15 Special Applications

Fred L. Walls

Time and Frequency Division
National Bureau of Standards
Boulder, Colorado

Jean-Jacques Gagnepain

Laboratoire de Physique et Métrologie des Oscillateurs
Besançon, France

The high resolution achievable with frequency metrology often makes it attractive to connect the measurement of physical parameters to a frequency measurement via a suitable transducer. Quartz crystal resonators are sensitive to mass loading and, via nonlinear effects, to temperature and stress. The sensitivities are generally low; however, the excellent short-term stability of precision quartz resonators makes high-resolution measurements of temperature, pressure, vibration, acceleration, film thickness, some gas-phase chemical reaction rates, and absorption feasible.

PRECISION FREQUENCY CONTROL
Volume 2
Oscillators and Standards
ISBN 0-12-280602-6

15.1 MICROBALANCES, THIN-FILM MEASUREMENT, AND OTHER MASS-LOADING PHENOMENA

The sensitivity of quartz resonators to added mass has been widely studied and used to measure the deposition rate, thickness, etc., of various materials. This technique was first suggested by Sauerbrey (1959). Further analyses have been carried out by many researchers [see, e.g., Warner and Stockbridge (1963), Mueller and White (1968), EerNisse (1975a), and Lu (1975)].

For changes in crystal-resonator mass loading of several percent or less, the frequency change $\Delta\nu/\nu$ is linear, that is,

$$\Delta\nu/\nu = K\,\Delta m/m,$$

where K depends only on the crystal and deposition area. As the thickness of the coating grows, the elastic and inelastic properties of the coating and the inherent stress of the coating play increasingly important roles in determining the resonator frequency (EerNisse, 1975b; Lu, 1975). Ultimate resolution for coatings of aluminum and copper is typically about $\Delta m/m = 10^{-12}$.

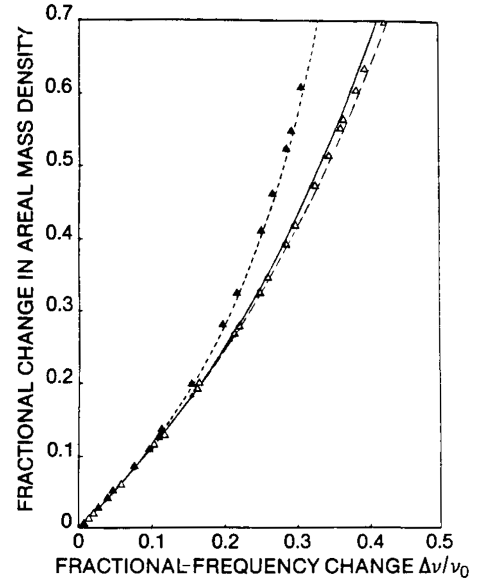


FIG. 15-1 Comparison of measured and computed fractional-frequency changes for quartz resonators loaded by copper and aluminium. The symbol ▲ denotes the experimentally measured points for copper, while △ denotes the experimentally measured points for aluminum. The theoretical curve for copper is shown as - - - -, that for aluminum is shown by — — —, and that for quartz is shown by a solid line. [From Lewis and Lu (1975).]

Film coatings ranging from a few picograms per square centimeter to 0.05 g/cm^2 (Lu, 1975) can be measured with accuracies that are typically better than 3% (see Fig. 15-1). Since quartz resonators are also sensitive to stress and temperature, schemes must be used to minimize these spurious effects. Usually these effects are compensated by using several resonators with either different exposures or different sensitivities [see, e.g., Warner and Stockbridge (1963), Warner *et al.* (1965), Mueller and White (1968), Shiojiri *et al.* (1969), Mecea and Bucur (1974), EerNisse (1975a), and Van Ballegooijen *et al.* (1978)] as frequency-determining elements in two or more oscillators in order to distinguish between the various effects.

A new possibility could be offered by doubly rotated crystals that exhibit, in addition to the regular C mode, a second resonance. The B mode (see Chapter 2) is very temperature sensitive and can therefore be used as a temperature probe for compensation in a dual-mode oscillator (Kusters *et al.*, 1978).

By using a cryogenically cooled pair of quartz resonators, Scialdone (1974) measured the outgassing of condensable gasses from a spacecraft. The high sensitivity to mass changes achievable with quartz resonators makes it possible to monitor chemical reactions between an electrode material and a gas. The sensitivity to mass change typically exceeds 10^{-3} monolayers. Benndorf *et al.* (1977) used such an arrangement to study the initial oxidation of aluminum. Warner *et al.* (1965) used this technique to study the effect of carbon dioxide on gold. Florio (1968) studied *alkali-antimonide* films. Shiojiri *et al.* (1969) studied sulfuration and oxidation of metal films, and Bucur *et al.* (1972) studied palladium–deuterium systems.

Mecea and Bucur (1974) showed that the amplitude of oscillation of a quartz crystal resonator decreases linearly with added mass and that many nonmetallic materials have a relatively larger effect than the same mass of copper. Water, for example, decreases the amplitude some 200 times faster than copper, while mineral oil decreases it about 60 times faster than copper. This inelastic effect is due to the added damping of the oscillation, which is due to dissipation within the coating. This technique could possibly be used to detect phase changes in coatings by simultaneously measuring changes in the amplitude and frequency of oscillation.

Quartz crystals can also be used as detectors by coating one electrode with a material that can absorb one specific gas (King, 1971). For instance, ambient-air hydrocarbons or auto-exhaust hydrocarbons can be analyzed in this manner. Generally, polymers are used as coating material. There is a potential for application in the field of meteorological monitors by employing simultaneously several sensors for humidity, temperature, and pressure measurements (Kertzman, 1971).

15.2 MEASUREMENTS OF FORCE, PRESSURE, AND ACCELERATION

When the propagation medium of an elastic wave is submitted to static or low-frequency mechanical perturbations, the quasistatic stresses and strains that are induced in the crystal are coupled to the high-frequency wave by the elastic nonlinearities of the crystal, thereby causing wave-velocity and frequency shifts.

15.2.1 Force

Force sensitivity was studied in the case of diametric or bending forces applied at the periphery of circular plates (Ballato, 1960; Gerber and Miles, 1961a,b; Keyes and Blair, 1967; Ratajski, 1966, 1968). These first measurements, made with AT-cut resonators, were then complemented by theoretical analyses and extended to doubly rotated cut resonators (EerNisse *et al.*, 1978; Lee *et al.*, 1976; Janiaud *et al.*, 1978). As an example, Fig. 15-2 shows the frequency change per diametrically applied force for an AT-cut plate as a function of the azimuth angle (Gerber and Miles, 1961a).

The temperature dependence of the force-sensitivity effect was also investigated (Dauwalter, 1972; EerNisse *et al.*, 1978, 1979), and in some particular cases attempts were made to use the force-sensitivity effect for temperature compensation (Gerber and Miles, 1961a,b).

This force sensitivity is typically on the order of 1.4×10^{-5}/N for AT-cut crystals under diametric forces along the x-axis. The force sensitivity depends on the directions of application of the forces. Particular azimuthal angles can be found either with zero or maximum force sensitivities. Quartz force

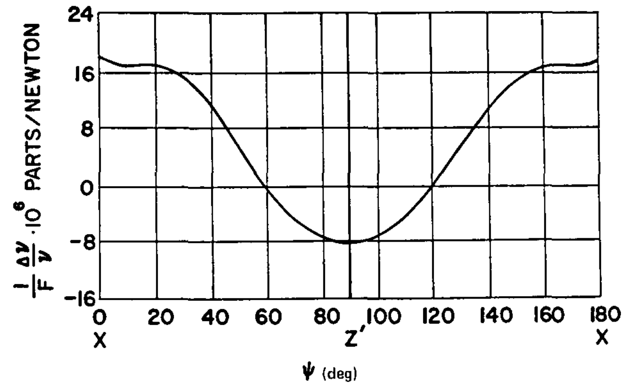


FIG. 15-2 Frequency change $\Delta\nu/\nu$ per applied force F as a function of the azimuth ψ for an AT-cut plate. [From Gerber and Miles (1961a).]

sensors were studied in this last case (Hammond and Benjaminson, 1969; Karrer and Ward, 1977).

Surface-acoustic-wave (SAW) devices also are sensitive to forces. Sensitivity to compressional and bending forces on rectangular plates and to diametric forces on circular plates were also investigated (Hauden *et al.*, 1980; Dias and Karrer, 1974). The largest sensitivity was obtained with bending forces (typically 1200 Hz/N for ST-cut quartz at 100 MHz). Such sensitivity opens the possibility of measuring pressures and accelerations through the force-frequency effect.

15.2.2 Pressure

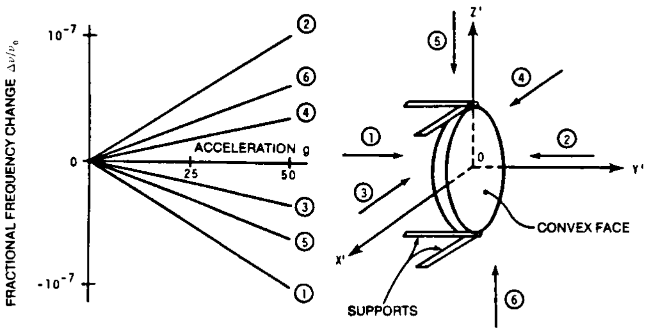
Warner *et al.* (1965) and Stockbridge (1966) examined the sensitivity of quartz resonators to the hydrostatic pressure of inert gasses and found a sensitivity of about 1×10^{-7}/Pa for a 5th-overtone AT-cut resonator. This phenomenon of viscous damping on bulk-acoustic-wave (BAW) devices can be exploited to yield a pressure sensor. An example of this approach is illustrated by the work of Genis and Newell (1977). They used a bellows arrangement to isolate an X–Y-flexure watch crystal from humidity and contamination effects. The transfer gas was dry nitrogen. They achieved an accuracy of about 700 Pa over the range from 0 to 1.4×10^5 Pa.

A much different approach is that described by Hammond and Benjaminson (1969) and Karrer and Ward (1977), where the pressure is transformed to diametric forces applied on the periphery of a BT-cut resonator. They reported a sensitivity of about 70 Pa, an accuracy of order ± 5000 Pa $\pm$ 0.025%, and an operating range of 100 to 8×10^7 Pa. A very special feature of their resonator was an integral resonator–mounting structure machined out of a single piece of quartz. This gave a total pressure range extending over six orders of magnitude.

SAW devices can also be exploited as pressure–force sensors. Their sensitivity to hydrostatic pressure is relatively small. An ST-cut SAW device at 100 MHz yields sensitivities of order 3×10^{-3} Hz/Pa (Hauden *et al.*, 1980). By utilizing a small circular diaphragm, a differential pressure device has been built with a sensitivity of 0.4 Hz/Pa. This differential device also has excellent thermal properties, with offsets of order ± 400 Pa for temperatures from -40 to 80°C (Reeder and Cullen, 1976).

15.2.3 Acceleration

When a crystal is in an acceleration field, the body forces and the induced reaction forces (at the fixation points) also give a static or quasistatic deformation and, again through nonlinear coupling, the wave velocity is



(a) (b)

FIG. 15-3 (a) Frequency variation of a quartz resonator for several different directions of applied acceleration, shown schematically in (b). [From Valdois *et al.* (1974).]

changed. The result is a variation of the resonance frequency related to the applied acceleration field direction, as shown in Fig. 15-3 [Valdois *et al.* (1974); see also Ballato and Bechmann (1960)]. This effect, a major source of environmental disturbance in precision oscillators, can be used to produce an acceleration transducer. However, since the acceleration sensitivity varies widely (even polarity) depending on the direction of applied force, a single resonator provides little information on acceleration. By a careful choice of mounting several resonators, one can fabricate a sensor with calibrated sensitivity to only a single directional component of acceleration (vibration). The work of Onoe *et al.* (1977) describes one such approach. Two near-identical retangular plates are separated by a small distance and clamped along the same edge. Both are made to oscillate at their respective thickness-shear resonance. The beat frequency between the two oscillators, derived by mixing the two oscillator outputs, is proportional to the acceleration component perpendicular to the plane of the crystal plates. Other force components that normally produce a signal in single-resonator accelerometers cancel out to a high degree. They achieved a sensitivity of 500 Hz/g for the range from 0 to 100. Deviations from linearity were typically less than 0.2% of the full range, or 0.2 g.

SAW resonators exhibit a sensitivity to forces of order 1 kHz/N at 100 MHz, which can be used to fabricate an acceleration sensor by transforming the acceleration into a force using an auxiliary mass. Due to their relatively recent introduction and a preoccupation with using them for complex data processing, their application to acceleration measurement is not well developed yet.

An interesting aspect is the sensitivity of propagating acoustic waves to Coriolis acceleration: when a point mass moves with a velocity relative to a rotating frame, it experiences a Coriolis force. Thus, the velocity of a wave therefore varies with the angular velocity of the substrate. This effect could be used for measuring rotation rates; however, it occurs only for propagating waves and not for standing waves. This necessitates the use of delay lines rather than resonators to control the frequency of the oscillator.

Theoretical evaluations of sensitivity to Coriolis forces have been made for surface acoustic waves and bulk flexure waves (Lao, 1980; Tiersten *et al.*, 1980). An interesting effect is the fact that reversing the propagation direction of the wave reverses the sign of the velocity or frequency shift. It is therefore possible to operate with a differential configuration that improves sensitivity and reduces some spurious effects.

15.3 TEMPERATURE MEASUREMENTS

The present accuracy limit of temperature measurements near 300 K is on the order of 50–100 μK and is obtained using platinum resistance thermometers (Riddle *et al.*, 1973). Thermistors used as thermal sensors yield a resolution of approximately 10 μK and a temperature stability of order 1 mK/100 days (Dror and Cannel, 1974; Wood *et al.*, 1978). Quartz crystal thermometers presently have a temperature resolution of order 2 μK and inherently yield a digital output; however, they are plagued by hysteresis effects due to thermal shock and cycling. Several new experimental quartz crystal resonators show promise of achieving temperature resolutions of less than 1 μK with daily variations of less than 10 μK and greatly reduced thermal-shock–cycling-induced hysteresis.

The potential for using a quartz crystal resonator to obtain a high-resolution digital thermometer has long been recognized (Gorini and Sortori, 1962; Hammond *et al.*, 1965; Hammond and Benjaminson, 1969; Holland, 1974). Indeed, Smith and Spencer (1963) used a high-quality quartz resonator as the frequency-determining element of an oscillator and obtained a temperature resolution of approximately 5 μK for a 10-sec measurement time and a drift of less than 100 μK/hr, as illustrated in Fig. 15-4. The frequency

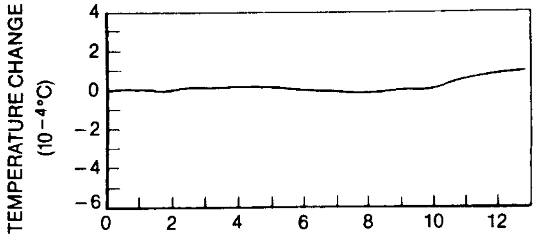


FIG. 15-4 Temperature variation of a double oven versus time measured using a 5° Y-cut quartz resonator. [From Smith and Spencer (1963).]

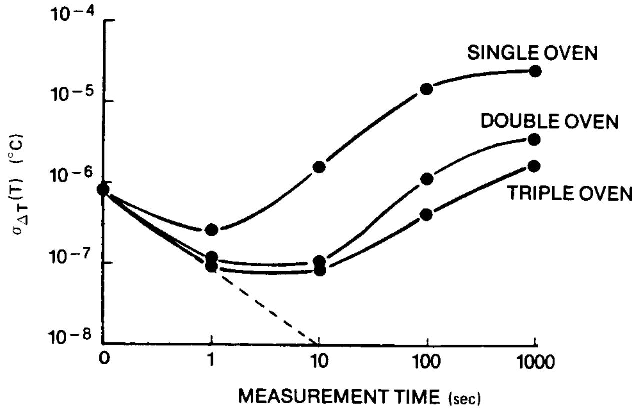


FIG. 15-5 Temperature stability of BVA SC-cut resonators contained in various ovens that were digitally controlled with an LC-cut quartz temperature probe. The dashed line shows the measurement limit due to noise. [From Marianneau and Gagnepain (1980).]

dependence was approximately 74.6 ppm/°C from −20 to 100°C. Presently available quartz thermometers are linear to within a few millikelvin from 0 to 200°C, have a time constant of order 10 sec, a resolution of order 2 μK, and a drift of only a few millikelvin per month (Hammond *et al.*, 1965). LC-cut quartz probes were used by Marianneau and Gagnepain (1980) for controlling the temperature of very stable ovens, as shown in Fig. 15-5. Temperature can also be measured by using the B mode of SC-cut crystals (Kusters *et al.*, 1978). Accurate temperature control and thermal filtering enable one to lower the residual temperature fluctuation of a vacuum-enclosed quartz crystal down to 0.1 μK over a few seconds.

However, LC-cut resonators suffer from thermal stress effects that result in spurious temperature readings on the order of 10 mK following thermal cycling (Fig. 15-6). The apparent temperature typically drifts approximately 10 mK over several days immediately following a temperature shock of many degrees. Because of these hysteresis effects, quartz crystal resonators have not generally been used in precision thermometry where temperature cycling is required.

Stress-induced frequency transients have received considerable attention in the past 5 years because they are responsible for much of the frequency instability of high-precision quartz crystal resonators used in frequency control (Holland, 1974; Ballato and Vig, 1978; Stein *et al.*, 1978; Theobald *et al.*, 1979). It appears likely that they are responsible for the thermal hysteresis as well as the noise in quartz sensors. In the past several years great strides have been made in designing crystallographic cuts that are less sensitive to

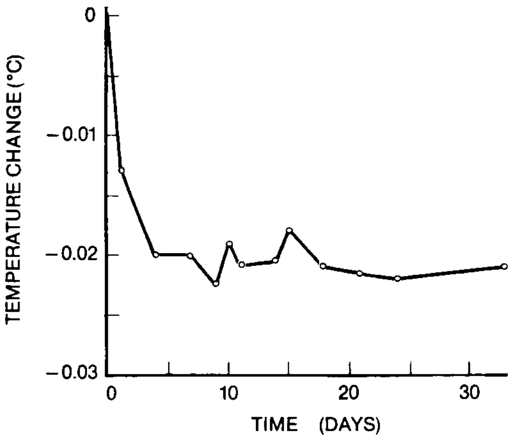


FIG. 15-6 Temperature error of an LC-cut quartz thermometer as a function of time after a temperature transient. [From Hammond *et al.* (1965).]

stress and in new mounting techniques that help to minimize temperature-induced (i.e., stress-induced) transients (EerNisse, 1975b, 1976; Besson, 1976, 1977; Kusters *et al.*, 1977).

For example, a fifth-overtone, 5-MHz quartz resonator has a parabolic static temperature sensitivity of approximately $\Delta\nu/\nu = 10^{-9}/\mathrm{K}^2$, yielding a linearized sensitivity of $\Delta\nu/\nu = 2 \times 10^{-8}/\mathrm{K}$, 1 K away from turnover. Since the frequency stability of such precision units is $\Delta\nu/\nu = 10^{-13}$, one would expect to achieve temperature resolution of 5 μK; however, the thermal-transient-induced response is $\Delta\nu/\nu = 10^{-5}\, dT/dt$, requiring that dT/dt be less than 0.01 μK/sec in order to achieve 1-μK temperature resolution and stability. Most ovens and test systems do not have the low-temperature transients required to use AT-cut resonators for temperature sensors.

The new SC-cut resonators (Besson, 1977; Kusters *et al.*, 1977; Theobald *et al.*, 1979) have a measured transient response that is 50–100 times smaller than that for AT-cut resonators. Therefore, dT/dt of only 0.5–1 μK/sec is required in order to resolve 1 μK. SC-cut resonators are therefore excellent candidates for thermal sensors. These new SC-cut resonators have another very interesting feature, namely, they can be made to oscillate on both the B and C modes simultaneously (Kusters *et al.*, 1978). The C mode can be made with $\Delta\nu/\nu = 10^{-9}/\mathrm{K}^2 + 10^{-7}\, dT/dt$, while the B mode has a linear response of $\Delta\nu/\nu = 2.5 \times 10^{-5}/\mathrm{K}$. It may be possible to use the C mode as the frequency reference for the microprocessor-based counter measuring the frequency of the B mode. With such a system temperature resolutions of approximately 0.1 μK are contemplated. Using only the B mode temperature stabilities of 1 μK over hours and 10 μK/day appear likely. The application of the so-called BVA_2 technology developed by Besson (1977) to the LC cut (Hammond *et al*., 1965) or the Y cut (Smith and Spencer, 1963) may yield a thermal sensor with resolution of order 0.1 μK, linearity of order 10 mK/100 K, and a daily stability of order $< 10\ \mu K$.

SAW devices are also sensitive to temperature. Hauden *et al* (1980) examined several cuts and found that a cut that is near $\phi = 11°24'$, $\theta = 59°24'$, and $\psi = 35°$ has a nearly linear frequency versus temperature curve. The first-order coefficient is ~ 31 ppm/°C or 3.2×10^{-4} °C/Hz at 93 MHz. The second-order coefficient was 2×10^{-3} ppm/°C^2. Given a typical SAW oscillator stability of 10^{-9} to a few parts in 10^{-10} would indicate possible resolutions on the order of 10 to 30 μK. Data on hysteresis effects appear to be nonexistent, but an interesting feature of such a SAW temperature probe is its short response time, which is typically 0.3 sec or less. This is 30 times shorter than for typical LC-cut sensors.