

The Quartz Crystal Microbalance

Early History of the Quartz Crystal Microbalance

Piezoelectricity is defined as electric polarization produced by mechanical strain in certain crystals, the polarization being proportional to the strain (1). The Curies first observed piezoelectricity in 1880 as a potential difference generated across two surfaces of a quartz crystal under strain (2). The converse piezoelectric effect, the deformation of a piezoelectric material by an applied electric field, was predicted by Lippman (3). Thus, when a thin wafer from a piezoelectric crystal such as quartz is placed in an alternating electric field of the right frequency it will oscillate in a mechanically resonant mode of the wafer. The resonance frequency depends upon the angles with respect to the optical axis at which the wafer was cut from a single crystal and inversely on the crystal thickness. Figure 1 shows typical cuts used to produce such wafers from a quartz single crystal. The angle most commonly chosen is referred to as the AT cut, 35° 15' from the Z or optic axis of the crystal. The AT-cut angles are chosen so that the temperature dependence of the resonant frequency is essentially zero at 25°C. These thin quartz plates with attached electrodes are called *transverse shear mode (TSM) resonators*.

The development and applications of quartz plate TSM resonators is a venerable field in electrical engineering. In the early 1920's the National Bureau of Standards (U.S.) began studies of quartz-crystal oscillators as frequency standards (4). To meet the growing demand for better accuracy, NBS sought outside partners, and began collaboration on oscillators with the Naval Research Laboratory and Bell Telephone Laboratories. In 1929 Bell Labs delivered four complete temperature-controlled 100 kHz oscillators to NBS, and these oscillators quickly became the national primary standard of radio frequency. By 1952 the facility involved a larger number of oscillators and the measurement uncertainty had been reduced to about 2 parts in 10⁸.

An entertaining account of the history of the history of the quartz crystal industry in the USA (5) indicates the critical role that quartz resonators played in the development of radio communications during World War II. Quartz resonators are presently found in many commercial products from quartz timepieces to ultra-stable frequency counters. Quartz plate resonators have been used as sensitive microbalances for thin adherent films since the late 1950's, following the pioneering work of Sauerbrey (6), who coined the term *quartz crystal microbalance* (see Figure 2). A widely used acronym is QCM.

The literature of thermal analysis and of the quartz crystal microbalance

It is useful to compare the history of the development of thermal analysis with the history of the development of the quartz crystal microbalance. Scopus (www.Scopus.com) is the largest online abstract and citation database of scientific and technical research literature and quality web sources. We have searched on the term “thermal analysis” and the term “QCM” or “quartz crystal microbalance” in Scopus, and have found all references dating

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to 1966. A Scopus literature search on the terms “QCM” or “quartz crystal microbalance” shows about 4500 citations since 1966. Figure 3 shows the number of publications per year for thermal analysis and for the quartz crystal microbalance. The QCM publications remain at 1-4% of the thermal analysis publications until about 1990, when they gradually increase to 15-18% by 2005 (reasons for this expansion are discussed below). Yet the number of publications involving BOTH thermal analysis and QCM is miniscule (5, all in the last five years). The number involving both QCM and calorimetry is not much larger (28, again in the last few years). These data show that the techniques of thermal analysis and the quartz crystal microbalance have developed independently of each other until very recently.

The following figures present a breakdown of the fields of the published references in thermal analysis and in QCM and how they have changed since 1971. Figures 4-7 show the professional fields assigned to all thermal analysis publications in the time intervals 1966-1980, 1981-1990, 1991-2000, and 2001-2003. Figures 8-11 show the fields assigned for QCM in the same time intervals.

For thermal analysis, materials science has the largest number of publications in each time interval. The next largest category is engineering in 1966-1980, but this shifts to chemistry and chemical engineering in 2001-2003.

For the quartz crystal microbalance, however, the pattern of dominant fields is quite different. 78% of the early literature (1966-80) is in engineering (predominantly electrical) and physics and astronomy, with only 18% in materials science and chemistry. The 61 references before 1980 are in engineering and physics journals, and deal with applications of the QCM in vacuum science and technology to determine the mass and thickness of deposited metallic films. The 1980's show a significant increase in materials science and chemistry (to 33%) and in chemical engineering (to 11%), at the expense of engineering. In the 1990's the field with the largest number of publications on QCM is chemistry, with materials science second. This trend is continued in 2001-2003. As we discuss below, during the mid-to-late 1980's it was shown that the QCM can function as a sensor when immersed in water or other liquids or solutions. This discovery led to rapid increases both in the total number of publications (Figure 3) and the number in chemistry and chemical engineering in such sub-disciplines as electrochemistry, analytical chemistry, and surface chemistry.

Table I shows the journals with the most thermal analysis publications, 1965-2005, and Table II shows the Journals with the most QCM publications, 1965-2005. The complete lack of overlap between these two lists is another indication that the quartz crystal microbalance is unknown to the thermal analysis and calorimetry community.

Principles of Operation of the QCM

The resonant frequency of the fundamental acoustic mode of vibration of a quartz TSM resonator of thickness h_q is

$$f_0 = (\mu_q/\rho_q)^{1/2}/2h_q \quad (1)$$

where μ_q and ρ_q are the shear modulus and density of quartz(7). The shift in frequency due to deposition of a film of the same acoustic impedance as quartz is proportional to the deposited mass per unit area of the film, $\Delta m/A$, a relationship first given by Sauerbrey (6):

$$\Delta f = -(2f_0^2 /(\mu_q\rho_q)^{1/2})\Delta m/A = -(2f_0^2 /(\mu_q\rho_q)^{1/2}) h_f\rho_f = -C h_f\rho_f = -C\Delta m/A \quad (2)$$

In Eq. (2) ρ_f and h_f are the density and thickness of the deposited film. For an AT-cut 5 MHz crystal at room temperature, $C = 56.6 \text{ Hz}/(\mu\text{g}/\text{cm}^2)$. Because it is easy to measure frequencies to $\pm 0.1\text{Hz}$, changes in mass per unit area of $< 1\text{ng}/\text{cm}^2$ are measurable with the QCM.

The electrical characteristics of a QCM are well represented by a simple RLC damped resonator equivalent circuit (7), termed the Butterworth-Van Dyke equivalent circuit (Figure 12). The series resonant frequency f of an RLC resonant circuit is given by

$$f_s = \frac{1}{2\pi} \sqrt{\frac{1}{L C_s}} \quad (3)$$

Here L is the dynamic inductance, a measure of the oscillating mass of the quartz, and C_s is the dynamic capacitance, a measure of the elasticity of the oscillating body (8). The resistance of the RLC circuit is related to the *quality factor* Q (the width of the resonance), the *dissipation* D (9), and the *full width at half maximum* δf of the resonance by the relationship

$$R_{\text{mot}} = 2\pi f L D = 2\pi f L /Q = 2\pi L \delta f \quad (4)$$

where R_{mot} is the motional or dynamic resistance of the quartz resonator. For an uncoated resonator, R_{mot} is a measure of the internal frictional damping of the quartz; coatings provide additional damping. The width of the resonance for an uncoated 5 MHz resonator is about 50 Hz, (i.e. $Q = 10^5$), and the damping within the quartz that gives rise to this broadening can be determined by measuring the motional resistance R of the uncoated resonator, typically 10 ohms. When thin, stiff films are deposited on the QCM surface the increase in R is small, but softer, thicker films (i.e., rubbery polymers 5-20 microns thick) can increase R by hundreds or even thousands of ohms.

Since the mid 1980's (10) it has been recognized that TSM resonators can also operate in fluid media if electronic oscillator drivers of suitable gain are employed to excite the resonator and to offset the losses due to damping of the resonator by the fluid. When immersed in water, the motional resistance of a 5 MHz TSM resonator increases to ~ 360 ohms. For an infinite viscoelastic liquid in contact with the TSM, the frequency shift is

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$$\Delta f_{liq} = - (2\rho_q h_q)^{-1} (\rho_l \eta_l f_0 / \pi)^{1/2} \quad (4)$$

where ρ_l and η_l are the density and viscosity of the liquid. For a 5 MHz QCM immersed in water at 25°C, $\Delta f_{liq} = -710$ Hz.

More complete theories of the operation of transverse shear mode resonators have been given by Kanazawa (10,11), Martin et al (12) (13), Lucklum and Hauptmann (14-16), Voinova, Jonson and Kasemo(17), Johannsmann (18,19), Tsionsky(20)and Arnau (21). In these theories the electrical impedance of the QCM Z_q is complex. The impedance of a TSM resonator damped by a finite viscoelastic film can be described as the sum of two complex impedances:

$$Z = Z_q + Z_L \quad (5)$$

where the acoustic load impedance due to the film Z_L contains both an inductive and a resistive part. Equations are given relating the complex impedance of a TSM resonator damped by a finite viscoelastic film to four parameters characterizing the film: the thickness h_f , the density ρ_f , the shear storage modulus G_f' and the shear loss modulus G_f'' . Shear moduli are functions of the frequency at which they are measured, so for TSM resonators G' and G'' are determined at the QCM resonant frequency f_0 or one of its overtones.

The acoustic load impedance Z_L of a film measured at frequency $\omega = 2\pi f$, is

$$Z_L = (i\omega h_f \rho_f) \tan \varphi / \varphi, \quad (6)$$

where φ is the (complex) acoustical phase shift ,

$$\varphi = \omega h_f \sqrt{(\rho_f / G)} \quad (7)$$

Here the modulus $G_f = G_f' + iG_f''$ is also complex.

Two convenient experimental measures of the film properties are

(a) the difference in resonant frequency $\Delta f = f(\text{crystal} + \text{film}) - f(\text{crystal})$

(b) the difference in motional resistance $\Delta R = R(\text{crystal} + \text{film}) - R(\text{film})$.

For thin films (the gravimetric region) the frequency shift Δf is proportional to $\rho_f h_f$, the mass per unit area of the film (the Sauerbrey relation, Eq. 2). It is possible to define an “ideal rigid mass layer” with small acoustic phase shifts (22), for which the acoustic load impedance is purely imaginary and the Sauerbrey limit is reached.

The relationship between Z_L and the measured quantities is (23)

$$\Delta f / f_0 = -\text{Im}(Z_L) / \pi Z_{cq} \quad (8)$$

$$\Delta R / 4\pi f_0 L_q = \text{Re}(Z_L) / \pi Z_{cq} \quad (9)$$

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Here f_0 , Z_{cq} , and L_q are the resonant frequency, acoustic impedance, and motional inductance of the bare quartz crystal.

Both Δf and ΔR are zero in the limit of zero film thickness. Voinova et al (17) and Johannsmann(18,19) present equations for both quantities in a power series expansion in the thickness h_f . The result for Δf and ΔR , to third order in h_f , is

$$\frac{\Delta f}{f_0} = \frac{\rho_f h_f}{\rho_q h_q} \left\{ 1 + \frac{h_f^2}{3} \frac{4\pi f_0^2 \rho_f G'}{G'^2 + G''^2} \right\} \quad (10)$$

$$\Delta R = \frac{2L_q}{3\pi Z_q} \omega^4 \rho_f^2 h_f^3 \frac{G''}{G'^2 + G''^2} \quad (11)$$

The compliance can be used instead of the modulus to quantify storage and loss behavior in viscoelastic solids. The shear storage compliance is defined as

$$J' = \frac{G'}{(G'^2 + G''^2)} \quad (12)$$

and the shear loss compliance is defined as

$$J'' = \frac{G''}{(G'^2 + G''^2)} \quad (13)$$

Thus, the thin film limit equations can be rewritten as

$$\frac{\Delta f}{f_0} = \frac{\rho_f h_f}{\rho_q h_q} \left\{ 1 + \frac{4h_f^2 \pi f_0^2 \rho_f J'}{3} \right\} \quad (14)$$

and

$$\Delta R = \frac{2L_q}{3\pi Z_q} \omega^4 \rho_f^2 h_f^3 J'' \quad (15)$$

Eq. (14) is useful in estimating the thickness of compliant films at which deviations from the Sauerbrey equation are noticeable. Eq. (15) is useful in interpreting motional resistance measurements of thin films. In the thin film limit, the motional resistance change is proportional to the square of the film density, the cube of the film thickness,

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and the loss compliance of the film. For a 5 MHz QCM, typical values for L_q and Z_q are 0.0402 Henry and 8.84×10^6 Pa s/m, respectively.

Detection electronics

Simple QCM driving circuits

Simple circuits to drive quartz resonators were developed in the 1960's and 70's. The most common and least expensive detection electronics involves such a driving circuit and a frequency counter. It is the series resonance frequency that is recorded. For Figure 12 the series resonant frequency is given by Eq. (3), whereas the parallel resonance frequency is given by

$$f_p = \frac{1}{2\pi\sqrt{L_1 C^*}} \quad (16)$$

where

$$C^* = \frac{C_s C_p}{C_s + C_p} \quad (17)$$

The static parallel capacitance C_p is the capacitance between the quartz electrodes, the crystal holder, and the leads to the driving circuit. Typical values are between 4 pF and 30 pF. For a typical 5 MHz quartz oscillator with $C_p = 20$ pF, $L_1 = 0.033$ H, $C_1 = 0.0307$ pF, and $R_1 = 10 \Omega$, the series resonant frequency $f_s = 5.0000$ MHz, the quality factor is 96,500, the difference between parallel and series resonant frequencies is 3.30 kHz, and the resonance line width δf is 52 Hz.

When QCM's began to be used with liquids there was a need to develop more specialized circuits. The damping produced by liquids causes a decrease in Q by 2-3 orders of magnitude and a corresponding broadening of the resonance. Eichelbaum et al (8) give references to Handbooks that present standard crystal oscillator circuits. They discuss the developments needed for interface circuits to operate with a fluid in contact with one of the crystal faces.

Frequency and damping measurements

Beginning in the 1990's, driving circuits that produce both resonance frequency outputs and analog outputs that measure the motional resistance began to be commercially available (see, for example, www.maxtekinc.com). A list of companies now providing such electronics is given in Appendix I.

Impedance analysis

Using an impedance analyzer, it is possible to measure both the real and imaginary parts of Z_q for TSM resonators(24) at the resonant frequency and many of its overtones. With

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suitable analysis software is in possible to determine both the shear modulus G' and the loss modulus G'' of the QCM (18).

Is the transverse shear mode resonator a true microbalance?

This is actually still a controversial question, after many years of discussion. We give verbatim quotes from some of the leaders in the field:

Comments in the literature

V. Tsionsky, in *Electroanalytical Chemistry*, Vol. 22, Ed. A.J. Bard and I. Rubenstein, 2003

“ Is the quartz crystal microbalance really a *microbalance*? For one thing, it should rightly be called a nano-balance, considering that the sensitivity of modern-day devices is on the order of 1-2 ng/cm² and could be pushed further, if necessary. More importantly, calling it a balance implies that the Sauerbrey equation applies strictly, namely that the frequency shift is the sole result of mass loading. It is well known that [in the case of operation of the resonator in a liquid] this is not the case, and the frequency shift observed could more appropriately be expressed by a sum of terms of the form

$$\Delta f = \Delta f_m + \Delta f_\eta + \Delta f_p + \Delta f_R + \Delta f_{sl} + \Delta f_T \quad (18)$$

where the different terms on the right hand side of this equation represent the effects of mass loading, viscosity and density of the medium in contact with the vibrating crystal, the hydrostatic pressure, the surface roughness, the slippage effect, and the temperature, respectively, and the different contributions can be interdependent. It should be evident from the above arguments that the term quartz crystal microbalance is a misnomer, which could (and indeed has) led to erroneous interpretation of the results obtained by this useful device. It would be helpful to rename it the *quartz crystal sensor* (QCS) which describes what it really does – it is a sensor that responds to its nearest environment on the nano-scale. However, it may be too late to change the widely used name. The QCM or its analogue in electrochemistry, the EQCM, can each act as a nano-balance under specific conditions, but not in general.”

R. Lucklum, *Anal. Bioanal. Chem. Comm.* 2006, 384, 667-682

“The name microbalance implies that acoustic sensors measure mass or mass changes only. Indeed, in many applications acoustic sensors are used to convert a mass accumulated on the surface into a frequency shift. In chemical and, especially, biochemical applications, however, this basic understanding of the sensor principle can easily lead to misintepretation of experimental results, especially when working in a liquid environment. It also hinders recognition by the experimenter of the outstanding capabilities of quartz crystal resonators, sensors, and other acoustic devices not available to other sensor principles. In a more general view acoustic sensors enable sensitive probing of changes within films attached to the transducer surface and at solid-solid and solid-liquid interfaces...”

V. Mecea, Sensors and Actuators 2006, 128, 270-277

“This article reveals that the local mass sensitivity of the quartz crystal microbalance (QCM) depends on the local intensity of the inertial field developed on the crystal surface during crystal vibration. ...The maximum intensity of this field in the center of the quartz resonator is a million times higher than the intensity of the gravitational field on the Earth. Experimental results reveal that the product of the minimum detectable mass and the intensity of the field acting on that mass is a constant for both QCM and beam balances, explaining thus why QCM is more sensitive than conventional analytical balances. It is show that the apparent effect of liquid viscosity on the frequency response of a quartz crystal resonator is, in fact, the result of the field intensity dependency of the mass sensitivity, being thus clear than QCM is really a mass sensor. “

M. Thompson, Phys. Chem. Chem. Phys. 2004, 6, 4928-4938

“For some considerable period of time it was assumed that the TSM structure employed in water simply responded to added or lost material on the sensor surface... In recent times it become clear that the device is exquisitely sensitive to changes in interfacial conditions. This observation is of great significance when biochemical interactions are detected using the TSM device. This technology involves the placement of biochemical receptors, such as antibody or nucleic acid species, on surfaces where the coupling processes described in the present paper area prevalent. Accordingly, modulation of such coupling by biochemical interactions instigated at the sensor surface constitute a new and highly sensitive detection strategy.”

Calibration

For a film interacting with a gas, Eq. 14 provides a quantitative means of determining if any calibration is needed for the mass measurement. The numerator of the factor outside the brackets can be expressed as $m_{\text{film}}/A_{\text{film}}$, the mass per unit area of the film. If the second term inside the brackets is $\ll 1$, then the Sauerbrey equation is obeyed and the QCM is a true gravimetric device. The correction factor is proportional to the square of the film thickness, the film density and the film’s shear compliance. Since virtually all polymers at room temperature are below their glass transition temperature at frequencies of 5 MHz, the time-temperature superposition principle (25,26) can be used to estimate the magnitude of J' and thus the thickness at which the Sauerbrey equation becomes inaccurate. At 20 °C for a rubbery polymer such as polyisobutylene, the correction is 1% for a film 4 μm thick. For a glassy polymer such as polystyrene, the mass correction factor is 1% for a thickness of 45 μm .

For QCM’s interacting with liquid films, the problem is much more complex. Tsionsky et al(20)discusses thoroughly the various limiting cases in which it is still possible to apply the Sauerbrey equation, but they are much more limited than in the case of film/gas interaction.

Comparison of gravimetric and Sauerbrey masses

As long as the correction factor in Eq. (14) relating frequency shift to change in mass per unit area is small, the QCM functions as a true balance with nanogram sensitivity. To

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prove this fact, we determined the resonant frequencies of 20 uncoated QCM crystals, then weighed the crystals with a 5-place analytical balance (Mettler 261). We spray-coated each crystal uniformly with a multi-component polymer coating used in the electronics industry, attempting to obtain films of thickness $\sim 1 \mu\text{m}$. Each crystal was dried at 200°C for 2 minutes to drive off residual solvents. We reweighed the coated crystal and divided each mass difference by the area of the coated crystal, 5.06 cm^2 to determine a *gravimetric film mass* per unit area for each sample. From the measured frequency of each coated crystal and Eq. (2) we determined the *Sauerbrey film mass per unit area*. Comparison of the two results is shown in Figure 14. The mean difference in mass between gravimetric and Sauerbrey masses was $2.4 \pm 4.6 \%$, well within the experimental error of the less accurate gravimetric mass determination. Nonuniformity in film coating and incomplete drying also may contribute to the scatter in the data.

Determination of shear and loss modulus at QCM frequencies

The determination of shear storage and loss moduli of thin viscoelastic films with TSM resonators has been reviewed (19,27,28). Even though the basic physics of damped TSM resonators is well understood, the effort to determine G_f' and G_f'' from measurements of frequency shift and motional resistance change has been fraught with problems. For very thin, rigid films, the frequency shift contains no information on either G_f' or G_f'' because the Sauerbrey limit (Eq. 2) is reached. For thicker and/or lossier films the frequency shift and motional resistance depend on G_f' and G_f'' in a complex manner not obvious by examining the equations.

Sample Preparation

In order for both mass and heat flow sensors to operate, the thin film sample must adhere to the top surface of the QCM and be of uniform thickness. The mechanical behavior of films on the quartz microbalance has been modeled by Kanazawa(11), who examined the amplitude of the shear displacement in the quartz crystal and in the overlying film for several cases. For a 1 volt peak RF applied voltage typical of the Stanford Research Systems oscillator driver, the amplitude of the shear wave of a bare crystal is 132 nm. Mecea (29) has calculated the inertial acceleration at the center of a similar quartz resonator, and finds that it is roughly $10^6 g$, where g is the gravitational constant. At these extremely high accelerations, powder or polycrystalline samples cannot be used because they do not adhere to the surface and follow the transverse motion of the QCM surface.

Many methods have been used to prepare thin film samples for the QCM. For metallic and inorganic materials, vacuum or electrochemical deposition has been traditionally used, but methods such as sol-gel formation of films can also be employed. Uniform films of polymers can be made by dip coating, drop coating, spray coating, or spin coating. To achieve sample homogeneity and uniformity the best of these methods is spin-coating, if the film material is amenable to this treatment. Self-assembled monolayer (SAM) chemistry (30) can be used to construct planar micro- and nano-structures. The effect of non-uniform thickness of films on the operation of the QCM has been treated by several authors(20), (31).

Since the measured frequency difference $\Delta f = f(\text{crystal} + \text{film}) - f(\text{crystal})$ is proportional to the mass per unit area of the film, the total sample mass is obtained from Eq. 2 as $(\Delta m/A)A_{\text{film}}$ where A_{film} is the area of the film exposed to the gas.

Chemical and Biological Applications of the QCM

Film thickness monitors in vacuum deposition

QCM's have been used as film thickness monitors in vacuum deposition of metals and inorganic solids since the 1970's. The monograph by Lu and Czanderna, while over 20 years old, still is a very good summary of early applications of the quartz crystal microbalance in physics and engineering as well as applications as thickness monitors in the vacuum deposition industry(32). Well before the full acoustical models of the past fifteen years it was realized that for thick deposited films there are deviations from the Sauerbrey equation that depend upon the acoustical transmission properties of the deposited film. The most successful method of analyzing frequency shifts of thick films is the Z-match method, reviewed by Benes (33). The working equation is

$$\frac{m_F}{m_Q} = -\frac{z_F f_Q}{z_Q \pi f} \arctan\left(\frac{z_Q}{z_F} \tan \frac{\pi f}{f_Q}\right) \quad (19)$$

where m_F and m_Q are the areal masses (mass per unit area) of the applied film and of the quartz resonator, z_F and z_Q are the acoustical impedances of the film and the quartz, f is the resonant frequency of the composite quartz + film, and f_Q is the frequency of the bare quartz resonator. Benes gives a table of acoustical impedances of 53 metals and simple inorganic salts, the hardest of which is iridium and the softest graphite. From Eq. 14 it can be seen that the acoustical impedance is a measure of the shear storage compliance J' of the film.

The metal/solution interface in electrochemical cells

The first subdiscipline of chemistry in the QCM that was widely applied was electrochemistry. In 1992 Buttry and Ward published a review entitled “Measurement of interfacial processes at electrode surfaces with the electrochemical quartz crystal microbalance”, with 133 references (7). This is the most widely cited paper on quartz crystal microbalances. After presenting the basic principles of AT-cut quartz resonators, the authors discuss the experimental aspects and relation of electrochemical parameters to QCM frequency changes. In their review of the investigation of thin films, they discuss electrodeposition of metals, dissolution of metal films, electrovalency measurements of anion adsorption, hydrogen absorption in metal films, bubble formation, and self-assembled monolayers. The review concludes with a brief section on redox and conducting polymer films.

In 2003, Tsionsky, Daikhin, Urbakh, and Gileadi (34) published a very thorough treatment of the metal/solution interface as examined by the electrochemical quartz

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crystal microbalance, with emphasis on the misinterpretations of data that can occur if the basic physics and chemistry at the interface is not understood. Topics covered include the electrical double layer/electrostatic adsorption, the adsorption of organic and inorganic species, metal deposition, and the influence of roughness on the response of the QCM in liquids.

Faraday Society Discussion No. 107, 1997

This entire volume has articles devoted to the theory and application of acoustic sensors. The quartz crystal microbalance is discussed in the following articles in this discussion:

- (1) L Daikhin, M Urbakh: Influence of surface roughness on the quartz crystal microbalance response in a solution - New configuration for QCM studies. Faraday Discussions (1997) 27-38.
- (2) KK Kanazawa: Mechanical Behavior of films on the quartz microbalance. Faraday Discussions 107 (1997) 77-90.
- (3) O Wolff, E Seydel, D Johannsmann: Viscoelastic properties of thin films studied with quartz crystal resonators. Faraday Society Discussions 107 (1997) 91-104.
- (4) HL Bandey, AR Hillman, MJ Brown, SJ Martin: Viscoelastic characterization of electroactive polymer films at the electrode/solution interface. Faraday Discussions 107 (1997) 105-21.
- (5) R Lucklum, P Hauptmann: Determination of polymer shear modulus with quartz crystal resonators. Faraday Discussions 107 (1997) 123-40.
- (6) BA Cavic, FL Chu, LM Furtado, S Ghafouri, GL Hayward, DP Mack, ME McGovern, H Su, T M.: Acoustic waves and the real-time study of biochemical macromolecules at the liquid/solid interface. Faraday Discussions 107 (1997) 159-76.
- (7) EJ Calvo, R Etchenique, PN Bartlett, K Singhal, C Santamaria: Quartz crystal impedance studies at 10 MHz of viscoelastic liquids and films. Faraday Discussions 107 (1997) 141-57.
- (8) JW Grate, SN Kaganove, VR Bhethanabotla: Examination of mass and modulus contributions to thickness shear mode and surface acoustic wave vapour sensor responses using partition coefficients. Farady Discussion 107 (1997) 259-83.
- (9) K-H Stellnberger, M Wolpers, T Fili, C Reinartz, T Paul, M Stratmann: Electrochemical quartz crystal microbalance in modern corrosion research. Faraday Discussions 107 (1997) 307-22.
- (10) V Tsionsky, E Gileadi, L Daikhin, G Zilberman: Response of the EQCM for electrostatic and specific adsorption on gold and silver electrodes. Faraday Discussions 107 (1997) 337-50.

Chemical sensors and biosensors

When a reactant molecule reacts with a metal, inorganic, or polymer film the magnitude of the mass change at the interface depends on whether the products are small enough to diffuse into the film, or whether they remain bound only to the surface. If the film is chemically compatible with the reactant a solid solution may be formed; for example, the

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absorption of water by a hydrophilic polymer. In this case the mass change and the corresponding viscoelastic damping may be large enough to yield large signal-to-noise changes when the reaction occurs on a coated QCM. But to be really useful a sensor must be *both sensitive and selective*. It is much more difficult to devise a surface coating that absorbs selectively only a single chemical species. For this reason, the concept of using solubility interactions to design chemically selective sorbent coatings for chemical sensors and arrays was proposed and developed (35). In a more recent review with 208 references, Grate has summarized the development and use of acoustic wave microsensor arrays for vapor sensing (36). To quote from the introduction to this review, “The advantages that sensor arrays offer over individual sensors are sensitivity to a wider range of analytes, improved selectivity, simultaneous multicomponent analysis, and the capability for analyte recognition rather than mere detection. By analogy with olfaction systems comprising multiple receptors and neuronal pattern recognition, sensor arrays for gas-phase detection are sometimes dubbed ‘electronic noses’.”

The field of piezoelectric mass-sensing devices as biosensors is well covered in a review published in 2000 with 194 references by Janshoff, Galla, and Steinem (28). To quote from the abstract of this review, “In the last decade absorption of biomolecules on functionalized surfaces turned into one of the paramount applications of piezoelectric transducers. These applications include the study of the interaction of DNA and RNA with complementary strands, specific recognition of protein ligands by immobilized receptors, the detection of virus capsids, bacteria, mammalian cells, and last but not least the development of complete immunosensors. Piezoelectric transducers allow a label-free detection of molecules; they are more than mere mass sensors since the sensor response is also influenced by interfacial phenomena, viscoelastic properties of the adhered biomaterial, surface charges of absorbed molecules, and surface roughness. These new insights have recently been used to investigate the adhesion of cells, liposomes, and proteins onto surfaces, thus allowing the determination of the morphological changes of cells as a response to pharmacological substances and changes in the water content of biopolymers without employing labor-intensive techniques. However, the future will show whether the quartz crystal microbalance will assert itself against established label-free sensor devices such as surface plasmon resonance spectroscopy and interferometry.”

Because quartz crystal microbalances are compact and sensitive, a large literature has developed on their use as sensors of both chemical and biomolecular reactions and processes at surfaces. A current review of this literature, with 176 references, is by K. A. Marx (37). To quote from the abstract of this review, “The technique possesses a wide detection range. At the low mass end, it can detect monolayer surface coverage by small molecules or polymer films. At the upper end, it is capable of detecting ...complex arrays of biopolymers and biomacromolecules, even whole cells. Another important and unique feature of the technique is the ability to measure mass and energy dissipation properties of films while simultaneously carrying out electrochemistry on solution species or upon film systems bound to the upper electrode of the oscillating quartz crystal surface.” As examples of chemical reactions, the review discusses in more detail the QCM studies of biopolymer film formation,

Final Draft of “The Quartz Crystal Microbalance”, by Allan Smith, a chapter for Volume 5 of the **Handbook of Thermal Analysis and Calorimetry**, Elsevier

electropolymerization, micellar-polymer film systems, self-assembled monolayer adsorption, Langmuir-Blodgett monolayer films, molecular imprinted polymer films and chemical sensors, and nanoarchitecture and layer-by-layer films.

A useful comparison of experimental methods used to interrogate biomolecular interactions has been published by Cooper (38). To quote from the abstract, “ The majority of techniques currently employed to interrogate a biomolecular interaction require some type of radio- or enzymatic- or fluorescent-labeling to report the binding event. However, there is an increasing awareness of novel techniques that do not require labeling of the ligand or the receptor, and that allow virtually any complex to be screened with minimal assay development. This review focuses on three major label-free screening platforms: surface plasmon resonance biosensors, acoustic biosensors, and calorimetric biosensors. ... The capabilities and advantages of each technique are compared and key applications involving small molecules, proteins, oligonucleotides, bacteriophage, viruses, bacteria, and cells are reviewed. The role of the interface between the biosensor surface (in the case of SPR and acoustic biosensors) and the chemical or biological systems to be studied is also covered with attention to the covalent and non-covalent coupling chemistries employed.”

Biological surface science

QCM is one of the many experimental methods discussed by Kasemo in his wide-ranging review of biological surface science (39). In Kasemo’s words, “Biological surface science (BioSS), as defined here is the broad interdisciplinary area where properties and processes at interfaces between synthetic materials and biological environments are investigated and biofunctional surfaces are fabricated. Six examples are used to introduce and discuss the subject: Medical implants in the human body, biosensors and biochips for diagnostics, tissue engineering, bioelectronics, artificial photosynthesis, and biomimetic materials. They are areas of varying maturity, together constituting a strong driving force for the current rapid development of BioSS. The second driving force is the purely scientific challenges and opportunities to explore the mutual interaction between biological components and surfaces.

“Model systems range from the unique water structures at solid surfaces and water shells around proteins and biomembranes, via amino and nucleic acids, proteins, DNA, phospholipid membranes, to cells and living tissue at surfaces. At one end of the spectrum the scientific challenge is to map out the structures, bonding, dynamics and kinetics of biomolecules at surfaces in a similar way as has been done for simple molecules during the past three decades in surface science. At the other end of the complexity spectrum one addresses how biofunctional surfaces participate in and can be designed to constructively participate in the total communication system of cells and tissue.”

Kasemo’s laboratory at Chalmers University of Technology and Goteborg University was the source of the QCM-D technique (9), now embodied in instrumentation offered by Q-Sense AB. They define the dissipation, D , as the inverse of the quality factor Q of the quartz crystal resonator (40) (see Eq. 4). In the Q-Sense instrumentation, the driving RF

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power to the oscillator causing it to respond at resonant frequency f is switched off and the exponentially damped sinusoidal wave decays with a time constant τ , where $D = 1/(\pi f \tau)$. More than 100 recent and archived publications on the QCM-D method are available at the Q-Sense website, www.q-sense.com. The publications stress real-time biointerface characterization with QCM-D.

Acoustic microsensors – the challenge behind microgravimetry

One of the more prolific author-teams who have developed the theory and applications of the QCM is R. Lucklum and P. Hauptmann. Their most recent review with 235 references (16) addresses the future of this field. To quote, “In this review we give an overview of recent developments in resonant sensors including micromachined devices and also list recent activity relating to the (Bio)chemical interface of acoustic sensors. Major results from theoretical analysis of quartz crystal resonators, descriptive for all acoustic microsensors are summarized and non-gravimetric contributions to the sensor signal from viscoelasticity and interfacial effects are discussed.”

Piezoelectric sensors

The final reference in this section is to a book not yet published, but in press as of November 2006. It contains current reviews by many of the authors quoted in this chapter, and promises to be the most current and comprehensive review of piezoelectric sensors published so far. Here is a description of the contents:

Piezoelectric Sensors

Claudia Steinem and Andreas Janshoff (Eds.)

Springer Series on Chemical Sensors and Biosensors, Volume 5

Available December 2006, ISBN 10-3-540-36567-2

Part I: Physical Aspects of QCM-Measurements:

Ralf Lucklum, Frank Eichelbaum: Interface Circuits for QCM Sensors.

Diethelm Johannsmann: Studies of Viscoelasticity with the QCM.

Michael Urbakh, Vladimir Tsionsky, Eliezer Gileadi, Leonid Daikhin: Probing the Solid/Liquid Interface with the Quartz Crystal Microbalance.

Diethelm Johannsmann: Studies of Contact Mechanics with the QCM.

Part II: Chemical and Biological Applications of the QCM:

Franz L. Dickert, Peter, A. Lieberzeit: Imprinted Polymers in Chemical Recognition for Mass-Sensitive Devices.

Maria Minnuni, Sara Tombelli, Marco Mascini: Analytical Applications of QCM-Based Nucleic Acid Biosensors.

Robert D. Vaughan, George G. Guilbault: Piezoelectric Immunosensors.

Claudia Steinem, Andreas Janshoff: Specific Adsorption of Proteins on Solid Supported Membranes.

Vanessa Heitmann, Björn Reiß, Joachim Wegener: The Quartz Crystal Microbalance in Cell Biology: Basics and Applications.

Part III: Applications Based on Advanced QCM-Techniques: Yoshio Okahata, Toshiaki Mori, Hiroyuki Furusawa: Enzyme Reactions on a 27 MHz Quartz-Crystal Microbalance.

Final Draft of “The Quartz Crystal Microbalance”, by Allan Smith, a chapter for Volume 5 of the **Handbook of Thermal Analysis and Calorimetry**, Elsevier

Kenneth A. Marx: The Quartz Crystal Microbalance and the Electrochemical QCM: Applications to Studies of Thin Polymer Films, Electron Transfer Systems, Biological Macromolecules, Biosensors, and Cells.

Fredrik Höök, Bengt Kasemo: The QCM-D Technique for Probing Biomacromolecular Recognition Reactions.

Matthew A. Cooper: Resonant Acoustic profiling (RAPTM) and Rupture Event Scanning (REVSTM).

While not yet in print, this volume has articles by the world’s leaders in QCM theory and application, and should be valuable for anyone wishing current and in-depth coverage of the applications of the QCM.

The Quartz Crystal Microbalance/Heat Conduction Calorimeter

A recent report entitled “Chemical Industry Roadmap for Nanomaterials by Design” (41) states

“The largest barrier to rational design and controlled synthesis of nanomaterials with predefined properties is the lack of fundamental understanding of thermodynamic and kinetic processes at the nanoscale. ... Bulk material properties are not size-dependent, but the properties of nanomaterials are a function of size. The underlying principles governing the properties at all lengths, organization complexity, and structural and property stability over time must be understood to enable the nanoscale materials by design approach.”

Quartz crystal microbalance/heat conduction calorimetry, (QCM/HCC) (42) is a new measurement technology that permits high sensitivity measurements in real time of three properties of a nanoscale coating or film undergoing chemical reaction: the mass change (to ± 10 nanograms), the heat generated (to ± 1 microwatt), and the change in loss compliance of the film. These sensitivities are sufficient to examine the energetics of the formation of a self-assembled monolayer as well as the thermodynamics of the chemical processes in nanoscale polymer coatings. Here we describe the development of this measurement technology and give a number of applications that illustrate its potential to be a key instrumental method of measuring thermodynamic and kinetic processes at the nanoscale.

Beginnings of QCM/HCC

In 1997 the author spent a six-month sabbatical leave from the chemistry department at Drexel University in the Department of Thermochemistry of Lund University, hosted by Professor Gerd Olofsson and Professor Ingemar Wadsö. We discussed over coffee one morning the need to measure tiny mass changes in a sample of low volatility inside a heat flow calorimeter. The goal was to determine the enthalpy of sublimation of the material. Heat flow signals from the subliming material were quite high, but the need to remove the sample container and reweigh it on an analytical balance introduced substantial errors in the needed measurement of the mass of material evaporated. I suggested to my hosts that what was needed was to build a small, sensitive balance into the sample chamber itself.

Shortly thereafter, we began work on a sensor that would combine two mature technologies: transverse shear resonators (quartz crystal microbalances) (32) and heat flow sensors and their use in isothermal microcalorimetry (43). Both have been employed in research laboratories and in commercial instrumentation for many years. Quartz crystal microbalances have been widely used since the 1970's as thickness monitors of thin films deposited in vacuum. Peltier heat flow sensors are the basic sensor in many calorimeters and thermal analysis instrumentation, including those designed and built at Lund University. Our goal was to develop and use a sensor that simultaneously measures the mass change and the heat generated or absorbed when a chemical process occurs on the surface of a bare or coated sensor. The quartz crystal microbalance can measure mass changes at the sub-monolayer coverage because of its nanogram sensitivity. With suitable thermal shielding and temperature control, heat conduction calorimetry can continuously measure sub-microwatt heat flows to or from a reacting sample. If a method could be devised to combine these two technologies in a single sensor, then chemical processes in a thin film sample on the sensor surface could be followed in real time by measuring both the heat and mass changes induced by the chemical or biological process. Since heat and mass are the two fundamental extensive variables needed to determine thermodynamic state variables such as enthalpy, entropy, and Gibbs free energy, we predicted that such a mass/heat flow sensor could be used to determine the thermodynamic quantities associated with the reactions of gases or liquids with thin films.

Here we make a simple estimate of the sensitivity in mass and heat detection needed to detect the energy of binding per unit mass of a monolayer of water on the gold surface of a QCM crystal. The area of the gold electrode exposed to the sample vapor is 2 cm^2 . We assume that the monolayer has the density of water itself and a thickness of 0.3 nm, the length of the water molecule. There are thus 2×10^{15} water molecules in this monolayer, and their mass is 60 ng. If the binding energy of the water to the gold is taken to be the enthalpy of condensation of water, 44 kJ/mole, then the heat liberated at the surface in forming this monolayer is 0.15 mJ. The mass resolution of the QCM depends on the integration time of the frequency counter used to measure the QCM resonant frequency, but nanogram sensitivity has been widely reported in the literature. Detecting a heat evolution of 150 microjoules in a heat conduction calorimeter is more challenging, but it has been achieved.

By June of 1997 there was a working mass/heat flow sensor in the Lund laboratory based on the principles described above.

Development of QCM/HCC

Upon returning to Drexel in the summer of 1997, the author worked with graduate student Hamid Shirazi to develop a quartz crystal microbalance/heat conduction calorimeter based on this mass/heat flow sensor. The development, testing, and initial

Final Draft of “The Quartz Crystal Microbalance”, by Allan Smith, a chapter for Volume 5 of the **Handbook of Thermal Analysis and Calorimetry**, Elsevier

uses of the QCM/HCC are very well documented in Shirazi’s Ph.D. thesis, available online (44). Shirazi performed the following experiments with this new technology:

Solvent vapor sorption into an aliphatic polyurethane film (Tecoflex™) (45). Solvents employed were ethanol, carbon tetrachloride, chloroform, toluene, acetone, and hexane. The sorption enthalpy and sorption isotherm of each solvent vapor in Tecoflex was determined.

Hydrogen sorption in thin palladium films (42). Both the sorption isotherm and sorption enthalpy of hydrogen in palladium were measured. The response of the mass/heat flow sensor during the palladium-catalyzed hydrogenation of ethylene was also measured.

Detection of the formation of a self-assembled monolayer of nonylthiol on gold (46). This experiment was done to test the sensitivity of the apparatus, and it showed that both the mass change and the heat release upon forming a self-assembled monolayer could be detected with the QCM/HCC.

Hydration and dehydration of a thin film of the protein lysozyme (44).

The next graduate student to work on the QCM/HCC was Sister Rose Mulligan, I.H.M.. Her contributions to the development are also described in a Ph. D. thesis available online (47):

Thermodynamic and rheological properties of Tecoflex upon ethanol vapor and water vapor sorption (48). Sorption isotherms, sorption enthalpies, and diffusion coefficients of the two gases were determined.

Hydration studies of protein films (49). Water sorption isotherms, sorption enthalpies and diffusion coefficients were determined in thin films of both lysozyme and myoglobin.

The final Drexel graduate student to work on the QCM/HCC was Jun Tian. His Ph.D. thesis (50) contains the following applications:

Solvent vapor sorption by C₆₀ and C₆₀-piperazine films (51). Solvents used were water, 1,3 dichlorobenzene, carbon tetrachloride, methylene chloride, and benzene.

Water vapor sorption by pharmaceutical film coatings.

All three of these Ph.D. theses contain sections on the theory of operation of each component of the mass/heat flow sensor and experimental details such as block diagrams of the apparatus, sample preparation, data acquisition and control, calibration, and data analysis.

Biological applications

Dr. Galit Zilberman joined the research group at Drexel in November 2003. Her previous research at Tel Aviv University with QCM measurements at the solution/electrode interface (52) led us to explore the use of the QCM/HCC as a detector of protein-ligand interactions in aqueous solution (53), and as a detector of the growth of E Coli bacteria on thin film of nutrient medium deposited on the QCM (54).

The Masscal G1

In 2001, the author founded Masscal Corporation to commercialize the developments we had achieved in the laboratory at Drexel. The goal was to make this technology more widely available to the research community. The first commercial product, the Masscal™ G1, was introduced at the 2004 PITTCON. Its capabilities are well described in company literature, but here are some key specifications:

- Operating temperature from ambient to 100°C; temperature stability of ± 0.005 °C without the use of water baths. Ambient operating pressure.

- 10 ng sensitivity in mass measurement and 500 nW sensitivity in heat flow measurements with a time constant of 12 seconds (5 datapoints per minute)

- Continuous measurement of motional resistance of the coated quartz crystal, a quantity that can be used to determine the loss compliance of the coating.

- Provisions for the software control of external mass flow controllers to provide a versatile program of gas composition vs time in the sample chamber.

- Provision for collection of an external analog signal from a detector such as a relative humidity meter.

With funding from the Department of Energy’s SBIR program at Masscal, it was shown that the G1 could measure both the catalyzed rate of reaction and the mass build-up or depletion at a platinum or palladium surface when H₂ reacted with C₂H₄ (55).

Recent applications

The following applications of the QCM/HCC technique have been performed with the Masscal G1:

- Moisture sorption, transport, and hydrolytic degradation in polylactide films (56).

- Monitoring the drying and curing of an alkyd spray enamel (57).

- Gravimetric analysis of the non-volatile residue from an evaporated droplet, using the quartz crystal microbalance/heat conduction calorimeter (58).

Final Draft of “The Quartz Crystal Microbalance”, by Allan Smith, a chapter for Volume 5 of the **Handbook of Thermal Analysis and Calorimetry**, Elsevier

Sorption Isotherms, Sorption Enthalpies, Diffusion Coefficients and Permeabilities of Water in a Multilayer PEO/PAA Polymer Film using the Quartz Crystal Microbalance/Heat Conduction Calorimeter (59)

Energetics of a self-assembled monolayer of butylthiol on gold (in progress).

Sorption isotherms, sorption enthalpies, and viscoelastic damping produced by water absorption in pharmaceutical film coat materials (in progress).

Conclusion

Since many of the materials now being made and characterized in nanotechnology are ultrathin films of thickness < 1 micrometer, their thermodynamic and kinetic properties must be measured with methods more sensitive than the normally employed calorimetric techniques. We believe that the QCM/HCC is ideally suited for such studies, as the references in this article will attest. One key question of importance to nanotechnology is the long-term stability of materials with nanostructures. With atomic compositions varying systematically at the nanometer scale, these nanomaterials contain many more contacts between different functional groups and molecular subunits than do typical materials. How stable are these nanomaterials to moisture, to oxidative degradation? Answers to these questions will determine the ultimate usefulness of the many extraordinary new nanomaterials being synthesized today. Knowledge of the thermodynamics and kinetics of these materials is thus essential in assessing their performance.

Commercially available QCM systems

Akubio

<http://www.akubio.com/default.aspx>

Institute of Physical Chemistry, Polish Academy of Sciences

<http://ichf.edu.pl/offers/instrum/quartz.htm>

KSV

<http://www.ksvltd.com/content/index/dissipativeqcm>

Masscal

<http://www.masscal.com/>

Maxtek

<http://www.maxtekinc.com>

Final Draft of “The Quartz Crystal Microbalance”, by Allan Smith, a chapter for Volume 5 of the **Handbook of Thermal Analysis and Calorimetry**, Elsevier

Princeton Applied Research

<http://www.princetonappliedresearch.com/Products/Polarographic.cfm>

Q-Sense

<http://www.q-sense.com/>

Stanford Research Systems

<http://www.thinksrs.com/products/QCM200.htm>

Resonant Probes

<http://www.resonant-probes.de/index.htm>

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