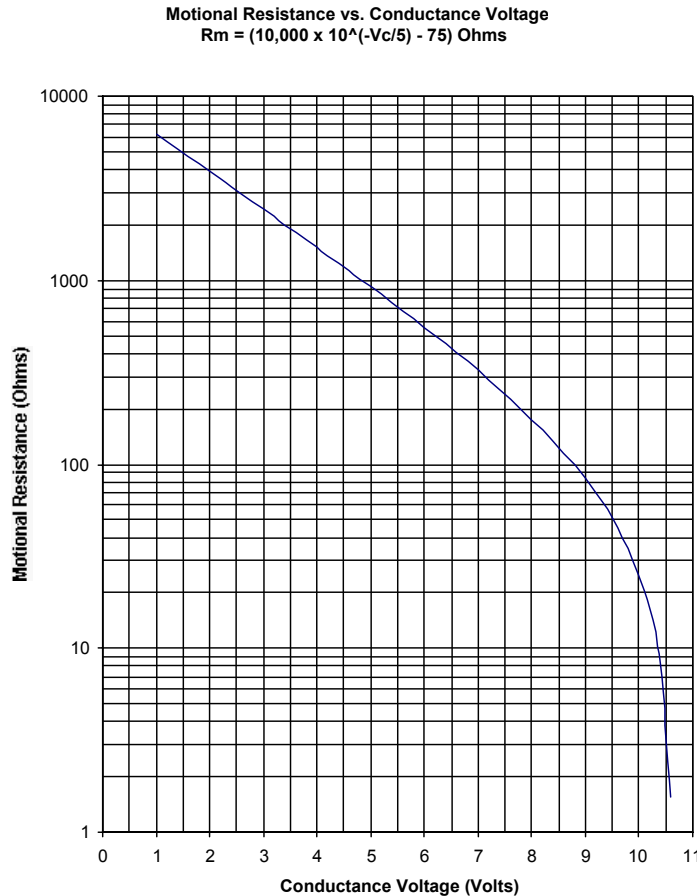
Motional Resistance vs. Conductance Voltage
Rm = (10,000 x 10^(-Vc/5) - 75) Ohms

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 3Ω + 3% of R_m (for R_m < 2kΩ), and are dominated by the departure of the voltage controlled attenuator from its nominal (voltage,gain) characteristic.

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

Noise in the measurement of R_m

V_c varies logarithmically with R_m over most of the range of interest. There is an important advantage in this: the fractional resolution of the resistance is nearly independent of the resistance and so allows detailed and low-noise

measurement of the viscous losses. To estimate the noise in resistance measurements, we can take the derivative of the equation for the motional resistance (units are Ohms and Ohms/Volt):

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

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

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

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

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

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

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

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 Controller/QCM100 are calibrated by replacing the crystal with a precision resistor in parallel with a 15pF capacitor. Two resistor values are used: 51.10Ω and $1.000k\Omega$. 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.)

$$\textbf{R}_m = (\textbf{10{,}000} \cdot \textbf{10}^{-V_c/5} - \textbf{75})$$

$$\textbf{V}_c = \textbf{5 log [10{,}000 / (R}_m + \textbf{75)]}$$

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

www.thinkSRS.com

Gas-Phase Measurements

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

Sauerbrey Equation

Sauerbrey's equation (equation 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.)

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

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}, and
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 active 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 dividing the mass per unit area provided by Sauerbrey's equation by the material's density:

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

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), and

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 specially simple equation (equation 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.

$\Delta m = [(N_q \cdot \rho_q)/(\Pi \cdot Z \cdot f_L)] \cdot \tan^{-1}[Z \cdot \tan[\Pi \cdot (f_U - f_L) / f_U]]$ (equation 5)

where,

Δm - change in mass per unit area, in g/cm^2,
N_q - Frequency Constant for AT-cut quartz crystal: 1.668*1013 Hz. Å,
ρ_q - density of quartz: 2.648 $g \cdot cm^{-3}$,
ρ_f - density of film material, in $g \cdot cm^{-3}$,
f_U - Frequency of unloaded crystal (prior to deposition), in Hz,
f_L - Frequency of loaded crystal, in Hz,
μ_q -shear modulus of quartz: $2.947 \cdot 10^{11}$ $g \cdot cm^{-1} \cdot s^{-2}$,
μ_f - shear modulus of film material, and
Z: Z-Factor of film material = $[(\rho_q \cdot \mu_q) / (\rho_f \cdot \mu_f)]^{1/2}$.

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 viscoelastic, 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 hoping 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) spitting of source material resulting in non-uniform films, etc.

Liquid Contact Measurements

Until recently, its 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 solid-solution interface. For many years, QCMs have been used in direct contact with liquids and/or viscoelastic films to assess changes in mass and viscoelastic properties during chemical and electrochemical surface processes.

When the QCM comes in contact with a solution, there is a decrease in frequency that is dependent upon the viscocity 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 (equation 6) permits the prediction of the change in resonance frequency which accompanies immersion of the crystal into a viscous medium:

$$\Delta f = - f_u^{3/2 \cdot} \left[(\rho_L \cdot \eta_L) / (\Pi \cdot \rho_q \cdot \mu_q) \right]^{1/2}$$ (equation 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$\cdot$10^{11} g$\cdot$cm$^{-1}\cdot$s^{-2},
 ρ_L - density of the liquid in contact with the electrode, and
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 (i.e. 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:

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

Where,

ΔR - change in series resonance resistance, in Ω,

n - number of sides in contact with liquid,

ω_s - angular frequency at series resonance (= $2 \cdot \Pi \cdot f_s$, where f_s is the oscillation frequency in solution in Hz), and

L_u - Inductance for the unperturbed (i.e. 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 equation 7) as required for compatibility with electrochemical QCM measurements. The QCM25 Crystal Controller provides both frequency and resistance change signals and will maintain oscillation up to a series resonance resistance of about 5 KΩ (i.e. it will support crystal operation in highly viscous solutions up to 88% (w/w) glycerol in water).
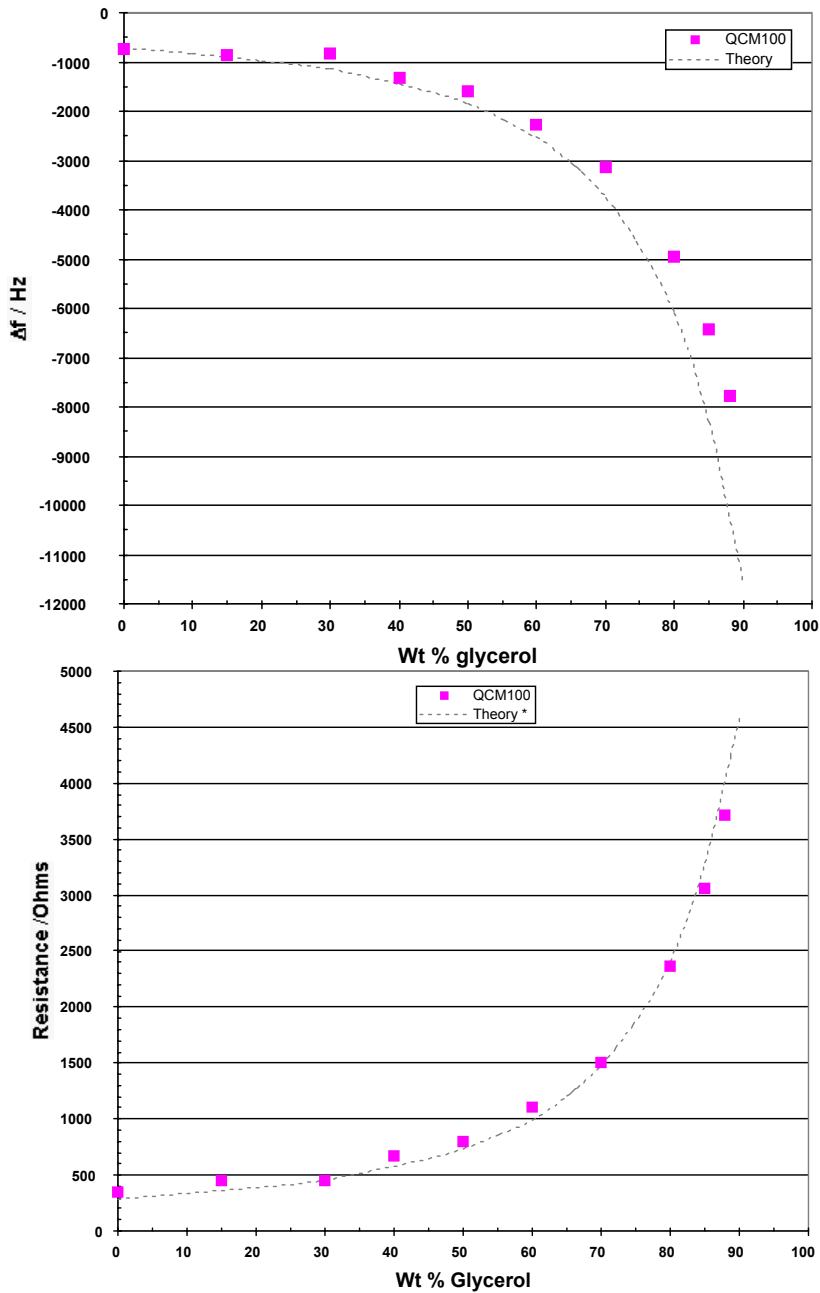
Figure 7. Δf and ΔR versus glycerol weight percentage (in water) as predicted by theory and as measured with QCM100 and a 5MHz polished crystal.

As an example, equation 6 predicts a decrease in f_0 of 715Hz on transfer from vacuum to pure water[18] at 20°C, in agreement with the results observed with a QCM100 using 1inch diameter, polished, 5MHz 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

Stanford Research Systems   *(408)744-9040*

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 (equations 6 & 7) and experiment is clearly illustrated by **Figure 7**.

Dissipation Technique

An alternative method[21] 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[22] have shown that as long as the effect of the parasitic capacitance (C_0) is properly cancelled, the results provided by the Dissipation Technique should be in good agreement with the measurements provided by the QCM100 System.

Temperature

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

Much larger changes in frequency with temperature are observed when QCM crystals are immersed in liquids. This is due to the coupling of the shear mode oscillation with the temperature dependent viscosity and density of the fluid- the temperature coefficient due to this effect is ≈ 8Hz/ °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. In electrochemical experiments this is often achieved with temperature controlled baths and jacketed cells. If temperature control is not possible or practical, it is always good practice to wait at least 30 minutes before performing any accurate measurements after the crystal comes in contact with a new medium and measure the temperature of the solution around the crystal during the experiments to perform temperature compensation. It is also common practice to soak the mounted crystal(s) in the solution overnight before performing any experiments to assure more stable readings.

Careful control of the temperature is required in high accuracy measurements to avoid frequency hysterisis effects- the dependence of resonator frequency at a

specific temperature on the prior temperature history of the resonator. For example, it is often observed that the frequency vs temperature curve obtained going from T1 to T2 will not coincide with the one obtained immediately after going from T2 to T1. This effect must be carefully considered during accurate determinations.

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

Electrode Polishing

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

System Checkup

A comparison against the theoretical predictions of equation 6 (&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 5MHz, _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 5MHz 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 (i.e. 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[24], corrosion, oxide formation, dissolution studies[25], adsorption/desorption of surfactants[26] and changes in conductive polymer films during redox processes[27].

The basic principles and applications of the QCM to electrochemical processes have been extensively reviewed in the electrochemical literature[28] 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 1inch 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 Controller, 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 Controller). 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.
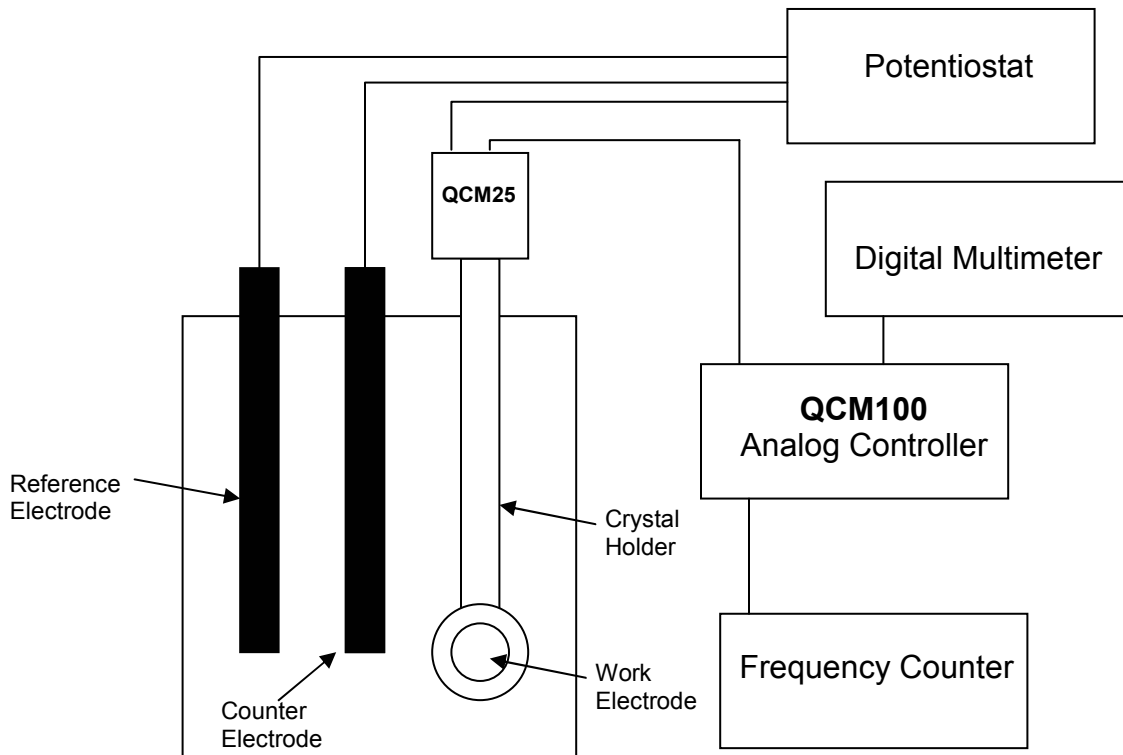
Figure 8. Schematic of EQCM apparatus

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 Controller provides transformer isolation of the crystal front face electrode. This allows direct electrical connection of the quartz crystal face to the "working electrode" pin of any standard potentiostat/galvanostat.

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

Figure 9 is an example of a typical voltammogram-massogram plot obtained from a 10mM solution of CuSO4 in 0.1M H_2SO4, using a 1inch diameter, Au coated, quartz crystal mounted in a standard holder as the working electrode.
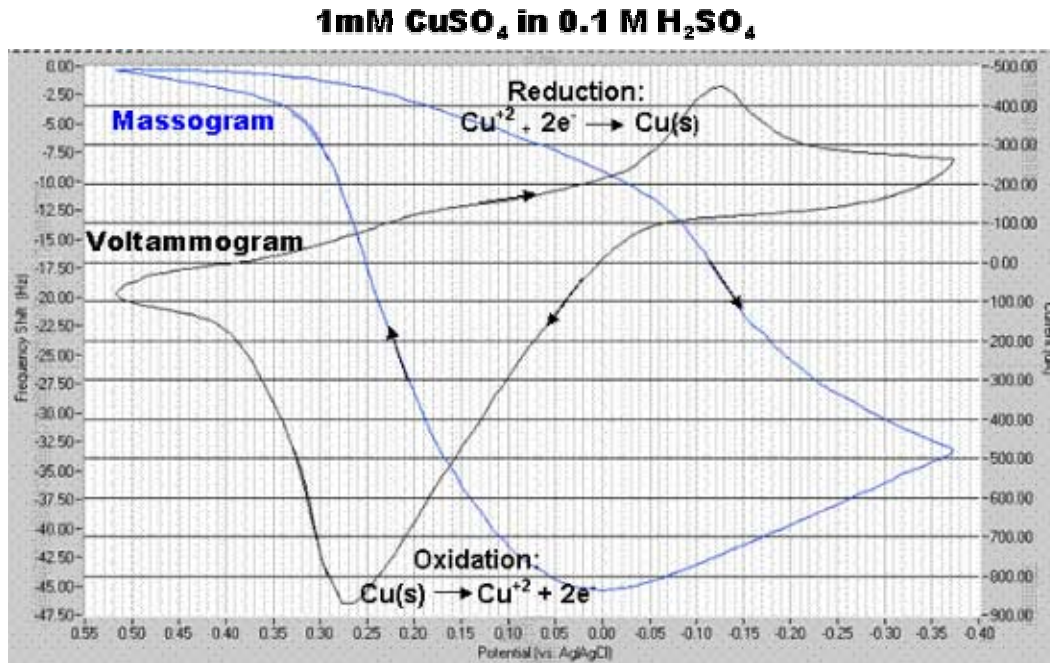
1mM CuSO₄ in 0.1 M H₂SO₄

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

Calibration

It has been amply demonstrated in the literature that when experiments involve only relative frequency shifts which are measured in a fixed solution, the offset caused by the viscous loading of the liquid, has negligible effect on the accuracy of the Sauerbrey equation for the determination of small mass changes in rigid deposits[29]. Quantitative interpretation of the EQCM data in those cases is based on the combination of the Sauerbrey equation (equation 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:

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

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 equation 1),

Q - integrated charge during the reduction, in Coulomb,

A - Active deposition area of the working (i.e. liquid contact) electrode, in cm^2 ,

F - Faraday's constant: $9.648 \cdot 10^4$ Coulomb/mole, and

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

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

A plot of "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 equation 8, the EQCM must be calibrated in order to properly derive (1) the proportionality constant, Cf, 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 50mM solution of $AgNO_3$ in 0.5M HNO_3 is subjected to a reducing potential and Ag is deposited with a fixed cathodic current density of 50-500 $\mu A/cm^2$. 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 $\mu g/cm^2$, providing a very reliable way to calibrate the proportionality constant of equation 8.

Several calibration procedures are also described in the electrochemistry literature[30], 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[31]. However, for the linear frequency-to-mass relationship (described by equation 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[32]. 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!
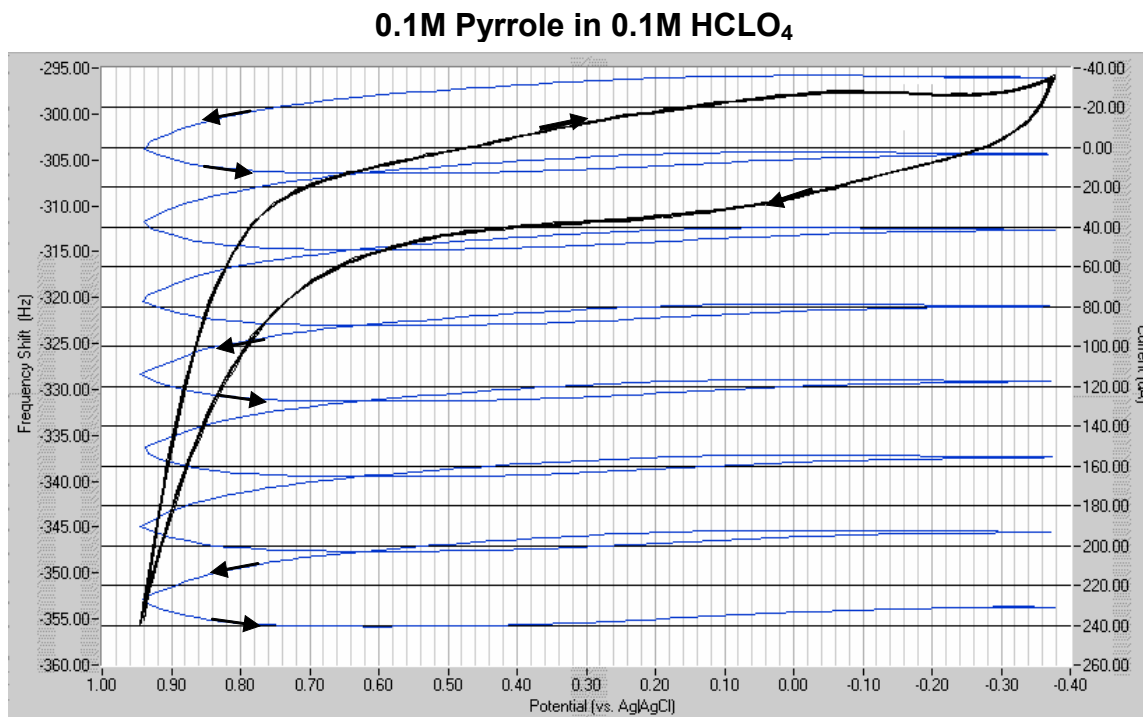
0.1M Pyrrole in 0.1M HCLO₄

Figure 10. Votammogram 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 0.65V. 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 starightforward 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[33]. Some theoretical models[34], 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 analyis 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[35].

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[36].

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 interferences. For analytical purposes, it is imperative to find ways of getting the QCM sensor to respond only to what you are interested in (i.e. build sensitivity into the device). This usually involves the addition of a sensitive layer on the surface of the crystal[37].

Organic polymers comprise the most common type of coating used with QCM sensors due to their capability to reversibly sorb vapors and liquids[38]. 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[39], as well as for the investigation and/or monitoring of biochemcially significant processes. Sensitive, selective detection of biochemically active compounds can be achieved by employing antigen-antibody[40], 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[41]. QCM studies have provided detailed information about the functionalized surfaces developed for a range of biochip and biosensor applications.

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

References

[1] G. Sauerbrey, Z. Phys. 155 (1959) 206

[2] Daniel Buttry, "Applications of the QCM to Electrochemistry", in A Series of Advances in Electroanalytical Chemistry, edited by Allen Bard, Marcel Dekker, 1991, p. 23-33.

[3] John Henderson, "Electronic Devices. Concepts and Applications", Prentice Hall, NJ, (1991) p. 357

[4] For example, QCM10 crystal holder with a 1inch, 5MHz crystal, connected directly to an SRS QCM25 Crystal Controller.

[5] C. Chagnard, P. Gilbert, N. Watkins, T. Beeler and David W. Paul, "An electronic oscillator with automatic gain control:EQCM Applications", Sensors and Actuators B 32(1996) 129-136.
A. Arnau, T. Sogorb and Y. Jimenez, "Circuit for continuous motional series resonat frequency and motional resistance monitoring of quartz crystal resonators by parallel capacitance cancellation", Rev. Sci. Instrum. 73(7)(2002) 2724.

[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).

[8] For example, Agilent 34401A, with 6 digit resolution or 3458, with eight digits resolution.

[9] D.R. Denison, "Linearity of a Heavily Loaded Quartz Crystal Microbalance", J. Vac. Sci. Technol. 10(1) (1973) 126
Klaus H. Behrndt, "Long Term Operation of Crystal Oscillators in Thin-Film Deposition", J. Vac. Sci. technol. 8(5)(1971) 622.

[10] C. Lu and O. Lewis, "Investigation of film-thickness determination by oscillating quartz resonators with large mass load", J. Appl. Phys. 43 (1972) 4385.
Chih-shun Lu, "Mass determination with piezoelectric quartz crystal resonators", J. Vac. Sci Technol., 12(1) (1975) 578.

[11] D. R. Denison, "Linearity of Heavily Loaded Quartz Crystal Microbalance", J. Vac. Sci. Technol. 10(1973) 126. K. H. Behrndt, "Long Term Operation of Crystal Oscillators in Thin-Film Deposition", J. Vac. Sci. Technol. 8(5) (1971) 622.

[12] T. Nomura and M. Okuhara, Anal. Chim. Acta 142(1982) 281.

[13] A. P. M. Glassford, "Response of a Quartz Crystal Microbalance to a liquid Deposit", J. Vac. Sci. Technol., 15(6)(1978) 1836

[14] K. Keiji Kanazawa and Joseph Gordon II, "Frequency of a Quartz Microbalance in Contact with Liquid", Anal Chem. 57(1985) 1770
K. Keiji Kanazawa and Joseph G. Gordon II, Analytica Chimica Acta, 175(1985) 99-105.

[15] Stephen J. Martin, James J. Spates, Kurt O. Wesendorf, thomas Schnneider and Robert J. Huber, "Resonator /Oscillator Response to Liquid Loading", Anal Chem 69(1997) 2050.

[16] Stephen Martin, Victoria Edwards Granstaff and Gregory C. Frye, "Characterization of a Quartz Crystal Microbalance with Simultaneous Mass and Liquid Loading", Anal. Chem. 63 (1991) 2272.

[17] Operation in liquids requires that the crystal be mounted in a holder such that only the front surface of the crystal is in contact with the fluid, while at the same time providing an electrical connection to both electrodes.

[18] For pure water, at 20C, ρ_L: 0.9982 g cm^{-3}, and η_L: 1.002$\cdot$10^{-2} g cm^{-1} s^{-1}.

[19] H. Muramatsu, Eiichi Tamiya and Isao Karube, "Computation of Equivalent Circuit Parameters of Quartz Crystals in Contact with Liquids and Study of Liquid Properties", Anal. Chem. 60(1988) 2142
S.J. Geelhood, C. W. Frank and K. Kanazawa, "Transient Quartz Crystal Microbalance Behaviors Compared", Journal of the Electrochemical Society, 149(2002) H33-H38.
Mengsu Yang and Michael Thompson, "Multiple Chemical Information from the Thickness Shear Mode Acoustic Wave Sensor in the liquid Phase", Anal. Chem. 65(1993) 1158

[20] S. J. Martin, R. W. Cernosek and J.J. Spates, "Sensing Liquid Properties with Shear-mode Resonator Sensors", in Proceeds from Transducers/Eurosensors IX, Stockholm, Sweden (1995)

[21] Michael Rodahl, Fredrik Hook, Anatol Krozer, Peter Brzezinski and Bengt Kasemo, "QCM setup for frequency and Q-factor measurements in gaseous and liquid environments", Rev. Sci. Instrum. 66(7)(1995)3924.

[22] S. J. Geelhood, C.W. Frank and K. Kanazawa, "Transient QCM Behaviors Compared", J. of the Electrochemical Society", 149(1)(2002)H33

[23] Stephen Martin, et. al. ,"Effect of Surface Roughness on the Response of Thickness-Shear Mode Resonators in Liquids", Anal. Chem., 65(1993)2910.
Michael Ward and Edward J. Delawski, "Radial Mass Sensitivity of the Quartz Crystal Microbalance in Liquid Media", Anal. Chem. 63(1991) 886.

[24] Mark R. Deakin and Owen Melroy, "Underpotential Metal Deposition on Au, monitorred in situ with a Quartz Microbalance", J. Electroanal. Chem. 239(1988) 321
O. Melroy, K. Kanazawa, J.G. Gordon II and D. Buttry, "Direct Determination of the Mass of an Underpotentially Deposited Monolayer of Lead on Gold", Langmuir 2(1986)697.
Masahiro Seo, Masaki Aomi and Kengo Yoshida, "A combined Piezoelectric and EQCM study of Underpotential Deposition of Silver on Gold Electrodes", Electrochimica Acta, 39(8/9) (1994) 1039
Youngran Lim and Euijin Hwang, "An Electrochemical QCM study of Oxygen reducttion during the Underpotential Depoosition of Lead on a Gold Electrode", Bull. Korean Chem Soc. 17(12)(1996)1091.

[25] EQCM/Wall Jet Split-Ring Disk Electrode study on Copper dissolution in Chloride Aqueous solution", Anal. Sciences,16(2000)1049
Michael Benje, Matthias Eiermann, Udo Pittermann and Konrad G. Weil, "An improved Quartz Microbalnce. Applications to Electrocrystallizatuion and dissolution of Niquel", Ber. Bunsenges, Phys. Chem. 90(1986) 435.

[26] Jorg Auge, Peter Hauptmann, Frank Eichelbaum and Stephen Rosler, "QCM sensor in liquids", Sensors and Actuators B, 18-19 (1994) 518.

[27] Adrian W. Bott, "Characterization of Films Immobilized on an Electrode Surface Using the EQCM", Current Separations 18:3(1999)79.

[28] Mark Deakin and Daniel Buttry, "Electrochemical Applications of the Quartz Crystal Microbalance", Anal Chem, 61(20)(1989)183
Daniel Buttry and Michael Ward, "Measurement of Interfacial Processes at electrode surfaces with the EQCM", Chem. Rev. 92(6) (1992) 1355

[29] Wolfgang Stockel and Rolf Schumacher, "In situ Microweighing at the Junction Metal/Electrolyte", Ber. Bunsenges. Phys. Chem. 91(1987)345.

[30] C. Gabrielli , M. Keddam and R. Torrei., "Calibration of the Electrochemical Quartz Crystal Microbalance", J. Electrochem. Soc. 139(9) (1991) 2657. Note: A calibration procedure based on the deposition of Ag on Au electrodes is described.
Graeme Andrew Snook, "Investigation of Solid-State Reactions by Electrochemical and Quartz Crystal Microbalance Measurements" Ph.D. Thesis, 2000, Department of Chemistry, Monash University, Clayton 3168, Melbourne, Australia and Division of Minerals, CSIRO, Clayton South 3169 Melbourne, Australia, under the supervision of Professor Alan Maxwell Bond (Monash) and Professor Stephen Fletcher (CSIRO).

Available for download from: http://www-bond.chem.monash.edu.au/theses/ Note: the use of Lead acetate is proposed as a better alternative to Cu and Ag deposition.
Bruckenstein S. and Shay M., "Experimental aspects of use of the quartz crystal microbalance in solution", Electrochim. Acta 30(1985) 1295

[31] Duke Orata and Daniel A. Buttry, "Determination of Ion Populations and Solvent Content as fucntions of Redox State and pH in Polyaniline", J. Am. Chem. Soc. 109(1987)3574.

[32] Michael Ward, "Investigation of Open Circuit Reactions of Polymer Films Using the QCM. Reactions of Polyvinylferrocene Films", J. Phys. Chem. 92(1988)2049.
Charles K. Baker and John R. Reynolds, "A quartz microbalance study of the electrosynthesis of polypyrrole", J. Electroanal Chem, 251(1988) 307.

[33] Stephen Martin, Victoria Edwards Granstaff and Gregory C. Frye, "Characterization of a Quartz Crystal Microbalance with Simultaneouus Mass and Liquid Loading", Anal. Chem. 63 (1991) 2272.
Ralf Lucklum and Peter Hauptmann, "The Df-DR QCM technique: an approach to an advanced sensor signal interpretation", Electrochimica Acta, 45(2000) 3907.

[34] R.A. Etchenique and E. L. Calvo,"Gravimetric measurement in redox polymer electrodes with the EQCM beyond the Sauerbrey limit", Electrochemistry Communications, 1(5)(1999)167.
R.A. Etchenique and E. J. Calvo, "Electrochemical Quartz Crystal Impedance Study of Redox Hydrogel Mediators for Amperometryic Enzyme Electrodes", Anal. Chem. 69(1997)4833.

[35] E. J. Calvo , R. Etchenique, P. N. Bartlett, K. Singhal and Santamaria, "Quartz Crystal Impedance studies at 10MHz of viscoelastic liquids and films", Faraday Discuss.,107(1997)141.
Diethelm Johannsmann, "Viscoelastic Analysis of Organic Thin Films" on quartz resonators", Macromol. Chem. Phys. 200(1999)501.

[36] C. E. Reed, K. Keiji Kanazawa and J. Kaufman, "Physical description of a viscoelastically loaded AT-cut quartz resonator", J. Appl. Phys. 68(5) (1990) 1993.

[37] D. S. Ballantine, R. M. White, S. J. Martin. A. J. Rico, E. T. Zellers, G. C. Frye and H. Woltjen, "Acoustic Wave Sensors: Theory, Design and Physico-Chemical Applications", Acad. Press, London, UK, 1997. Chapter 5 (Chemical and Biological Sensors), p. 222.

[38] G.G. Guilbault and J. Jordan, "Analytical uses of piezoelectric crystals", CRC Reviews 19, p. 1-28.
W. H. King, "Piezoelectric Sorption Detector", Anal. Chem. 36 (1964) 1735.

[39] Iddo Ben-Dov and Itamar Willmer, "Piezoelectric Immunosensors for Urine Specimens of Chlamidia trachomatis Employing QCM Microgravimetric Analysis", Anal. Chem. 69(1997) 3506.

[40] A. Hengerer, C. Kösslinger1, J. Decker, S. Hauck1, I. Queitsch2, H. Wolf and S. Dübel2, "Determination of Phage Antibody Affinities to Antigen by a Microbalance Sensor System", *BioTechniques 26:956-964 (May 1999)*

[41] G. G. Guibault, "Analytical uses of immobilized Enzymes: Modern Monographs in Analytical Chemistry", Vol. 2,Marcel Dekker, New York (1984)
G. M. Minunni, M. Mascini, G.G. Guilbault, B. Hock, "The Quartz Crystal Microbalance as Biosensor. A Status Report on its Future", Anal. Lett. 28, 5(1995), 749.
S. Tombelli, M. Mascini, "Piezoelectric Quartz Crystal Biosensor: Recent Immobilisation Schemes", Anal. Lett. 33(11), 2000, pp. 2129-2151

Kim R. Rogers, "Principles of Affinity Based Biosensors", Molecular Biotechnology 14(2000)109.

[42] Fredrik Hook, et. al., "Structural changes in hemoglobin during adsorption to solid surfaces: effects of pH, ionic strength and ligand binding", Proc. Natl. Acad. Sci. USA 95(1998)12271.

[43] C. Fredriksson, S. Kihlman, M. Rodahl and B. Kasemo, "The Piezoelectric Quartz crystal Mass and Dissipation Sensor: A means of studyinng Cell adhesion", Langmuir, 19(1998) 248.

Ann-Sofie Cans, et. al.., "Measurement of the Dynamics of Exocytosis and Vesicle Retrieval at Cell Populations Using a QCM", Anal. Chem. 73(2001)5805.

C. A. Keller and B. Kasemo,"Surface Specific Kinetics of Lipid Vesicle Adsorption Measured with a QCM", Biophysical Journal, 75(1998) 1397

[44] Wei, W. Z. et. al. , "Selective pharmaceutical analyis technique with sensitive piezoelectric quartz sensors", Anal. Lett. 26(11)(1993)2371.

[45] Storri, S, Santoni, T., Mascini, M.,"A piezoelectric biosensor for DNA hybridization detection", Anal. Lett. 31(11)(1998)1795.