

USING A TEMPERATURE-CONTROLLED QUARTZ CRYSTAL MICROBALANCE  
IN A SPACE EQUIPMENT CLEANROOM  
TO MONITOR MOLECULAR CONTAMINATION

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**ABSTRACT**

There is a need for continuous monitoring for molecular contamination in cleanrooms where spaceflight equipment is assembled, integrated, and tested to insure that contamination budgets are met. The TQCM (temperature-controlled quartz crystal microbalance) can be used to provide both a real time warning and a cumulative measurement of molecular contamination. It has advantages over the other measurement methods such as witness mirrors, NVR(non-volatile residue) plates, and gas analyzers. A comparison of the TQCM sensitivity and ease of operation is made with the other methods. The surface acoustic wave microbalance (SAW), a newly developed instrument similar to the TQCM, is considered in the comparison. An example is provided of TQCM use at Goddard Space Flight Center when the Wide Field Planetary Camera 2(WFPC-2) and the Corrective Optics Space Telescope Axial Replacement(COSTAR) were undergoing integrated testing prior to their installation in the Hubble Space Telescope on its first servicing mission. Areas for further investigation are presented.

**INTRODUCTION**

Molecular contamination is a serious concern when spaceflight equipment is assembled, tested, and integrated in cleanrooms at government and industry facilities. Molecular contamination, sometimes called non-volatile residue (NVR), is the result of emitted gas, vapors, or aerosols condensing on a surface. The molecular layers will degrade performance of optics and sensors by reducing their throughput. As part of system performance considerations, the loss of signal due to contamination must be budgeted. For example, the total allowable molecular contamination coating for the COSTAR optics was determined and then budgeted for the various stages of assembly, test, integration, and on-orbit life. Eight (8) angstroms of molecular contamination was allowable during the integration and testing stage at GSFC. If the budget was exceeded, cleaning, with its inherent risks, would be necessary to prevent a degradation in performance. It is therefore desirable to monitor the contamination deposited at each stage and to know as early as possible if excessive contamination is occurring.

Although contamination deposited directly on critical surfaces such as optics or sensors is the immediate concern, contamination on other surfaces may later desorb and transfer to the critical areas particularly in the vacuum environment of a test chamber or space as temperatures of the surfaces change.

In some cases, contamination of a critical surface can be measured directly by checking transmission, reflectivity, or detector response with a standard source. In other cases, the contamination may be inferred from sample collection of contamination made in the vicinity of the spaceflight equipment. This has traditionally been done with witness mirrors and NVR collection plates. More recently the TQCM is being used for this purpose(ref. 1) and the surface acoustic wave (SAW) microbalance, a newly developed instrument similar to the TQCM, is in limited use(ref. 2). Gas analyzers, although more difficult to relate to deposited molecular contamination, give an indication of molecular contaminants in the cleanroom atmosphere.

The purpose of this paper is to compare the TQCM with the other measuring techniques in terms of sensitivity and ease of operation and to describe in more detail the TQCM use. The advantages of each technique will be discussed and the need for a coordinated use of the various techniques is stressed. An example of TQCM use in a clean room at Goddard Space Flight Center(GSFC) will be presented including a description of the installation, operation, results, and analysis. Areas for investigation in the use of the TQCM are discussed.

#### **MOLECULAR CONTAMINATION MONITORING METHODS**

The molecular contamination monitoring methods discussed herein are the witness mirror, NVR plate, gas analyzer, TQCM, and SAW.

##### **Witness Mirrors**

Witness mirrors are typically one inch diameter by one quarter inch thick flat glass mirrors front-surface coated with aluminum and magnesium fluoride or some other coating that is representative of the optics of concern. They are made with a highly uniform reflective surface and are normally serialized for easy identification. A baseline reflectivity measurement is made of a control mirror and a test mirror in one or more wavelengths using a reflectometer and typically ranges from 75 to 85%. The test mirror is placed in the vicinity of the spaceflight equipment. It is periodically removed and returned to the lab for reflectivity measurement where a decrease in reflectivity is an indication of contamination. The control mirror is transported and handled in the same manner as the test mirror except that it is not exposed to the environment being monitored. The mirrors must be carefully handled to avoid scratches, smudges, or any other damage or contamination that would give misleading results. The purpose of the control mirror is to determine if any damage or contamination occurs in transportation and handling as well as provide a check on the reflectometer.

For the purpose of comparison of the different measuring methods, the ability to detect a change equivalent to one molecular layer of water will be discussed. (Some forms of contamination have considerable greater molecular thickness than water). The measuring accuracy of the reflectometer is usually  $\pm 1.5\%$  (or greater) for a uncertainty range of 3% (see Table 1). A typical conversion factor (depending on measuring wavelength and contaminant material) is 0.5%/angstrom. Therefore the 3% range of measurement uncertainty is equivalent to 6 angstroms. Thus, the minimum thickness that can be detected would be slightly over six angstroms. One molecular layer of water is about 3 angstroms(ref. 9) and could not be detected by a witness mirror.

The advantage of the witness mirror is that it can be coated similar to the optics in space equipment and measured in the wavelength of interest. If positioned properly it should be a very representative sample. The disadvantage is in the careful handling required, the lack of sensitivity to low levels of contamination, and the lack of real time warning capability.

##### **NVR Plates**

NVR plates are normally 1 foot square polished aluminum plates. They are cleaned to an ultraclean level and then carefully transported to the cleanroom and installed in a holder. It is common to position four or more plates in a large cleanroom on wall mounts with their collecting surface parallel to the wall facing into the room. After a period of time (usually one to six months) the plate(s) are removed and carefully transported to the lab for analysis. Analysis is by solvent wash, evaporation of solvent, and weighing of the remaining non volatile residue (NVR). Normal lab procedures would not detect much less than 0.1 mg/ft<sup>2</sup> (see Table 1). This is equivalent to about 10.8 angstroms of coating(using the density of water). Obviously one monolayer of 3 angstroms is beyond detection level.

The advantage of the NVR plates is that the NVR produced can be analyzed by infrared and mass spectroscopy and the contents, such as esters, phthalates, silicones, and aliphatic hydrocarbons, can be identified. This can sometimes reveal the source and allow for corrective action. A periodic check with NVR plates is a nice facility control measure. The disadvantages are lack of sensitivity which requires fairly long collection time and the laboratory time and effort required for processing the plates.

#### **Gas Analyzer**

Gas analyzers can be used in cleanrooms to collect air samples, analyze the samples, and print out results on a near real-time basis. They are usually Fourier transform infrared spectrometers that periodically sample the air and measure content of water, carbon dioxide, methane, hexane, etc., in parts per million. The results are printed out and displayed on a screen and alarm levels can be set. An increase above normal range could indicate increased molecular contamination being deposited and investigation and corrective action can be taken. However, the vapor pressure of many of the species detected by the analyzer may not allow their condensation on optics at clean room temperature and pressure. Thus, the measurements of air content cannot be correlated to the thickness of the contamination being deposited on the spaceflight equipment. Thus, the sensitivity of parts per million (Table 1) cannot be compared to the other methods.

The advantage of the gas analyzer is that it provides a real time measurement which can be used to take timely corrective action. The disadvantage is it cannot be correlated with levels of molecular contamination being deposited.

#### **TQCM**

The TQCM is an instrument that uses quartz crystal oscillators operating in the dual difference mode to measure the mass of small amounts of molecular contamination deposited on the exposed crystal (see Figure 1 for an illustration of TQCM sensors). The mass deposited results in an increase in the TQCM frequency which is normally directed to a computer and displayed on its screen, printed out, and recorded on disk. The screen and printout can be monitored on a periodic basis and limits can be set for investigation. The sensitivity is such that the TQCM can provide a real time warning of contamination events in a clean room. Also, the recorded frequency can be compared over any length of time to get an indication of cumulative deposit. Table 1 shows the sensitivity of a 10 MHz TQCM and a 15 MHz TQCM. Note that the minimum thickness that can be detected is shown for comparison with other methods. The conventional expression for sensitivity is shown at the bottom of the table in mass per unit area to cause 1 Hz change. This is converted to frequency change caused by one angstrom thick coating assuming that the molecular contamination has the density of water. The measuring accuracy of the TQCM,  $\pm 2$  Hz or a range of 4 Hz, is divided by the conversion factor to result in the minimum thickness detected.

A 3 angstrom layer of molecular contamination would result in about 19 Hz change on the 15 MHz TQCM, well within its ability to detect. For the 10 MHz TQCM, a three angstrom deposit would result in about 7 Hz change, more than the range of uncertainty of 4 Hz. Thus, both TQCMs could detect the hypothetical 3 angstrom layer.

The advantage of the TQCM is that it can provide a real time warning and cumulative record of molecular contamination, it does not require laboratory effort, and it is more sensitive than the witness mirror or NVR plate. The disadvantage might be the greater equipment cost (estimate \$10,000 to \$20,000 for one TQCM and support equipment). Also it is difficult to analyze the small quantities deposited on the crystal to identify molecular species.

## **SAW**

The SAW microbalance also uses quartz crystals operating in the dual difference mode. However its frequency is developed by a "surface acoustic wave" as opposed to a shear wave(ref. 5). It operates at a higher frequency and has considerably greater sensitivity(ref. 3, 4). See Table 1 for the improvement in sensitivity over the TQCM. The practical benefit of the considerably greater sensitivity, particularly at less than one molecular layer where surface behavior may not be uniform, is still to be demonstrated.

### **TQCM/SAW Advantages**

Due to their greater sensitivity, the TQCM and SAW can provide near real time indication of molecular contamination. Their results can be displayed on computer screen and limits set for allowable increases over various time periods. They can also provide a cumulative measurement over any period of time as the frequency is recorded for later reference. Their data is easily recorded and displayed and no separate laboratory procedures and measurements are required. Their frequency increase is directly relatable to deposit on a surface where the gas analyzer measurements are not.

### **Coordinated Use**

Other methods should not be discarded because the TQCM and SAW have certain advantages in sensitivity and ease of recording and use of data. The witness mirror may give the optical designer the most direct measurement of the effect of contamination on a specific optical surface at a specific wavelength if minimum detectable levels of contamination are exceeded. (The TQCM might allow for a similar reflectance measurement from the exposed crystal depending on reflectometer configuration and crystal size.) The NVR plate is a good long-term measurement of contamination that allows for chemical analysis of the contamination constituents. The gas analyzer supplements the TQCM real time capability.

It is important to take a coordinated look at all methods available. If NVR plates are analyzed on a three month basis as a facility check, the TQCM readings for that period of time should be presented and a comparison made. Witness mirrors and NVR plates can corroborate each other if their results are obtained for the same time period and compared to historical trends. If there is an important space instrument in the cleanroom, additional witness mirrors and NVR plates can be installed at the start of the period and analyzed at the end to provide cumulative data for comparison with the TQCM.

### **USE OF TQCMs AT GSFC**

TQCMs have long been used at GSFC in vacuum chamber testing to measure outgassing of condensable products. In March 1993, several TQCMs were installed in the cleanroom of the Spacecraft Systems Development and Integration Facility. The temperature of the TQCMs was controlled at a few degrees Farenheit below nominal room temperature. Two TQCMs were selected for their stability and were returned to the manufacturer for coating with magnesium flouride, similar to the optics of the flight instruments for the first HST Servicing Mission, the WFPC-2 and the COSTAR. The TQCMs were then installed in the clean room and operated before and during the period that the instruments were there and have been operating since as a facility monitor.

### **Installation**

Figure 2 illustrates the TQCM installation. Each TQCM (Faraday Mod. 82-E with 15 MHz crystals) was connected to a controller (Faraday Mod. 72-DET) with a 15 foot long electrical cable. The controller allows for setting and controlling of the operating temperature of the TQCM. It also provides the temperature diagnostic and TQCM frequency thru a coax cable to the data acquisition unit (Hewlett Packard Mod. 3421A) which is connected to a Hewlett

Packard Integral Personal Computer. The data acquisition unit and the computer are located outside the clean room in a test control room where personnel are available to monitor the TQCM data.

One TQCM was installed on a specially built platform in the High Fidelity Mechanical Simulator (HFMS), a test station that simulates the aft section of the HST where the instruments are located. During testing of the WFPC-2 and COSTAR they are placed in the HFMS with their optics exposed. (At other times they are covered and purged). Thus, this TQCM was located as close as possible to the critical optics.

The other TQCM was located in the northeast corner of the clean room at the input air filter bank and is more indicative of the input air to the clean room.

### Operation

TQCM frequency and temperature were displayed on the computer screen and printer every half hour. (Interval can be set as desired and recording can be more or less frequent than printout). During the time the critical instruments were in the cleanroom, the responsible personnel would monitor the readings hourly. Limits were set for notification of the contamination engineer and project personnel.

### Results

WFPC-2 arrived at GSFC on June 4, 1993, and was in the clean room for 74 days thru August 17, 1993. The TQCM data is shown in Figure 3. TQCM #3, located in the NE corner, showed no change for the period. There was very little personnel or equipment activity in this area, so TQCM #3 is indicative of the input air quality. TQCM #4 was located in the enclosed HFMS hub area near the WFPC-2 and COSTAR. Its frequency increased from 913 to 932 Hz, a difference of 19 Hz. At 6.4 Hz/angstrom (see Table 2) this amounts to about a 3 angstrom coating. This was well within the WFPC budget of 108 angstroms.

The WFPC budget was based on external surface degrading from 1 milligram per square foot to 2 milligram per square foot (MIL-STD 1246B, Level B). The budget considered the planned cleaning after the testing at GSFC, the fact that the flight pickoff mirror would be installed at the launch site, and the fact that the internal optics were protected by an aperture cover and purge.

Note on Figure 3 (point 2) that the TQCM frequency increased about 8 Hz on June 23, the highest single day increase. This day marked the start of a period of heavy activity in and around the HFMS which included the installation and removal several times of large tooling using the overhead crane and a balance beam. As many as six people were needed inside and immediately outside the HFMS. Thus, the increase in TQCM frequency occurred during a period of peak personnel and tooling activity. Note that TQCM #3, which is not in the area, did not react to the activity.

TQCM #3 did react to its physical movement (point 1), and to cleanroom input air variations at point 3 where temperature was lowered from 68F to 65F and TQCM temperature from 19C(66.2F) to 17C(62.6F), and at point 4 where the cleanroom relative humidity increased from 44 to 56% before returning to 44%. It has been noticed on numerous occasions that the TQCM frequency is affected by changes in humidity and temperature and by changes in physical orientation or the vibration associated with relocation.

The COSTAR arrived at GSFC on July 9, 1993, and was in the clean room for 50 days until it was installed in its shipping container on August 27. The TQCM readings are shown for this period in Figure 4. TQCM #3 readings showed no significant change during this period. TQCM #4 increased from 930 to 934 Hz, a difference of 4 Hz which is less than one angstrom of molecular coating. Part or all of the increase could be due to instrument random variation. The 4 Hz increase is negligible when compared to the budget of 48 Hz (8 angstroms). Note

that the COSTAR budget was much more stringent than that of WFPC-2 due to greater exposure of the flight optics.

Thus, the TQCM data indicated that both instruments were well within their molecular contamination budgets while at GSFC.

A total of nine witness mirrors were placed in the HFMS during the time the WFPC-2 and COSTAR were at GSFC. No statistically significant change was seen in the mirrors when considering the measuring accuracy of the reflectometer (+, - 1.5%) although a slight trend toward a reflectance decrease could be seen when all data was viewed together. This correlates with the TQCM data as the 3 angstroms coating indicated by the TQCM for the WFPC and less than 1 angstrom for the COSTAR are below the measuring accuracy of a witness mirror (see Table 1).

NVR plates were not read to correlate with the period of time that WFPC and COSTAR were in the clean room.

### **Analysis of Deposition on Crystal**

Several methods were considered for analyzing the contaminant deposited on the TQCM. Problems result due to the very small mass and thickness of coating available for analysis. The 19 Hz frequency increase noted during the WFPC II exposure in the cleanroom indicates about 3 angstroms coating or 0.008 micrograms on the approximately 0.6 cm diameter crystal.

McKeown et. al. reported on analysis of the TQCM crystal surface done with a Nicolet MX-1 FTIR spectrometer with a specular reflectance attachment (ref. 6). The IR beam was reflected off the crystal at near normal incidence and compared to the signature of a clean crystal for reference. However, in this case there was about 25 micrograms deposit. This method "detects films down to a few hundred angstroms region" and is not feasible for the small amount detected above.

Experiments are currently underway at GSFC using a Nicolet Model 710SX Infrared Spectrometer and IR microscope with grazing angle objective to analyze thin films on a TQCM crystal.

Thermogravimetric analysis is a method by which the crystal temperature is increased at a controlled rate and the TQCM frequency monitored to determine the temperatures at which desorption takes place (ref. 7). If there are a small number of species involved and they are placed on the crystal in the right order, they can be identified by their desorption temperature. In practice, the more volatile species tend to sweep the less volatile from the surface (ref. 8).

### **AREAS FOR INVESTIGATION**

Three areas for future investigation have been noted. They are the stability of the TQCM, methods of calibration, and the analysis of the deposition on the crystal.

#### **Stability**

All TQCMs operated to date in the GSFC cleanroom at temperatures a few degrees below room temperature appear to require some time from hours to days to stabilize. The frequency usually increases initially and then levels off.

Once the TQCMs have stabilized after initial turn-on, they have a random variability that may be due to the cooling device cycling, electronic noise, and variation of the temperature and humidity in the room. More work could be done in this area. The standard deviation for three TQCMs over an eight day period was calculated and ranged from 0.7 Hz to 1.2 Hz.

The TQCMs will vary with temperature and humidity. See Figure 5 for an instance where cleanroom humidity went out of control but temperature was held

fairly constant. In this case the TQCM frequency immediately followed the relative humidity and varied about 0.5 Hz per 1% RH change. It has been suggested that a crystal coated with magnesium flouride, as was the case in this example, is hygroscopic and will react in this manner. As the reference crystal was not coated with magnesium flouride, it would not be expected to react to the humidity. It would be advantageous to eliminate or reduce the reaction to temperature and humidity. At present the TQCMs can only be used in a well controlled area where any significant change due to humidity or temperature is known and allowed for.

### **Calibration**

There is no method for periodic calibration of the TQCM. If a method could be developed to apply a known mass to the exposed crystal for calibration purposed and then remove it by physical means or heating, confidence in the readings would be improved.

### **Analysis of the Deposition on the Crystal**

The analysis of the molecular contamination deposited on the crystal is important so the source of the contamination can be identified and corrected. More effort needs to be applied to methods such as thermogravimetric and spectroscopic analysis of the adsorbed material.

### **CONCLUSIONS**

The TQCM is considerably more sensitive to molecular contamination than witness mirrors and NVR plates. When operated in a cleanroom at ambient pressure, the TQCM provides a real-time warning of low levels of molecular contamination and reliable and convenient measurement of cumulative contamination deposition.

### **REFERENCES**

1. W. J. Mitchell, "Monitoring deposition of molecular contamination of optics using a temperature controlled quartz crystal microbalance (TQCM)", SPIE Vol. 2261, Optical Systems Contamination, pp. TBP, 1994. (TBP = to be published)
2. P. A. Mogan, "Real time measurements of nonvolatile residue contamination in cleanroom environments", SPIE Vol. 2270, NASA Spin Off Technologies, pp. TBP, 1994.
3. D. A. Wallace, W. D. Bowers, "Mass flux comparisons of a 200-MHz SAW resonator microbalance to a 15 MHz TQCM in a high vacuum environment", SPIE Vol. 2261, Optical Systems Contamination, pp. TBP, 1994.
4. A. P. M. Glassford, J. W. Garrett, W. D. Bowers, "Mass sensitivity calibration of the SAW QCM at ambient temperature", SPIE Vol. 2261, Optical Systems Contamination, pp. TBP, 1994.
5. W. D. Bowers, "A high sensitivity real time NVR monitor", SPIE Vol. 1754, Optical Systems Contamination, pp. 344-351, 1992.
6. D. McKeown, J. A. Fountain, V. H. Cox, and R. V. Peterson, "Analysis of TQCM Surface Contamination Adsorbed During the Spacelab I Mission," AIAA Shuttle Environment and Operations Conference, pp. 108-115, November 13-15, 1985, Houston, Tx.
7. D. A. Wallace and S. A. Wallace, "Use of a cryogenically cooled TQCM in conjunction with a programmable data acquisition system to detect and examine excreted mass on the sensing crystal caused by environmental contamination," SPIE Vol 1165 Scatter from Optical Components pp. 424-431, 1989.

8. R. J. Bryson, A. B. Bailey, B. L. Seiber, W. T. Bertrand, J. H. Jones, and B. E. Wood, "Cryogenic quartz crystal microbalance - characterization and calibration for Midcourse Space Experiment (MSX) program," SPIE Vol. 1754, Optical Systems Contamination, pp. 205-214, 1992.

9. E. H. Kennard, Kinetic Theory of Gasses, McGraw Hill, 1938, p. 149.

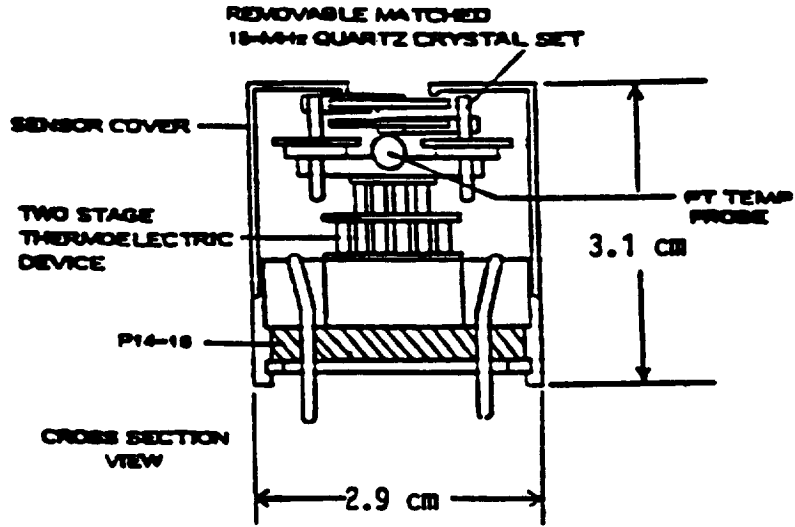
Table 1. Sensitivity of Molecular Contamination Measuring Devices

	<u>MEASURING ACCURACY</u>	<u>CONVERSION FACTOR</u>	<u>DETECT 1 MONOLAYER (3 angstroms)</u>	<u>MINIMUM THICKNESS DETECTED (angstroms)</u>
WITNESS MIRROR (reflectance measurement)	+,-1.5%	0.5% per angstrom	No	6
NVR PLATES, 1 ft. square rinse, weigh	0.1mg/ft <sup>2</sup> minimum	9.26x10 <sup>-6</sup> g/ft <sup>2</sup> /ang.	No	10.8
FTIR GAS ANALYZER	+,-1 ppm	*	No	*
TQCM 10 MHz	+,-2 Hz	2.3 Hz/ang.	Yes	1.7
TQCM 15 MHz	+,-2 Hz	6.4 Hz/ang.	Yes	0.63
SAW 200 MHz	+,-2 Hz	920 Hz/ang.	Yes	0.0043

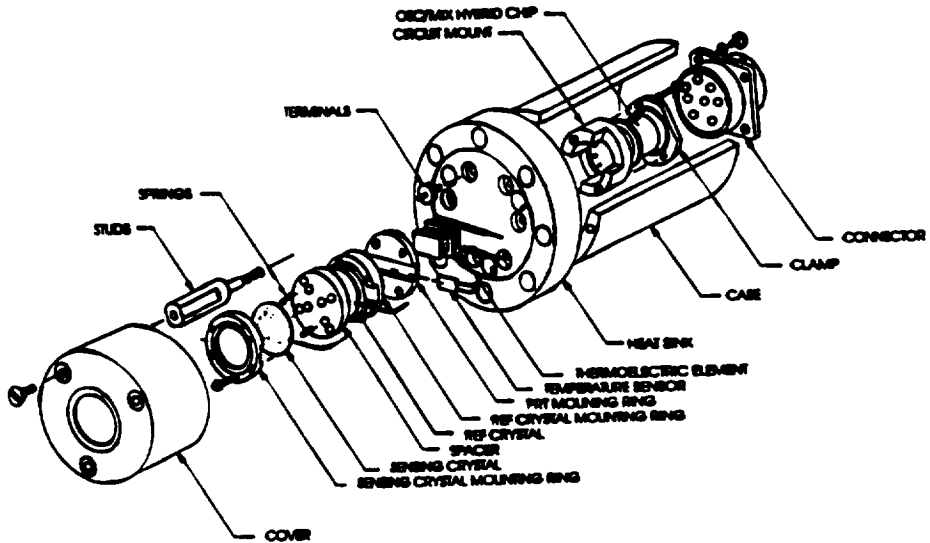
For Reference:

	TQCM SENSITIVITY	
	<u>ngm/cm<sup>2</sup> - Hz</u>	<u>Hz cm<sup>2</sup> - ng</u>
10 MHz TQCM	4.42	0.23
15 MHz TQCM	1.56	0.64
200 MHz SAW	0.0109	92.0





TQCM Sensor Design, Paraday Labs, La Jolla, CA.



TQCM Sensor Design, QCM Research, Laguna Beach, CA.

Figure 1 : TQCM Sensor Design

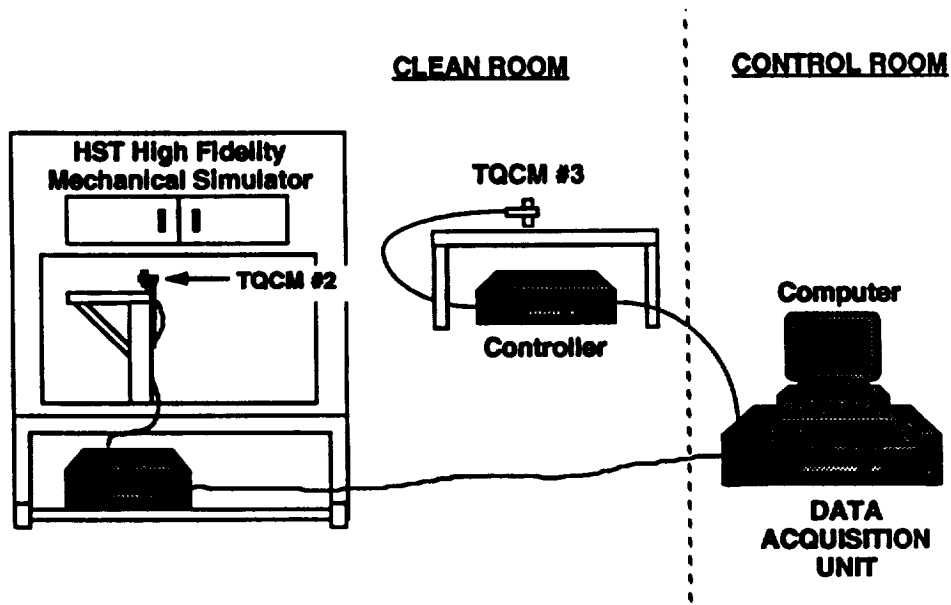


Figure 2 : TQCM Installation

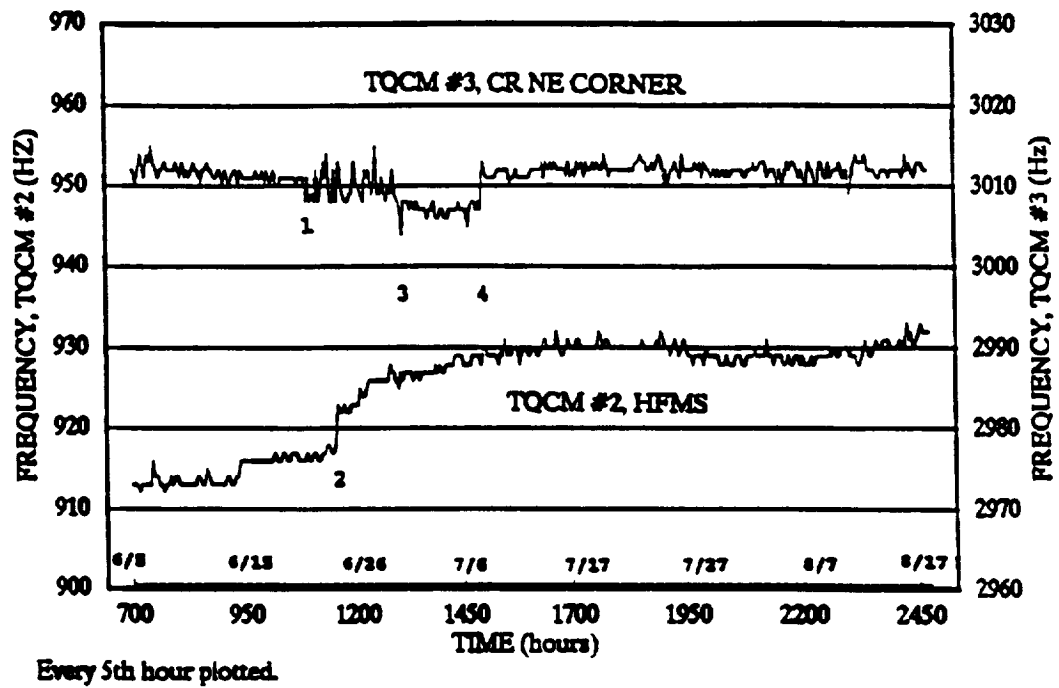


Figure 3 : TQCM Readings, WFPC II Integration and Test at GSFC

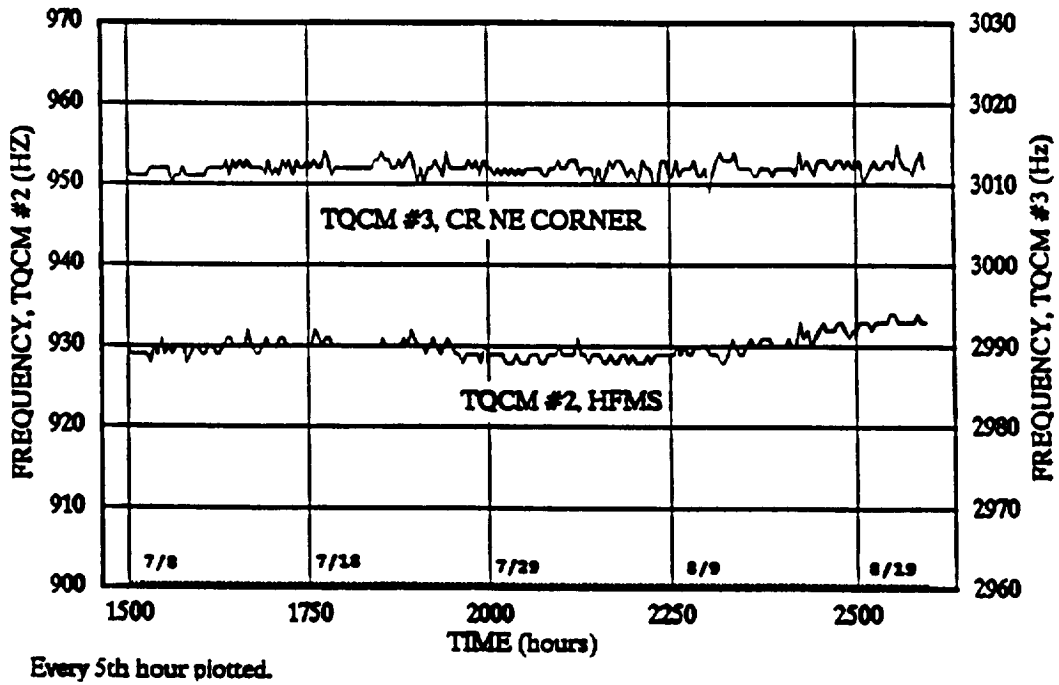


Figure 4 : TQCM Readings, COSTAR Integration and Test at GSFC

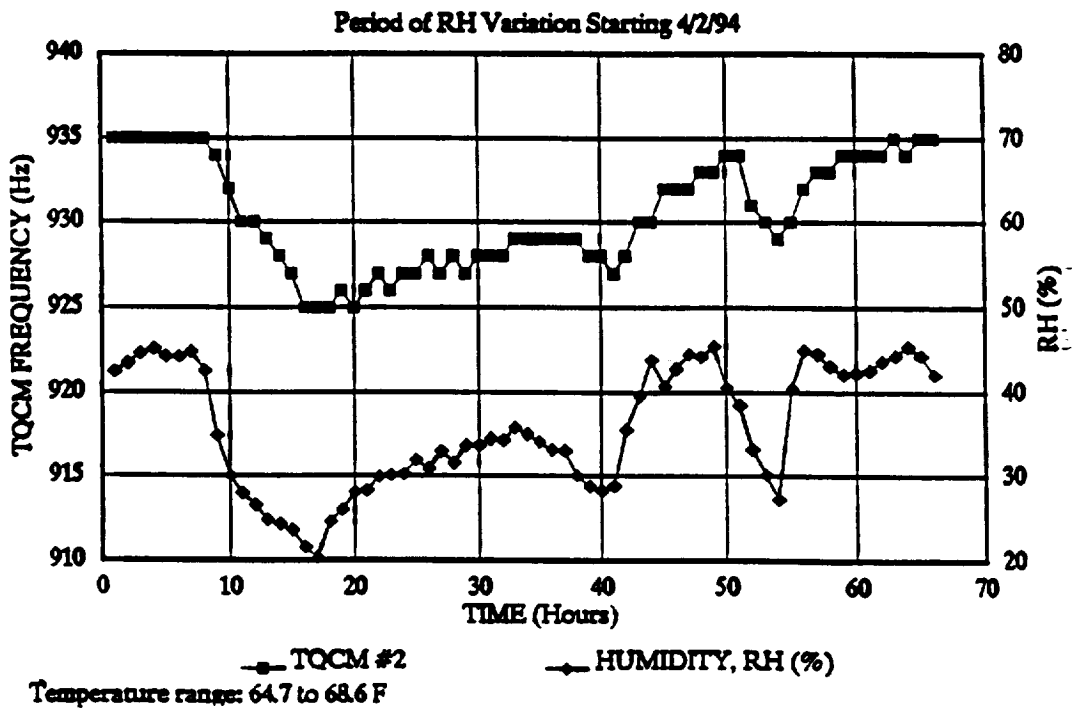


Figure 5 : TQCM #2 Correlation with Humidity

