



Designation: E2311 – 04(Reapproved 2009)

Standard Practice for QCM Measurement of Spacecraft Molecular Contamination in Space¹

This standard is issued under the fixed designation E2311; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice provides guidance for making decisions concerning the use of a quartz crystal microbalance (QCM) and a thermoelectrically cooled quartz crystal microbalance (TQCM) in space where contamination problems on spacecraft are likely to exist. Careful adherence to this document should ensure adequate measurement of condensation of molecular constituents that are commonly termed “contamination” on spacecraft surfaces.

1.2 A corollary purpose is to provide choices among the flight-qualified QCMs now existing to meet specific needs.

1.3 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:²

E595 Test Method for Total Mass Loss and Collected Volatile Condensable Materials from Outgassing in a Vacuum Environment

E1559 Test Method for Contamination Outgassing Characteristics of Spacecraft Materials

2.2 U.S. Federal Standards:³

MIL-STD-883 Standard Test Method, Microcircuits

MIL-S-45743 Soldering, Manual Type, High Reliability Electrical and Electronic Equipment

FED-STD-209E Airborne Particulate Cleanliness Classes in Cleanrooms and Clean Zones

NOTE 1—Although FED-STD-209E has been cancelled, it still may be used and designations in FED-STD-209E may be used in addition to the ISO designations.

2.3 ISO Standards:⁴

ISO 14644-1 Cleanrooms and Associated Controlled Environments—Part 1: Classification of Air Cleanliness

ISO 14644-2 Cleanrooms and Associated Controlled Environments—Part 2: Specifications for Testing and Monitoring to Prove Continued Compliance with ISO 14644-1

3. Terminology

3.1 Definitions:

3.1.1 *absorptance*, α , n —ratio of the absorbed radiant or luminous flux to the incident flux.

3.1.2 *activity coefficient of crystal*, Q , n —energy stored during a cycle divided by energy lost during a cycle, or the quality factor of a crystal.

3.1.3 *crystallographic cut*, Φ , n —rotation angle between the optical axis and the plane of the crystal at which the quartz is cut; typically 35° 18' AT cut for ambient temperature use or 39° 40' cut for cryogenic temperature use.

3.1.4 *collected volatile condensable materials*, (CVC), n —tested per Test Method **E595**.

3.1.5 *equivalent monomolecular layer*, (EML), n —single layer of molecules, each 3×10^{-8} cm in diameter, placed with centers on a square pattern. This results in an EML of approximately 1×10^{15} molecules/cm².

3.1.6 *field of view*, (FOV), n —the line of sight from the surface of the QCM that is directly exposed to mass flux.

3.1.7 *irradiance at a point on a surface*, n — E_e , $E(E_e = dI_e/dA)$, (watt per square metre, Wm⁻²), ratio of the radiant flux incident on an element of the surface containing the point, to the area of that element.

¹ This practice is under the jurisdiction of ASTM Committee E21 on Space Simulation and Applications of Space Technology and is the direct responsibility of Subcommittee E21.05 on Contamination.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401.

⁴ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036.

3.1.8 *mass sensitivity, S, n*—relationship between the frequency shift and the arriving or departing mass on the sensing crystal of a QCM. As defined by theory:

$$\Delta m/A = (\rho_q c/2f^2) \Delta f \quad (1)$$

where:

- Δm = mass change, g,
- A = area on which the deposit occurs, cm²,
- f = fundamental frequency of the QCM, Hz,
- ρ_q = density of quartz, g/cm³, and
- c = shear wave velocity of quartz, cm/s.

3.1.9 *molecular contamination, n*—molecules that remain on a surface with sufficiently long residence times to affect the surface properties to a sensible degree.

3.1.10 *optical polish, n*—the topology of the quartz crystal surface as it affects its light reflective properties, for example, specular (sometimes called “clear polish”) or diffuse polish.

3.1.11 *optical solar reflector, (OSR), n*—a term used to designate thermal control surfaces on a spacecraft incorporating second surface mirrors.

3.1.12 *quartz crystal microbalance (QCM), n*—a piezoelectric quartz crystal that is driven by an external electronic oscillator whose frequency is determined by the total crystal thickness plus the mass deposited on the crystal surface.

3.1.13 *reflectance, p, n*—ratio of the reflected radiant or luminous flux to the incident flux.

3.1.14 *surface of interest, n*—any immediate surface on which contamination can be formed.

3.1.15 *super-polish, n*—polish of a quartz crystal that produces less than 10 Å root mean square (rms) roughness on the surface.

3.1.16 *QCM thermogravimetric analysis, (QTGA), n*—raising the temperature of the QCM deposition surface causes contaminants to evaporate, changing the QCM frequency as a function of time and the mass loss. Relevant vapor pressures can be calculated for various species and can be used to identify the molecular species.

3.1.17 *total mass loss, (TML), n*—when tested per Test Method E595.

3.1.18 *thermoelectric quartz crystal microbalance, (TQCM), n*—The temperature of the crystal is controlled with a thermoelectric element so that the rate of deposition and the species that condense onto the QCM can be related to the temperature.

3.2 Constants:

3.2.1 *density of quartz*—at $T = 25^\circ\text{C}$, $\rho_q = 2.6485 \text{ g/cm}^3$ **(1)**⁵; at $T = 77 \text{ K}$, $\rho_q = 2.664 \text{ g/cm}^3$ **(2)**.

3.2.2 *mass sensitivity*—AT or rotated cut crystal **(3)**.

4. Summary of Practice

4.1 Measurement of molecular contamination on spacecraft can be performed in a variety of ways. The specific methods

depend upon such factors as knowing its contamination source and the approximate level of outgassing, the ability or inability to place a sensor in the immediate area of concern, the variation of the solar thermal radiation striking the sensor, the power dissipation of the QCM and how it affects certain critical spacecraft cooling requirements, cost to the program, and the schedule. Therefore, it is not desirable or possible to include all QCM testing in one test method. The engineers must determine and provide the detailed monitoring procedure that will satisfy their particular requirements and be fully aware of the effects of any necessary deviations from the ideal.

5. Significance and Use

5.1 Spacecraft have consistently had the problem of contamination of thermal control surfaces from line-of-sight warm surfaces on the vehicle, outgassing of materials and subsequent condensation on critical surfaces, such as solar arrays, moving mechanical assemblies, cryogenic insulation schemes, and electrical contacts, control jet effects, and other forms of expelling molecules in a vapor stream. To this has been added the need to protect optical components, either at ambient or cryogenic temperatures, from the minutest deposition of contaminants because of their absorptance, reflectance or scattering characteristics. Much progress has been accomplished in this area, such as the careful testing of each material for outgassing characteristics before the material is used on the spacecraft (following Test Methods E595 and E1559), but measurement and control of critical surfaces during spaceflight still can aid in the determination of location and behavior of outgassing materials.

6. General Considerations

6.1 A QCM sensor is used to measure the molecular contamination of critical surfaces on spacecraft at one or more temperatures for an extended period of time. A piezoelectric crystal is exposed next to a “surface of interest” or in the plane where molecular flux is expected. It is then cooled to the temperature at which the crystal should condense whatever molecular contaminant exists at that temperature (according to the vapor-pressure characteristics of that constituent). By measuring the frequency-shift of the crystal and knowing the mass sensitivity (frequency to mass-added factor for that crystal), the mass accumulated can be determined. Sunlight striking the solar panels may cause outgassing that intercepts the surface of interest. The probable source and extent of contamination can be determined from known components of the spacecraft and probable sources.

6.2 Potential contamination problem areas are shown in Fig. 1.

6.2.1 The performance of thermal control surfaces is degraded as a result of the accumulation of contaminants, which may increase the surfaces’ solar absorptance;

6.2.2 Optics may be degraded by increasing “light” scattering or reflectance loss;

6.2.3 Electronic modules with high rates of outgassing components may have voltage arc-over;

6.2.4 Internal to the spacecraft there may be outgassing sources which will degrade (for instance, mass spectrometer causing signal overload conditions);

⁵ The boldface numbers in parentheses refer to the list of references at the end of this practice.

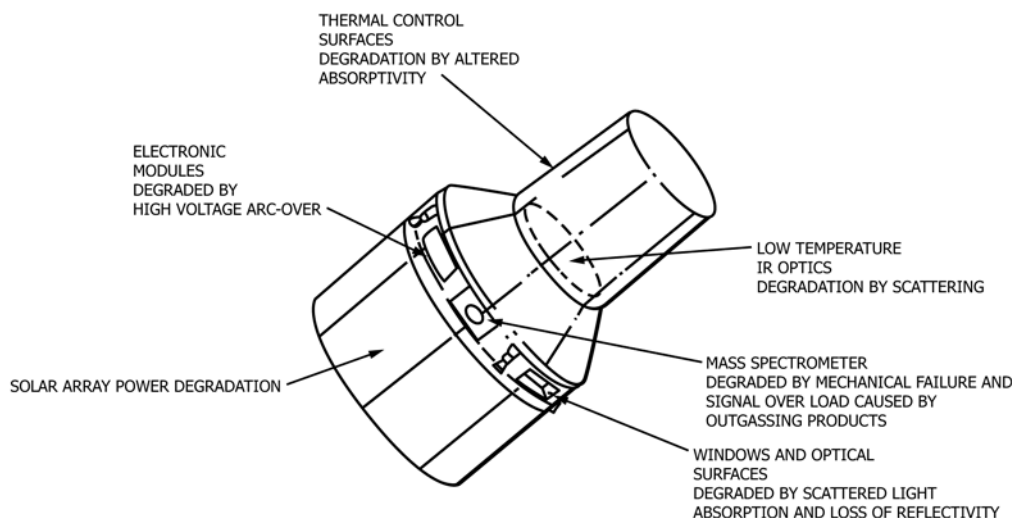


FIG. 1 Examples of Spacecraft Component Degradation Due to Contamination

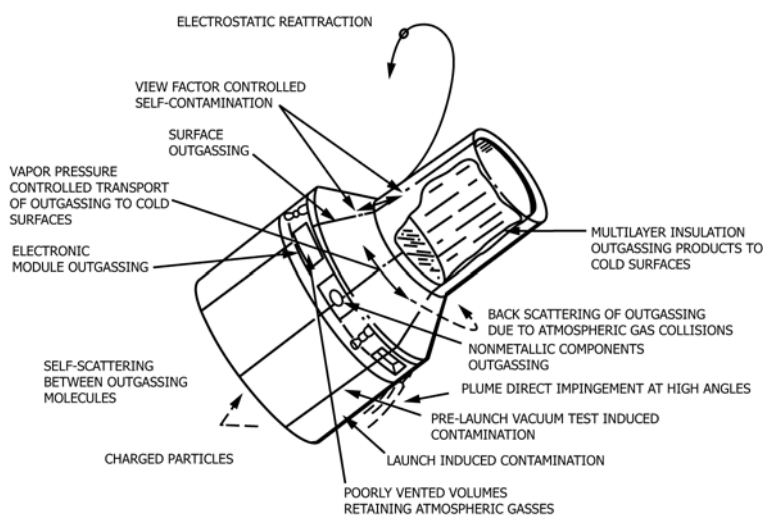


FIG. 2 Sources of Contamination and Transport Mechanisms

6.2.5 Windows and optical elements may be degraded by adsorption of a contaminant film leading to a loss of transmittance, reflectance, or an increase in scattered light; and

6.2.6 Solar arrays are adversely affected by the absorbance of contaminants.

6.3 Some of the sources of contamination and mechanisms for transporting them are shown in Fig. 2. Pre-launch, vacuum test-induced contamination remains a problem as well as launch-induced contaminants. High-angle plume impingement from spacecraft orientation thrusters, as well as multi-layer insulation surrounding cryogenic surfaces, are also sources of contamination. Frequently, the largest long-term sources are warm, relatively thick, non-metallic materials of the spacecraft construction. High vapor pressure (low molecular mass) molecules may photo polymerize on surfaces to become low vapor pressure (high molecular mass) stable contaminants. Vapor pressure-controlled self-contamination needs to be in the design engineer's mind; however, some parameters are still

uncertain, that is, back scattering of outgassed molecules due to atmospheric gas collisions, influence of free oxygen and charged particles as they impact the spacecraft surface.

6.4 Some typical spacecraft outgassing rates and the experimental determination of the resolution of QCMs are shown in Fig. 3. Some actual deposition rate conditions on a spacecraft have been observed to be $1.2 \times 10^{-12} \text{ g cm}^{-2} \text{ s}^{-1}$ for a sunlit vent-viewing OSR (4), $2 \times 10^{-13} \text{ g cm}^{-2} \text{ s}^{-1}$ for a mature large satellite (4), and a projected Space Station budget of $1 \times 10^{-14} \text{ g cm}^{-2} \text{ s}^{-1}$ (daily average) (5).

7. Defining Molecular Contamination

7.1 The process termed outgassing is a combination of events (Fig. 4) including the solid state diffusion of molecules to the surface, followed by desorption into the high-vacuum environment of space. When those molecules reach a sensitive surface, either by line-of-sight or indirect (non-line-of-sight)

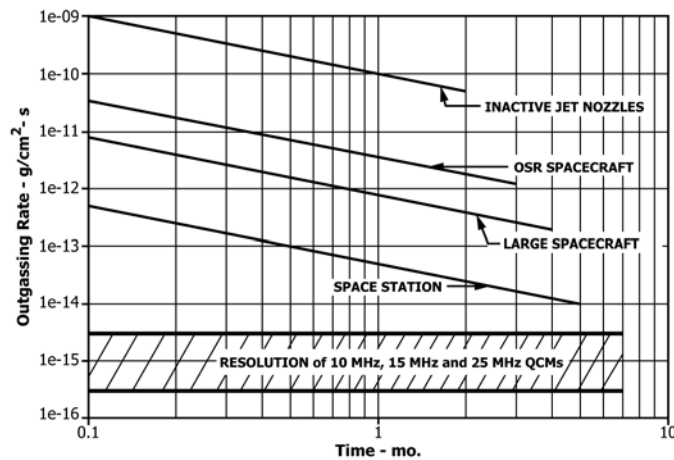


FIG. 3 Typical Outgassing Rates

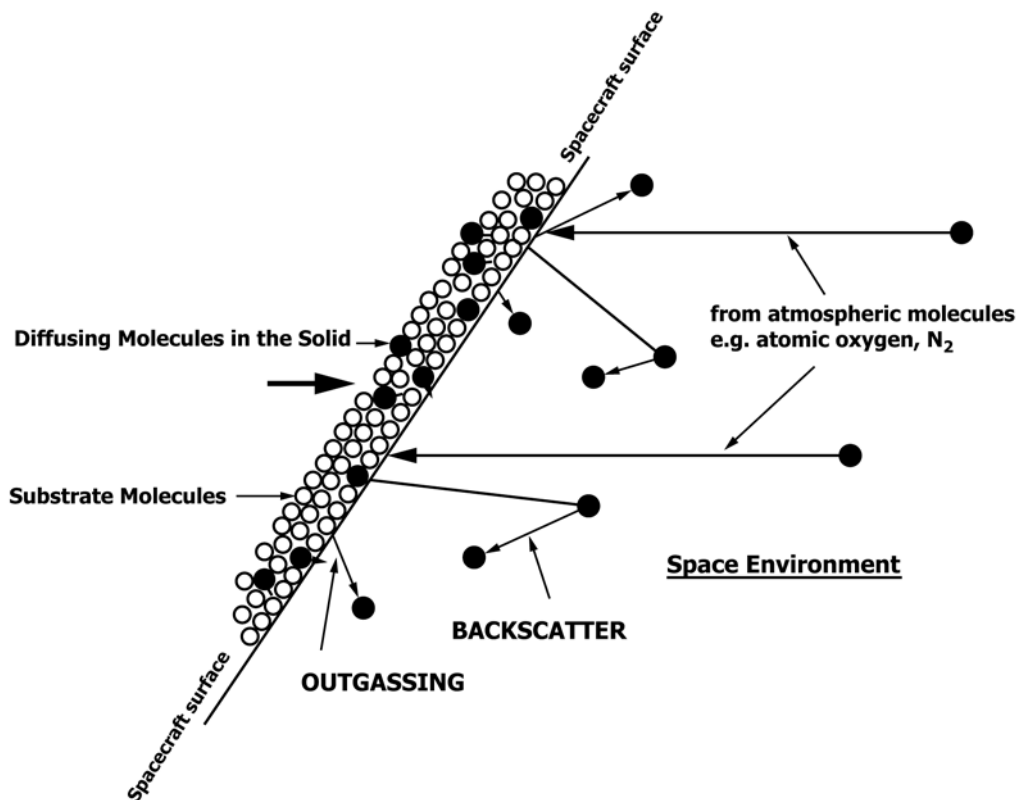


FIG. 4 Outgassing Combination of Events from Atmospheric Molecules on External Surfaces

transport and deposit, the deposit is termed “molecular contamination.” At low altitudes atmospheric molecules sometimes play a role in these processes by scattering or deflecting molecular contamination.

7.2 The definition of equivalent monomolecular layer (EML) of water on a surface (Fig. 5) is based on the concept of a uniform single layer of molecules, each 3×10^{-8} cm in diameter, placed with centers on a square pattern. This results in an EML being defined as approximately 1×10^{15} molecules/cm². However, molecular deposits are not always formed as uniform films.

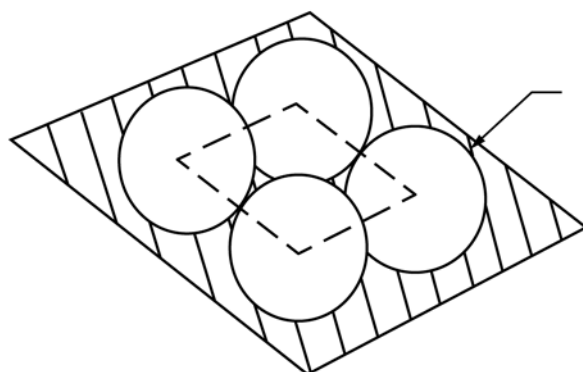
7.3 Given, for instance, water with a gram molecular mass of 18 g/mole and Avogadro’s number of 6×10^{23} molecules/g mole, this results in 3×10^{-8} g/EML or 3×10^{-8} g/cm².

8. QCM Theory

8.1 Crystal Frequency:

8.1.1 A piezoelectric quartz crystal (Fig. 6) is externally driven by an electronic oscillator attached to two metal plates (usually deposited by vacuum evaporation) placed on both sides of the quartz blank. This imposes a time dependent electric field across the plate, which causes the crystal to

Molecules on a square pattern



$\sim 3 \times 10^{-8} \text{ cm } \Phi$ – molecular diameter

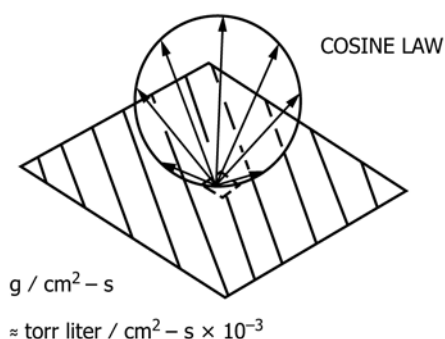
$1 \times 10^{15} \text{ molecules / cm}^2$ — monomolecular layer

water: 18 g / mole

Avogadro's number: $6 \times 10^{23} \text{ molecules / g mole}$

$\therefore 3 \times 10^{-8} \text{ g / EML or } 3 \times 10^{-8} \text{ g / cm}^2$

(a)



COSINE LAW

$\text{g / cm}^2 - \text{s}$

$\approx \text{torr liter / cm}^2 - \text{s} \times 10^{-3}$

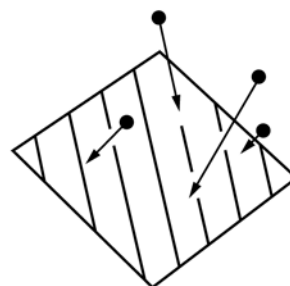
(b)

$\rho_{\text{N}_2} = 0.91 \text{ g / cm}^3$

$\rho_{\text{H}_2\text{O}} = 0.917 \text{ g / cm}^3$

if ρ is known,

$$\frac{\text{\AA}}{S} = \frac{\text{g / cm}^2 - \text{s} \times 10^8}{\rho - \text{g / cm}^3}$$



(c)

FIG. 5 Equivalent Monomolecular Layer (EML)

oscillate at a frequency determined by the total thickness of the crystal plus any mass on these electrodes. The oscillation appears as a Gaussian distribution of displacement, peaking at the center and vanishing at the electrode edge. The frequency of the surface motion decreases as a layer of contaminant is formed (mass addition), according to the degree to which each element is being displaced by the oscillation. The arriving or departing molecules (mass flux) are deposited or desorbed randomly. Therefore, integrating the distribution of surface displacements provides us with a valid sensitivity (mass flux to change in frequency) for the quartz plate. Experimental confirmation that the mass sensitivity of the plano-plano (p-p) crystal is as predicted by theory (3, 6-11) has been provided many times.

8.1.2 The resonant frequency of the QCM used is normally 10 MHz, 15 MHz, or up to 200 MHz, depending on the application. The p-p piezoelectric quartz crystal is approximately 1.27 cm (0.5 in.) in diameter and 0.0112 cm (0.0044 in.) in thickness for the 15 MHz crystal, or 0.0168 cm (0.0066 in.) in thickness for the 10 MHz crystal, which is, as already stated

above, set in vibration by an oscillation circuit that measures the frequency change as mass flux occurs. In the case of the higher frequency QCMs, such as the 25 MHz sensor, the crystal may be approximately 0.635 cm (0.25 in.) in diameter. The quartz plate electrode may have a different diameter on the topmost surface than on the bottom because the α/ϵ value for aluminum, which is commonly used as an electrode material, for irradiation from the sun is lower than for quartz. Electrodes of gold, platinum, and other metals are also often used. Aluminum is commonly chosen because of its low absorptance coefficient for solar radiation but gold resists the formation of oxides between the lead wire and the gold electrode making it more reliable for long-term space use. The electrode-to-crystal outer diameter ratio is usually approximately on half in order for the crystal to have a high “Q” (activity coefficient). While one of the electrodes must have this ratio to contain the electric field, the other side of the quartz crystal may have an electrode that covers the blank completely. The controlling electrode is the one smallest in diameter. (The smaller of the two electrodes defines the “active area” of the crystal).

Frequency of Crystals: 10 MHz or 15 MHz

$$f = c / 2t$$

$$c = 3.369 \times 10^5 \text{ cm/s (12)}$$

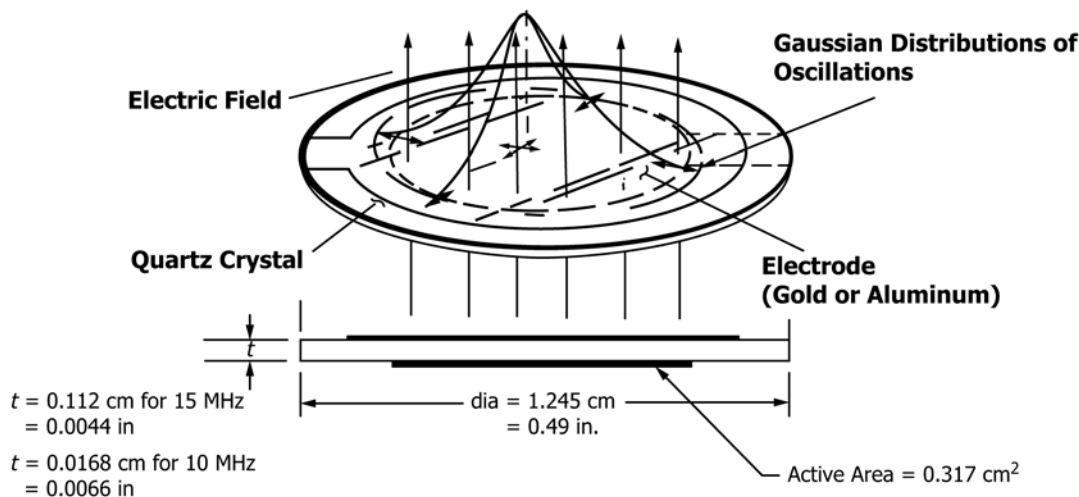


FIG. 6 Piezoelectric Quartz Crystal

Normally, this controlling electrode diameter is 0.625 cm (0.25 in.), which results in an active area of 0.317 cm². Molecules that strike the crystal outside the active area do not affect the crystal frequency even though the crystal is wholly plated.

8.2 Sensitivity:

8.2.1 The integration sensitivity of a quartz plate (mass flux to change in frequency) is a function of Φ (cut angle of the crystal), ρ_q (crystal density) and the transverse shear wave velocity, c , through the quartz plate (12) (see 3.1.8).

8.2.2 The frequency to mass relationship is:

$$d(-\Delta f)/d(\Delta m/A) = 2f^2/\rho_q c = S \quad (2)$$

where:

- f = crystal resonant frequency,
- Δf = change in frequency due to a change in mass per unit area on the crystal $\Delta m/A$,
- ρ_q = density of the quartz,
- c = shear wave velocity perpendicular to the crystal surface, and
- S = sensitivity.

8.2.3 The machined properties of quartz due to its hexagonal structure are characterized by six independent stress constants, C_{ij} , where $ij = 11, 13, 14, 33, 44$ and 66 . The shear wave velocity, c , can then be determined from:

$$\rho_q c^2 = (C_{66} + 0.76311 \times 10^{10}) \cos^2 \Phi + C_{44} \sin^2 \Phi + 2C_{14} \sin \Phi \cos \Phi$$

8.2.4 The density of the quartz also varies from 2.6485 g/cm³ at room temperature to 2.664 g/cm³ at 77K (see 3.2.1).

8.2.5 The usual practice is to use a p-p AT or rotated cut crystal (thickness shear vibration) at 35° 18' to 39° 40' crystallographic cut angle (13, 14) (Fig. 7) for use in a QCM over the wide temperature range to which it will be applied.

8.2.6 The mass sensitivity, S , is cited in Table 1 for 5, 10, and 15 MHz p-p crystals, and in Table 2, further approximate sensitivities for 1 to 25 MHz are given.

8.3 *Overcoating the Electrodes*—An overcoating of dielectric layers may be placed over the electrodes if desired, usually up to a thickness of approximately 800 nm (8000 Å). When used, overcoating is intended to simulate the material of the surface of interest or attempt to match the van der Waals' force effects when the first deposited molecules strike the surface. An overcoating of magnesium fluoride (MgF), silicon dioxide (SiO₂), aluminum oxide (Al₂O₃), zinc sulfide (ZnS) and indium oxide (In₂O₃), to name a few, may be made over the aluminum or gold electrode. When deposited, SiO₂ first forms SiOx which, with exposure to ultra-violet, becomes SiO₂. However, since this molecular transformation results in mass being added to the crystal; this needs to be considered if long-term stability is a requirement.

8.4 *Radiation Effects*—Natural quartz contains minute amounts of unwanted materials that cause detrimental effects in the processing of quartz blanks, for example, etch channels, in completed crystal performance, there may be high-energy electron and photon effects. Crystal vendors, when required, apply high temperatures along with high voltage (electrodiffusion or "sweeping") to the crystal blank to greatly diminish this effect. Swept crystals are normally 1/200 as sensitive to induced frequency changes from radiation. Therefore, in the space environment, especially in the case of polar orbits, swept crystals are recommended.

8.5 *Mass Sensor Range*—The usual stated mass sensor dynamic range is 1/100 of the resonant fundamental frequency, that is, 100 000 Hz for a 10 MHz crystal and 10 000 Hz for a

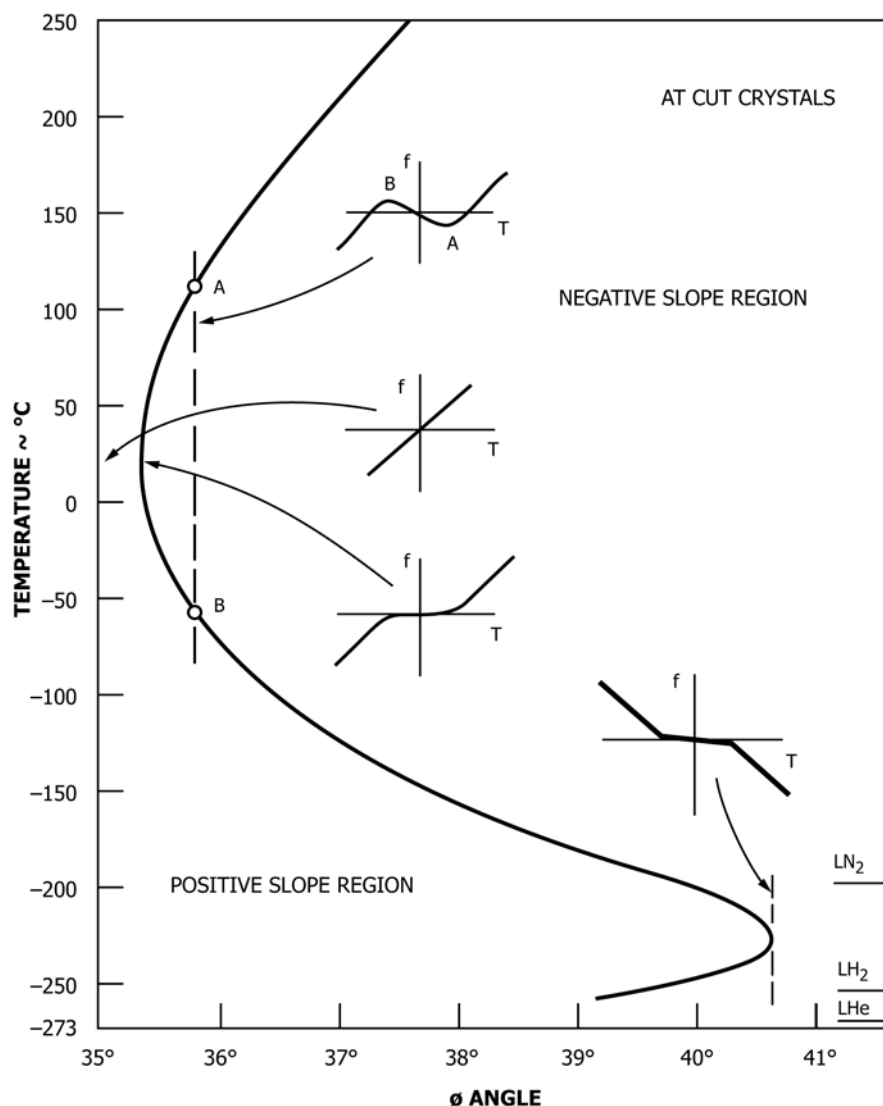


FIG. 7 Locus of First Order Zero Temperature Coefficient of Frequency for Crystals in Thickness-Shear Oscillation

TABLE 1 Mass Sensitivity of Crystals

Crystal Temp.	Mass Sensitivity	$f = 5 \text{ MHz}$	$f = 10 \text{ MHz}$	$f = 15 \text{ MHz}$
25°C	$S \approx \text{Hz/g/cm}^2$	5.6569×10^7	2.2627×10^8	5.0912×10^8
	$1/S \approx \text{g/cm}^2 \cdot \text{Hz}$	1.7677×10^{-8}	4.4195×10^{-9}	1.9642×10^{-9}
LN ₂ -LHe	S	5.6417×10^7	2.2566×10^8	5.0775×10^8
	$1/S$	1.7725×10^{-8}	4.43124×10^{-9}	1.9695×10^{-9}

TABLE 2 Approximate Sensitivities of Various P-P Crystals

Crystal Oscillator Frequency (MHz)	Approximate Sensitivity at 20°C ($\text{cm}^2 \text{g}^{-1} \text{Hz}$)
1	2.26×10^6
2	9.05×10^6
5	5.66×10^7
10	2.26×10^8
15	5.09×10^8
20	9.05×10^8
25	1.41×10^9

15 MHz crystal. This means that the sensitivity can be assumed to be essentially constant over that range. This is true only if the deposit is a solid polycrystalline or amorphous layer, for example, water vapor, carbon dioxide, oxygen or nitrogen. However, if the deposit consists of liquid or droplets (as can occur in the case of plasticizers and solvents from polymeric materials, nucleation of outgassed products, evaporating liquids, and so forth, onto a “warm” crystal) this range may be considerably reduced due to damping of the crystal oscillation (15-18).

8.6 QCM Thermogravimetric Analysis—The QCM measures the amount of mass flux on the crystal. It can also be used to do an elemental analysis on the mass. By raising the temperature of the crystal from the deposition temperature, a QCM Thermogravimetric Analysis (QCM TGA) can be obtained. At increasing temperatures the contaminants tend to evaporate, and from the frequency change as a function of time the mass change and the relevant vapor pressures can be calculated for the actual temperature. If the vapor pressure