OPERATION AND SERVICE MANUAL

RQCM

Research Quartz Crystal Microbalance

IPN 603800 Rev. J

INFICON

OPERATION AND SERVICE MANUAL

RQCM

Research Quartz Crystal Microbalance

IPN 603800 Rev. J

INFICON Instruments for Intelligent Control®

www.inficon.com reachus@inficon.com

Trademarks

Disclaimer

Disclosure

The disclosure of this information is to assist owners of INFICON equipment to properly operate and maintain their equipment, and does not constitute the release of rights thereof. Reproduction of this information and equipment described herein is prohibited without prior written consent from INFICON, Two Technology Place, East Syracuse, NY 13057-9714. Phone 315.434.1100. See www.inficon.com.

Copyright

First Edition, March 2002; Revision A, May 2002; Revision B, October 2002; Revision C, December 2002; Second Edition Revision D, June 2003; Revision E, July 2004; Revision F, October 2004; Revision G, August 2005; Revision H, November 2005

WARNING

All standard safety procedures associated with the safe handling of electrical equipment must be observed. Always disconnect power when working inside the controller. Only properly trained personnel should attempt to service the instrument.

INFICON

DECLARATION OF CONFORMITY

This is to certify that this equipment, designed and manufactured by:

INFICON Inc.
Two Technology Place
East Syracuse, NY 13057
USA

meets the essential safety requirements of the European Union and is placed on the market accordingly. It has been constructed in accordance with good engineering practice in safety matters in force in the Community and does not endanger the safety of persons, domestic animals or property when properly installed and maintained and used in applications for which it was made.

Equipment Description:	RQCM (Research Quartz Crystal Microbalance) Thin Film Deposition Controller, including the SO-100 Oscillator Package.
Applicable Directives:	73/23/EEC as amended by 93/68/EEC (LVD) 89/336/EEC as amended by 93/68/EEC (EMC) 2002/95/EC (RoHS)
Applicable Standards:	EN 61010-1:2001 (Safety) EN 61326-1:1997/A1:1998/A2:2001, Class A: Emissions per Table 3 Immunity per Table A.1 Due to the classification of this product it is currently exempt from the RoHS directive.
CE Implementation Date:	October 1, 2007
Authorized Representative:	Duane H. Wright Quality Assurance Manager, ISS INFICON Inc.

ANY QUESTIONS RELATIVE TO THIS DECLARATION OR TO THE SAFETY OF INFICON'S PRODUCTS SHOULD BE DIRECTED, IN WRITING, TO THE QUALITY ASSURANCE DEPARTMENT AT THE ABOVE ADDRESS.

10/01/07

Warranty

INFICON warrants the product to be free of functional defects in material and workmanship and that it will perform in accordance with its published specification for a period of (twenty-four) 24 months.

The foregoing warranty is subject to the condition that the product be properly operated in accordance with instructions provided by INFICON or has not been subjected to improper installation or abuse, misuse, negligence, accident, corrosion, or damage during shipment.

Purchaser's sole and exclusive remedy under the above warranty is limited to, at INFICON's option, repair or replacement of defective equipment or return to purchaser of the original purchase price. Transportation charges must be prepaid and upon examination by INFICON the equipment must be found not to comply with the above warranty. In the event that INFICON elects to refund the purchase price, the equipment shall be the property of INFICON.

This warranty is in lieu of all other warranties, expressed or implied and constitutes fulfillment of all of INFICON's liabilities to the purchaser. INFICON does not warrant that the product can be used for any particular purpose other than that covered by the applicable specifications. INFICON assumes no liability in any event, for consequential damages, for anticipated or lost profits, incidental damage of loss of time or other losses incurred by the purchaser or third party in connection with products covered by this warranty or otherwise.

INFICON

www.inficon.com reachus@inficon.com

TABLE OF CONTENTS

Table of Figures

List of Tables

1 GENERAL DESCRIPTION

The RQCM is designed for many types of research applications where QCM (Quartz Crystal Microbalance) measurement is desired. Included with each instrument is a Windows™ based software package that allows the user to configure the RQCM, setup multiple experiments, log data with real-time graphing and review results from previous experiments.

The QCM portion of this system accurately measures crystal frequency and crystal resistance for up to three crystals simultaneously. The software uses this data to derive various physical parameters of the deposited film and/or the liquid or gas environment at the surface of the crystal. The heart of the system is a high performance phase lock oscillator (PLO) circuit that provides superior measurement stability over a wide frequency range (3.8 to 6.06 MHz, or 5.1 to 10 MHz). The circuit incorporates adjustable crystal capacitance cancellation reducing error caused by the parasitic capacitance of the crystal, cable and fixture. Capacitance cancellation is essential for accurate measurements of lossy (soft) films.

Data collection from external sources is accomplished with an optional Data Acquisition Card, which provides three temperature inputs (RTD, Thermocouple and Thermistor) as well as five scalable analog inputs. For example, you can use the analog inputs to acquire potential and current data from a potentiostat during a cyclic voltammogram. The RQCM allows you to combine this data with the mass data of the QCM to create a graph of mass and current versus potential.

Control of external instruments and peripheral devices is accomplished with an optional input/output card. Each remote I/O card provides eight remote inputs and eight relay outputs. The functions of the inputs and outputs are defined in the RQCM's software with some typical uses including the control of pumps, heaters, valves, instrument initiation, etc.

1.1 FEATURES

1.1.1 VERY WIDE FREQUENCY RANGE

The RQCM supports a wide frequency range from 3.8 to over 6 MHz. It will support both 5 and 6 MHz crystals; and with a low limit of 3.8 MHz it will support 1.2 MHz of frequency shift on a 5MHz crystal. A frequency range of 5.1 to over 10 MHz is also available.

1.1.2 SUPPORT FOR VERY LOW Q, HIGHLY DAMPED, CRYSTALS

The RQCM will accurately measure crystals with resistances up to 5 KΩ. In most cases it will maintain lock up to a resistance of 10 KΩ or more. It will support crystal oscillation in highly viscous solutions of more than 88% glycol in water.

1.1.3 DIRECT REAL-TIME MEASUREMENTS OF CRYSTAL FREQUENCY, MASS, AND RESISTANCE

The RQCM accurately measures crystal frequency, mass, and resistance. The software uses this data to derive various physical parameters of the deposited film or media at the surface of the crystal.

1.1.4 MULTIPLE CRYSTAL MEASUREMENT CHANNELS

The RQCM can be configured to measure up to three crystal measurement channels simultaneously.

1.1.5 ELECTRODE CAPACITANCE CANCELLATION

The total quartz crystal impedance includes a shunt capacitance (due to the capacitance of the crystal electrodes, cable and holder) in parallel with the series resonant arm. The total current through the crystal is the sum of the current through the shunt capacitance plus the current through the series resonant arm. The physical motion of the crystal is reflected in the values of the L, R and C in the series arm of the crystal only, and therefore we want to subtract out or otherwise cancel the current through the shunt electrode capacitance. The Crystal Measurement Card includes a method of canceling the electrode capacitance insuring that the measured crystal current does not include the current through the electrode capacitance and therefore is essentially the current through the series resonant arm of the crystal only.

1.1.6 “AUTOLOCK”

When the PLO loses lock, the VCO (Voltage Controlled Oscillator) is ramped up to the maximum frequency at which time it is automatically reset to the minimum frequency and a new scan is initiated.

To insure that the VCO ramps up in frequency, a small amount of quadrature current is injected into the current to voltage buffer whenever the PLO is unlocked. This current is equivalent to a shunt capacitance of about 1.5 pfd. As soon as lock is detected, the quadrature current is turned off.

1.1.7 CRYSTAL FACE ISOLATION

The Crystal face is galvanically (transformer) isolated from earth ground. The Crystal Face connection allows the crystal face electrode to be easily connected to an external voltage or current source such as a potentiostat.

1.1.8 FULLY INTERGATED COMPUTER SOFTWARE

Computer software is included with each RQCM, allowing the user to set up, graph and log frequency and resistance of the crystals from a computer. It also allows the setup, graphing and logging of temperature and analog data – if the hardware is installed.

1.1.9 INPUTS AND OUTPUTS CAPABILITY

As an option, the RQCM can be outfitted with an I/O Card. This card provides eight remote discrete inputs and eight relay outputs. These I/O’s can be used to monitor or control external instruments and peripheral devices.

1.1.10 DATA ACQUISITION

To support the simultaneous logging and display of additional analog information, such as voltage, current, or temperature, the RQCM can be outfitted with an optional Data Acquisition Card. This card supports three types of temperature sensors (RTD, Thermocouple and Thermistor) as well as five scalable analog inputs.

1.2 SPECIFICATIONS

1.2.1 CRYSTAL MEASUREMENT

Crystal measurement channels:	One standard, three maximum.
Frequency range:	3.8 to 6.06 MHz, or 5.1 to 10 MHz
Frequency resolution:	0.03 Hz @ 6.0MHz
Mass resolution:	<0.4 ng/cm^2 (0.014 Å Aluminum)
Capacitance compensation range:	40 to 200 pfd
Achievable capacitance cancellation:	± 0.3 pfd
Crystal resistance range:	5 Ω to 5.0 KΩ
Phase angle accuracy:	± 2 degrees
Phase angle stability:	± 0.5 degrees
Frequency error vs. phase error and crystal Q:	Q= 100,000 0.087 ppm per degree Q=10,000 0.87 ppm per degree Q=1,000 8.7 ppm per degree
Measurement update rate:	From 0.5 to 20 updates/sec
Operating temperature range:	0 to 50°C
Operating temperature range for stated stability:	20 ± 10°C
Controls:	Reset Switch Capacitance Adjustment Trimmer, Course and Fine
Indicators:	Green “Lock” LED Red “Unlock” LED Yellow “Sweep Rate” LED
Crystal Drive Voltage, open circuit:	125 mV RMS
Crystal Drive Source Impedance:	20 Ω ± 1%
Crystal Power:	200 microwatt, maximum
Crystal Face Isolation:	Transformer, ± 200 VDC maximum

1.2.2 DATA ACQUISITION ANALOG CARD (OPTIONAL)

Except where noted. All specifications @ 25°C. All specifications are within 90 days of calibration.

1.2.2.1 Analog Inputs

Number of channels:	5
Resolution:	16 bits (see Section 8.1)
Selectable range:	0-5V, 0-10V, ± 5V, ± 10V
Zero offset:	± 2mV
Gain accuracy:	± 0.01% (± 0.02% for ±5V & ±10V)
Gain non-linearity:	< 2 LSB
Single ended input impedance:	1 MΩ
Differential input impedance:	2 MΩ
Input protection:	± 200V
Common mode range:	± 200V
Common mode rejection:	70 dB up to 200 Hz

1.2.2.2 Thermocouple Input

Type:	Type “T” thermocouple
Temperature range:	0 to 371°C
Accuracy:	± 2°C + sensor error

1.2.2.3 RTD Input

Type:	100 Ω Thin film platinum
Temperature range:	0 to 600°C
Accuracy:	± 4°C + sensor error

1.2.2.4 Thermistor Input

Type:	100 KΩ
Temperature range:	0 to 150°C
Accuracy:	± 0.5°C + sensor error

1.2.3 I/O CARD (OPTIONAL)

Number of Discrete Inputs:	8, ground true 4.7KΩ pulled up to 5V
Number of Discrete Outputs:	8, SPST relays, 120VA, 2 A max.

1.2.4 COMMUNICATIONS

RS-232 serial port standard.

RS-485 serial port optional.

IEEE-488 optional.

1.2.5 FRONT PANEL INDICATORS

Communication Status LED’s

System Ready LED

1.2.6 POWER REQUIREMENTS

100, 200, 220, 240 VAC @ 50/60Hz, 25 W

1.2.7 PHYSICAL

Size: 4” H (including feet) x 13” W x 9 ¾” D
Weight: 7 lbs.
Shipping Weight: 10 lbs.

1.3 ACCESSORIES

Part Number	Description
172205	CHT-100 Crystal Holder, Teflon®, SMB Connector
173205	CHC-100 Crystal Holder, CPVC, BNC Connector
184204	CHK-100 Crystal Holder, Kynar®, SMB Connector
184208	FC-550 Flow Cell
603211	DB25S to Terminal Strip for Passive I/O Card
603212	DB37S to Terminal Strip for Data Acquisition Card
603216-2	Cable, SMB Plug-SMB Plug, 2' length, RG174A/U coax
888023	Adapter, BNC Male to SMB Jack
803081	Power Cord
803312	Capacitance Tuning Tool
885072	2.5 mm Male Connector – For Crystal Face

Refer to INFICON Price List for more accessories and other products.

1.4 OPTIONAL CARDS

Part Number	Description
603208	Crystal Measurement Card (3.8 to 6 MHz)
603208-2	Crystal Measurement Card (5.1 to 10 MHz)
603209	Data Acquisition Card
603210	Passive I/O Card

2 GETTING STARTED

2.1 UNPACKING

Your RQCM was released to the carrier in good condition and properly packed. It is essential to all concerned that the contents of the shipment be carefully examined when unpacked to assure that no damage occurred in transit. Check the material received against the packing list to be certain that all elements are accounted for. Basic items included with your RQCM are:

1 RQCM Unit
1 Operation and Service Manual
1 Power cord
1 Capacitance Adjustment Tool (1 per Crystal Channel)
1 2.5 mm Male Connector for mating to Crystal Face (1 per Crystal Channel)
1 9-Pin Female-Female D-sub Computer Interface Cable
1 CD-ROM contains computer application software

In addition, you may have ordered one or more of the accessories listed in Section 1.3 and 1.4.

If there is evidence of loss or damage:

a) Notify the carrier or the carrier agent to request inspection of the loss or damage claimed.
b) Keep the shipping containers until it is determined whether or not they are needed to return the equipment to INFICON.

2.2 SAFETY PRECAUTION

All standard safety procedures associated with the safe operation and handling of electrical equipment must be observed to avoid personal injury and damage to the unit. In addition, the following guidelines must be observed.

2.2.1 LINE VOLTAGE

The RQCM can be set to operate at one of the four line voltages, namely 100, 120, 220, 240 VAC @ 50 or 60 Hz line frequency. Verify the power entry module is correctly set for your local line voltage.

2.2.2 GROUNDING

A chassis-grounding lug is located in the rear panel of next to the power entry module. Use a foil or braided wire of #12 AWG or larger to connect the ground lug directly to a facility earth ground to provide additional protection against electrical shock.

2.2.3 LINE FUSES

The RQCM is protected by two miniature Type T fuses. They are located inside the power entry module and replaceable. The fuse rating is 4/10 amperes, 250 V.

2.3 SYSTEM CHECKOUT

Connect the DB9S computer cable to the RS-232/RS-485 port located on the rear of the RQCM. Connect the other end of the cable to the computer serial port. If you have the

IEEE-488 communication option, install the proper cable.

Refer to Section 7.1 to install, setup and run the RQCM software.

Connect the crystal holder, with a crystal installed, to the SMB connector labeled Crystal by means of the 24-inch SMB coaxial cable.

Observe the AC voltage setting on the rear panel. Make sure it is set for your local line voltage. Plug one end of the power cord to a power outlet and plug the other end into the power entry module in the rear of the RQCM.

Refer to Figure 4, and Figure 7 for complete system connections. If your RQCM is equipped with optional cards, refer to their appropriate section for detail instruction on installation and operation.

Switch the front panel power switch to **on**. All of the red communication LEDS on the front panel will light up for two seconds then some will turn off reflecting the status of the communication lines. The green System Ready LED will come on and remain on until the RQCM power is turned off. If the System Ready LED fails to turn on then there is an internal problem with the RQCM. Please refer to section 10 for troubleshooting.

Start the RQCM computer program. Note that you may have to set the RQCM address and select the correct COMM port in the Setup Menu in order for the RQCM to communicate with your PC. Click on the View Status button to bring up the Status Screen. The Status Screen should indicate a crystal frequency within the specified range for the type of crystals being used. The frequency should be stable to within a few hertz and the crystal resistance should be between 5 Ω and 15 Ω for an uncoated polished crystal in air.

Check the capacitance cancellation by pressing and holding the Reset switch. The green, Lock LED should light. Keeping the Reset switch pressed, adjust the fine capacitance trimmer counterclockwise (decreasing the capacitance) by about 5 degrees. The yellow, Sweep LED should flash. Back the trimmer clockwise to the point where the Sweep LED just stops flashing. The capacitance cancellation should be checked and readjusted every time the environment of the crystal and holder is changed. i.e. if the crystal and holder are moved from air to liquid or liquid to air.

Remove the crystal. The red, Unlock, LED should light. The green, Lock, LED should go off. The Sweep LED should not flash. If the Sweep LED flashes the capacitance is under compensated. Reinstall the crystal in the holder and repeat the process until it is perfectly compensated (Sweep LED not flashing when the crystal is removed). Refer to Section 3.4 for more details on adjusting the capacitance cancellation.

2.3.1 CRYSTAL MEASUREMENTS VERIFICATION

A quick way to test your RQCM is to verify its measurements of frequency and resistance in air and in water. The measurement values of frequency and resistance are as follows. For a thorough test, the crystal can be immersed in a series of viscous glycerol/water solutions at 20ºC and compare its measurement values against the predicted results shown in Figure 14 and Figure 15.

2.3.1.1 In Air

If you are using INFICON 1” Polished, 5 MHz Gold Electrode Crystal, after compensated for the capacitance, the frequency should be between 4.976 to 5.020 MHz, and the resistance should be between 5 to 15 ohms. Record the frequency and resistance values.

2.3.1.2 In Water

Submerge the crystal holder into room temperature water (20°C) and adjust for capacitance. The frequency should decrease ~ 721 Hz and the resistance should increase ~ 364 ohms from the values recorded in air.

3 OPERATION

The heart of the RQCM is the crystal measurement methodology. It is important that the user understand its operation to ensure proper setup and application.

3.1 GENERAL DESCRIPTION OF THE CRYSTAL MEASUREMENT

The INFICON Phase Lock Oscillator (used on the Crystal Measurement Card) was developed specifically to support the use of the quartz crystal microbalance in the measurement of lossy films and in liquid applications. In addition to accurately tracking the frequency of heavily damped crystals, the RQCM also tracks the crystal's resistance. This provides additional information in the study of lossy films and/or viscous solutions.

The PLO utilizes an internal oscillator referred to as a Voltage Controlled Oscillator (VCO) to drive the crystal. The crystal current is monitored and the frequency of the oscillator is adjusted until there is zero phase between the crystal voltage and current. Assuming that the crystal's electrode capacitance has been effectively cancelled, this point of zero phase between the crystal current and voltage is the exact series resonant point of the crystal. The magnitude of the current at this point is directly proportional to the crystal's conductance. This current is monitored by the RQCM and displayed as crystal resistance. The PLO contains a phase detector that continuously monitors the phase difference between the crystal's current and voltage. At frequencies below the crystal's resonant frequency the current leads the voltage and the phase goes to 90 degrees as the frequency separation continues to increase, see Figure 19. Above the resonant point the current lags the voltage and the phase go to minus 90 degrees. As the frequency increases through the resonant frequency, the phase goes from plus 90 through 0 to minus 90. It is interesting to note that the phase angle is 45 degrees when the VCO frequency is one half of the crystal's bandwidth above or below the crystal's resonant frequency.

The output of the phase detector is fed into an integrator. The integrator accumulates the phase error such that any positive phase error causes the integrator output to climb; a negative phase causes the integrator output to fall. With zero phase error the Integrator output holds steady.

The integrator output is connected to the VCO. Thus, if the VCO frequency is initially below the crystal resonant frequency, the phase will be positive, producing a positive output at the phase detector. This causes the Integrator output to climb, which causes the VCO frequency to increase. When the VCO frequency matches the resonant frequency of the crystal the phase will decrease to zero, the phase detector output will go to zero, the Integrator output will hold steady and the VCO frequency will be "locked" to the crystal's resonant frequency.

If the crystal's resonant frequency moves up or down, a phase difference between the crystal voltage and current will develop, producing a phase detector output. The non-zero phase detector output will drive the Integrator output up or down until the phase is zero once again, thus keeping the VCO frequency locked to the crystal's resonant frequency.

Once the frequency of the VCO is locked to the series resonant frequency of the crystal, the in-phase component (at zero phase error, there is no out of phase component) of the crystal current is demodulated to a DC voltage. This voltage is amplified and converted into resistance value which the RQCM outputs to the computer.

3.2 UNDERSTANDING AND SETTING UP A CRYSTAL MEASUREMENT CHANNEL

The RQCM can have up to three independent crystal measurement channels. Each channel has a crystal input, three status LED's, fine and course capacitance adjustments, a reset switch and a crystal face connection. Refer to Figure 2.

3.3 FRONT PANEL DESCRIPTION

3.3.1 LOCK INDICATOR

The green, Lock LED is **on** when the oscillator is locked on a crystal's resonant frequency.

3.3.2 UNLOCK INDICATOR

The Red, Unlock LED will be **on** whenever the oscillator is not locked on a crystal.

3.3.3 SWEEP INDICATOR

The Yellow, Sweep LED flashes each time the frequency ramp is reset to its low starting point. In normal operation, the sweep light will only flash while adjusting the capacitance compensation. The Sweep LED will not light when locked on a crystal.

3.3.4 RESET SWITCH

The Reset switch should be pressed while adjusting the capacitance compensation. This switch forces the VCO to its lowest frequency independently of the Integrator output. The Reset switch also forces the Lock LED on, thus turning off the quadrature current injection which is required for proper capacitance cancellation adjustment. The equivalent of about 1.5 pfd of capacitance is added as quadrature current to insure that the VCO ramps up in frequency when not locked onto a crystal. The quadrature current is turned off as soon as a lock is detected.

3.3.5 CRYSTAL CONNECTOR

The SMB connector labeled Crystal provides connections to the crystal. When used with a INFICON crystal holder, the center pin connects to the crystal's rear electrode, and the connector housing connects to the crystal's front electrode.

3.3.6 CRYSTAL FACE CONNECTOR

The Crystal Face connector provides a direct connection to the crystal's front electrode. Note that the mating connector (2.5 mm male plug) provided with each Crystal Measurement Channel must be used for proper connection. When the mating connector is inserted, the crystal face electrode is galvanically (transformer) isolated from earth ground allowing a potential to be applied. Use this connection to connect the crystal face electrode to the working electrode of a potentiostat or galvanostat for electrochemical experiments. When this connection is not in use, the crystal face electrode is grounded to minimize effects of capacitance that may couple to crystal face electrode in non-electrochemical experiments.

3.3.6.1 Crystal Face Mating Connector

The mating connector to the Crystal Face Connector is a 2.5 mm male plug. The plug carries two contacts, the tip and the sleeve (see Figure 1). However, only the tip contact is used to connect to the working electrode of a potentiostat. You can solder the working electrode wire directly to the tip terminal. The sleeve terminal is not used. You can disregard it or break it off.

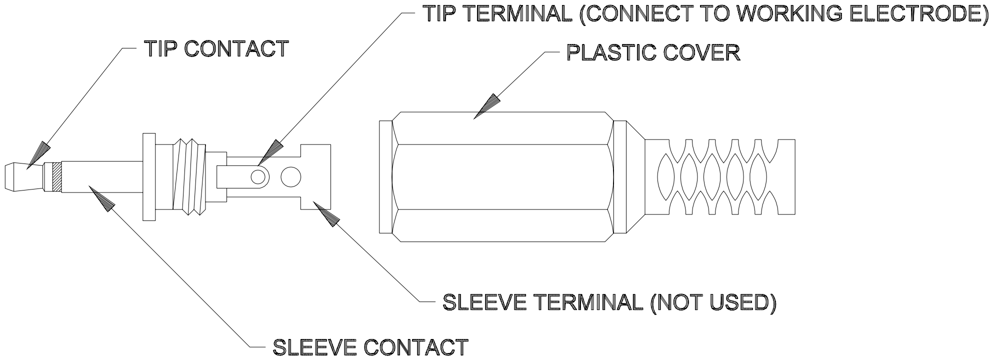


Figure 1 Crystal Face Mating Connector

3.3.7 FINE AND COURSE CAPACITANCE ADJUSTMENTS

The Fine and Course capacitance adjustments are used together to cancel out the unwanted static capacitance of the crystal, the crystal holder, and the connecting cable. Refer to Section 3.4 for procedure on the proper adjustment.

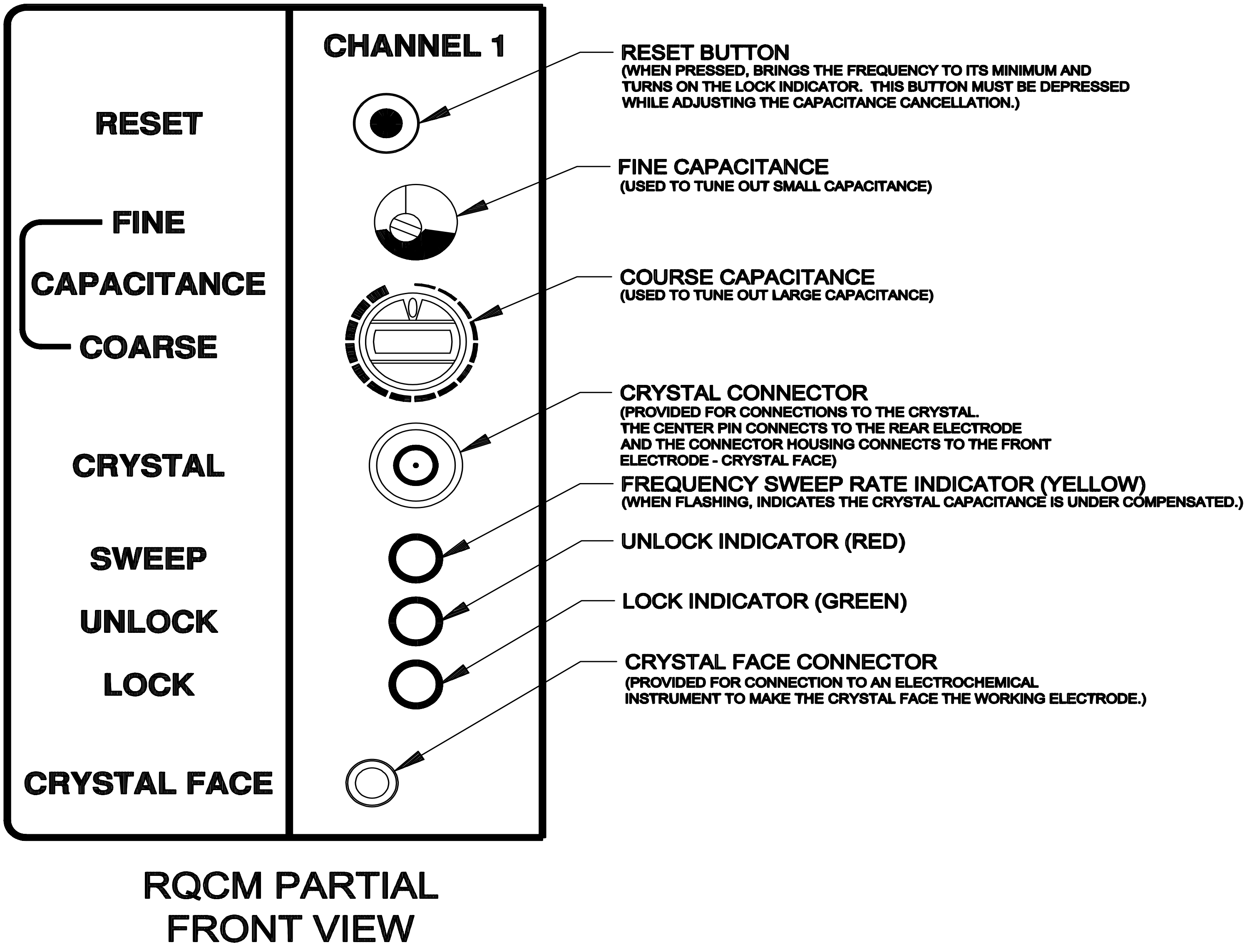


Figure 2 Crystal Channel Description

3.4 ADJUSTING THE CAPACITANCE CANCELLATION

Proper adjustment of the Capacitance Cancellation is critical in obtaining accurate results with high resistance (heavily damped) crystals. See Section 5.8. The cancellation adjustment should be performed with the crystal holder and crystal in the measurement environment. For instance, if liquid measurements are to be made, insert the crystal and its holder into the liquid where the measurement will be made.

With the crystal and holder in the measurement environment, press and hold the Reset switch. Pressing and holding the Reset switch forces the VCO to its minimum frequency, turns on the Lock LED, and turns off the quadrature current injector. Forcing the VCO to its minimum frequency insures that the crystal is being driven at a frequency far from its resonant frequency where its impedance is essentially due only to the shunt electrode capacitance. With the quadrature current injector turned off, the measured current is due only to the net shunt capacitance. The measured net shunt capacitance is the capacitance of the cable, holder and crystal electrodes minus the compensation capacitance. If the capacitance is under compensated, the phase of the measured current leads the voltage, (a phase angle of plus 90 degrees). If the capacitance is over compensated, it lags the voltage, (a phase angle of minus 90 degrees).

The Yellow Sweep LED is used to determine whether the crystal capacitance is over compensated or under compensated. The Sweep LED flashes whenever the crystal capacitance in under compensated.

If the Sweep LED is not flashing, turn the fine adjustment counterclockwise until it begins to flash then back up until it just stops. If it is flashing, turn the fine adjustment clockwise until it just stops flashing. This is a very fine adjustment. Go back and forth until you are sure you are right on the edge. The sensitivity of the fine adjustment is approximately 0.05 pfd per degree. In situations where the crystal resistance is very high (over 1 KΩ) a net capacitance of over 0.5 pfd can result in a significant frequency error so try to get this adjustment to within a couple of degrees. Remember to keep the Reset switch depressed while making this adjustment.

3.5 ADJUSTING CAPACITANCE CANCELLATION TRIMMER & SWITCH

Setting up the capacitance cancellation is fairly straightforward. The thing to remember is that there are two adjustments, a course (rotary switch) and a fine (capacitor trimmer) with the total compensation capacitance being the sum of the two. The trim capacitor has no stops so it's not obvious when it is at its minimum or its maximum.

The fine adjustment capacitor has circular, rotor plates that mesh into fixed stator plates. The capacitance is at a maximum when the plates are fully meshed and a minimum when rotor plates are above the stator plates and not meshed. As the capacitor is rotated clockwise it goes through a full cycle from maximum to minimum and back to maximum. Or, depending on where you start it may go first toward a minimum, then to a maximum and then back toward a minimum. To avoid confusion, always turn the fine adjustment clockwise as we approach the desired capacitance and we want the capacitance to be decreasing.

The coarse adjustment is a rotary switch. Like the fine adjustment, it goes from its minimum to its maximum, then back to its minimum capacitance value in a full rotation. The difference is that it has 16 positive stops. Observe the "V" notch on the switch (Figure 3). The coarse adjustment is at its minimum capacitance when the "V" notch is pointing straight upward (zero position). The capacitance is increased with each stop as the switch is rotated clockwise. It reaches maximum capacitance at the 15th stop – one stop before returning to the zero position.

The RQCM is setup for a standard INFICON crystal holder and cable from the factory so you should not have to change the course adjustment. Simply connect the cable and crystal holder to the SMB connector labeled Crystal but don't install a crystal.

If the Sweep LED is flashing, press and hold the Reset button and then turn the fine trimmer clockwise until it just stops flashing. Go back and forth a few times to get a feel for the point where the Sweep LED just stops flashing. Release the Reset button and the Sweep LED should begin to flash again.

Install a crystal. The PLO should lock. Even so, press and hold the Reset button and again adjust the fine trimmer to the point where the flashing just stops. The capacitance cancellation adjustment is now perfect. Remember to check this adjustment whenever the crystal's environment changes.

If you could not find the proper zero capacitance point using the fine trimmer alone, then the coarse rotary switch needs to be adjusted. Follow the instructions below to set the coarse rotary switch.

First adjust the fine trimmer so that it is 50% meshed and the rotor plates are below the shaft. You can see these plates through the oversize adjustment hole. See Figure 3. Next connect a cable and crystal holder, and the crystal, if you haven't already done so.

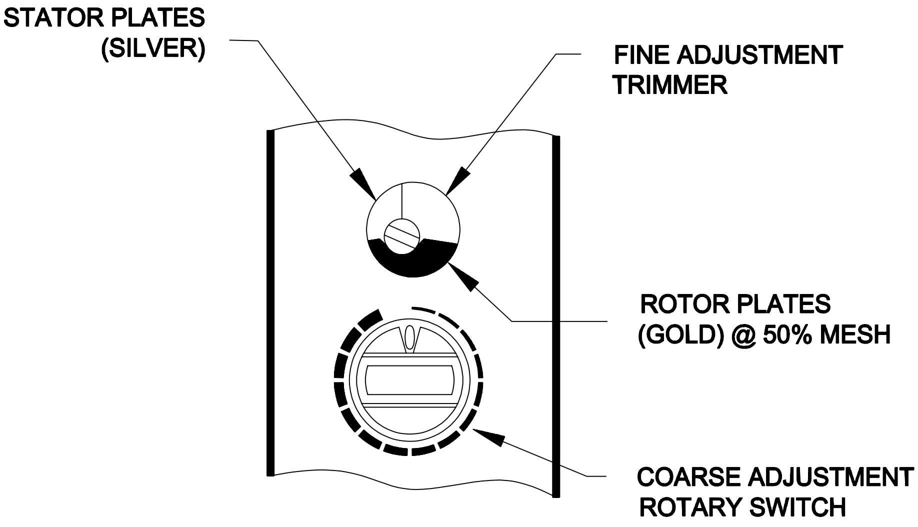


Figure 3 Capacitance Adjustments

Set the course rotary switch to its minimum. Depress the Reset button, and observe the yellow, Sweep, LED. It should be flashing very fast, indicating the capacitance is grossly under compensated. Now rotate the course switch clockwise, one step at a time. At each stop observe the yellow, Sweep, LED, at some point it will cease to flash. Back off one stop so the flashing begins again. The course adjustment is complete.

Slowly adjust the fine trimmer clockwise (increasing capacitance) until the flashing of the Sweep LED just stops. The capacitance compensation adjustment is now complete. Release the Reset button and assuming the crystal is not dead or out of range, the RQCM will lock on it.

3.5.1 AS A GENERAL RULE

- The Reset switch must be depressed during the adjustment for capacitance cancellation.
- Capacitance cancellation is essential for accurate measurements of liquids and lossy (soft)

films.

- Use a shortest cable possible for connection from the Crystal Holder to the RQCM. Cables' capacitance changes with temperature and position, the longer the cable the larger the capacitance; hence the larger change in capacitance.
- Capacitance cancellation should be checked and readjusted every time the environment of the crystal is changed, for example, transition from air to a liquid phase.
- The capacitance cancellation adjustment must be performed with the Crystal Holder and crystal in the actual measurement environment.

3.6 WORKING WITH VERY LOW Q CRYSTALS

Very low Q crystals require very close adjustment of the compensating capacitance to insure a successful lock. To adjust the compensation capacitance one pushes the Reset button and adjusts the capacitance to the point where the Sweep LED just ceases to flash. With very low Q crystals, the PLO may not lock upon release of the Reset button. The Unlock LED will be on and the Sweep LED will be flashing. This is normal. Even so it may be possible to lock on the crystal by slowly adjusting the fine capacitance clockwise until the Sweep LED again ceases to flash. Lock is evidenced by the Lock LED turning on or by a crystal resistance of less than 10 KΩ.

Once lock is achieved the true series resonant point can be found by adjusting the capacitance for minimum resistance value. The limits of the crystal bandwidth can be determined by adjusting the capacitance and reading the maximum frequency and the minimum frequency just before the RQCM loses lock.

3.7 NORMAL OPERATION

The RQCM comes set up for operation with a INFICON cable and crystal holder. If a INFICON cable and crystal holder is being used, then no initial adjustments should be needed.

During normal operation with a crystal installed and connected to the oscillator, the green Lock LED will be on and the frequency output will reflect the crystal resonance. The red Unlock LED will be off.

If the Unlock LED is on, the Sweep LED should slowly flash. Continuous sweeping of the frequency range indicates that the crystal's resonant frequency is outside of the PLO's frequency range or the crystal's conductance is below the conductance threshold.

No flashing of the Sweep LED when the Unlock LED is on can mean one of two things. First, if the VCO frequency is sitting at its low limit, it means the electrode capacitance is over compensated. Second, in some cases, even though the crystal conductance has fallen below the threshold necessary to indicate lock, the internal signals are still sufficient to keep the VCO locked to the crystal. In that case, the PLO really is locked and the VCO frequency will be sitting at the crystal frequency somewhere between its minimum and maximum frequencies.

If the VCO frequency is sitting at its low limit, press and hold the Reset switch and adjust the fine capacitance trimmer a few degrees counterclockwise (not more than ten) until the Sweep LED begins to flash.

3.8 HOOKUP FOR ELECTROCHEMICAL EXPERIMENTS

Figure 4 shows a typical connection diagram for an electrochemical QCM using the INFICON RQCM. Note that the crystal's front electrode becomes the "working electrode" when the Crystal

Face Connector on the RQCM is connected to the potentiostat's "working electrode" port. 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 5 is an example of a typical voltammogram plot obtained from the INFICON RQCM with a PC. This particular experiment involved a 0.1 M solution of CuSO4 in 0.5 M H_2SO4, using a 5 MHz, 1 inch diameter, polished, gold coated crystal mounted in a CHC-100 Crystal Holder as the working electrode.

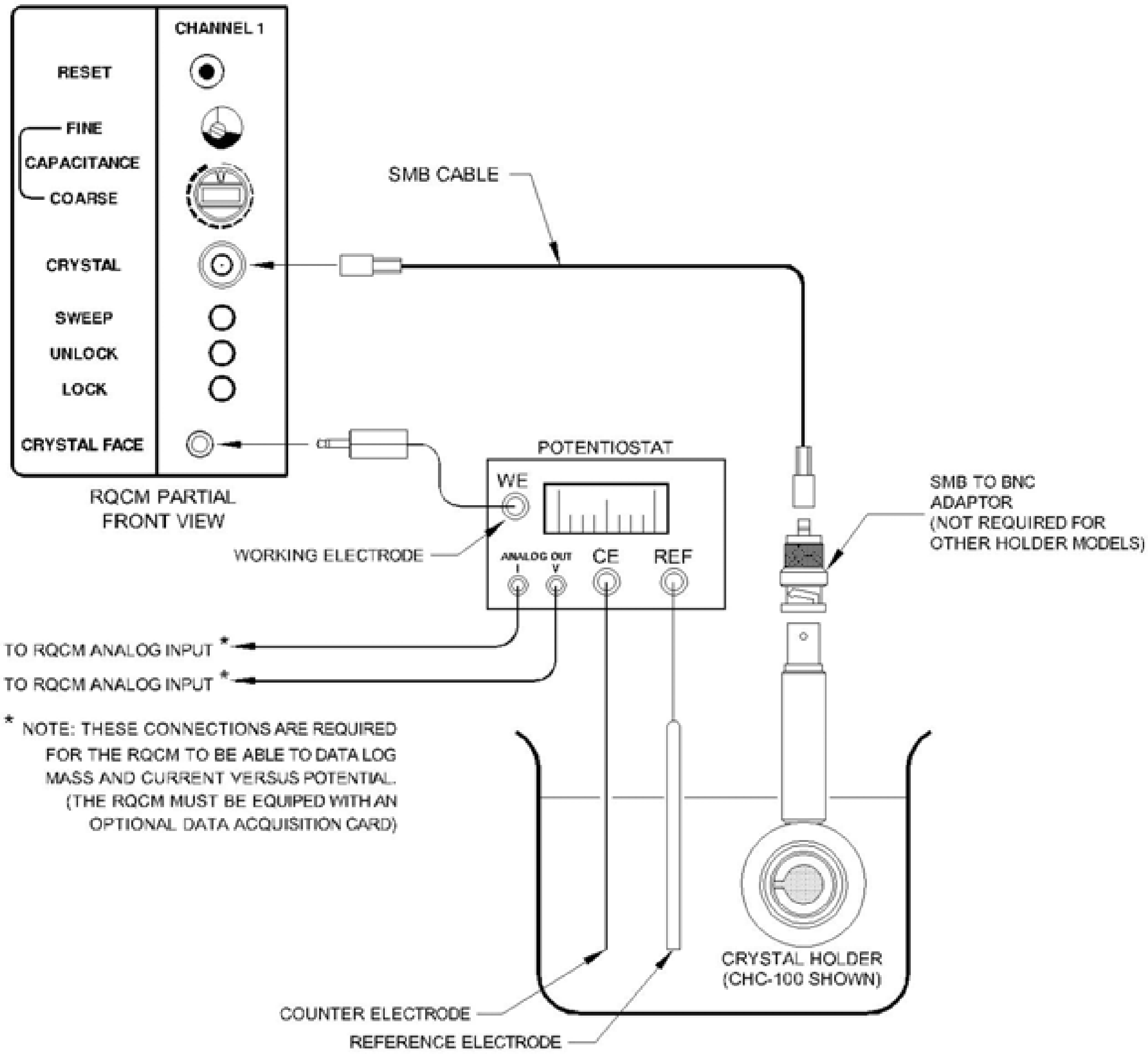
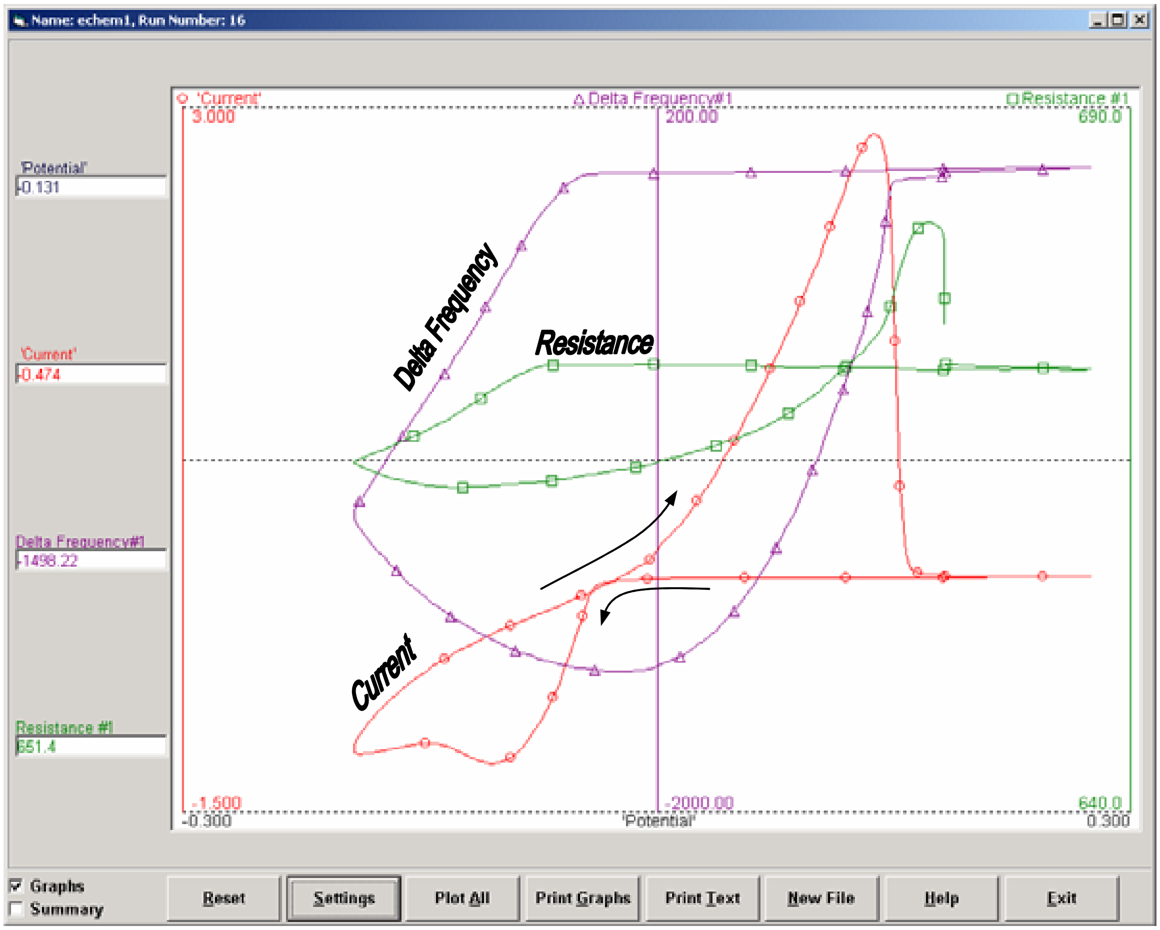


Figure 4 Typical Connections For An Electrochemical QCM Experiment



Name: echem1, Run Number: 16

'Potential' 0.131

'Current' 0.474

Delta Frequency#1 -1498.22

Resistance #1 651.4

Figure 5 Typical Voltammogram Plot Obtained Using the RQCM

3.9 OPERATION GUIDELINES

This section offers some general guidelines to help minimize errors in the measurements due to the environment of the sensor crystal. It is the user's discretion as which are best to utilize for a particular experiment. Keep the following tips in mind when setting up an experiment.

3.9.1 ALLOW THE RQCM TO WARM UP

Allow for about one to two hours of warm-up time for the RQCM's electronics to reach temperature equilibrium.

3.9.2 ISOLATE THE RQCM FROM TEMPERATURE CHANGE

Limit temperature changes of the RQCM's environment as this will cause small changes in the measured crystal frequency. The most likely source that alters the RQCM temperature is the room air-conditioning system. Keep the RQCM away from the direct path of air-conditioning vents.

3.9.3 FOR OPERATION IN AIR

In gas-phase measurements, the single factor that is most likely to induce frequency instability or drift is temperature. Review section 4.1.9 for more information on the crystal's response to temperature.

3.9.3.1 Operate at or Near The Crystal's "Turn-Around-Point"

When possible, perform the experiment at the sensor crystal's "turn-around-point". At or near this temperature, most of the errors due to temperature are negligible. The "turn-around-point" is where the temperature coefficient of the crystal is zero. That is, there is no change in resonance frequency due to a change in the temperature of the crystal at the turnaround point. INFICON's 1 inch crystals are optimized for two operating temperatures namely 90ºC and 25ºC.

3.9.3.2 Control The Temperature

If operation at or near the crystal's zero turn-around-point is not possible, the operating temperature should be controlled within a degree or a fraction of a degree of its desired value. How tightly the temperature should be controlled depends on how far the operating temperature is from the zero turn-around-point, the further away from the turn-around-point, the larger the error. For example, for 90ºC-cut-crystal, about 1.5 Hz/ºC error is expected if operating at 80ºC. However, as much as 5 Hz/ºC error is expected when operating at 60ºC.

3.9.3.3 Keep the Test Chamber Clean

Keep the test chamber clean, as any particle attached to the crystal's sensing surface will result in a frequency change.

3.9.3.4 Keep a Constant Gas Flow

If a gas is used, keep the flow constant throughout the experiment. The crystal's frequency is also sensitive to changes in pressure, which will result, if the flow rate is not constant.

3.9.4 FOR OPERATION IN LIQUIDS

Since the sensor crystal is dampened by the liquid, any error in the measurements will be amplified. Extra care must be taken to ensure minimal error. The sample liquid should be prepared carefully. Changes in temperature or the properties of the solvent as well as air bubbles will affect the sensor signal.

3.9.4.1 Degas The Sample Liquid

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

3.9.4.2 Wait For Mechanical Disturbances To Stabilize

To minimize random fluctuations cause by vibrations, it is best to immerse the holder, with a crystal installed, in the sample solution several hours before the experiment is started.

3.9.4.3 Wait For The Temperature To Stabilize

To avoid the formation of air bubbles and reduce temperature related artifacts, the sample liquid should have approximately the same temperature as the measurement chamber's working temperature (±2°C). Wait at least one hour after a holder is immersed in a liquid to allow for the crystal to come to equilibrium, before performing any accurate measurements.

3.9.4.4 Prepare Your Solutions Carefully

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

3.9.4.5 Avoid Using A Stirrer

If possible, avoid using a magnetic stirrer. Stirrers create turbulences. However, many solutions often require the use of a magnetic stirrer to keep a solution well mixed. If this is the case, keep the stirrer rotating speed constant throughout the experiment.

3.9.5 FOR OPERATION WITH THE FC-550 FLOW CELL

The FC-550 is used in place of the Crystal Retainer Ring to create a flow chamber of ~ 0.1 mL. This setup can be used for either gas or liquid flow. In both cases, observe the following tips to avoid unwanted effects in the measurements.

3.9.5.1 Avoid Excessive Differential Pressure

The differential pressure from the front to the back of the crystal must be minimized to avoid frequency errors due to stress on the crystal and to avoid crystal breakage. INFICON's 1-inch, 5 MHz, AT cut crystal will fracture at pressure differentials above 5 PSI.

3.9.5.2 Keep a Constant Line Pressure

Using a pumping system that minimizes pulsation and maintains a constant line pressure throughout the experiment. A syringe pump is a good choice because it provides pulse-less flow. If a peristaltic pump is used then it is better to pull the liquid through the flow cell to reduce frequency fluctuations caused by pulsing. Gravity flow is another good method for flowing fluid through the cell without the pulsation effects. However, the line pressure does change as the volume of the fluid reduces in the reservoir. Care must be taken to maintain the volume in the reservoir.

3.9.5.3 Allow Ample Time For the Crystal To Come to Equilibrium

Expose the flow cell's chamber and the sensor crystal to the medium. Wait for it to come to equilibrium and establish a baseline prior to making measurements.

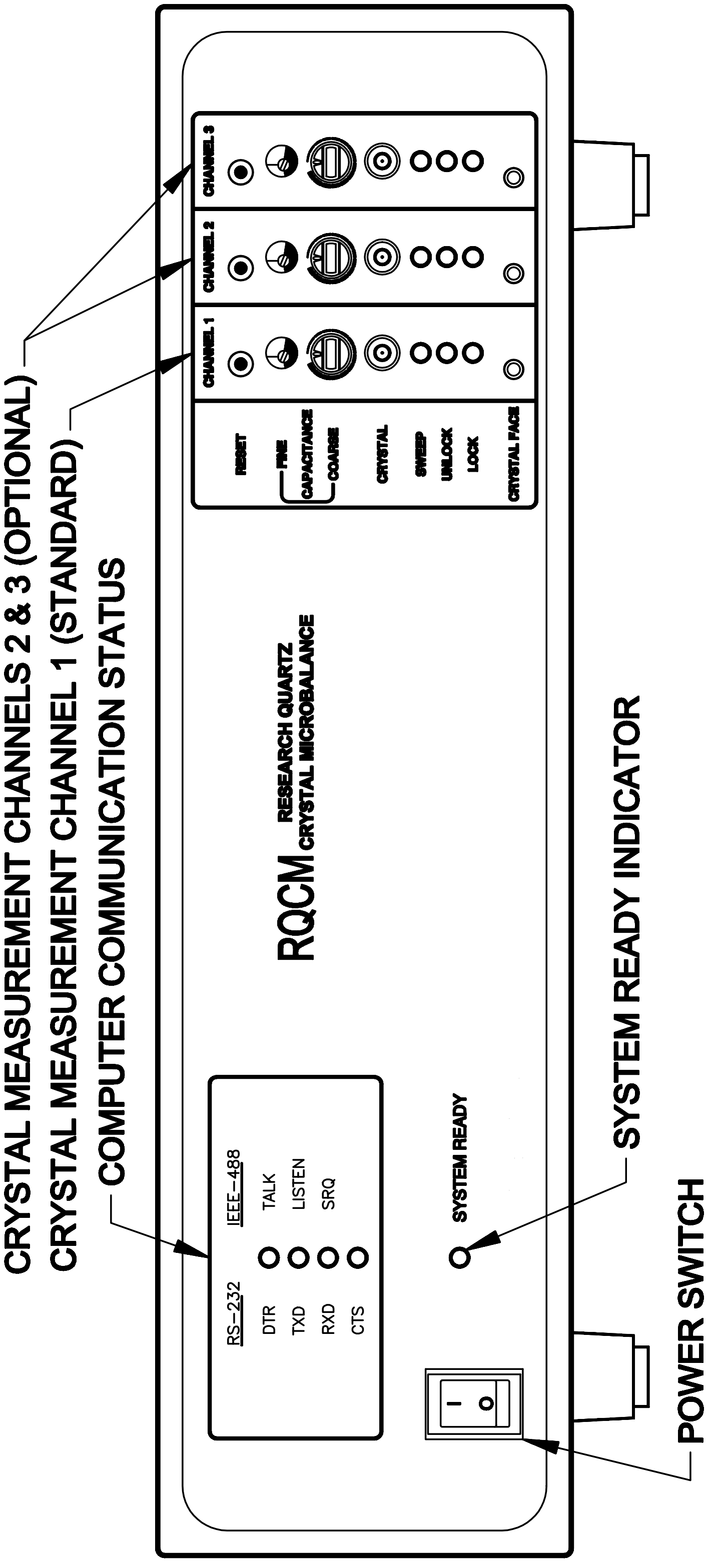


Figure 6 RQCM Front Panel

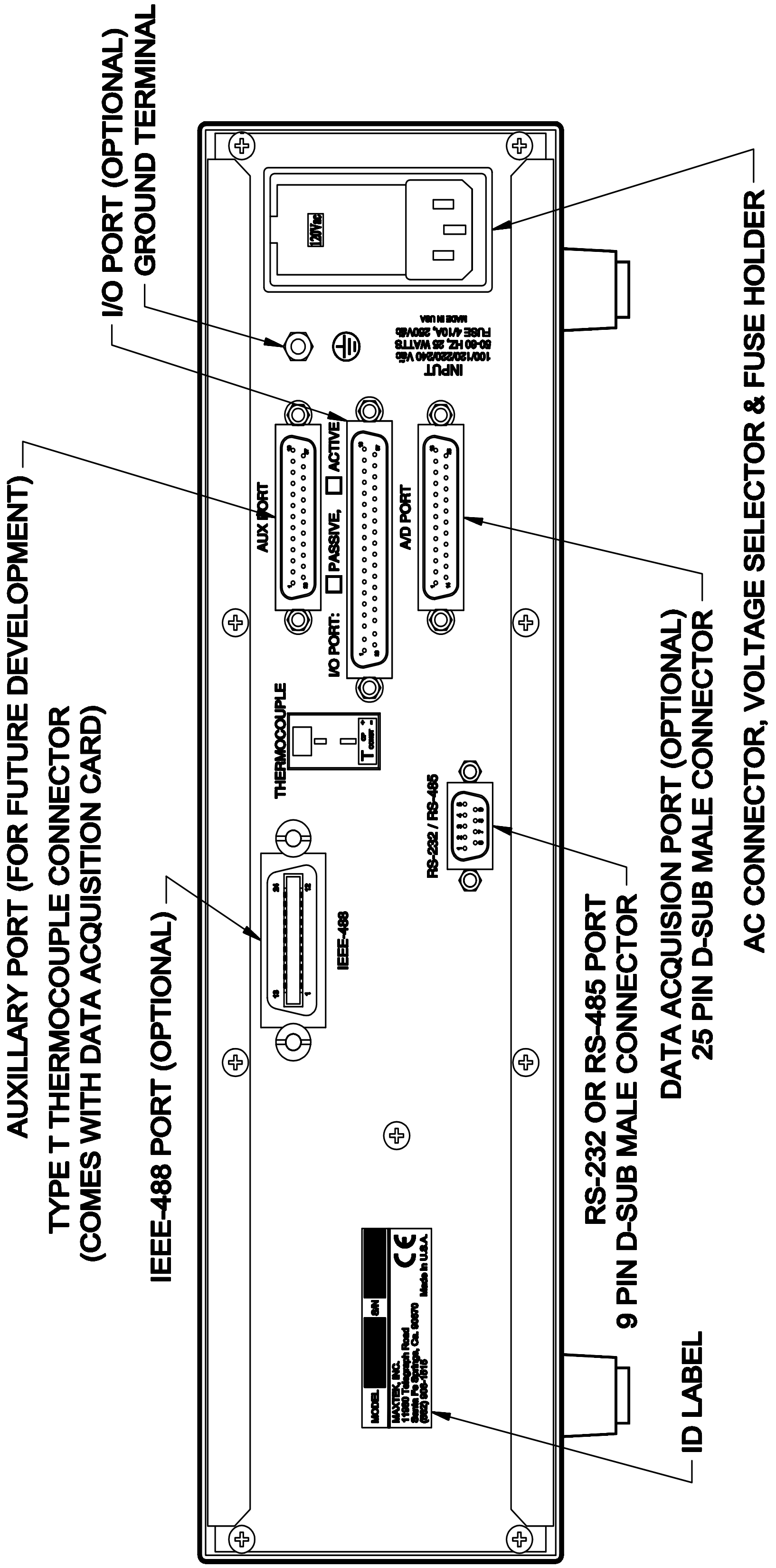


Figure 7 RQCM Rear Panel

4 CRYSTALS, HOLDERS AND FLOW CELL

An essential part of the RQCM system is the sensing crystal. Careful handling of both the crystal and the crystal holder must be observed to ensure proper and reproducible measurements. Furthermore, the sensing crystal, the crystal holder and the connecting cable must be orientated and connected correctly in order for the RQCM to work properly. This is especially true if you design your own crystal or holder.

If you have purchased a INFICON crystal, holder and cable, the installation is simple. Follow the instructions below.

If you plan to build your own crystal or holder or cable, see Section 4.3.2.

4.1 1 INCH DIAMETER CRYSTALS

IINFICON pioneered the standard AT-cut, 5 MHz, 1-inch diameter crystals for use in liquid applications. The AT-cut quartz is chosen for its superior mechanical and piezoelectric properties, and the angle of cut can be adjusted to obtain a zero temperature coefficient at a desired operating temperature. The 1 inch diameter was chosen to allow enough distance between the active area of the crystal and the mounting o-ring. This improves the overall stability of the crystal by reducing the frequency changes due to mounting stress.

4.1.1 ELECTRODE CONFIGURATION

Figure 8 below shows INFICON's 1" crystal electrode patterns. The left figure shows the ½ inch diameter front electrode (also called sensing electrode) with an extended electrode that wraps around the edge of the crystal and extends into a semicircle shown in the top half of the right figure. The lower half of the right figure shows the ¼ inch diameter rear electrode (also called contact electrode).

This configuration enables both electrical contacts to be made on the backside of the crystal allowing measurement in conductive liquids.

The oversized front electrode (½ inch in diameter as oppose to the ¼ inch diameter rear electrode) was chosen to ensure a more consistence deposition across the active area of the crystal. The exposed area of the front electrode is 0.212 in^2 (137 mm^2), but the active oscillation region (displacement area) is limited to the overlapping area of the front and rear electrodes (0.053 in^2 or 34.19 mm^2).

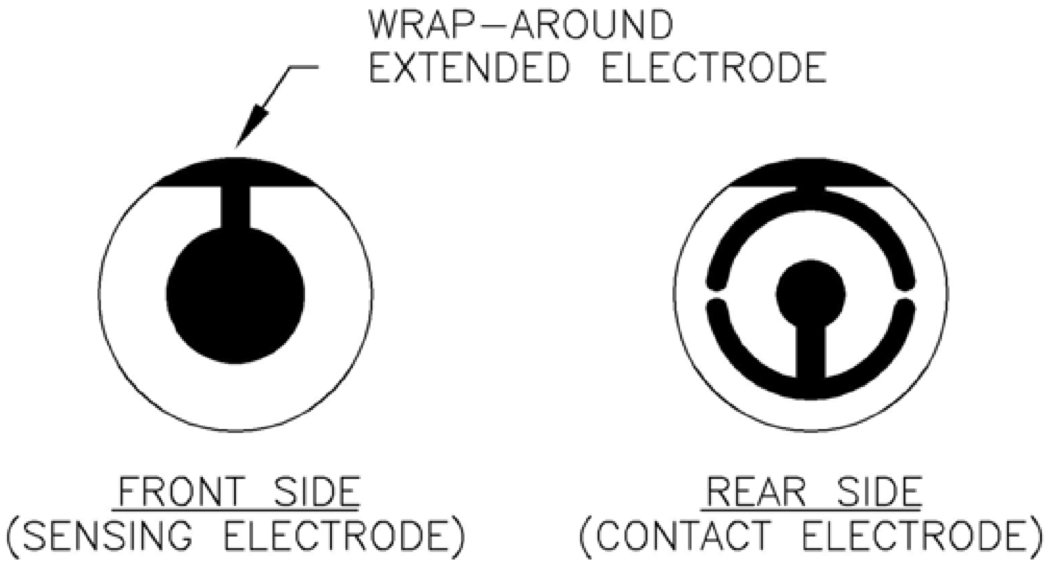


Figure 8 INFICON 1-Inch Diameter Crystals – Electrode Configuration

The figure below shows a INFICON 1" diameter as seen from the front side.

Figure 9 INFICON 1" Crystal - as Seen From The Front Side

4.1.2 CRYSTAL PARAMETERS

Polished one-inch diameter crystals that are commonly available for liquid work have the typical values as listed below.

Type	Frequency Range (MHz)	Electrode Material	Resistance (ohms)	Q Factor
5 MHz	4.976 – 5.020	Gold	~10	120,000
9 MHz	8.976 – 9.036	Gold	~7	55,000

4.1.3 CRYSTAL SURFACE FINISH

Studies have shown that electrode surface roughness can cause large apparent mass loadings due to the liquid that is trapped within pores at the crystal surface [1] . INFICO's crystals are optically polished to 50 Å average surface roughness to minimize this effect. Polished crystals are required to obtain good agreement between theory and measurement during liquid immersion experiments. Polished crystals are also required to obtain measurements reproducibility from crystal to crystal[2].

Non-polished crystals (R_a=1.8 microns) are also available at reduced costs for applications that do not require the accuracy and reproducibility of the polished crystals.

4.1.4 CRYSTAL ELECTRODE MATERIALS

INFICON's crystals are available in a variety of electrode materials including Gold, Platinum, Aluminum, Silver, Titanium, etc. INFICON also offers Gold electrode crystals with an additional SiO2 outer layer to create a hydrophilic surface needed for some biological applications.

4.1.5 CRYSTAL THICKNESS

INFICON AT cut, 1-inch diameter crystals are plano-plano. Their physical thickness is determined by a frequency constant and their final frequency. The frequency constant for an AT cut crystal is 1.668E5 Hz × cm or 65.5 kHz × in. Therefore, the crystal thicknesses for various frequencies are as follows.

5 MHz AT cut thickness = 333 microns (0.013 inch)

6 MHz AT cut thickness = 227 microns (0.0109 inch)

9 MHz AT cut thickness = 185 microns (0.007 inch)

4.1.6 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 $\mu g/cm^2$ range.

Sauerbrey 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[3]. 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:

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

where

Δf = the observed frequency change in Hz,

C_f = the sensitivity factor of the crystal in Hz/ng/cm^2

(0.056 Hz/ng/cm^2 for a 5 MHz crystal @ 20° C)

(0.081 Hz/ng/cm^2 for a 6 MHz crystal @ 20° C)

(0.181 Hz/ng/cm^2 for a 9 MHz crystal @ 20° C)

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

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 equipment used to measure frequency shifts. For example, the INFICON RQCM has a frequency resolution of 0.03 Hz @ 6 MHz, therefore, its minimum detectable mass change is 0.37 ng/cm^2.

The Sauerbrey equation relies on a sensitivity factor, C_f, which is a fundamental property of the QCM crystal. Thus, in theory, the QCM mass sensor does not require calibration. This ability to calculate the mass sensitivity from first principles is obviously a very attractive feature of these devices. However, it is very important to notice, that the Sauerbrey equation is only strictly applicable to uniform, thin-film deposits originating from a low pressure (i.e. vacuum) gas environment[21]. Thick deposits and operation in liquid environments or in contact with lossy films, relies on the use of more complex equations relating the frequency shifts to mass loading, and often requires calibration of the setup for accurate results. Several articles have been published on simple ways to calibrate the mass sensitivity of QCMs for electrochemical applications[4] and for vacuum thin-film deposition processes[5] [6] [7], and some useful calibration guidelines are also described herein.

Many studies have shown that the crystal's sensitivity is approximately Gaussian. The maximum sensitivity is in the center of the crystal and it tapers off towards the edge of the active area[8] [9] [10]. The mass sensitivity distribution has also been shown to become slightly more confined to the electrode region as the mass loading is increased.

4.1.7 STABILITY

A sensor crystal cannot distinguish the difference between a frequency shift due to deposited material or that due to other disturbances. Thus any extraneous factors, other than the deposited mass, which may cause the quartz crystal to change its resonant frequency, must be properly controlled. Factors that can influence the stability of a sensor crystal are categorized as follows[11]:

- The crystal itself: Improper design, localized stress, damage to the crystal
- The crystal holder: Improper seating of the crystal, large mechanical coupling between the crystal and the holder
- Thermal input: Radiation from evaporation source, radiation from substrate heater, bombardment by charge particles, energy released by condensates
- Stress: Thermal stress, stress release in the deposited materials
- Temperature: See section 4.1.9 for data on frequency versus temperature for INFICON’s crystals.

Other factors that can affect stability are humidity, shock, vibration and change in pressure. Controlling those conditions is a must to insure accurate measurements of small mass changes over long periods of time.

4.1.8 CRYSTAL LIFE EXPECTANCY

It is difficult to predict the useful life of a crystal since it depends on many factors. Some of these factors are[11]:

- The quality of the quartz
- The amount of deposited material
- The stress generated in the crystal due to deposited material

- The acoustic losses in the deposited material
- The design of the oscillator circuitry

Other aspects that affect the crystal life include the type of the deposited material, spitting of source material resulting in non- uniform films, film flakes that landed on the crystal's active area, and of course, physical damage to the crystal such as chipping, cracking, or peeling of the electrode, etc.

In general, a sensor crystal can be used until its frequency drops below 50% of its uncoated value. However, for the reasons stated above, crystal failures often occur well before a 40% shift in frequency is reached.

The sensor crystals are considered expendable. However, a crystal may be reused up to 20 times on average in experiments that don't physically alter the crystal electrode. In experiments where a film is deposited, the crystal can be stripped using a chemical etchant . Care must be taken so only the deposited material is stripped and not the crystal electrodes. The amount of times that a crystal can be reused greatly depends on its condition after each experiment or stripping. Needless to say, careful handling and cleaning of the crystal is required to maximize its re-usability.

Noisy or erratic measurement indicates that the crystal is about to fail. It might even be difficult to obtain a stable baseline. Spurious signals might become evident in electrochemical QCM experiments. Visually, traces of consumption and wear can often be seen on the crystal surface. Edges of the sensor crystal might become cracked and the deposited film, even the electrode, starts to show scratches and tears.

The crystal motional resistance R does reflect the influence of deposited material on the performance of a crystal. This resistance is associated with the damping of acoustic waves by the electrodes, deposited materials, and the supporting structure. This resistance increases as more material is being deposited onto the crystal[11]. This resistance value can be used to determine when a crystal reaches a maximum loading.

4.1.9 TEMPERATURE COEFFICIENT

The temperature coefficient of quartz crystals is normally specified in units of parts per million per degree of temperature change. A one part per million change in frequency of the sensing crystal corresponds to an indicated thickness change of approximately 7.4 Å for a material with a density of 1.0 gm/cm^3. For Aluminum with a density of 2.7 gm/cm^3, this is equivalent to approximately 2.7Å. This intrinsic dependence of resonance frequency of a sensor crystal on temperature is generally small in experiments in gas phase when operating at or near its "turn-around-point". The "turn-around-point" is where the temperature coefficient of the crystal is zero. That is, there is no change in resonance frequency due to a change in the temperature of the crystal at the turnaround point. INFICON 1 inch crystals are optimized for two operating temperatures namely 90ºC and 25ºC. These crystals have very good temperature stability when operating close to their specified temperature.

Even though AT cut crystals are designed to minimize the change in frequency due to temperature, the effect of temperature can be significant when attempting to resolve small mass (frequency) changes over long periods of time. This frequency change due to temperature is magnified when the sensor crystal is submerged in liquids. This is due to the coupling of the shear mode oscillation with the temperature dependent viscosity and density of the fluid. For experiments in liquid phase in which the frequency is to be monitored over long periods of time, 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. 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. This allows the crystal to come to equilibrium with the medium. If temperature control is not possible or practical, attempts should be made to measure the temperature of the solution around the crystal during the experiments and perform temperature compensation.

In short, each RQCM 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.

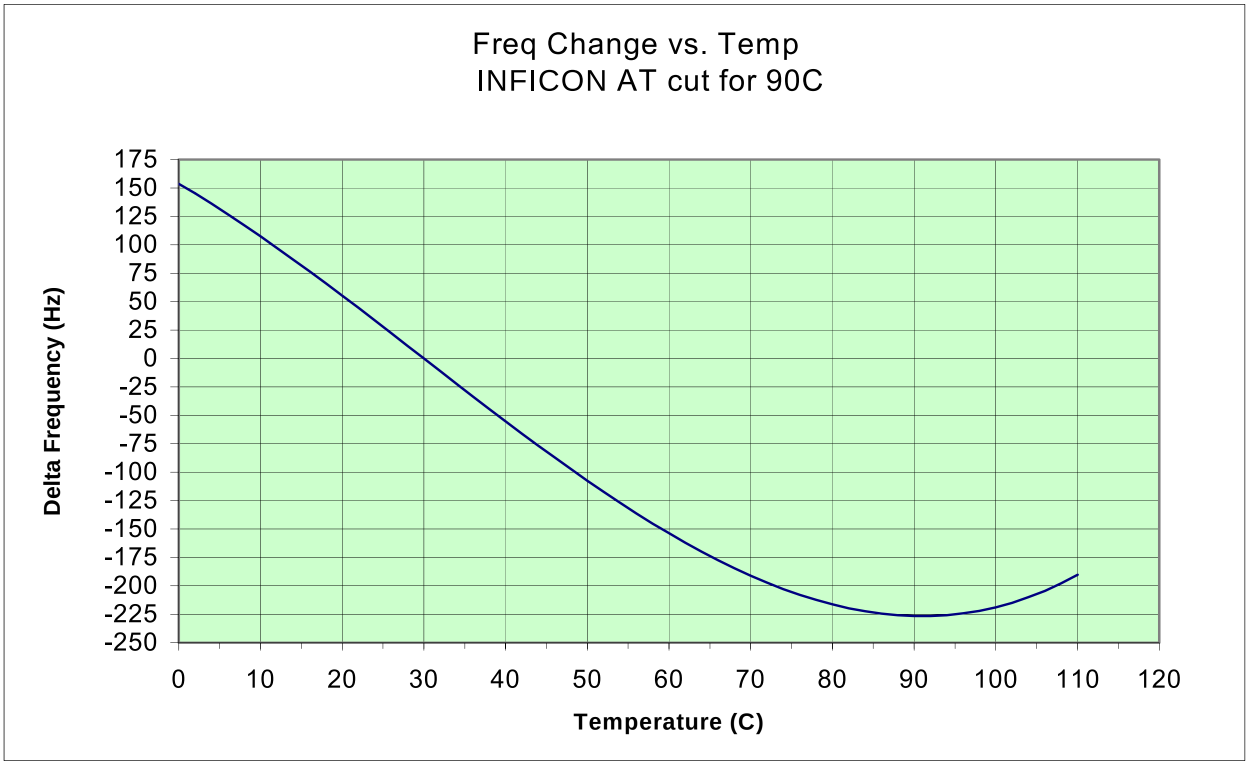


Figure 10 Frequency vs. Temperature of INFICON 1" AT-Cut Crystal for 90 C

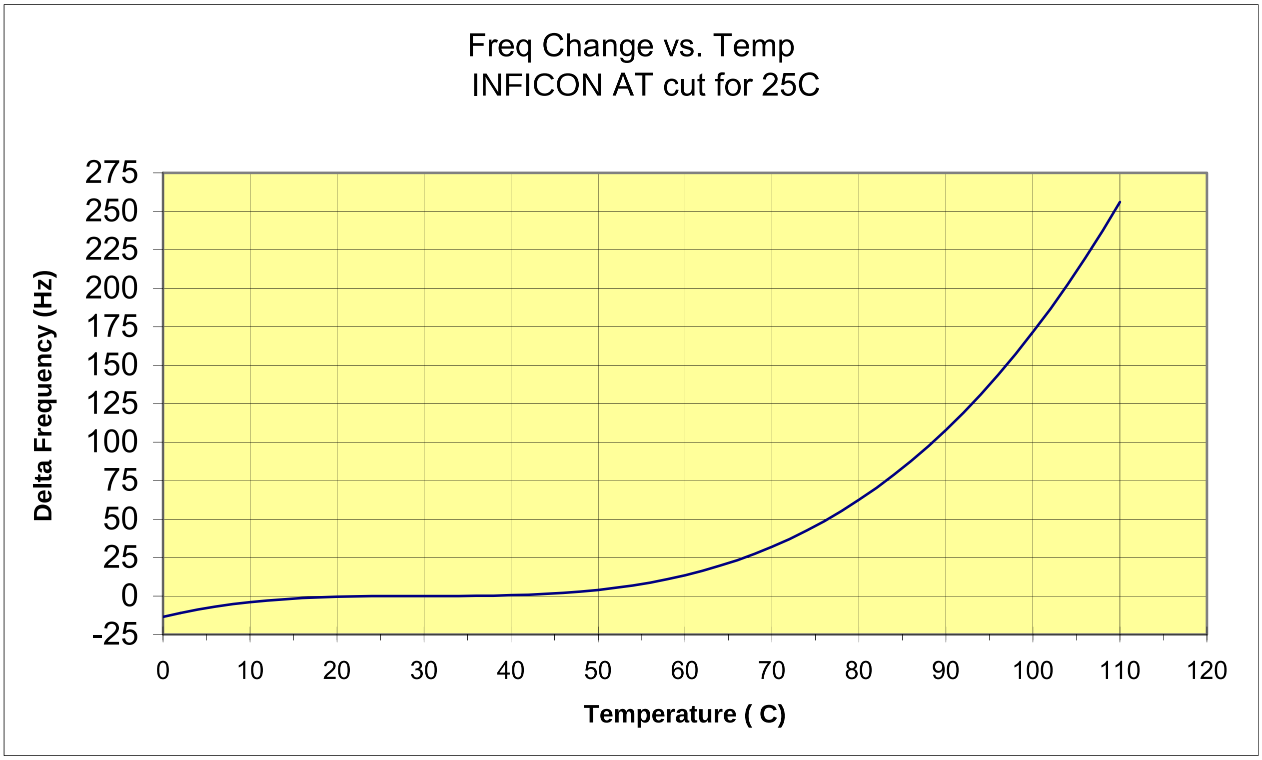


Figure 11 Frequency vs. Temperature of INFICON 1" AT-Cut Crystal for 25 C

4.2 CRYSTAL CARE AND HANDLING

It is essential that a sensor crystal is clean and free of foreign matter that may react with the experiment inducing errors in the measurements. The following guidelines are recommended for general handling of the sensor crystals.

- Keep the crystals in a clean environment. Store them in their original package until use.
- Never handle the crystals with bare hands.
- Always use plastic tweezers around the edge of the crystal during handling.
- Do not touch the center of a sensor crystal, as any oil, dirt, dust, or scratches will quickly degrade the quality of the crystal.
- When using a chemical agent to clean the crystal, ensure that the crystal electrode material(s) will not be damaged by the chemical.
- Never use cleaner that will etch the quartz surface.
- Always rinse with deionized water, or another appropriate pure liquid, before drying the crystal.
- Always use a flow of dry, oil-free, non-reactive gas (e.g. filtered nitrogen) to blow-dry the crystal. It is better to chase liquid off the crystal than to let it evaporate off the crystal.
- Never wipe the crystal – even soft, lint-free cloth will scratch the crystal.

4.2.1 CRYSTAL CLEANING

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

> **CAUTION** – When developing a cleaning procedure, always perform a test run on a crystal before committing to a larger batch cleaning. Follow the crystal handling guidelines throughout the cleaning process to protect the crystal quality. Avoid using high pH cleaners since they will etch the crystal surface.

4.2.1.1 General Cleaning

For general purpose applications such as electrochemistry and liquid or viscoelastic film experiments, it is usually sufficient to use ultrasonic cleaning method to clean 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 filtered nitrogen gas.

4.2.1.2 Organic (hydrocarbon contaminants)

UV/ozone treatment[12] is a powerful tool for removing hydrocarbon impurities which have been adsorbed from the ambient air. This method utilizes irradiation with ultra violet light that breaks up the organics on the surface of the sample being cleaned. A flow of air or a weak vacuum carries off the organics. This method does not affect the quartz surface; it is low cost and is very efficient.

Oxygen plasma cleaning is another effective method that will remove organic matters. In this method, the plasma reaction breaks up organic matters at the surface of the sample being cleaned into smaller molecules and a vacuum pump removes them from the surface of the sample.

4.2.1.3 Biomaterials (lipids, proteins and similar biomolecules)

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

4.2.1.4 Lipid vesicles on SiO_2 surfaces

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

4.2.1.5 Polystyrene removal

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

4.2.1.6 Polymer Removal

To clean polymers from the crystals a combination of plasma cleaning with O2 plasma and piranha solution is recommended. However, it is best to remove the bulk of the material with organic solvents prior to oxidative cleaning. Polymers that are very intractable may be particularly difficult to clean. In this case, refluxing toluene of Tetrahydrofuran helps to facilitate the removal of the polymer. Then the following procedure is recommended:

A. Wash with Organic Solvents: Methylene Chloride, Toluene, or THF to remove most organic material. Reflux if needed.

B. Wash with Isopropanol and dry.

C. Clean in hot piranha (70% sulfuric acid/ 30% hydrogen peroxide) for 1 – 2 minutes.

D. Rinse with DI water.

E. Rinse with isopropanol and dry.

F. O2 plasma cleaning for 5 minutes or longer if needed.

G. Rinse with ethanol.

H. O2 plasma clean for 3 minutes.

> **Caution** – Beware when working with piranha solution since it is a strong oxidizer and should not be contacted with any organic solvents. Also, if you leave the QCM crystal in the hot piranha too long it can leech the chromium or titanium (adhesion layer) from under the gold leading to delaminating of the gold from the crystal surface.

I. Use the crystal as soon as possible or store in a Nitrogen environment.

4.2.2 ELECTRODE SURFACE MODIFICATIONS

A QCM will response to *anything* that has mass. Thus, it is imperative for the QCM user to develop a “condition” where the QCM will only responsed to the substance of interest. This usually involves a chemically or biologically sensitive layer applied to the surface of the crystal[13].

INFICON offers a wide variety of standard electrode materials for you to choose from. Contact us if you don’t see one that fits your needs. If you choose to do your own crystal surface modification, use the following guidelines.

4.2.2.1 SPIN COATING

Thin films (nm to microns) of polymers and other materials can be applied by spin coating[14]. Polystyrene is a common material spin-coated on QCM sensor crystals. UV/Ozone treatment can be used to change the hydrophobicity of organic polymeric coatings[15] [16].

4.2.2.2 SELF-ASSEMBLED MONOLAYERS (SAM)

Self-assembling monolayers can be laid down on gold or silver surface by thiolization[17] [18] [19] or on SiO_2 by silanization[20] to control surface properties.

4.2.2.3 PHYSICAL VACUUM DEPOSITION (PVD)

Thin films of metals or metal oxides can be applied by sputtering or thermal evaporation in a vacuum chamber. To ensure quality and reproducible films, careful attention to cleanliness must be observed, both in the vacuum chamber and in the preparation of the crystals prior to coating. INFICON is an expert in PVD. Consult us for any special needs.

4.3 CRYSTAL HOLDERS

Figure 12 shows a INFICON CHC-100 Crystal Holder (without a crystal, the crystal retainer or the retainer cover). It has a cavity for a 1-inch diameter crystal. Inside the cavity there are two Pogo® pins providing connections to the crystal's front and rear electrodes. Note the locations of the Pogo® pins. These pins are internally connected to the BNC connector (SMB Jack for CHT-100 and CHK-100 holders) via an internal coaxial cable.

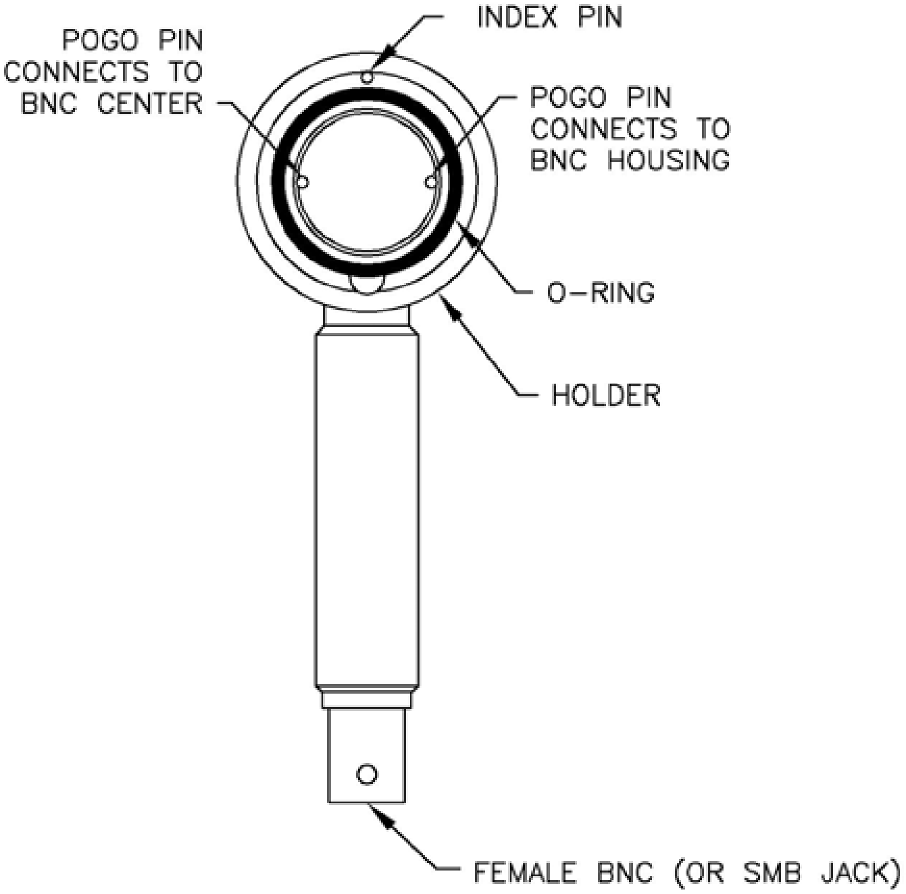


Figure 12 CHC-100 Crystal Holder

4.3.1 HOW TO INSTALL A CRYSTAL IN A INFICON CRYSTAL HOLDER

1. Identify the Front and Rear Sides of the crystal. See Section 4.1.

2. Clean & Dry the Crystal Holder cavity, then insert the Crystal with the Front Side (Sensing Electrode) exposed. The "Wrap-Around Extended Electrode" MUST be in the 60º region as in Figure 13 below.

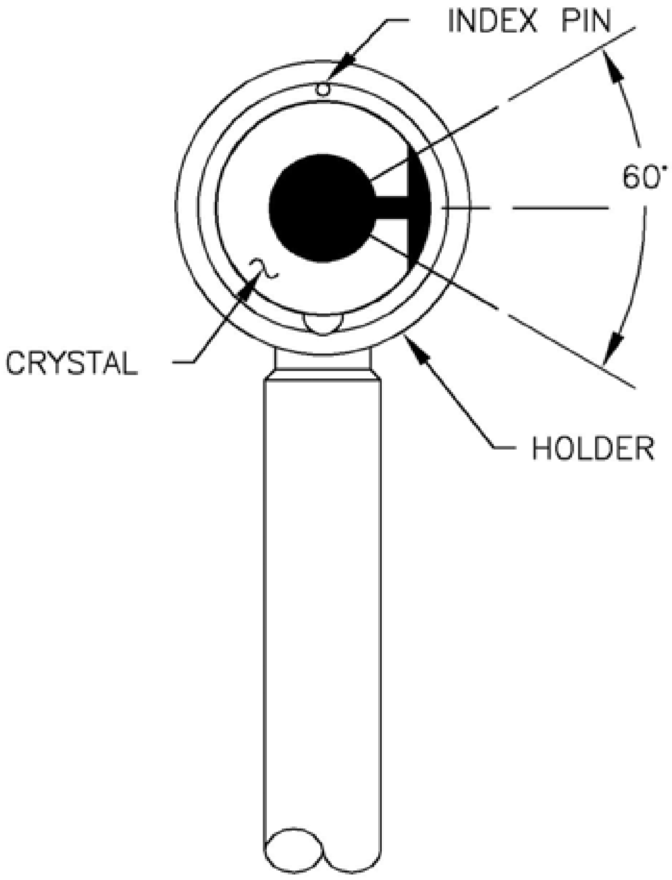
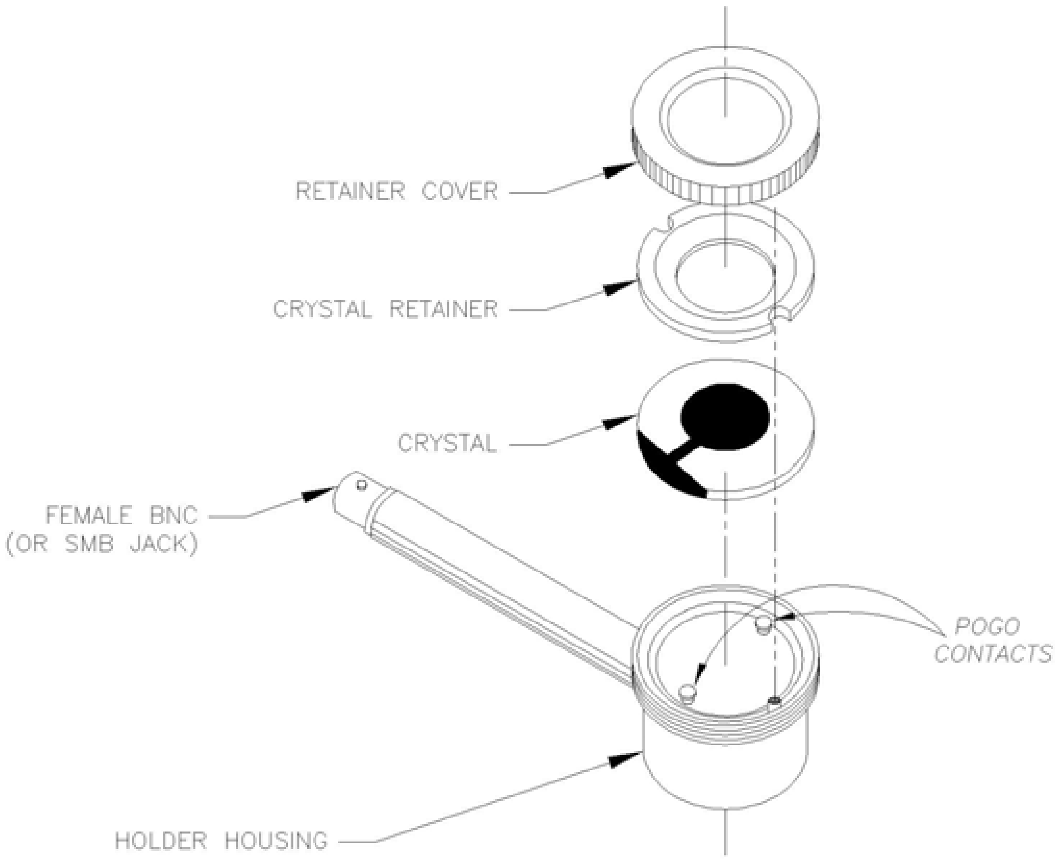


Figure 13 Crystal Installation

3. Place the Retainer Ring over the Crystal, with the Notch mating to the Index Pin.

4. Mount and turn the Retainer Cover approximately ¼ turn. Then with a gloved-finger or cotton swab *gently* press the Retainer Ring down at the Notch to make sure that it stays mated to the Index Pin. Finish tightening the Cover until it's snug.



4.3.2 HOLDER CARE AND HANDLING

With a robust design, INFICON crystal holders require little care. However, the crystal holder is in direct contact with the sensor crystal and your experiment environment. Thus, care must be taken to ensure its cleanliness eliminating any contaminants that may react with the crystal or the experiment media. The following guidelines are recommended for general handling of the holders.

- ♦ Always keep the holder clean and dry when not in use.
- ♦ Always use clean room grade gloves while handling the holder and its components.
- ♦ Never handle the holder with bare hands as human skin oils may deposit on it and react with your experiment.
- ♦ Always ensure that your holder is compatible with your experiment environment.
- ♦ Never submerge the holder unassembled or without a crystal.
- ♦ Never submerge the holder pass its terminal connector at the end of the rod.
- ♦ Always rinse the holder generously with deionized water and thoroughly blow dry using filtered air after each experiment. This is especially important if the holder has been exposed to oxidizing acids.
- ♦ Always act fast in the event that liquids or chemicals have entered the crystal cavity in the holder. Immediately clean the holder using the following procedure.

- Remove the crystal to expose the crystal cavity.
- Remove both Pogo® contact pins from their sockets. Use a pair of tweezers (or gloved fingernail), grab the Pogo® head firmly and pull it straight out of its socket.
- Rinse the holder, the crystal cavity and the Pogo® sockets generously with deionized water to remove all traces of chemicals and thoroughly blow-dry the whole holder using filtered air. Ensure all liquids that may have been trapped inside the sockets are removed.
- Generously rinse the Pogo® contact pins with deionized water, occasionally squeeze the pins to push out any liquids that may have been trapped inside the pins. Thoroughly blow-dry the pins using filtered air.
- Install the Pogo® pins back into their sockets. Use the tip of a pair of tweezers and push down on each Pogo® pins to verify their deflection.

4.3.3 CONSIDERATIONS FOR BUILDING YOUR OWN HOLDER

You MUST consider the following aspects when building your own crystal holder.

The holder must be designed so that when a crystal is installed, the its front electrode (sensing electrode) is connected to the housing (shell) of the SMB Crystal Connector on the RQCM (see Section 3.3.5); and the rear electrode is connected to the center pin of the SMB Crystal Connector.

The crystal should be clamped, as close as possible, to the edge of the crystal to avoid damping of the crystal's oscillations.

The holder clamping mechanism should have a positive stop to avoid excessive clamping force on the crystal.

If the crystal is to be used in a conductive fluid or conductive gas, the rear electrode must be sealed from the conductive environment to avoid an electrical short between the electrodes. The electrodes should be designed so the rear electrode and the electrodes contacts can be sealed. Only the front electrode should be exposed.

The connecting cable must be coaxial all the way, from SMB on the RQCM, on up to the crystal. The shield of the coaxial must connect to the front electrode and the center conductor must connect to the rear electrode of the crystal. In addition, the coaxial cable must be free of kinks, knots, etc. to avoid unbalanced capacitance in the cable. Note that a one-foot of well balance RG174A/U coaxial cable has approximately 29 picofarads.

The total capacitance of the crystal, the crystal holder and the cable must be within the RQCM's capacitance compensation limits (between 40 and 200 pfd).

4.4 FLOW CELL

The FC-550 Flow Cell is designed to be used with any of INFICON's 100 series crystal holders. The FC-550 is made from Kynar®. The cell has two stainless steel inlet and outlet tubes with a .047" I.D. x .062" O.D., compatible with 0.062" I.D. tubing. A Viton® O-ring provides sealing between the cell and the face of the sensor crystal. The cell is used in place of the Crystal Retainer Ring. Once installed in a probe, it creates a flow chamber of approximately 0.1 mL.

5 THEORY OF OPERATION

Sauerbrey was the first to recognize the ability of the Quartz Crystal Microbalance (QCM) to measure very small mass changes on the crystal surface. His seemingly simple equations have been used for many years and in many different applications.

5.1 SAUERBREY EQUATION

Equation 1

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

Where:

Δf = Frequency change in Hz.

C_f = Sensitivity factor of the crystal in Hz/ng/cm^2

(0.0566 Hz/ng/cm^2 for a 5 MHz crystal @ 20° C)

(0.0815 Hz/ng/cm^2 for a 6 MHz crystal @ 20° C)

(0.1834 Hz/ng/cm^2 for a 9 MHz crystal @ 20° C)

Δm = Change in mass per unit area in g/cm^2.

The Sauerbrey equations assumed that the additional mass or film deposited on the crystal has the same acousto-elastic properties as quartz. This assumption resulted in a sensitivity factor, C_f, which is a fundamental property of the QCM crystal as shown in equation 2.

Equation 2

$$C_f = \frac{2n \times f^2}{\sqrt{\rho_q \times \mu_q}}$$

Where:

n = Number of the harmonic at which the crystal is driven.

f = Resonant frequency of the fundamental mode of the crystal in Hz.

ρ_q = Density of quartz = 2.648 g · cm^{-3}

μ_q = Effective piezoelectrically stiffened shear modulus of quartz = 2.947 · 10^{11} g · cm^{-1} · sec^{-2}.

Solving these equations for Δm yields

Equation 3

$$\Delta m = \frac{-\Delta f}{C_f} = \frac{(f_q - f)\sqrt{\rho_q \times \mu_q}}{2n \times f^2}$$

Where:

f_q = Resonant frequency of unloaded crystal in Hz.

f = Resonant frequency of loaded crystal in Hz.

It is important to note that under these assumptions, the change in frequency is a function of mass per unit area. Therefore, in theory, the QCM mass sensor does not require calibration. However, keep in mind that the Sauerbrey equation is only strictly applicable to uniform, rigid, thin-film deposits [21]. 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.

5.2 Z-MATCH EQUATION

Sauerbrey's original assumptions were of course, questionable and indeed work with crystals heavily loaded with certain materials showed significant and predictable deviations between the measured mass and that predicted by Equation 3. Lu and Lewis[22] analyzed the loaded crystal as a one-dimensional composite resonator of quartz and the deposited film which led to the equation shown below which is also referred to as the Z-Match equation.

Equation 4

$$\Delta m = \left(\frac{N_q \cdot \rho_q}{\pi \cdot R_z \cdot f}\right) \cdot \tan^{-1}\left[R_z \cdot \tan\left[\pi \cdot \left(\frac{f_q - f}{f}\right)\right]\right]$$

where:

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

N_q = Frequency Constant for AT-cut quartz crystal = 1.668 x 10^5 Hz x cm = $\frac{\sqrt{\rho_q \mu_q}}{2\rho_q}$

ρ_q = Density of quartz = 2.648 g/cm^3.

f_q = Resonant frequency of unloaded crystal in Hz.

f = Resonant frequency of loaded crystal in Hz.

R_z = Z-Factor of film material = $\sqrt{\frac{\rho_q \cdot \mu_q}{\rho_f \cdot \mu_f}}$ = Acoustic Impedance Ratio

ρ_f = Density of material g/cm^3

μ_q = shear modulus of quartz = 2.947×10^{11} g · cm^{-1} · s^{-2}

μ_f = shear modulus of film material in g · cm^{-1} · s^{-2}.

This equation introduces another term into the relationship which is the ratio of the acoustic impedance of quartz to the acoustic impedance of the deposited film. The acoustic impedance is associated with the transmission of a shear wave in the deposited mass. Notice that the units of the frequency constant for quartz is length/time or velocity. Also note that if the acoustic impedance ratio is equal to one, quartz on quartz, then Equation 4 reduces to Equation 3.

5.3 THICKNESS CALCULATION

Film thickness is often the parameter of interest in many QCM applications. Thickness can be derived from Equation 4 as follows:

Equation 5

$$TK_f = \frac{\Delta m}{\rho_f} = \left(\frac{N_q \cdot \rho_q}{\pi \cdot R_z \cdot f \cdot \rho_f} \right) \cdot \tan^{-1}\left[R_z \cdot \tan\left[\pi \cdot \left(\frac{f_q - f}{f} \right) \right] \right]$$

where:

TK_f = thickness of the film in cm.

Δm = change in mass per unit area in g/cm^2 (calculated from the Lu and Lewis equation).

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

If the period of oscillation is measured rather than the frequency, 1/period can be substituted for frequency resulting in the following equation. (See INFICON TechNote RTK-101 for details discussion).

Equation 6

$$TK_f = \left(\frac{\rho_q}{\rho_f} \right) \cdot N_q \cdot \left(\frac{\tau}{\pi R_z} \right) \cdot \tan^{-1}\left[R_z \cdot \tan \pi \cdot \left(\frac{\tau - \tau_q}{\tau} \right) \right]$$

where:

τ_q = Period of unloaded crystal in seconds

τ = Period of loaded crystal in seconds

Although the above equation still involves a number of simplifying assumptions, its ability to accurately predict the film thickness of most commonly deposited materials has been demonstrated. The RQCM uses this equation to calculate film thickness.

The basic measurement is period, which can be thought of as a measurement of equivalent quartz mass. The actual film mass on the crystal is then found by applying the acoustic impedance correction factor.

When the mass is zeroed using the RQCM, the initial equivalent quartz mass and the initial corrected film mass are stored. For each subsequent measurement the new corrected total film mass is calculated, and the film mass deposited since the thickness was zeroed is determined by subtracting the initial corrected film mass from the total corrected film mass. The film thickness on the crystal is calculated by dividing by the film mass by the material density.

The Lu and Lewis equation is generally considered to be a good match to the experimental results[5] [6] for frequency changes up to 40% (relative to the unloaded crystal). Keep in mind that the Z-match equation strictly applies to elastic (lossless) films. Films which behave viscoelastically, such as some organic polymer films with large thickness or viscosity, will exhibit significant deviations from both Equation 3 and Equation 6.

Table 5-1 Material Density and Acoustic Impedance Value

Material	**Symbol**	**Density** gm/cm^2	**Impedance** 10^5gm/(cm^2sec)
Aluminum	Al	2.70	8.17
Aluminum Oxide	Al_2O_3	3.97	26.28
Antimony	Sb	6.62	11.49
Arsenic	As	5.73	9.14
Barium	Ba	3.5	4.20
Beryllium	Be	1.85	16.26
Bismuth	Bi	9.8	11.18
Boron	B	2.54	22.70
Cadmium	Cd	8.64	12.95
Cadmium Sulfide	CdS	4.83	8.66
Cadmium Telluride	CdTe	5.85	9.01
Calcium	Ca	1.55	3.37
Calcium Fluoride	CaF_2	3.18	11.39
Carbon (Diamond)	C	3.52	40.14
Carbon (Graphite)	C	2.25	2.71
Chromium	Cr	7.20	28.95
Cobalt	Co	8.71	25.74
Copper	Cu	8.93	20.21
Copper (I) Sulfide (alpha)	Cu_2S	5.6	12.80
Copper (I) Sulfide (beta)	Cu_2S	5.8	13.18
Copper (II) Sulfide	CuS	4.6	10.77
Dysprosium	Dy	8.54	14.72
Erbium	Er	9.05	11.93
Europium	Eu	5.244	----
Gadolinium	Gd	7.89	13.18
Gallium	Ga	5.93	14.89
Gallium Arsenide	GaAs	5.31	5.55
Germanium	Ge	5.35	17.11
Gold	Au	19.30	23.18
Hafnium	Hf	13.09	24.53
Holnium	Ho	8.8	15.2
Indium	In	7.30	10.50
Indium Antimonide	InSb	5.76	11.48
Iridium	Ir	22.40	68.45
Iron	Fe	7.86	25.30
Lanthanum	La	6.17	9.59
Lead	Pb	11.30	7.81
Lead Sulfide	PbS	7.50	15.60
Lithium	Li	0.53	1.50
Lithium Fluoride	LiF	2.64	11.41
Magnesium	Mg	1.74	5.48
Magnesium Fluoride	MgF_2	3.0	13.86
Magnesium Oxide	MgO	3.58	21.48
Manganese	Mn	7.20	23.42
Manganese (II) Sulfide	MnS	3.99	9.39
Mercury	Hg	13.46	11.93
Molybdenum	Mo	10.20	34.36
Nickel	Ni	8.91	26.68
Niobium	Nb	8.57	17.91

Palladium	Pd	12.00	24.73
Platinum	Pt	21.40	36.04
Potassium Chloride	KC	1.98	4.31
Rhenium	Re	21.04	58.87
Rhodium	Rh	12.41	42.05
Samarium	Sm	7.54	9.92
Scandium	Sc	3.0	9.70
Selenium	Se	4.82	10.22
Silicon	Si	2.32	12.40
Silicon (II) Oxide	SiO	2.13	10.15
Silicon Dioxide (fused quartz)	SiO_2	2.2	8.25
Silver	Ag	10.50	16.69
Silver Bromide	AgBr	6.47	7.48
Silver Chloride	AgCl	5.56	6.69
Sodium	Na	0.97	1.84
Sodium Chloride	NaCl	2.17	5.62
Strontium	Sr	2.620	----
Sulphur	S	2.07	3.86
Tantalum	Ta	16.60	33.70
Tantalum (IV) Oxide	Ta_2O_5	8.2	29.43
Tellurium	Te	6.25	9.81
Terbium	Tb	8.27	13.38
Thallium	Tl	11.85	5.70
Tin	Sn	7.30	12.20
Titanium	Ti	4.50	14.06
Titanium (IV) Oxide	TiO_2	4.26	22.07
Tungsten	W	19.30	54.17
Tungsten Carbide	WC	15.60	58.48
Uranium	U	18.70	37.10
Vanadium	V	5.96	16.66
Ytterbium	Yb	6.98	7.81
Yttrium	Y	4.34	10.57
Zinc	Zn	7.04	17.18
Zinc Oxide	ZnO	5.61	15.88
Zinc Selenide	ZnS	5.26	12.23
Zinc Sulfide	ZnS	4.09	11.39
Zirconium	Zr	6.51	14.72

5.4 LIQUID MEASUREMENTS

QCMs have been used as gas-phase mass detectors with lossless films for many years. However, only recently has their applications been extended to liquids and with viscoelastic deposits. In these cases, both frequency and series resonance resistance[*] of the quartz crystal are important to completely characterize the material and/or the liquid in contact with the crystal electrode. The development of QCM systems for use in liquids 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 many applications including: specific gas detection, environmental monitoring, biosensing and basic surface-molecule interaction studies.

---

[*] See Section 5.6 for a detail discussion.

When the QCM comes in contact with a liquid, there is a decrease in frequency that is dependent upon the viscosity and density of the liquid. Kanazawa's solution for the change in resonant frequency of the crystal due to liquid loading is shown in Equation 7.

Equation 7

$$\Delta f = -f_q^{3/2}\sqrt{\frac{\eta_L \cdot \rho_L}{\pi \cdot \mu_q \cdot \rho_q}}$$

Where:

f_q = Resonant frequency of unloaded crystal in Hz.

ρ_q = Density of quartz = 2.648×103 kg/m^3.

μ_q = shear modulus of quartz = 2.947×10^{10} Pa

ρ_L = density of the liquid in contact with the electrode in kg/m^3,

η_L = viscosity of the liquid in contact with the electrode in N · Sec/m^2

Liquid loading also dampens the resonant oscillation of the crystal causing an increase in series resonance resistance, R, of the crystal. 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[23].

A Butterworth-Van Dyke equivalent circuit model (Figure 16) was applied to derive a linear relationship between the change in series resonance resistance, ΔR, of the crystal and $\sqrt{\eta_L \cdot \rho_L}$ under liquid loading. Using the relations in this study the change in resistance, ΔR, can be put in the form:

Equation 8

$$\Delta R = \Delta f \cdot \frac{2\pi \cdot \left(\rho_q \cdot \mu_q\right)^{3/2}}{f^3 \cdot 32 \cdot A_r \cdot \left(\rho_q \cdot e_{26}\right)^2}$$

Where:

ΔR = change in series resonance resistance in Ω,

A_r = active area of INFICON 1-inch crystal = 3.419×10^{-5} m^2

e_{26} = piezoelectric constant for an AT cut quartz = 0.095 kg/sec^2/V

For example, moving the crystal from air to pure water @ 20°C, Equation 7 and Equation 8 predict a decrease in f of 714 Hz and an increase in R of 357.4 Ω, respectively. These values are in agreement with the results observed with an RQCM using a 5 MHz, 1-inch diameter, polished, gold coated mounted on a INFICON Crystal Holder. Note that pure water @ 20°C has a density (ρ_L) of 998.2 kg/m^3, and a viscosity (η_L) of 1.002×10^{-3} N · sec/m^2.

Excellent agreement between the frequency and resistance equations and the experimental results has been proved[24 25 26], making the QCM an excellent tool for the evaluation of fluid properties. Application examples include *in-situ* monitoring of lubricant and petroleum properties[27]. The tight correspondence between theory (Equation 7 and Equation 8) and the RQCM is clearly illustrated by Figure 14 and Figure 15, respectively. Note that some of the discrepancy in the resistance curve could arise from an error in estimating the active electrode area.

The RQCM utilizes the PLO technology which allows the sensor crystal to operate under heavy viscous loading. INFICON Crystal Holders support operation in gas and liquid environments and provide single-electrode exposure to liquids as required for compatibility with electrochemical QCM measurements. The RQCM 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% weight percentage of glycerol[28]. The RQCM computer software provides a friendly interface for setting up the RQCM to log and graph data collected from the sensor crystal such as frequency change, resistance change, mass, etc.

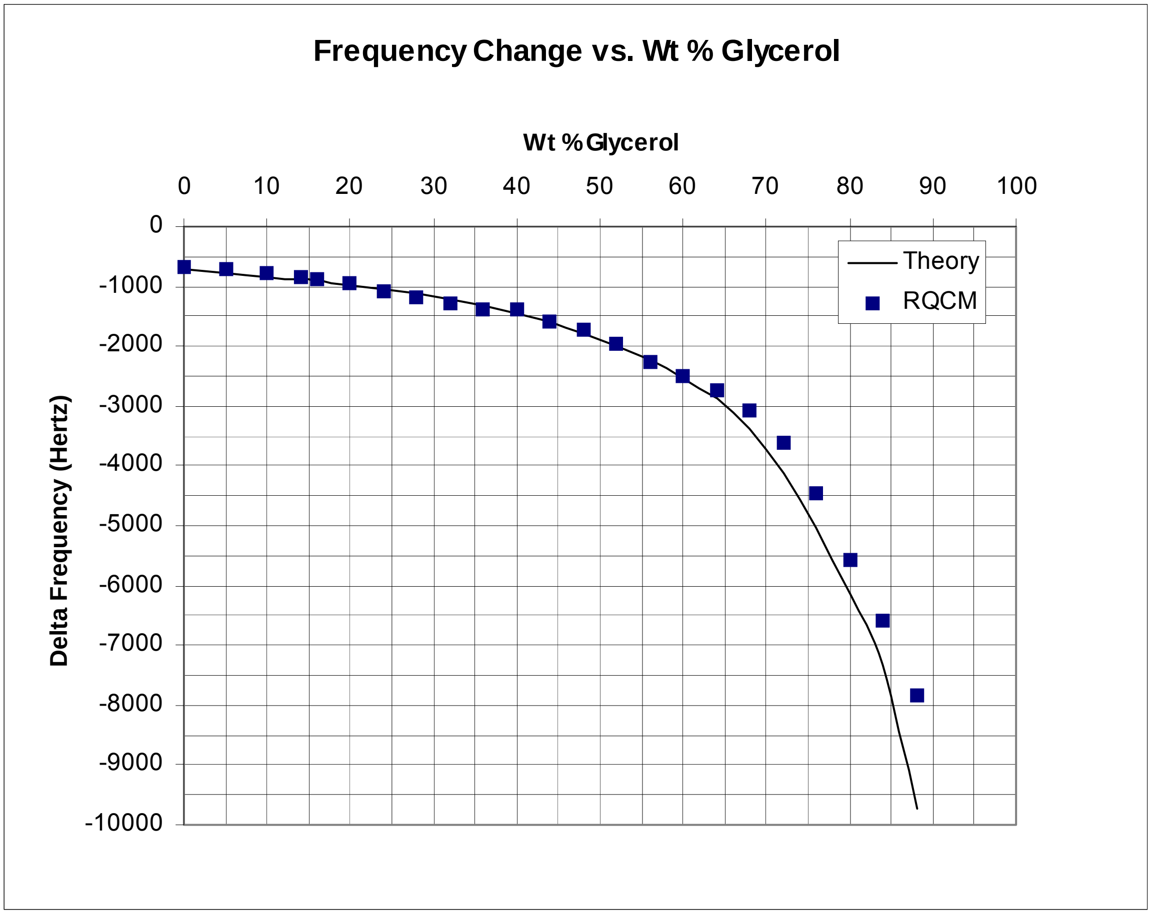


Figure 14 Frequency Change vs. Wt % Glycerol

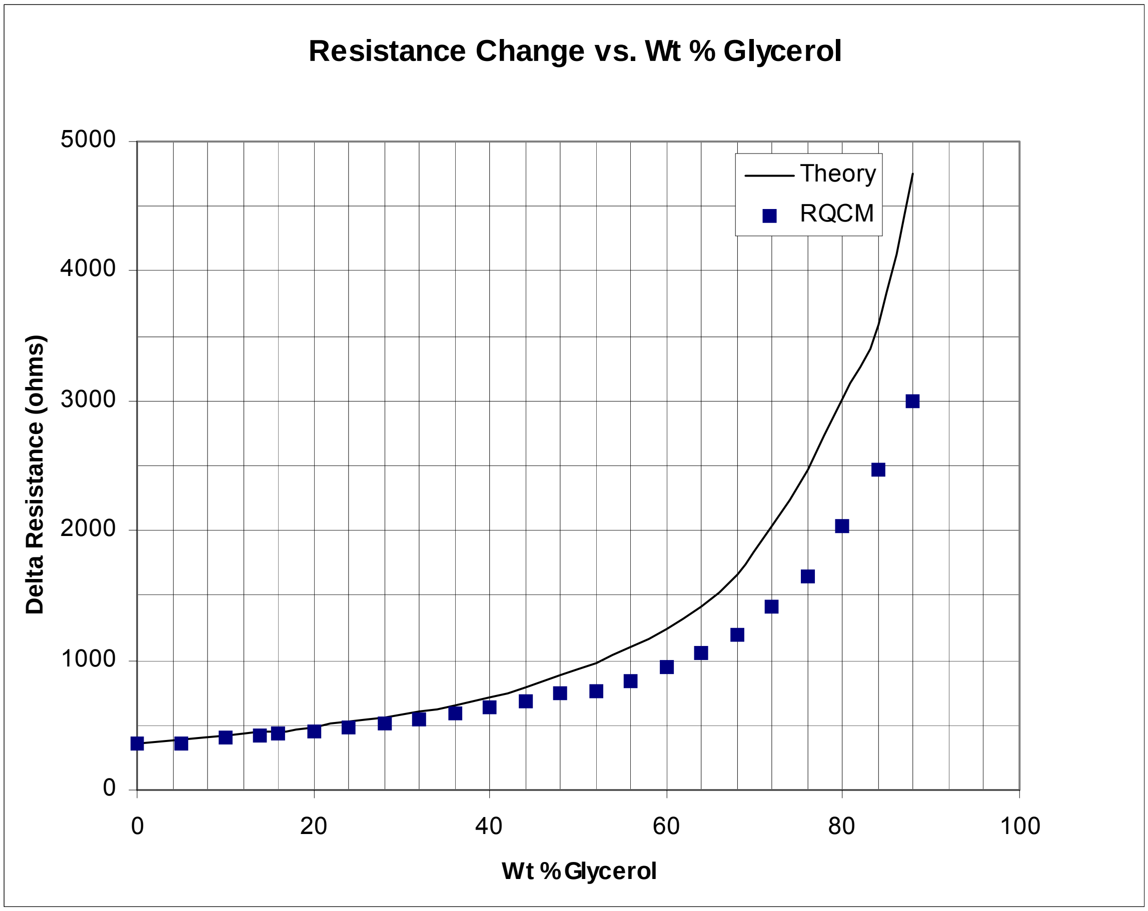


Figure 15 Resistance Change vs. Wt % Glycerol

5.4.1 DECAY LENGTH OF SHEAR WAVE IN LIQUID

As mentioned in the section above, when an oscillating crystal is in contact with a liquid, there will be a decrease in the resonant frequency and an increase in the motional resistance. The decrease in the resonant frequency is caused by the additional mass of the vibrating liquid. The increase in motional resistance is caused by the power dissipation of the shear wave that radiates into the liquid. The decay length of the shear wave into the liquid is defined by

Equation 9

$$L_D = \sqrt{\frac{2\eta_L}{\rho_L \cdot \omega_S}}$$

Where:

L_D = Decay length in m

ρ_L = Density of the liquid in contact with the electrode in kg/m^3

η_L = Viscosity of the liquid in contact with the electrode in kg/m/sec

ω_S = Angular frequency at series resonance ($2\pi f$)

For example, the decay length for a 5 Mhz crystal in water at 20°C is 2.5×10^{-7} m = 0.25 microns.

5.5 DISSIPATION METHOD

The *Dissipation Method* is an alternate way of measuring the crystal to determine the properties of the film and/or the liquid. In this method, the crystal is driven at its resonant frequency by an oscillator then the crystal shorted and both the resonant frequency and the oscillation decay time are measured. The crystal dissipation is related to Q and R as follows:

Equation 10

$$D = \frac{1}{Q} = \frac{R}{\omega_S \cdot L}$$

Where:

D = Dissipation

Q = Quality Factor

R = resistance in Ω

L = inductance in H

D can be determined from R if L is known. It has been shown that L will remain constant unless there is an acoustic resonance in the film on the crystal. Independent studies[25] have shown that as long as the effect of the parasitic capacitance (C_S) is properly cancelled, the results provided by the RQCM System are in good agreement with those obtained by the Dissipation Method.

5.6 ELECTRICAL DESCRIPTION OF THE QUARTZ CRYSTAL

Figure 16 shows the equivalent circuit of a quartz crystal. The circuit has two branches. The motional branch, which contains the L, R & C, is the branch that is modified by mass and viscous loading of the crystal. The shunt branch, which contains the lone Cs element, represents the shunt capacitance of the crystal electrodes and any cable and fixture capacitance.

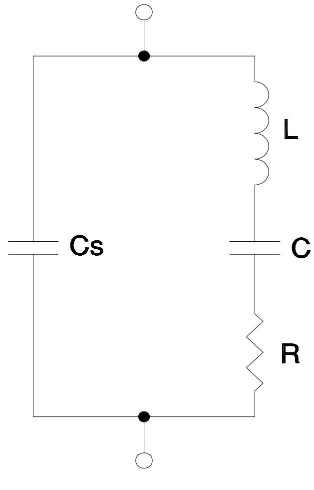


Figure 16 Crystal Equivalent Circuit

Because a crystal's impedance is minimum at resonance it is convenient to characterize a crystal in terms of admittance. Admittance is the inverse of impedance, (Y = 1/Z), thus the admittance reaches a maximum at resonance. While impedance is proportional to the voltage developed across a device when it is subjected to a current, the admittance is proportional to the current through the device when it is subjected to a voltage.

At any frequency the admittance of a quartz crystal is a complex value that can be expressed in terms of magnitude and phase or in terms of a real and imaginary value. The relationship of these two representations is shown in Figure 17.

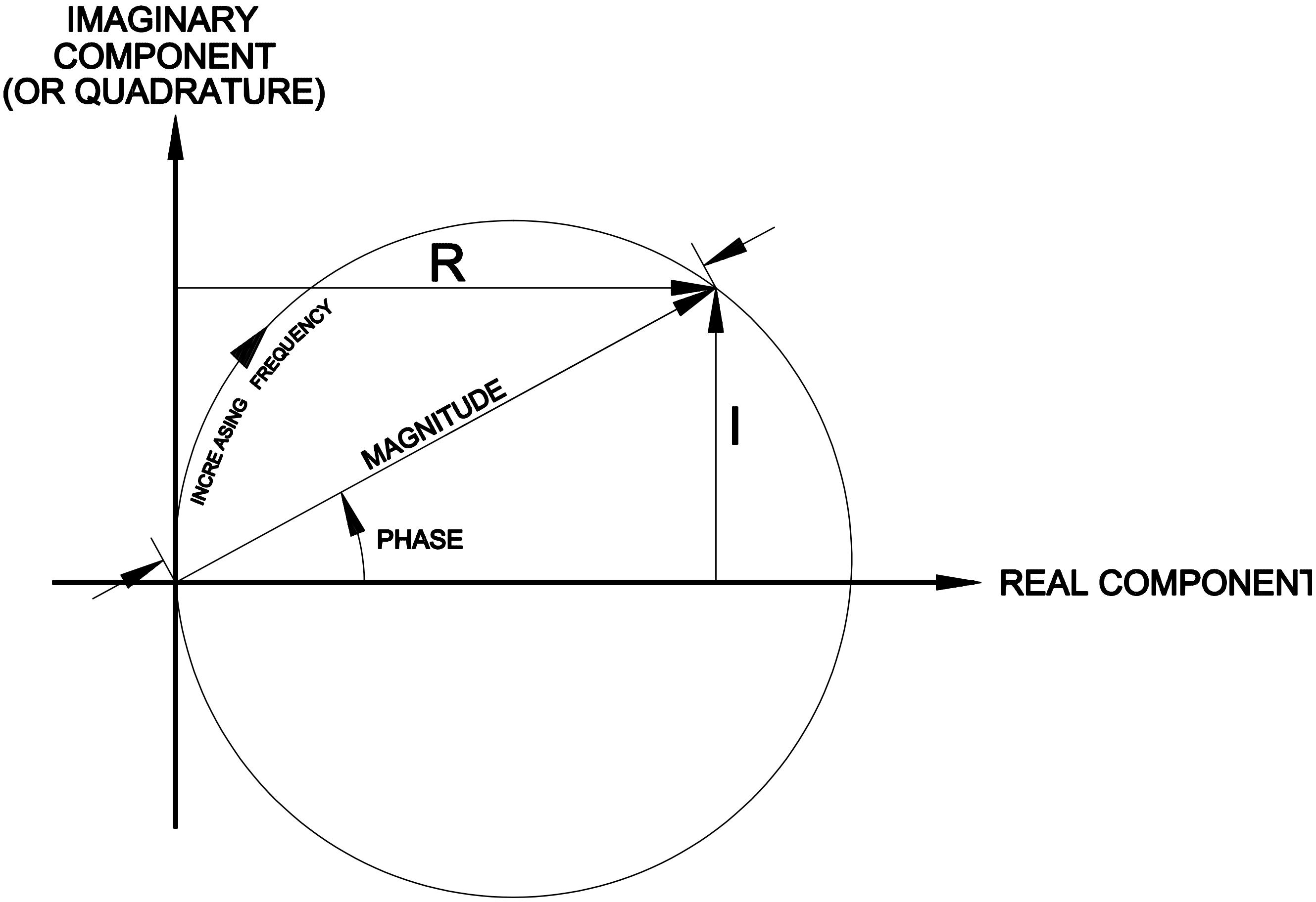


Figure 17 Polar Plot of Crystal Admittance

Figure 18 shows the conductance in terms of magnitude and phase, while Figure 19 shows the same information in terms of the imaginary and real part of the conductance.

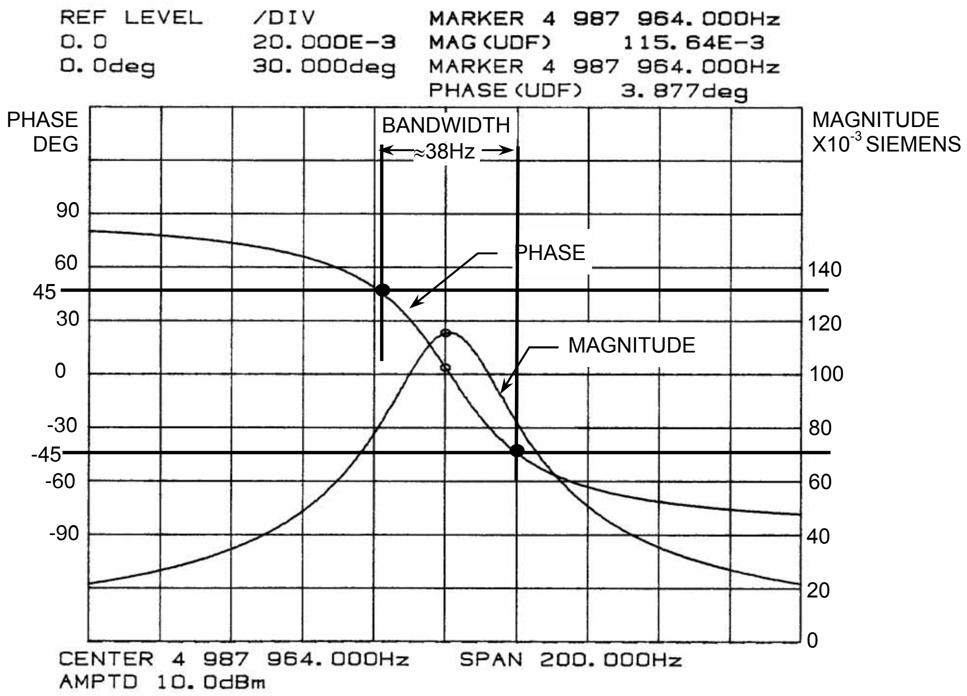


Figure 18 Admittance vs. Frequency, Magnitude and Phase of High Q Crystal

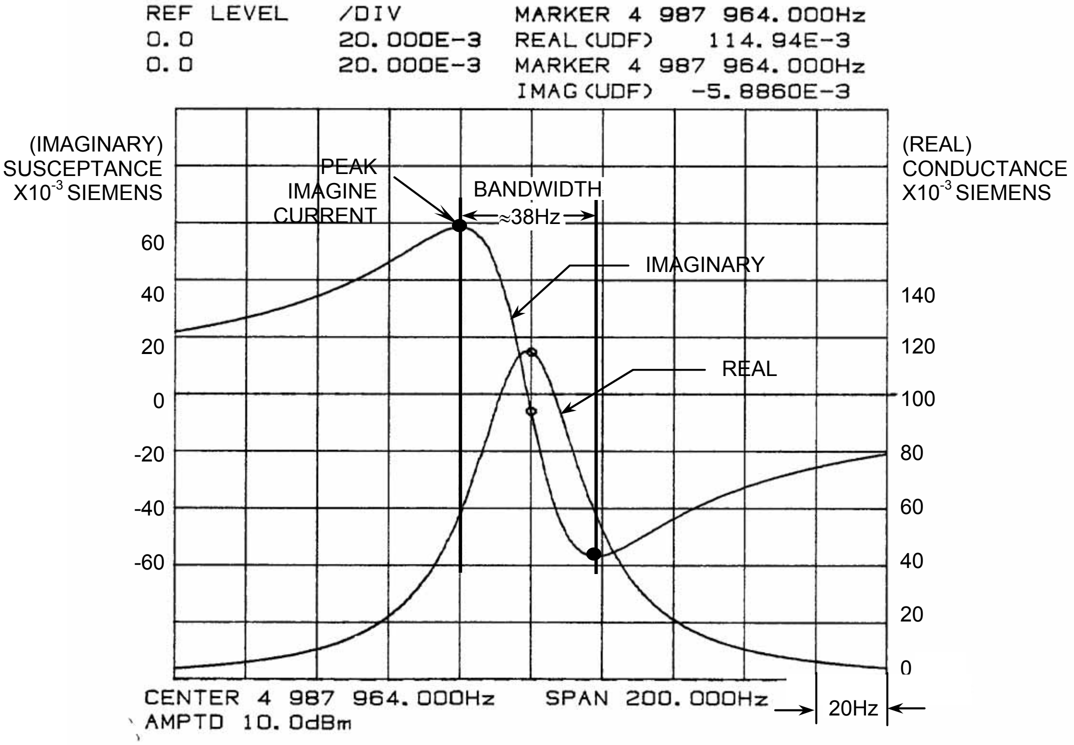


Figure 19 Admittance vs. Frequency, Real and Imaginary Components of High Q Crystal

When the above complex conductance is plotted in polar coordinates, one obtains a circle as shown in Figure 20. The vector V indicates the magnitude and phase of the crystal current divided by the applied voltage. The real part of the conductance is indicated by the vector R and the imaginary part is indicated by the vector I.

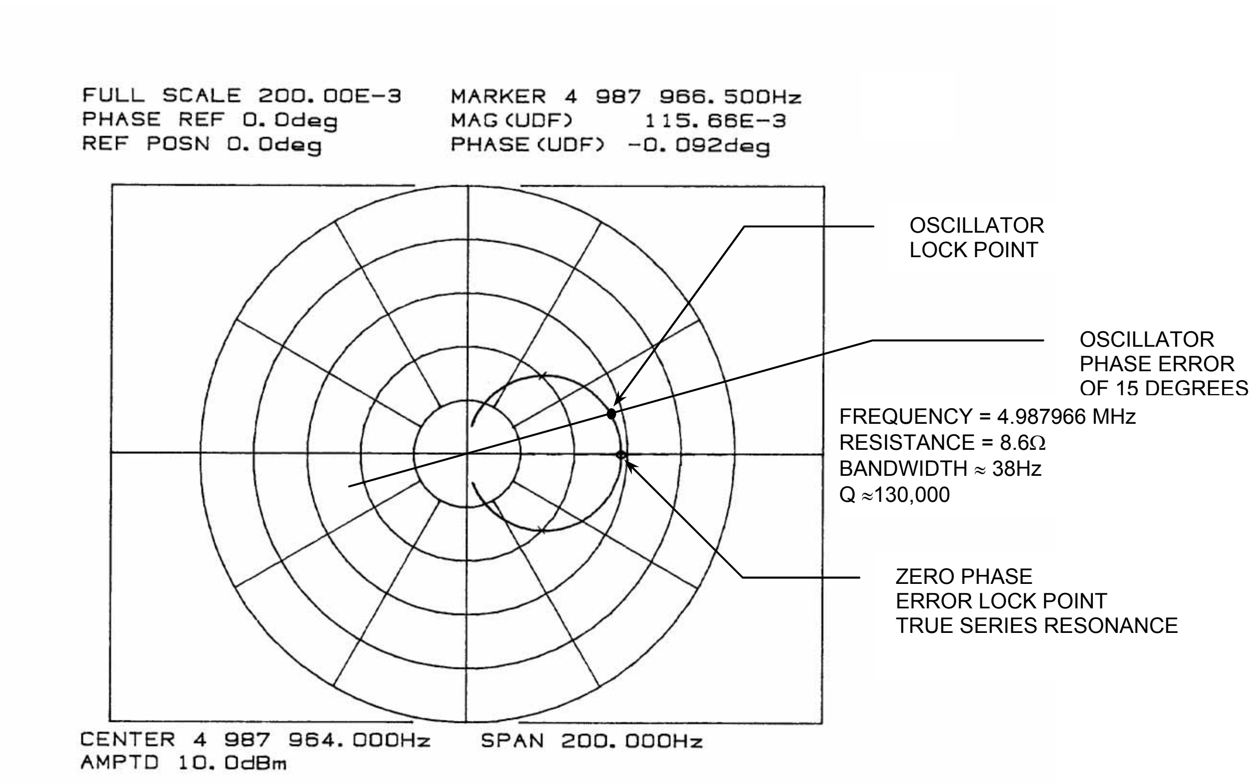
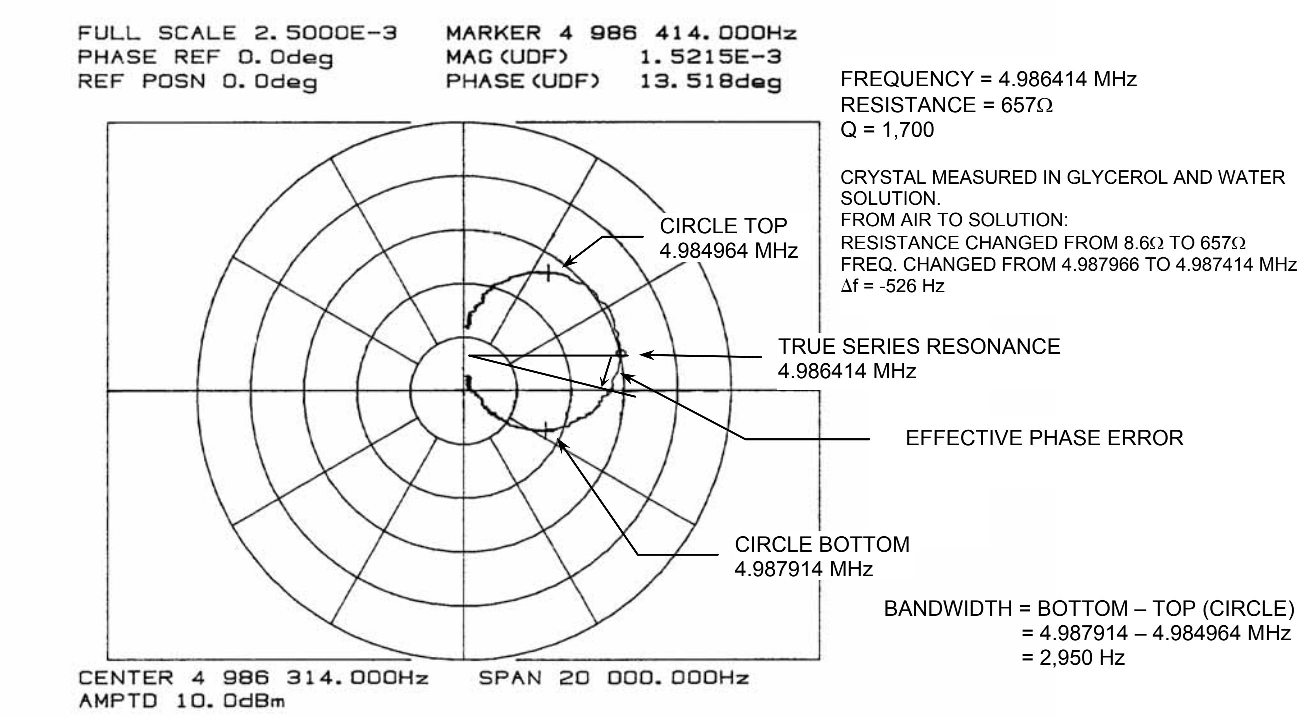


Figure 20 Polar Admittance Plot of High Q Crystal



FREQUENCY = 4.986414 MHz
RESISTANCE = 657Ω
Q = 1,700

CRYSTAL MEASURED IN GLYCEROL AND WATER SOLUTION.
FROM AIR TO SOLUTION:
RESISTANCE CHANGED FROM 8.6Ω TO 657Ω
FREQ. CHANGED FROM 4.987966 TO 4.987414 MHz
Δf = -526 Hz

CIRCLE TOP
4.984964 MHz

TRUE SERIES RESONANCE
4.986414 MHz

EFFECTIVE PHASE ERROR

CIRCLE BOTTOM
4.987914 MHz

BANDWIDTH = BOTTOM – TOP (CIRCLE)
= 4.987914 – 4.984964 MHz
= 2,950 Hz

Figure 21 Polar Admittance Plot of Low Q Crystal

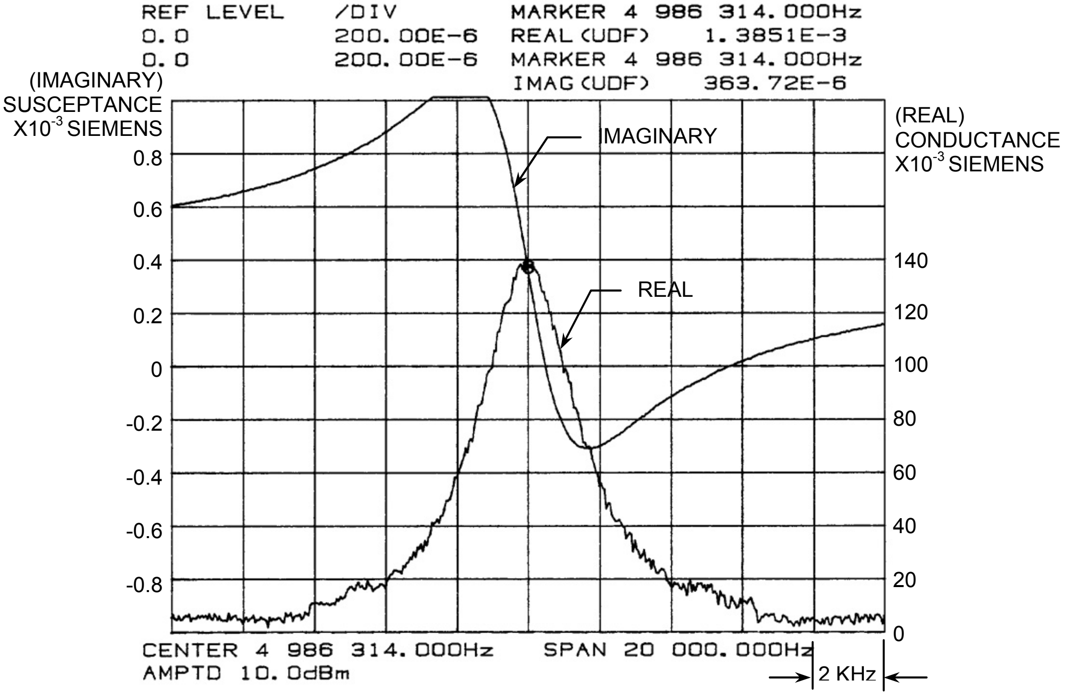


Figure 22 Admittance vs. Frequency, Real and Imaginary Components of Low Q Crystal

The conductance of the L, R & C series arm creates the circle in the polar plot with its center on the real axis. The effect of the shunt capacitance conductance is to offset the circle vertically. Figure 21 shows a heavily loaded crystal in which the offset is obvious. It is the imaginary (quadrature) current through the shunt capacitance that creates the offset. The RQCM provides a mechanism for canceling out the imaginary current effectively putting the center of the crystal back on the real axis. The true series resonant frequency of the crystal is then the point where the conductance circle crosses the real axis. This is the frequency at which the inductive and capacitive impedance's in the L, R & C branch cancel out and the crystal looks like a pure resistance of value R.

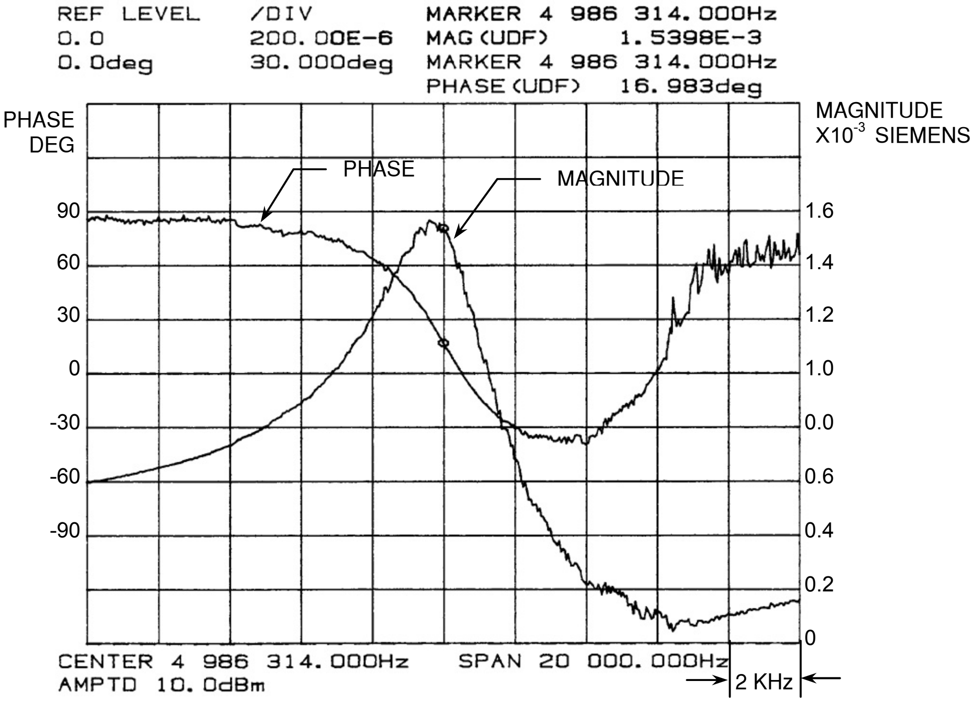


Figure 23 Admittance vs. Frequency, Magnitude and Phase of Low Q Crystal

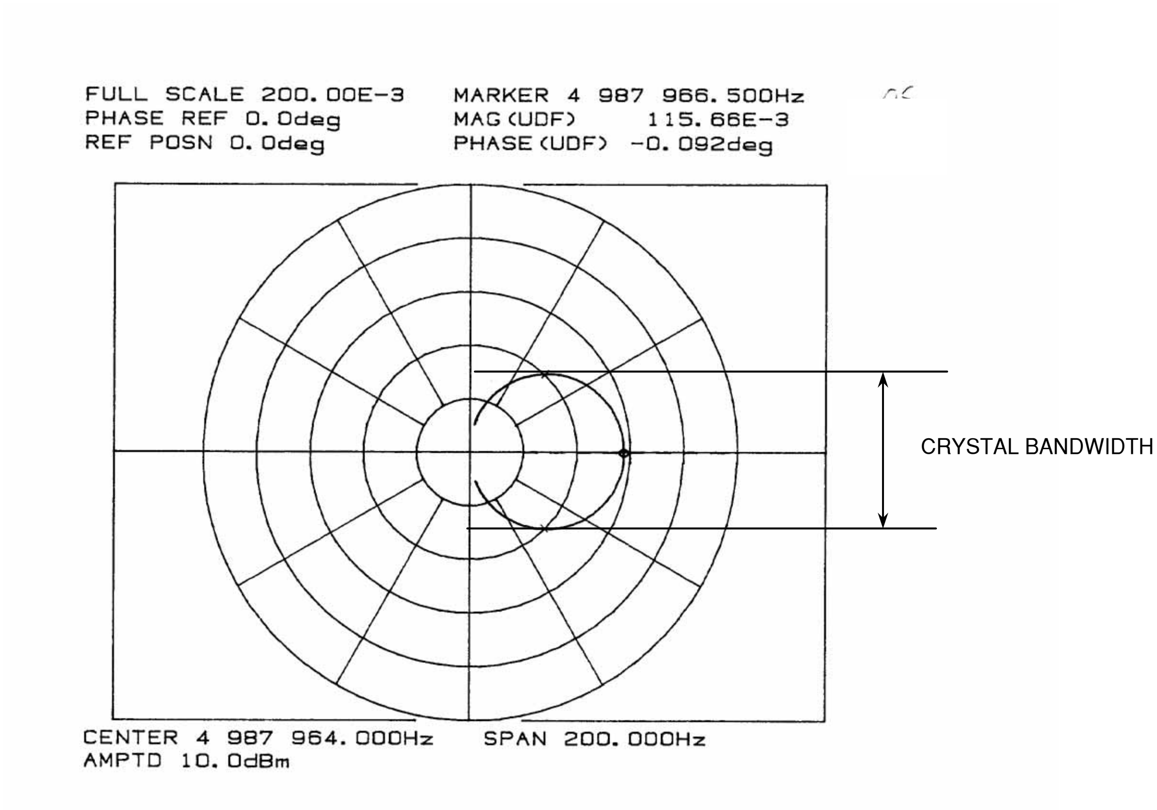


Figure 24 Non-zero Phase Lock

Figure 24 shows the result of a non-zero phase lock. Note that the frequency difference between the top of the conductance circle and the bottom is equal to the bandwidth of the crystal. For a high Q, (high conductance, low resistance) crystal, the bandwidth is very narrow and small errors in phase lock angle are insignificant. For a low Q crystal the bandwidth can be quite large and small phase errors can result in significant frequency errors. See the equations in the error discussion section.

5.7 CHARACTERIZING THE CRYSTAL MEASUREMENT

The INFICON Phase Lock Oscillator (used on the Crystal Measurement Card) was developed specifically to support the use of the quartz crystal microbalance in the measurement of lossy films and in liquid applications. In addition to accurately tracking the frequency of heavily damped crystals, the RQCM also tracks the crystal's resistance. This provides additional information in the study of lossy films and/or viscous solutions.

The PLO utilizes an internal oscillator referred to as a Voltage Controlled Oscillator (VCO) to drive the crystal. The crystal current is monitored and the frequency of the oscillator is adjusted until there is zero phase between the crystal voltage and current. Assuming that the crystal's electrode capacitance has been effectively cancelled, this point of zero phase between the crystal current and voltage is the exact series resonant point of the crystal. The magnitude of the current at this point is directly proportional to the crystal's conductance. This current is monitored by the RQCM and displayed as crystal resistance. The PLO contains a phase detector that continuously monitors the phase difference between the crystal's current and voltage. At frequencies below the crystal's resonant frequency the current leads the voltage and the phase goes to 90 degrees as the frequency separation continues to increase, see Figure 19. Above the resonant point the current lags the voltage and the phase go to minus 90 degrees. As the frequency increases through the resonant frequency, the phase goes from plus 90 through 0 to minus 90. It is interesting to note that the phase angle is 45 degrees when the VCO frequency is one half of the crystal's bandwidth above or below the crystal's resonant frequency.

The output of the phase detector is fed into an integrator. The integrator accumulates the phase error such that any positive phase error causes the integrator output to climb; a negative phase causes the integrator output to fall. With zero phase error the Integrator output holds steady.

The integrator output is connected to the VCO. Thus, if the VCO frequency is initially below the crystal resonant frequency, the phase will be positive, producing a positive output at the phase detector. This causes the Integrator output to climb, which causes the VCO frequency to increase. When the VCO frequency matches the resonant frequency of the crystal the phase will decrease to zero, the phase detector output will go to zero, the Integrator output will hold steady and the VCO frequency will be "locked" to the crystal's resonant frequency.

If the crystal's resonant frequency moves up or down, a phase difference between the crystal voltage and current will develop, producing a phase detector output. The non-zero phase detector output will drive the Integrator output up or down until the phase is zero once again, thus keeping the VCO frequency locked to the crystal's resonant frequency.

Once the frequency of the VCO is locked to the series resonant frequency of the crystal, the in-phase component (at zero phase error, there is no out of phase component) of the crystal current is demodulated to a DC voltage. This voltage is amplified and converted into resistance value which the RQCM outputs to the computer.

5.7.1 FREQUENCY ERRORS

The first thing we want to know regarding the performance of the crystal measurement is "What is the magnitude of the frequency error we can expect from the crystal measurement portion of the RQCM?"

In any oscillator and sensing crystal system, the error in the frequency measurement, is a function of both the oscillator and the sensing crystal. The same is true for phase locked loops. Any phase error will introduce a frequency error and this frequency error will be inversely proportional to the sensing crystal's Q. These errors are over and above any change in crystal frequency due to stress, temperature, adsorption, and humidity changes.

There are four important parameters that determine the frequency error of the PLO and sensing crystal system or indeed, any oscillator and sensing crystal system. The first two, the zero phase error and the electrode capacitance cancellation errors, are characteristics of the PLO. The second two are characteristics of the crystal, the Q of the crystal and the conductance (1/resistance) of the crystal.

5.7.2 FREQUENCY ERROR DUE TO PHASE ERROR

Given some finite zero phase error, the resulting frequency error depends on the sensing crystal's Q, the higher the Q, the lower the error. For phase errors below 10 degrees the frequency error is 0.087 PPM per degree for crystals with a Q of 100,000. Thus a one degree phase error in the PLO results in a 0.44 Hz frequency error for a 5MHz crystal with a Q of 100,000. For a 5 MHz crystal with a Q of 10,000, the error is 10 time greater or 4.4 Hz per degree.

$$\text{Frequency Error/deg} = df/f = \pi/(360*Q)$$

5.7.3 FREQUENCY ERROR DUE TO IMPERFECT CAPACITANCE CANCELLATION

The effect of imperfect electrode capacitance cancellation can also be viewed as an equivalent phase error. This error is directly proportional to crystal resistance. The equivalent phase error due to a non-zero shunt capacitance equal to 1 pfd is one degree for a crystal with a series resistance of 556 Ω. Since the equivalent phase error is proportional to the crystal resistance, a 1-pfd residual capacitance error will result in a 10-degree equivalent error for a sensing crystal with a resistance of 5.56 KΩ.

Polar Plot of Crystal Conductance

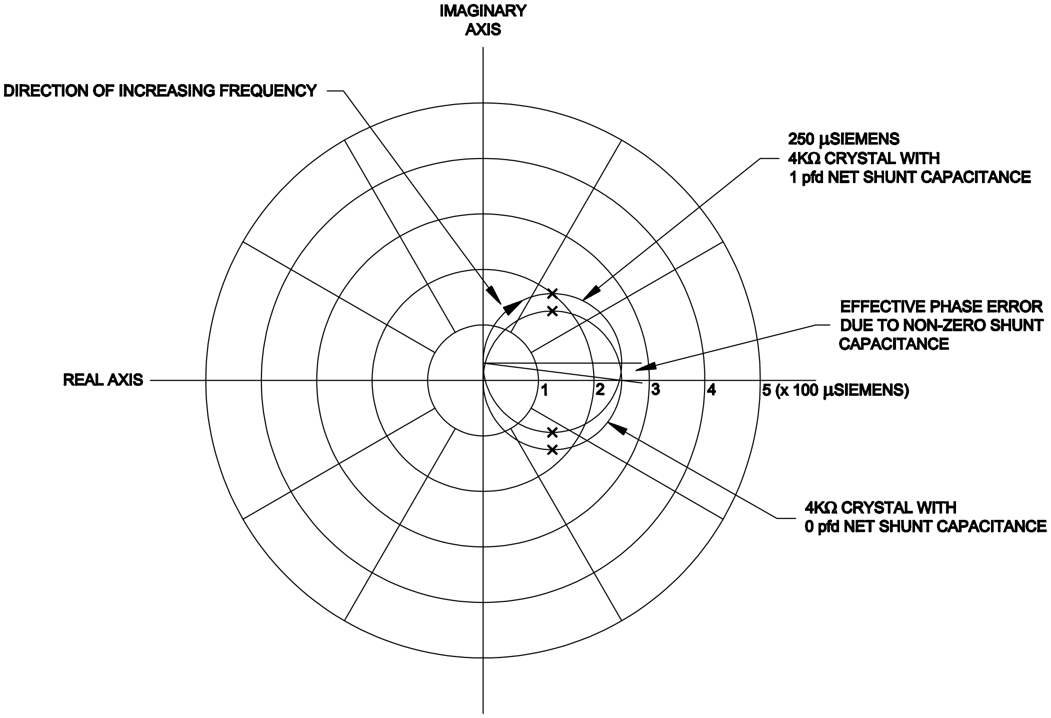


Figure 25 Equivalent Phase Error Due to Imperfect Capacitance Cancellation

5.8 FREQUENCY ERRORS DUE TO IMPERFECT CAPACITANCE CANCELLATION

There are two reasons that proper capacitance cancellation is so important with high resistance crystals.

The first is that to a first approximation, the frequency error resulting from a given phase error is proportional to the bandwidth of the crystal. The bandwidth of the crystal is proportional to the crystal's resistance. A ten-ohm crystal might typically have a bandwidth of 42 Hz, while a one thousand-ohm crystal will have a bandwidth of 4,200 Hz. A five thousand-ohm crystal will have a bandwidth of 21,000 Hz. Since the frequency error for a given phase error is proportional to the bandwidth, a phase error that would result in a 0.5 Hz frequency error in a ten ohm crystal will cause a 50 Hz error in a one thousand ohm crystal and 250 Hz error in a five thousand ohm crystal.

The second reason is that the effective phase error caused by a non-zero net quadrature current is inversely proportional to the real current, which is inversely proportional to the crystal resistance. In other words, the effective phase error is proportional to the crystal resistance. For instance, a net unbalance of 1 pfd leads to an effective phase error of 0.02 degrees for a ten ohm crystal, but it leads to a 2 degree error for a one thousand ohm crystal and a 10 degree error for a five thousand ohm crystal.

Examples:

A ten-ohm, 5 MHz crystal will have a Q (Quality Factor) of about 120,000. The bandwidth is equal to the crystal frequency divided by Q. Thus, the bandwidth of this crystal would be about 42 Hz. To a first approximation, near zero phase, the frequency error per degree of phase error is given by the following formula,

Frequency Error = -½(Phase Error, in radians)(Bandwidth)

Or,

Frequency Error = -(1/(2*57.3))(Phase Error, in degrees)(Bandwidth)

For the above ten-ohm crystal, the frequency error caused by a one-degree phase error is 42/114.6 or approximately 0.37 Hz. For a one thousand-ohm crystal, one degree of phase error results in a 37 Hz error and for a ten thousand-ohm crystal the frequency error is 370 Hz per degree of phase error.

Now, the effective phase error caused by a non-zero quadrature (imaginary) current is given by the following formula,

Effective Phase error = arctangent (imaginary current/real current)

And since current is proportional to conductance,

Effective Phase error = arctangent (imaginary conductance/real conductance)

The conductance of a one picofarad capacitor at 5 MHz is 31.4 microsiemens. The conductance of a ten-ohm crystal at resonance is 100 millisiemens.

Effective Phase error = arctangent ((31.4e-6)/(100e-3)) = 0.018 degrees

In other words a one picofarad capacitance unbalance will result in an effective phase error of only 0.018 degrees when measuring a ten-ohm crystal. However, when measuring a one thousand-ohm crystal the effective phase error will increase to 1.8 degrees and it will increase to 9 degrees when measuring a five thousand-ohm crystal.

Combining these two errors we can get an idea of the magnitude of the frequency error caused by imperfect capacitance cancellation.

For a 10 Ω crystal a one picofarad capacitance imbalance results in a 0.018 degree phase error and a 0.0067 Hz frequency error.

For a 100 Ω crystal, the phase error is 0.18 degrees and the frequency error is 0.67 Hz. For a 1000 Ω crystal, the phase error is 1.8 degrees and the frequency error is 67 Hz. For a 5000 Ω crystal, the phase error is 9 degrees and the frequency error is 1,635 Hz.

A two picofarad capacitance imbalance will result in approximately twice the above error.

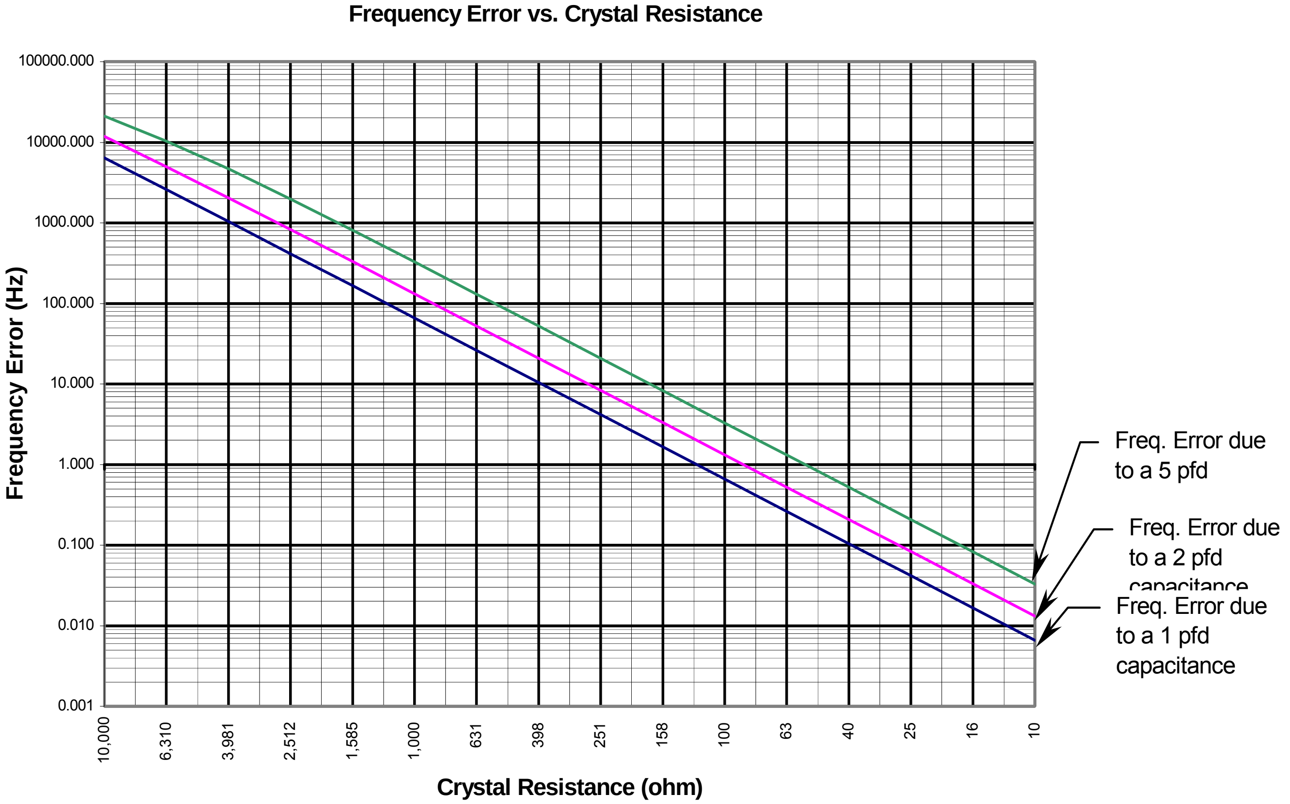


Figure 26 Frequency Error Due to Imperfect Capacitance Cancellation

5.9 CALCULATING CRYSTAL POWER

Crystal power can be calculated as follows:

Crystal power, $P_{cry} = i^2 * R_{cry}$

Crystal current, $i = V_{oc}/(R_s + R_{cry})$

Hence, $P_{cry} = i^2 * R_{cry} = [V_{oc}/(R_s + R_{cry})]^2 * R_{cry}$

Where:

V_{oc} = Open Circuit crystal drive voltage = 125 mV

R_s = Crystal drive source resistance = 20 ohms

R_{cry} = Crystal resistance value in ohms

Examples:

1. Crystal Resistance = 80 ohms

   $P_{cry,\ in\ watts} = [0.125/(20 + 80)]^2 * 80 = 1.25E^{-4}$ watts or 125 μW

2. Crystal Resistance = 4000 Ω

   $P_{cry,\ in\ watts} = [0.125/(20 + 4000)]^2 * 4000 = 3.87E^{-6}$ watts or 3.87 μW

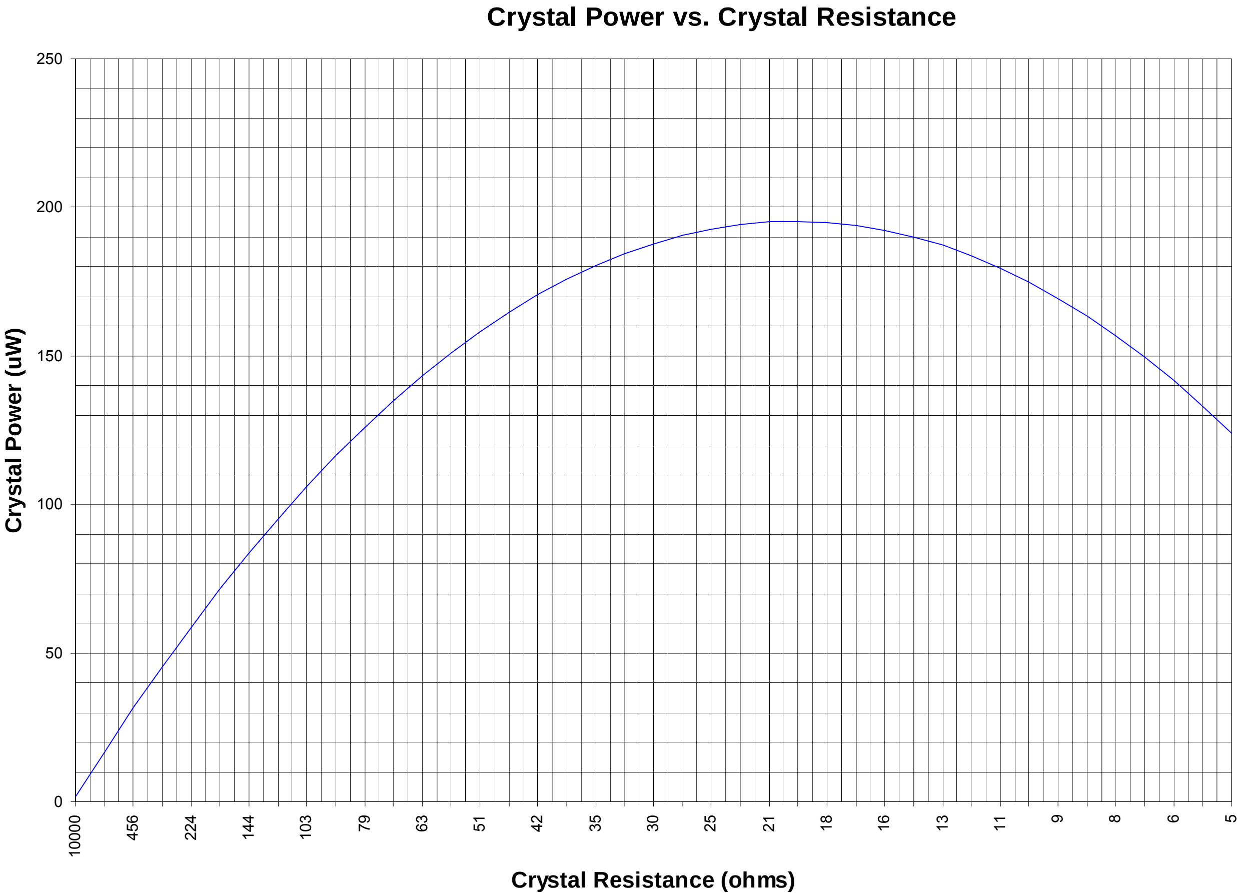


Figure 27 Crystal Power Dissipation vs. Crystal Resistance

6 APPLICATIONS

The RQCM will respond *very sensitively* to minute stress changes on its vibrating surface resulting from mass deposits or frictional forces. This makes it a powerful tool for a wide variety of applications, including: biofilms formations on surfaces, bio-sensing, specific gas detection, environmental monitoring, and basic surface-molecule interaction studies.

A full spectrum of its potential applications is beyond the scope of this manual. This section only describes a few typical applications. The user is advised to consult the publications listed in Section 12 for further information.

6.1 ELECTROCHEMICAL QUARTZ CRYSTAL MICROBALANCE

The basic principles and applications of the QCM to electrochemical processes have been extensively reviewed in the electrochemical literature[29 30].

In most electrochemical experiments, mass changes occur as material is deposited or removed from the "working" electrode. It is of interest to monitor those changes simultaneously with the electrochemical response, and the RQCM 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[31 32 33 34], corrosion[35], oxide formation[36], dissolution studies[37 38 39 40], adsorption/desorption of surfactants[41 42 43] and changes in conductive polymer films during redox processes[44].

6.1.1 CALIBRATION

Many published literature has demonstrated 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[45]. Quantitative interpretation of the EQCM data in those cases is based on the combination of the Sauerbrey equation and Faraday's law.

The Sauerbrey equation relates change in frequency to change in mass for thin, lossless deposited films, whereas Faraday's law 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 this next equation:

Equation 11

$$\Delta f = \frac{10^6 \cdot M_W \cdot C_f \cdot Q}{n \cdot F \cdot A_r}$$

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,

Q = integrated charge during the reduction in Coulombs,

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

A_r = active deposition area of the working (liquid contact) electrode in cm^2,

F = Faraday's constant = 9.648×10^4 Coulomb/mole,

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 11, 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 gold or platinum electrode. Several calibration procedures are described in the electrochemistry literature[46] [47] [48].

6.1.2 POLYMER MODIFIED ELECTRODES

The EQCM has been extensively used to study polymer-modified electrodes, particularly as a gravimetric tool to follow redox processes[49] [50]. However, for the linear frequency-to-mass relationship (described by Equation 11) to hold true, the polymer over layer 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[51] [52]. As a consequence, it is important to determine if viscoelastic properties of the polymer film influence the frequency measurement during polymer film experiments.

A straightforward method 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[53] [54]. Some theoretical models[55] [56], based on the simultaneous measurement of Δf and ΔR, have been discussed in the literature for the extension of EQCM gravimetric measurements to lossy 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, especially 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[57].

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[58].

6.2 CHEMICAL AND BIOLOGICAL SENSORS

A QCM will response to *anything* that has mass. Thus, it is imperative for the QCM user to develop a "condition" where the QCM will only response to the analyte of interest, i.e build a unique sensitivity into the sensor crystal. This usually involves a chemically or biologically sensitive layer applied to the surface of the crystal[13].

In recent years, QCM applications have seen a dramatic increase in field of biochemical analysis. QCM devices are routinely used as biochemical and immunological probes[59], as well as for the investigation and/or monitoring of biochemcially significant processes[60]. Sensitive, selective detection of biochemically active compounds can be achieved by employing antigen-antibody[61], enzyme substrates and other receptor–protein pairs. The potential analytical applications of these materials has been reviewed, particularly with respect to the development of biochemical sensors. QCM studies have provided detailed information about the functionalized surfaces developed for a range of biochip and biosensor applications.

INFICON RQCM is now being applied routinely by biologists and biochemists to obtain information about processes such as protein adsorption/desorption, cell adhesion, protein-protein interaction, degradation of polymers, biofouling and biofilm formation, drug analysis, and DNA biosensors.

7 COMPUTER INTERFACE

Three different interfaces are available to connect the RQCM hardware to your computer.

The RQCM system comes standard with an RS-232 serial interface. Both RS-485 and IEEE-488 interfaces are available as options. Currently the RQCM does not offer a Universal Serial Bus (USB) interface. However, you can use an inexpensive RS-232 to USB adaptor if your computer does not have an RS-232 port available. Refer to the RQCM Data Logging on-line help for more details.

7.1 COMPUTER INTERFACE SOFTWARE

Your RQCM software is supplied on a CD. Extensive on-line help makes a hardcopy manual unnecessary.

7.2 RECOMMENDED MINIMUM COMPUTER CONFIGURATION

- Pentium III 500 MHz PC
- 24 MB of RAM. (This is in addition to the Operating System requirements.)
- 35 MB of hard disk space. (Additional free hard disk space is required for data storage.)
- CD-ROM drive
- Microsoft Windows 9x/ME/NT4 (SP3 or later)/2000/XP.

7.3 SOFTWARE INSTALLATION

Follow the instruction below to install the software on the computer.

1. Insert the RQCM Software CD into the CD-ROM drive.
2. If your system supports the auto-run feature, installation begins automatically.
3. If your system does not support the auto-run feature, click Start, Run, then enter X:\setup, where X is the CD-ROM’s drive letter.
4. Follow the instructions in the windows as they appear.

7.4 CREATING YOUR OWN SOFTWARE

Although the RQCM includes a comprehensive Windows™ based interface program, some users may find it necessary to create their own interface program. This section describes the various computer interfaces and the protocol of the RQCM.

There are three types of computer interfaces offered. The RQCM comes standard with an RS-232 serial interface. Both RS-485 and IEEE-488 interfaces are available as options.

7.5 RS-232 SERIAL INTERFACE

The standard RS-232 serial interface of the RQCM allows one RQCM to be connected to any other device with an RS-232 serial interface. The RS-232 interface port is the D9P connector on the rear panel of the RQCM. The pin layout is shown in Figure 28 and Table 7-1 lists the pin signal assignments, including a definition of whether the signal is an input or an output of the RQCM.

The RQCM acts as DTE, and accordingly the 9-pin connector has 'plug' pins. It can be used with a DCE or a DTE host cable connection providing the sense of the RxD/TxD data lines and the control lines is observed. Pin 2 'TxD' transmits data from the RQCM to the host; pin 3 'RxD' receives data from the host. Pin 7 'CTS' is a control output signal, and pin 8 'RTS' is a control input signal.

In this implementation, pin 7 'CTS' means what is says, namely, this is an output control line, and when the RQCM asserts this control line 'true' the host can transmit to the RQCM. On the other hand, pin 8 'RTS' is not quite what it may seem because this is a signal input to the RQCM, and it is intended that the host should assert this line 'true' only when the RQCM is allowed to transmit data to the host. The RQCM does not generate an RTS 'request-to-send' as such for the host PC, so the host should assert pin 8 true whenever the RQCM is allowed to transmit to the host, without being asked to do so.

The RQCM's RS-232 port is automatically set up to operate with the following specifications:

19200 Baud, 8 Bit data, No Parity, 1 Stop bit

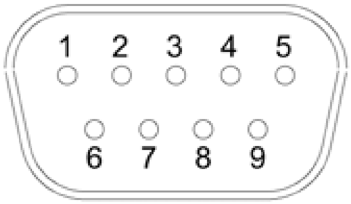


Figure 28 D9S DTE Rear-panel RS-232 socket connector

Pin	Signal	
Number	RS-232	RS-485
1	Not used	Rx- Input
2	Tx Output	Rx+ Input
3	Rx Input	Tx+ Output
4	Not used	Tx- Output
5	GND	GND
6	Not used	CTS- Input
7	CTS Input	CTS+ Input
8	RTS Output	RTS+ Output
9	Not used	RTS- Output

Table 7-1 D9 Rear Panel RS-232/RS-485 Connector Pin Assignments

7.6 RS-485 SERIAL INTERFACE

The optional RS-485 serial interface of the RQCM allows connection of up to 32 separate devices equipped with RS-485. The RS-485 serial interface is also ideal in electrically noisy environments and in applications where long cables are required. The RS-485 port of the RQCM is the same D9P connector on the rear panel used for RS-232. The pin layout is shown in Figure 28 and Table 7-1lists the pin signal assignments, including a definition of whether the signal is an input or an output of the RQCM.

The RQCM's RS-485 port is automatically set up to operate with the following specifications:

19200 Baud, 8 Bit data, No Parity, 1 Stop bit

7.7 IEEE-488 PARALLEL INTERFACE

The optional IEEE-488 interface provides the RQCM with the ability to communicate with computers and other devices over a standard IEEE-488 interface bus. The IEEE-488 interface, also known as GPIB or HPIB, provides an eight bit parallel asynchronous interface between up to 15 individual devices on the same bus. This means that one computer equipped with an IEEE-488 interface card can communicate with up to 14 RQCMs or other devices.

The pin layout of the IEEE-488 port is shown in Figure 29 and Table 7-2 lists the pin signal assignments, including a definition of whether the signal is an input or an output of the RQCM.

The RS-232 serial port can still be used with IEEE-488 installed. However, since both interfaces use the same input and output message buffers, they should not be used at the same time. This will result in communication errors.

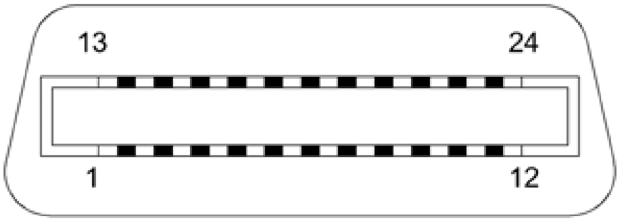


Figure 29 IEEE-488 Connector

Pin Number	Signal
1	DATA I/O 1
2	DATA I/O 2
3	DATA I/O 3
4	DATA I/O 4
5	End Or Identify
6	Data Valid
7	Not Ready For Data
8	Data Not Accepted
9	Service Request
10	Interface Clear
11	Attention
12	Shield or Wire GND
13	DATA I/O 5
14	DATA I/O 6
15	DATA I/O 7
16	DATA I/O 8
17	Remote Enable
18	GND
19	GND
20	GND
21	GND
22	GND
23	GND
24	Logic GND

Table 7-2 IEEE-488 Pin Assignments

7.8 PROTOCOL

All communications between the computer and the RQCM are in the form of messages with the format:

* Two byte header - (FFh, FEh i.e. Chr$(255), Chr$(254)) The header indicates the beginning of a message.

*One byte device address - (1 to 32) The device address byte defines the bus address of the instrument that sent or should receive the message. The device address will range from 1 to 32. A message sent to a device address of zero will be received by all RQCMs except in the case of the IEEE-488 interface. With this interface, only the addressed device will receive the message.

*One byte instruction code - (0 to 6) Defines the code number of the message.

*One byte message length - (0 to 249) Indicates the number of data bytes contained in the message.

* One byte checksum - (0 to 255) The checksum byte is used for transmission error detection. If the RQCM receives a message with an incorrect checksum, it will disregard the message. The checksum is the compliment of the one-byte sum of all bytes from, and including, the instruction code to the end of the message. If the one-byte sum of all these bytes is added to the checksum, the result should equal 255.

If the sum of all bytes occupies more than one byte, a single byte checksum can be generated using the expression: checksum=! (Sum MOD 256), i.e. the checksum is the complement of the remainder byte, which results from dividing the sum of all bytes by 256.

7.9 DATA TYPES

There are three data types stored in the RQCM: One byte, two byte, and three byte parameters. All data types are stored as integers in binary format with the most significant byte first. The one-byte data types are ASCII characters, numeric values (0-255), or 8 bit registers. Some of the multiple byte data types are decimal values stored as integers. To convert these values to their decimal equivalent, use the following equation:

Decimal Value = (Integer Value)/(10*DP)

Where:

DP = the value's decimal point position.

The decimal point positions for all the parameters are constant and are given in tables along with the parameters' range.

7.10 MESSAGE RECEIVED STATUS

Following the receipt of each message, the RQCM will send a one-byte 'received status' message, indicating how the message was received, with the following format:

Header

Address

Inst=253

Length=2

Instruction Code

Receive code

Checksum

A value of 253 for the instruction byte indicates that this is a received status message. The Instruction Code byte indicates the instruction code of the message that was received. The following table shows a list of possible receive codes:

Receive Code	Description
0	Message received O.K.
1	Invalid checksum.
2	Invalid instruction code.
3	Invalid message length.
4	Parameter(s) out of range.
5	Invalid message.

7.11 INSTRUCTION SUMMARY

The following table is a list of valid instruction codes.

Instruction Code	Description
0	Send RQCM configuration
1	Initiate automatic data logging of binary values
2	Set analog to digital board configuration
3	Internal command
4	Internal command
5	Internal command
6	Set Relay Outputs
7	Internal command
8	Set interface address

7.12 INSTRUCTION DESCRIPTIONS

The following is a description of the valid instructions along with an example of how they are used. All the examples assume the device address is 1.

1. Send RQCM hardware configuration (Code #0)

Instructs the RQCM to send its configuration data to the host computer. The following is a description of the configuration data message:

Name	Length (bytes)	Message
Software Version	35	INFICON RQCM Software Version X.XX
Communication Port	1	(1=RS232, 2=RS-485, 3=IEEE488)
Sensor Board Status	1	(Bit0=Ch. #1, Bit1=Ch. #2, Bit2=Ch. #3)
Accessory Board Status	1	(Bit0 = Digital I/O, Bit 1 = Analog Input)
Total 38 bytes		

Example: To instruct the RQCM to send the configuration data the computer would send:

Chr$(255)+Chr$(254)+Chr$(1)+Chr$(0)+Chr$(0)+Chr$(255)

2. Automatic Data Logging of Binary Values (Code #1)

This instruction allows the computer to setup the RQCM to automatically output selected binary values to the communication port every 50 milliseconds. The values sent are determined by the bit value of the message byte in the data logging instruction message.

Byte #	Bit #	Description	Length bytes	Format	Range	Units
1	0	Message counter	1	Binary	0 to 255	
	1	Sensor #1 Period	4	Binary		Counts/sec
	2	Sensor #1 Resistance	2	Binary	0 to 65535	Counts
	3	Sensor #2 Period	4	Binary		Counts/sec
	4	Sensor #2 Resistance	2	Binary	0 to 65535	Counts
	5	Sensor #3 Period	4	Binary		Counts/sec
	6	Sensor #3 Resistance	2	Binary	0 to 65535	Counts
	7	Analog Input #1	2	Binary	-33,333 to 33,333	--------
2	0	Analog Input #2	2	Binary	-33,333 to 33,333	--------
	1	Analog Input #3	2	Binary	-33,333 to 33,333	--------
	2	Analog Input #4	2	Binary	-33,333 to 33,333	--------
	3	Analog Input #5	2	Binary	-33,333 to 33,333	--------
	4	RTD Temperature	2	Binary	-33,333 to 33,333	0.1 °C or °F
	5	Thermocouple Temperature	2	Binary	-33,333 to 33,333	0.1 °C or °F
	6	Thermistor Temperature	2	Binary	-33,333 to 33,333	0.1 °C or °F
	7	Discrete Inputs	1	**		
3	0	Discrete Outputs	1	**		

** The discrete input and output bytes indicate the status of the inputs and outputs such that bit 0 corresponds to input/output #1, bit 1 to input/output #2, etc.

All values are sent in Binary format with the most significant byte first. To convert binary values to decimal, use the following formula:

Decimal Value = Sum of Byte[n]*256^(Y-n) where n goes from 1 to Y and Y is the total number of bytes that make up the value.

For example, say you want to read sensor frequency. You first have to setup the RQCM to send sensor period. Say you receive the four following bytes representing sensor period:

31,255,109,53

This equals (31*256^3 + 255*256^2 + 109*256 + 53) = 536,833,333

To convert period to frequency, use the following formula:

Frequency (Hz) = (3.221E15)/Period = (3.221E15/536,833,333) = 6,000,000.0 Hz

Like sensor period, sensor resistance is also in special units. Use the following formula to convert the resistance counts value sent by the RQCM to OHMs:

Sensor Resistance (OHMs) = (273,300/Counts) - 20

The scaling of the analog inputs depends on each inputs configuration as shown in the following table.

Input Range	Scaling (mV)
0 – 5	0.0001
+/- 5	0.0002
0 – 10	0.0002
+/- 10	0.0005

Example: To instruct the RQCM to output sensor #1 period and resistance, the computer would send the following message:

Chr$(255)+Chr$(254)+Chr$(1)+Chr$(1)+Chr$(3)+Chr$(6)+Chr$(0)+Chr$(0)+Chr$(245
)

The RQCM will then send one message every 50 milliseconds that it 12 bytes long and contains 6 bytes of data. The first four bytes of data is sensor period and the next two bytes are sensor resistance.

Data logging is stopped by sending the following message:

Chr$(255)+Chr$(254)+Chr$(1)+Chr$(1)+Chr$(3)+Chr$(0)+Chr$(0)+Chr$(0)+Chr$(251
)

3. Configure Data Acquisition Board (Code #2)

This instruction allows the computer to configure the input range and temperature units of the RQCM's Analog Input/Temperature card. The following table shows the byte configuration for this message.

Byte #	Description	Length bytes	Range
1	Input #1 Range	1	0 to 7
2	Input #2 Range	1	0 to 7
3	Input #3 Range	1	0 to 7
4	Input #4 Range	1	0 to 7
5	Input #5 Range	1	0 to 7
6	Temperature Configuration	1	0 or 7
	Total Bytes	6	

Each inputs voltage range and filter frequency can be independently configured. There are four voltage ranges and two frequency ranges. The available values are as follows:

Input Code	Voltage Range (Volts)	Filter Freq. (Hertz)
0	0 to 5	1
1	0 to 10	1
2	+/- 5	1
3	+/- 10	1
4	0 to 5	8
5	0 to 10	8
6	+/- 5	8
7	+/- 10	8

The temperature configuration byte sets the units for the three temperature inputs. A value of zero selects Fahrenheit and a value of seven selects Celsius.

Example: To set inputs 1 through 5 for 0 to 5 volt range and 1 hertz filter and the temperature inputs to Celsius, computer would send:

Chr$(255)+Chr$(254)+Chr$(1)+Chr$(2)+Chr$(6)+Chr$(0)+Chr$(0)+Chr$(0)+Chr$(0)+
Chr$(0)+Chr$(7)+Chr$(240)

4. Internal Command

5. Internal Command

6. Internal Command

7. Receive Relay Output Status (Code #6)

This instruction allows the computer to open or close the RQCM's relay outputs. Each bit of the one-byte command code in the message determines the status of one output. If the bit is 1 then that output relay will close. If the bit is 0 then that relay output will open. Bit 0 = relay #1, bit 1 = relay #2, etc.

For example: To instruct the RQCM to close relays 1 & 2 and open all other relays, the computer would send:

Chr$(255)+Chr$(254)+Chr$(1)+Chr$(6)+Chr$(1)+Chr$(3)+Chr$(245)

8. Internal Command

9. Set RQCM Interface Address (Code #8)

This instruction allows the computer to set the RQCM's interface address. The RQCM's interface address allows for multiple instruments to share the same communications bus. You can have multiple RQCM's on the same bus but each must have a unique interface address so the computer can communicate with each one individually.

The interface address can range from 1 to 32. All RQCM's are shipped with the interface address set to one.

For example: To set the RQCM's interface address to 2, the computer would send:

```
Chr$(255)+Chr$(254)+Chr$(1)+Chr$(8)+Chr$(1)+Chr$(2)+Chr$(244)
```

If using the IEEE interface then the computer must also send a device clear before the new interface address takes affect. The new interface address will take affect immediately when using either RS-232 or RS-485.

8 DATA ACQUISITION CARD (OPTIONAL)

The RQCM has one rear panel slot for the optional Data Acquisition Card. The card has three (3) temperature inputs to accommodate an RTD, thermocouple and thermistor. There are also five (5) scalable analog inputs for measuring and logging of DC voltages. Except for the thermocouple input, which has its own connector, all other temperature inputs and analog inputs are on a D-SUB 25 pin male connector. Figure 30 shows the connector pin configuration and Table 8-1 shows the pin signal assignments. Refer to the online help included in the RQCM software for instructions on setting up and programming of these inputs.

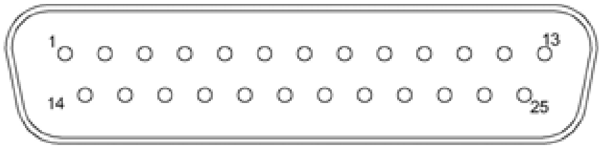


Figure 30 DB25P Data Acquisition Rear Panel Connector

Pin Number	Function
1, 2, 3	Voltage Input #1 (Input, Common, Shield)
4, 5, 6	Voltage Input #2 (Input, Common, Shield)
7, 8, 9	Voltage Input #3 (Input, Common, Shield)
10, 11, 12	Voltage Input #4 (Input, Common, Shield)
14, 15, 16	Voltage Input #5 (Input, Common, Shield)
17, 18, 19	Thermocouple Input (Hi, Lo, Shield)
20, 21, 22, 23, 24	RTD Input (Hi, Hi Sense, Lo Sense, Lo, Shield)
25	Voltage Reference
13	Not used

Table 8-1 DB25P Data Acquision Rear Panel Connector Pin Assignments

8.1 VOLTAGE INPUTS

Each of the five analog inputs can be configured as 0 to 5V, 0 to 10V, ±5V, or ±10V. The unipolar positive inputs can be connected as unipolar negative inputs. The resolution of the data is dependent on the range selection as shown in the table below.

Configuration	Resolution
0 to 5V	0.1 mV
0 to 10V	0.2 mV
±5V	0.2 mV
±10V	0.5 mV

Table 8-2 Input Voltage Resolution

The voltage input pairs are labeled as Input and Common. The Input pin is the positive input and the Common pin is the negative input. The common mode range is ±200V, so the Common pin can be used to read unipolar negative voltages with the input pin as common. Each input also has a Shield pin for shielded cable termination. Shielded, twisted pair cable is recommended for connections longer than a foot.

8.2 TEMPERATURE INPUTS

Three temperature inputs are included to support the three most commonly used temperature sensors: thermistor, Resistance Temperature Detector (RTD), and type T (copper constantan) thermocouple.

8.2.1 THERMISTOR INPUT

The Thermistor Input is designed to use an Omega 10 KΩ @ 25°C – Precision Interchangeable Thermistor P/N 44006, or equivalent. Shielded, twisted pair is recommended for the leads.

This thermistor has a range of 0 to 150°C. The use of a thermistor provides high accuracy measurements within its temperature range, or when long leads are required.

8.2.2 RTD INPUT

The RTD has a range of 0 to 600°C. The use of the RTD is for the measurements in the higher temperature ranges.

The RTD input is designed to use an RTD conforming to the European standard curve with an alpha of 0.00385 for the Calendar-van Dusen equation and a resistance of 100 ohms @ 0°C. The RTD is connected as a four-wire element, using a pair of wires for excitation and pair of wires to sense the voltage across the element. This configuration should be continued all the way to the probe for maximum accuracy. A single shielded cable with two twisted pairs, or two shielded, twisted pair cables should be used.

8.2.3 THERMOCOUPLE INPUT

The Type T Thermocouple input uses true internal cold junction compensation. For accurate measurements, thermocouple grade copper and constantan wire must be used from the thermocouple to the rear panel thermocouple connector. Figure 31 shows the rear panel thermocouple connector. The mating connector is an Omega NMP-T-M (included with each Data Acquisition Card), or equivalent. If it is desired to use shielded thermocouple wire, which is recommended, the shield drain wire can be connected to the RTD or thermistor shield pin.

The Type T Thermocouple has a range of 0 to 371°C. The use of a thermocouple is recommended in oxidizing, reducing, inert or vacuum atmosphere within its temperature range.

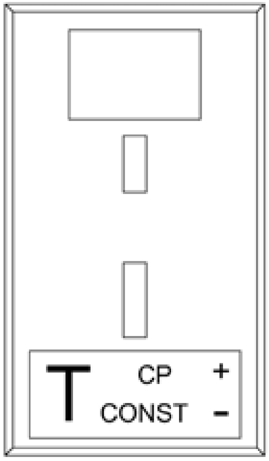


Figure 31 Rear Panel Type T Thermocouple Connector

8.3 GROUNDING CONSIDERATION

Proper grounding and shield termination is mandatory for accurate measurements.

8.3.1 VOLTAGE MEASUREMENT GROUNDING

If the voltage to be measured is returned to earth ground (within the common mode voltage range) at its source, neither the Input nor the Common lead should be grounded at the voltage measurement point, since the RQCM will return to earth ground through its power cord. The shield for the input leads must only be terminated at the Data Acquisition Card connector.

If the voltage to be measured is isolated from earth ground, the shield or its drain wire should be connected to the common side of the voltage to be measured at the voltage source as well as at the shield terminal on the RQCM Data Acquisition Card.

8.3.2 TEMPERATURE MEASUREMENT GROUNDING

All three temperature-sensors ***must*** be of the isolated or ungrounded type. Sensor lead wire shields should be terminated at the RQCM Data Acquisition Card connector only. The measured device should be connected to earth ground. Exposed junction probes should not be used to measure the temperature in a conductive media like water.

9 I/O CARD (OPTIONAL)

The RQCM has one rear panel slot for the optional I/O card. The card has eight (8) TTL level (0 to 5 volt DC) inputs. The inputs are pulled up to 5 volts internally through a 4.7 KΩ resistor and are set true, assuming the input's True level is set to Low, by shorting the input pins together.

There are eight (8) SPST relay outputs capable of handling 120 VA, 2A max. per relay.

These inputs and outputs can be used to control external instruments and peripheral devices such as pumps, heaters, valves, instruments, etc.

Figure 32 shows the connector pin configuration and Table 9-1 supplies pin signal assignments. Refer to the online help of RQCM computer software for I/O definition and programming instructions.

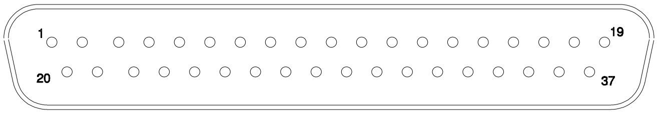


Figure 32 DB73P I/O Rear Panel Connector

Pin Number	Function
1, 20	Abort output
2, 21, 11	Output 1 (Common, N.O., N.C.)
3, 22, 29	Output 2 (Common, N.O., N.C.)
4,23	Output 3
5, 24	Output 4
6, 25	Output 5
7, 26	Output 6
8, 27	Output 7
9, 28	Output 8
30	Input 1
12	Input 1 Return
31	Input 2
13	Input 2 Return
32	Input 3
14	Input 3 Return
33	Input 4
15	Input 4 Return
34	Input 5
16	Input 5 Return
35	Input 6
17	Input 6 Return
36	Input 7
18	Input 7 Return
37	Input 8
19	Input 8 Return

Table 9-1 DB37P I/O Rear Panel Connector Pin Assignments

10 TROUBLESHOOTING GUIDE

This section is intended primarily as an aid in understanding the RQCM operation and to help insolate possible problems with the RQCM. If it is determined that the problem lies inside the unit, please contact the factory for further assistance.

Symptom	**Possible Cause**	**Remedy**
Line fuse blows when the power switch is switched to “on”.	Wrong line voltage is selected at the rear of RQCM	Set line voltage on RQCM rear panel to match with line voltage being used.
	Incorrect fuse rating.	Replace line fuse with correct fuse size.
None of the front panel LED indicators illuminated.	Blown line fuse.	Replace fuse
	Power switch is not on.	Switch front panel power switch to “on”.
	No power being applied to unit.	Check and correct power source and/or power cord.
	Wrong line voltage is selected at the rear of RQCM.	Set line voltage on RQCM rear panel to match with line voltage being used.
Unable to adjust fine and coarse adjustments to compensate for capacitance	The total capacitance of the cable, crystal, and crystal holder is out of the range of 40 to 200 pfd.	Adjust cable length to reduce/increase its capacitance.
Unit does not lock onto a frequency when a crystal is installed.	Crystal fundamental frequency exceeds the frequency range of the crystal channel.	Verify crystal frequency against crystal channel frequency range. (To verify the crystal channel frequency ranges, press Reset button and observe the output. A 3.8 MHz indicates the channel is set for 3.8 to 6 MHz. A 5.1 MHz indicates a 5.1 to 10 MHz.) Replace crystal.
	Crystal resistance exceeds the range of 5 and 5,000 Ohms.	Replace crystal.
Unit looses lock when crystal is exposed to liquid.	Total capacitance of the crystal, holder and cable changes when going from air to liquid.	Adjust capacitance compensation with crystal in the liquid. Refer to Section 3.4.
Unstable frequency reading when the crystal or the holder or the cable is being touched.	Same as above. The crystal measurement is reacting to the change in total capacitance when the setup is being touched.	Avoid contact with the hookup during an experiment. This is especially important if the crystal is a low Q crystal.
Frequency reading is unstable or drifting.	Temperature (of the crystal) is changing. An AT-cut crystal frequency may drift as much as 10 Hz/°C.	Control temperature of the test environment.
	Humidity (level on the crystal) is changing. Moisture being absorbed or exuded from the crystal surface.	Control humidity of the test environment.

	"Unbalanced" or damaged coaxial cable.	Check cable for any signs of damage such as broken shield. Replace cable.
Unit shows "Lock" with no crystal, holder and cable connected to the crystal channel.	The capacitance was probably adjusted with the crystal, holder and cable combined. With everything removed, the "Lock" light just means that the capacitance is now grossly out of adjustment.	This is normal. Re-connect the crystal, holder and cable.
Unit shows "Lock", but the frequency reading is at its lowest and the resistance reading is about 1 ohm.	An electrical short across the crystal input.	Check the cable, holder, and the crystal for short. Remove short or replace the defective part.
"No Clear to Send Signal" error message when attempting communications with RQCM.	Wrong COMM port number selected.	Set the correct COMM port number in the Setup|Comm Port Setting Menu.
	RS-232 Cable not connected to RQCM.	Connect RS-232 cable to RQCM
"Error reading data" message, "Timeout" when attempting communications with RQCM	Wrong COMM port number selected.	Set the correct COMM port number in the Setup|Comm Port Setting Menu.
	Incorrect RQCM Interface address.	Set an Interface Address in the Setup|Comm Port Settings Menu and click the Send Address button to send to RQCM
	COMM port not enabled.	Enable COMM port in PC's BIOS

11 GLOSSARY

Conductance	The ability to conduct. 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].
CPVC	Abbreviation for chlorinated polyvinyl chloride, a resin patented by Goodrich, it has excellent mechanical strength and stability over temperature, and offers good resistance over a selective range of chemicals.
Crystal Bandwidth	Refers to the crystal's frequency response range, bounced by the frequency values cross at half the resonance frequency's magnitude. It is defined as f_o /Q (resonance frequency/crystal Q).
Crystal Holder	A device that houses the crystal and provides connections to the crystal's electrodes via a coaxial connector.
Crystal Q	A figure of merit used in describing the "sharpness" of the crystal response. (It is also called crystal quality factor.)
Kynar®	Pennwalt's registered trademark of Polyvinilidene Fluoride (PVDF), 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. Visit www.atofinachemicals.com for more detailed information.
Picofarad	10^{-12} farads. A common unit of capacitance (abbreviated as pfd). By definition, 1 farad will store a 1 Coulomb charge when connected across a 1 volt potential.
PLO	Phase Lock Oscillator. A type of electronic circuit in which the frequency and the phase of the Voltage Controlled Oscillator (VCO) is locked to the frequency and the phase of a reference signal (in our case the signal from the sensing crystal).
Quadrature (current)	Refers to the imaginary component of the current through the shunt capacitance, C_S.
RQCM	INFICON QCM instrument's model name, which stands for Research Quartz Crystal Microbalance.
RTD	Resistance Temperature Detector. A device that changes its resistance as a function of temperature.
Shunt Capacitance	Effective capacitance due to the electrodes on the crystal. This is the "unwanted" capacitance we try to cancel out (along with the capacitance in the cable and the holder of course) while adjusting the Fine & Coarse capacitance cancellation on the Crystal Measurement Channel(s) on the RQCM.
Teflon®	DuPont Company's registered trademark of Perfluoroalkoxy Fluorocarbon Resin, a class of Teflon that offers excellent inertness to aqueous acid and aqueous alkaline, superior resistance over a wide range of pH. Visit www.dupont-dow.com for more information.
VCO	Voltage Controlled Oscillator. An oscillator circuit designed so that the output frequency can be controlled by applying a voltage to its control or tuning port.

Viton®	DuPont Dow Elastomers' registered trademark of Fluoroelastomer, offers superior mechanical properties and resistance to aggressive fuels and chemicals, well known for its excellent heat resistance. Visit www.dupont-dow.com/viton for more detailed information.
RTD	Resistance temperature detector. A device that senses temperature by measuring the change in resistance of a material.
Thermistor	A temperature-sensing element composed of sintered semiconductor material which exhibits a large change in resistance proportional to a small change in temperature.
Thermocouple	A device that has a junction of two dissimilar metals which has a voltage output proportional to the difference in temperature between the hot junction and the lead wires (cold junction).
I.D.	Abbreviation for Inside Diameter. Usually use in specifying a tube size in the form *inch* I.D. x *inch* O.D., where *inch* are the dimensions.
O.D.	Abbreviation for Outside Diameter. Usually use in specifying a tube size in the form *inch* I.D. x *inch* O.D., where *inch* are the dimensions.
Viscosity	The internal friction of a fluid, caused by molecular attraction, which makes it resist a tendency to flow.
Elastic	Flexible or springy - the property of immediately returning to its original size, shape, or position after being stretched, squeezed, flexed, etc.
Viscoelastic	Having or exhibiting both viscous *and* elastic properties.
Lipid	An organic compound found in tissue and that is soluble in nonpolar solvents.
Hydrophilic	Water-loving; attracted to water molecules and polar molecules.
Hydrophobic	Water-hating; not attracted to water molecules or polar molecules.
Hydrocarbon	A compound containing only the elements carbon and hydrogen.
nonpolar	Describing a molecule having no separation of centers of positive and negative electrical charge that would make the molecule assume certain orientations more than others in an electric field.
Organic	In chemistry, organic refers to a species containing carbon. Certain small ions and compounds containing carbon (such as carbon dioxide) are usually not considered to be organic, but rather are classed as inorganic.
UVO cleaning	Ultra-Violet/Ozone. The UVO cleaning method is a photo-sensitized oxidation process in which the contaminant molecules are excited and/or dissociated by the absorption of short-wavelength UV radiation. Near atomically clean surfaces can be achieved using this method. The basic instrumentation required this process includes a UVO chamber, a gas (oxygen) supply, or an exhaust system. For more information, visit http://www.jelight.com/uvo-ozone-cleaning.htm
Ultrasonic cleaning	This method utilizes high frequency (ultrasonic) and high intensity sound waves into a liquid producing cavitations (rapid formation and collapse of minute cavities in a cleaning liquid. For more information, visit http://www.aqueoustech.com/images/UltrasonicPrimer.PDF

Plasma Cleaning	A method that utilizes plasma reaction at the surface of the sample and volatile by-products are removed by the vacuum pump. The basic instrumentation required this process includes a reaction chamber, a power supply, and a vacuum source. The sample being cleaned is put into the chamber which is evacuated by the vacuum pump. Gas (oxygen) is introduced into the chamber and converted to reactive plasma by the power supply. For more information visit http://www.marchplasma.com/
Silanization	The chemical conversion of hydroxyl (OH) groups, which often act as adsorption sites on silica or glass stationary chromatographic phases, with silane coupling agents to give the inactive -O-SiR3 grouping. Silanization can neutralize surface charges, thus eliminating non-specific binding.
Redox	An oxidation-reduction reaction; the term "redox" is obtained from the first few letters of "reduction" and "oxidation."
Mole	That amount of a substance containing the same number of units as 12 g of carbon-12.
Molar mass	The mass of a mole of substance; the same as molecular weight for molecular substances.
Å	Symbol for angstrom, a unit of length equal to 10^{-10} meter.

12 REFERENCES

---

[1] Martin, Stephen, et. al., “Effect of Surface Roughness on the Response of Thickness-Shear Mode Resonators in Liquids”, Anal. Chem., 65 (**1993**) 2910.

[2] Sullivan, C. K. and Guilbault, G.G. “Commercial Quartz Crystal Microbalances- theory and applications”, Biosensors and Bioelectronics 14 (**1999**) 663-670.

[3] Sauerbrey, G. Z. Phys. 155 **(195**9) 206.

[4] Gabrielli, C. et. al., “Calibration of the Electrochemical Quartz Crystal Microbalance”, J. Electrochem. Soc. 139(9) (**1991**) 2657.

[5] Denison, D. R., “Linearity of Heavily Loaded Quartz Crystal Microbalance”, J. Vac. Sci. Technol. 10(**1973**) 126.

[6] Behrndt, K. H., “Long Term Operation of Crystal Oscillators in Thin-Film Deposition”, J. Vac. Sci. Technol. 8(5) (**1971**) 622.

[7] Lu, Chih-shun, “Mass determination with piezoelectric quartz crystal resonators”, J. Vac. Sci Technol., 12(1) (**1975**) 578.

[8] Rodahl, M. and Kasemo, B., “Frequency and dissipation-factor responses to localized liauid deposits on a QCM electrode”, Sensors and Actuators B37 (**1996**) 111-116.

[9] Ward, M. D. and Delawski, E. J., “Radial Mass Sensitivity of the Quartz Crystal Microbalance in Liquid Media”, Anal. Chem. 63(**1991**) 886.

[10] Cernosek, R.W. et. al., “Analysis of the radial dependence of mass sensitivity for Modified electrode quartz crystal resonators”, Anal. Chem.50(**1998**) 237.

[11] Lu, Chih-shun, “Monitoring And Controlling Techniques For Thin Film Deposition Processes”, AVS Course Material, published under the auspices of The Education Committee American Vacuum Soiety, (**1981**), p. 64-65.

[12] Vig, J. R., "UV/Ozone Cleaning of Surfaces," in Treatise on Clean Surface Technology, Vol. 1, ed. By K. L. Mittal, Plenum Press, (**1987)** p. 1-26.

[13] Cohen, Y., Levi, S., Rubin, S. and Willner, I., “Modified Monolayer electrodes for electrochemical and PZ analysis. Novel immunosensor electrodes”, J. ElectroAnal Chem. 417 (**1996**) 65. Minunni, M., Guilbault, G.G. and Hock, B., “Quartz Crystal microbalance as a biosensor”, Anal. Lett. 28 (**1995**) 749. Patel, Rupa, Zhou, R., Zinszer, K., Josse, F., and Cernozek, R., “Real-time Detection of Organic Compounds in Liquid Environments Using Polymer-coated Thickness Shear Mode Quartz Resonators”, Anal. Chem. 72 (**2000**) 4888.

[14] Stange, T. G. et. al. , “STM and AFM Characterization of Polystyrene Spin-coated onto Silicon Surfaces”, Langmuir 8 (**1992**) 920.

[15] Vig, J. R., “UV/Ozone cleaning of surfaces: A review”, in Surface contamination: Genesis, Detection and Control, K.L. Mittal Ed., Plenum Press, NY, (**1979)**, Pages 235-253.

[16] Krozer, A. and Rodahl, Michael, “X-ray Photoemission spectroscopy study of UV/ozone oxidation of Au under ultrahigh vacuum conditions”, J. Vac. Sci. Technol. A 15(3) (**1997**) 1704.

---

[17] Prime, K. L., Whitesides, G. M., Science, 252 (**1991**) 1164. Prime, K.L., Whitesides, G.M., J. "A Model System Using Self-Assembled Monolayers", Am. Chem. Soc., (**1993**), v.115, 10714-10721.

[18] Colorado Jr., Ramon, Villazana, Ramon J., and Lee, T. Randall, "Self-Assembled Monolayers on Gold Generated from Aliphatic Dithiocarboxylic Acids", Langmuir 14 (**1998**) 6337-6340.

[19] Duan, Lili and Garrett, Simon J., "Self-Assembled Monolayers of 6-Phenyl-n-hexanethiol and 6-(p-Vinylphenyl)-n-hexanethiol on Au(111): An Investigation of Structure, Stability, and Reactivity", Langmuir (**2001**) 17, 2986-2994.

[20] P. E. Hockberger et. al., "Cellular engineering: control of cell-substrate interactions" in Nanofabrication and Biosystems, H. C.Hoch, L.W. Jelinski and H.G. Craighead Eds., Cambridge University press (**1996**) 276-299.

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

[22] C. Lu and O. Lewis, "Investigation of film-thickness determination by oscillating quartz resonators with large mass load", J. Appl. Phys. 43 (**1972**) 4385.

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

[24] Muramatsu, H., Tamiya, Eiichi and Karube, Isao, "Computation of Equivalent Circuit Parameters of Quartz Crystals in Contact with Liquids and Study of Liquid Properties", Anal. Chem. 60 (**1988**) 2142.

[25] Geelhood, S.J., Frank, C. W. and Kanazawa, K., "Transient Quartz Crystal Microbalance Behaviors Compared", Journal of the Electrochemical Society, 149 (**2002**) H33-H38.

[26] Yang, Mengsu and Thompson, Michael, "Multiple Chemical Information from the Thickness Shear Mode Acoustic Wave Sensor in the liquid Phase", Anal. Chem. 65 (**1993**) 1158.

[27] 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**).

[28] Kanazawa, K., "Characterization of Operating Behavior of the PLO-10", A Report Submitted to Maxtek, Inc. by Process Monitor, April 2000, p. 6.

[29] Mark Deakin and Daniel Buttry, "Electrochemical Applications of the Quartz Crystal Microbalance", Anal Chem, 61 (20) (**1989**) 183.

[30] Buttry, Daniel and Ward, Michael, "Measurement of Interfacial Processes at electrode surfaces with the EQCM", Chem. Rev. 92 (6) (**1992**) 1355.

[31] 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.

[32] Mark R. Deakin and Owen Melroy, "Underpotential Metal Deposition on Au, monitored in situ with a Quartz Microbalance", J. Electroanal. Chem. 239 (**1988**) 321.

[33] 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.

---

[34] Youngran Lim and Euijin Hwang, “An Electrochemical QCM study of Oxygen reduction during the Underpotential Deposition of Lead on a Gold Electrode”, Bull. Korean Chem Soc. 17 (12) (**1996**) 1091.

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

[35] Jope, Dirk,Sell, Joachim, Pickering, Howard W.,Weil, Konrad G., “Application of a Quartz Crystal Microbalance to the Study of Copper Corrosion in Acid Solution Inhibited by Triazole-Iodide Protective Films”, J. Electrochem. Soc., (142) 34881, 2170-2172.

[36] Jiang, Xiang Chun,Seo, Masahiro,Sato, Norio, “Piezoelectric Detection of Oxide Formation and Reduction on Platinum Electrodes”, J. Electrochem. Soc., (138) 33239, 137-139.

[37] Benje, Michael, Eierman, Matthias, Pittermann, Udo, Weil, Konrad G., “An Improved Quartz Crystal Microbalance. Applications to the Electrocrystallization and -dissolution of Nickel”, Ber. Bunsen-Ges. Phys. Chem., 90 (**1986**) 435-439.

[38] Tudos, Anna J., Johnson, Dennis C., “Dissolution of Gold Electrodes in Alkanine Media Containing Cysteine”, Anal. Chem., 67 (**1995**) 557-560.

[39] Schumacher, R., Muller, A., Stockel, W., “An In Situ Study on the Mechanism of the Electrochemical Dissolution of Copper in Oxygenated Sulphuric Acid - An Application of the Quartz Microbalance”, J. Electroanal. Chem. Interfacial Electrochem., 219 (**1987**) 311-317.

[40] Ostrom, Gregory S., Buttry, Daniel A., “Quartz crystal microbalance studies of deposition and dissolution mechanisms of electrochromic films of diheptylviologen bromide”, J. Electroanal. Chem. Interfacial Electrochem., 256 (**1988**) 411-431.

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

[42] Mo, Yibo, Hwang, Euijin, Scherson, Daniel A., “Simultaneous Normalized Optical Reflectivity and Microgravimetric Measurements at Electrode/Electrolyte Interfaces: The Adsorption of Bromide on Gold in Aqueous Media”, 67 (**1995**) 2415-2418.

[43] Schneider, Thomas W., Buttry, Daniel A., “Electrochemical Quartz Crystal Microbalance Studies of Adsorption and Desorption of Self-Assembled Monolayers of Alkyl Thiols on Gold”, J. Am. Chem. Soc., 115 (**1993**) 12391-12397.

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

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

[46] Gabrielli, C., Keddam, M., and Torrei, R., “Calibration of the Electrochemical Quartz Crystal Microbalance”, J. Electrochem. Soc. 139 (9) (**1991**) 2657.

[47] 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/

[48] Bruckenstein S. and Shay M., “Experimental aspects of use of the quartz crystal microbalance in solution”, Electrochim. Acta 30 (**1985**) 1295.

---

[49] Orata, Duke and Buttry, Daniel A., “Determination of Ion Populations and Solvent Content as functions of Redox State and pH in Polyaniline”, J. Am. Chem. Soc. 109 (**1987**) 3574-3581.

[50] Topart, Patrice A., Noel, Marc A. M., “High-Frequency Impedance Analysis of Quartz Crystal Microbalance 2. Electrochemical Deposition and Redox Switching of Conducting Polymers”, Anal. Chem., 66 (**1994**) 2926-2934.

[51] Ward, Michael, “Investigation of Open Circuit Reactions of Polymer Films Using the QCM. Reactionsof Polyvinylferrocene Films”, J. Phys. Chem. 92 (**1988**) 2049.

[52] Baker, Charles K. and Reynolds, John R., “A quartz microbalance study of the electrosynthesis of polypyrrole”, J. Electroanal Chem, 251(**1988**) 307.

[53] Martin, Stephen, Granstaff, Victoria Edwards and Frye, Gregory C., “Characterization of a Quartz Crystal Microbalance with Simultaneous Mass and Liquid Loading”, Anal. Chem. 63 **(199**1) 2272.

[54] Lucklum, Ralf and Hauptmann, Peter, “The Df-DR QCM technique: an approach to an advanced sensor signal interpretation”, Electrochimica Acta, 45 (**2000**) 3907.

[55] Etchenique, R.A. and Calvo, E. L.,”Gravimetric measurement in redox polymer electrodes with the EQCM beyond the Sauerbrey limit”, Electrochemistry Communications, 1(5) (**1999**) 167.

[56] Etchenique, R.A. and Calvo, E. J., “Electrochemical Quartz Crystal Impedance Study of Redox Hydrogen Mediators for Amperometric Enzyme Electrodes”, Anal. Chem. 69 (**1997**) 4833.

[57] Johannsmann, Diethelm, “Viscoelastic Analysis of Organic Thin Films on quartz resonators”, Macromol. Chem. Phys. 200 (**1999**) 501.

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

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

[60] Lasky, Steven J., Buttry, Daniel A. “Sensors Based on Biomolecules Immobilized on the Piezoelectric Quartz Crystal Microbalance”, Chemical Sensors and Microinstrumentation, 0 (32387).

[61] 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**).