PNNL-11882
UC-900

Final Report

CRADA with Northwest Instrumentation Systems, Inc. and Pacific Northwest National Laboratory (PNL-070): Dual Quartz Crystal Microbalance Commercialization

G.C. Dunham

April 1998

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Prepared for U.S. Department of Energy
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Pacific Northwest National Laboratory
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by Battelle

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Dual Quartz Crystal Microbalance CRADA Project

Purpose/Objective

This CRADA continued the commercialization of the dual quartz crystal microbalance (DQCM) begun in 1994 as a Staff Exchange (CRADA PNL-070). The completion of PNL-070 resulted in NISI possessing the technology for the DQCM chemical sensor *precursor,* that is, the device that will sensitively detect mass changes and which becomes a chemical sensor with the addition of a chemically sensitive film. NISI also owned prototype DQCM probes and accompanying data measuring organics in water to show DOE/Westinghouse/Bechtel. The follow-on CRADA supported the instrumentation and manufacturing development at a low level but primarily provided funds for developing the active films. As a result of this research, NISI received PNNL specifications for particular polymer films, and characterizations of the chemical response of DQCM probes prepared with these films.

NISI collaborated with Bechtel and other interested parties in identifying specific DQCM applications at Hanford. NISI installed and operated prototype probes for Bechtel. NISI also identified industrial applications for the DQCM and attempted to develop industrial customers.

Summary of Activities Performed

TASK	COMPLETED?
Characterize chemically selective films	Yes
Optimize selective film deposition on DQCM	Yes
Demonstrate DQCM detection of selected chemicals	Yes
Complete optimization of manufacturing process	No
Complete optimization of electronics	No
Identify analytes, environments, interferents	Yes
Identify industrial applications	Yes
Install and operate DQCM's at Hanford	Yes
Market DQCM's for limited applications	No
Market DQCM's for general applications	No
Produce a multiple DQCM analyzer using chemometrics for broad spectrum quantitative analysis	No

The PNNL work resulted in technical presentations at Electrochemical Society meetings in Miami in October 1994 and San Antonio in October 1996, and a paper published in *Analytical Chemistry* in January 1995. An illustration of the DQCM technology developed and tested in the project is provided in Appendix A. A reprint of the paper published in Analytical Chemistry is provide in Appendix B.

Significant Accomplishments

The project culminated in a demonstration test December 11, 1995 at the soil vapor scrubbing site at Hanford 200W area. PNNL/NISI prepared a self-contained analyzer that was installed in an equipment trailer at the pump station. Grab samples from the vapor stream were brought to the DQCM analyzer and to an IR analyzer used by Bechtel to regularly monitor operations. The contaminant was carbon tetrachloride at about 100 ppm. Test results between the two methods were comparable within 20%.

Significant Problems

NISI failed to design and construct circuitry stable enough for the resolution required for low level DQCM measurements. Additionally, upon satisfying the Bechtel milestone of demonstrating DQCM at 200W, NISI received no further funding for this development. Finally, no commercial applications materialized.

DOE/Laboratory Benefits Realized

PNNL achieved the development of a chemical sensing device that provides a prototype for a potential commercial instrument based on the technology. However, although the 200W demonstration was successful, Bechtel declined to continue support for the development of DQCM technology. Thus, the long-term benefit to PNNL and DOE was less than we had hoped.

Industry Benefits Realized

NISI obtained a substantial amount of information and experimental data on the DQCM technology. However, since the project terminated before commercial viability was achieved, the long-term benefits to NISI were also less than originally planned.

Recommended Follow-on Work

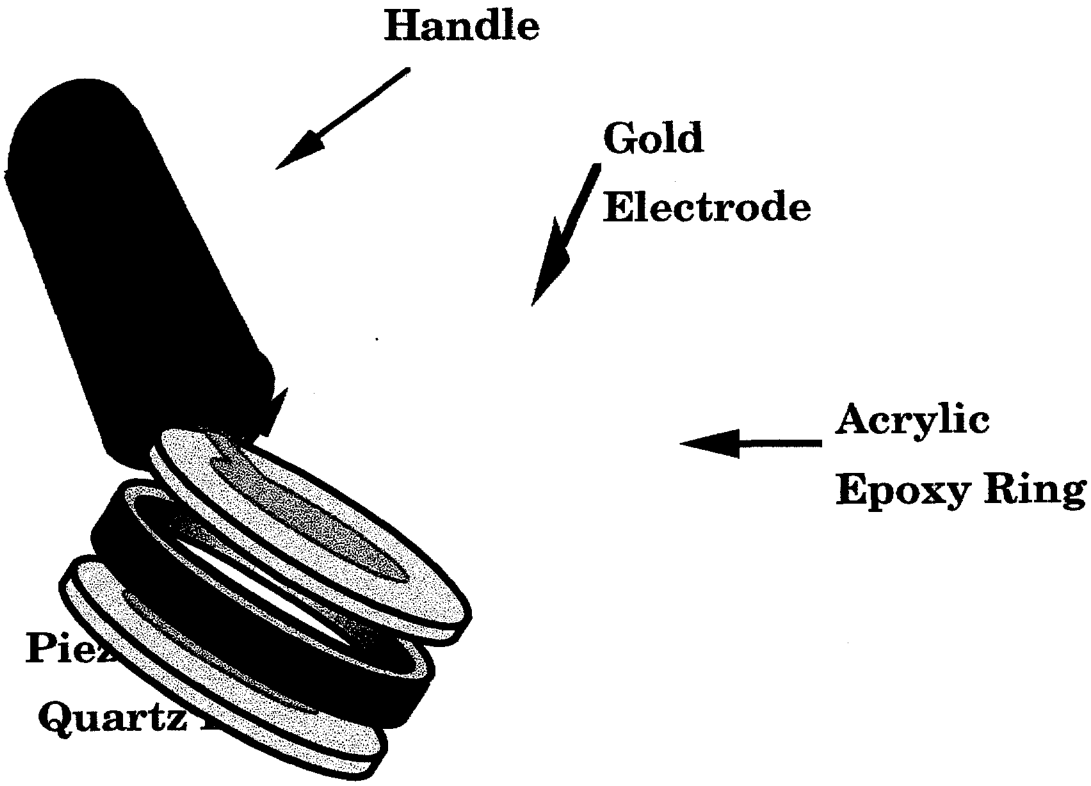
We found this cooperation difficult to manage, primarily because the DQCM technology was too immature for commercialization. Follow-on may be proposed in the future when the PNNL development is adequate.

Potential Benefits from Pursuing Follow-on Work

The initial claims for this technology remain valid: economical, real-time chemical sensing of air and water can be achieved.

APPENDIX A

DQCM SENSOR


Handle
Gold
Electrode
Acrylic
Epoxy Ring
Piez
Quartz

APPENDIX B

Reprint from Analytical Chemistry

Dual Quartz Crystal Microbalance

Reprinted from Analytical Chemistry , 1995, *34*.

Dual Quartz Crystal Microbalance

Glen C. Dunham, Nicholas H. Benson, Danuta Petelenz,[†] and Jiří Janata*

Environmental Molecular Sciences Laboratory, Pacific Northwest Laboratory, Richland, Washington 99352

Construction and performance of a dual quartz crystal microbalance is described. The final probe has a dipstick configuration that is particularly suitable for sensing and monitoring applications in viscous and/or conducting liquids. The differential (heterodyned) frequency measurement substantially eliminates the deleterious effects of viscosity, temperature, and conductivity. The corresponding performance coefficients are temperature $df/dT = 1.5$ Hz/°C, viscosity $df/d\eta_L = 103$ Hz/cP, and conductivity $df/dM = 108$ Hz/M, where conductivity is expressed in terms of molarity of sodium chloride. As an example, the etching of a 2000-Å-thick layer of aluminum has been monitored as a function of time.

We have developed a dual quartz crystal microbalance probe operable in gases and conducting or viscous liquids with no need for correction of effects due to conductivity, viscosity, or temperature changes over reasonable ranges of those parameters. The simultaneous sensitivity to mass change and insensitivity to environmental effects stimulates interest in this probe as a generic precursor of a chemical sensor. Application of thin selective layers with different chemical sensitivities to the two exposed faces creates a chemical sensor equally capable of functioning in air or liquid. Other possible applications include mass monitoring during electrochemical deposition, electroless plating and etching processes, or biological deposition and changes in elasticity of the added layer.

Applying thickness shear mode (TSM) piezoelectric quartz crystals, also known as quartz crystal microbalances (QCMs), to measurements in a liquid medium is no longer unique. Since the first reports by Nomura and Iijima[1] in 1981, QCMs have been used to measure deposition and dissolution in solution,[2] electrochemical oxidation and reduction,[3] biological cell growth,[4] and viscosity of liquids.[5] An obvious problem, however, is the sensitivity of the QCM to all these variables, since its resonant oscillation frequency in a liquid depends on three general factors: properties of the quartz, properties of a rigidly attached film, and properties of the liquid. Previous authors have compensated for undesirable effects by applying theoretical or empirical corrections, thereby largely isolating the effect of interest. This approach may yield unsatisfactory results if the real systems depart from theoretical predictions. An alternative approach is the development of an inherently self-compensating QCM able to produce a frequency change directly proportional to the measured phenomenon.

A thickness shear mode piezoelectric crystal wafer with opposing metal electrodes on its two faces can sustain a standing wave by the converse piezoelectric effect. Excitation of one electrode to ~1 V at 10-MHz frequency (for a crystal 170 μm thick) while holding the other electrode at ground creates the shear wave in the crystal with the physical displacement parallel to the planar surface and with antinodes at the surfaces. Thus, the frequency of the standing wave is related to crystal thickness by

$$f_0 = v/2t_q \qquad v = (\mu_q/\varrho_q)^{1/2} \tag{1}$$

where v is the velocity of sound in quartz, t_q is the wafer thickness, the quartz shear modulus is $\mu_q = 2.95 \times 10^{11}$ g cm^{-1} s^{-2}, and the quartz density is $\varrho_q = 2.65$ g cm^{-3}. When a rigid layer is added to the quartz surface, the additional thickness increases the wavelength, thereby reducing the standing wave frequency. Sauerbrey[6] expressed this in terms of the mass of the uniform rigidly attached film

$$\Delta f = -2f_0^2 \Delta m/(\mu_q \varrho_q)^{1/2} \tag{2}$$

where Δm is the change in mass per square centimeter and the negative sign indicates that frequency decreases with added mass. Substituting for the constants yields

$$\Delta f = (-2.26 \times 10^6 \text{ cm}^2/\text{Hz g}) f_0^2 \Delta m \tag{3}$$

These relationships assume operation of the QCM in air at standard conditions or in vacuum. In fact, the most common usage is as a thickness monitor for vacuum deposition systems. Immersing in a more viscous medium adds a viscosity term

$$\Delta f = C f_0^2 \Delta m + C f_0^{3/2} (\Delta \eta_L \Delta \varrho_L)^{1/2} \tag{4}$$
$$C = -2.26 \times 10^{-6} \text{ cm}^2/\text{Hz g}$$

which is strongly temperature dependent due to the temperature dependence of the liquid viscosity and density, η_L and ϱ_L, respectively. As a further complication, acoustoelectric effects or ionic conductivity effects become possible in polarizable or conductive liquids.[7] Finally, in any medium, film modulus changes could affect the frequency of oscillation.

[†] Present address: Hedco Microfabrication Facility, University of Utah, Salt Lake City, UT 84112.

(1) Nomura, T.; Iijima, M. *Anal. Chim. Acta* **1981**, *131*, 237.
(2) Bruckenstein, S.; Swathirajan, S. *Electrochim. Acta* **1985**, *30*, 851.
(3) Kaufman, J.; Kanazawa, K.; Street, G. *Phys. Rev. Lett.* **1984**, *53*, 2461.
(4) Redepenning, J.; Schlesinger, T.; Mechalke, E.; Puleo, D.; Bizios, R. *Anal. Chem.* **1993**, *65*, 3378.
(5) Kanazawa, K.; Gordon, J. *Anal. Chem.* **1985**, *57*, 1771.
(6) Sauerbrey, G. *Z. Phys.* **1959**, *155*, 206.
(7) Grate, J.; Martin, S.; White, R. *Anal. Chem.* **1993**, *65*, 940, 987.

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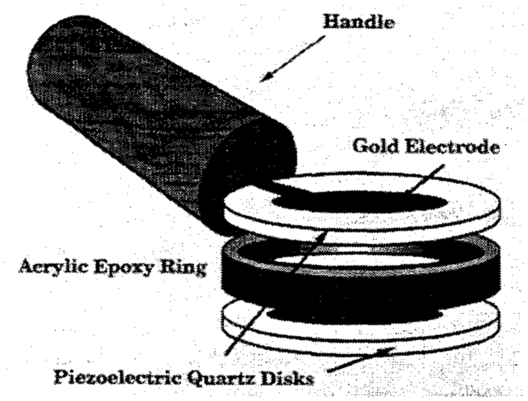

Figure 1. Exploded view of a DQCM. The crystals are 14mm in diameter with 9.9-mm-diameter outer and 5.1-mm-diameter inner electrodes. The spacer ring is 0.4−0.8-mm-thick acrylic epoxy. The insulated wires to the electrodes are threaded through the handle.

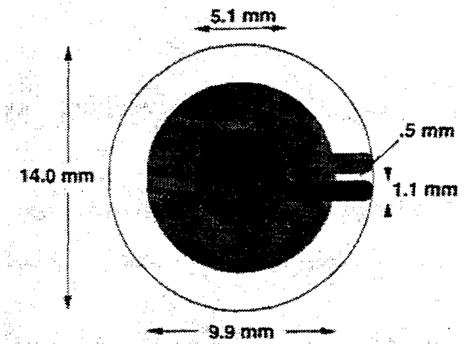

Figure 2. Electrode pattern for both crystals in a DQCM. The inner electrode is smaller in order to minimize edge effects in electrochemical processes.

The Dual Quartz Crystal Microbalance Probe. We have assembled and tested dual quartz crystal microbalance (DQCM) probes as depicted in Figure 1. Two QCM wafers are laminated together to form an air-gap sandwich. The spacer ring is DuPont Vacrel, a photosensitive acrylic epoxy film intended for circuit board patterning, applied 0.4−0.8 mm thick. The crystals were supplied AT-cut with the specified electrode configuration and polish (nominally 0.1 μm). Slightly different frequencies were chosen for the two crystals in each probe to minimize internal interferences. After wiring and testing, the crystal sandwich is epoxied onto a glass tube which serves as a handle.

A custom broad-band oscillator circuit was designed and constructed to drive the crystals. Each channel is entirely independent, with its oscillation frequency determined by the crystal's series resonance. The outer electrodes, those exposed to the sample, are on the ground side of the circuit. The frequencies of the two oscillators are heterodyned to extract the difference between the two frequencies. This frequency, typically $\sim$10 000 Hz, is exported to a frequency counter. Use of the heterodyned frequency is important for two reasons. First, since both crystals are exposed to the same environment, this frequency is substantially immune to interferences such as changing temperature. Second, heterodyning reduces the magnitude of the signal frequency by a factor of 1000, which reduces the sampling time for a given resolution by a similar factor.

The purpose of this work is the development of a DQCM probe that has a dipstick configuration and is usable in various environments without correcting for uncontrolled environmental effects. Combining the probe structure and driver circuitry described below achieves this goal. The efficacy of this approach will be demonstrated by showing that the two crystals do not physically interfere with each other, as well as by presenting probe performance as a function of liquid temperature, viscosity, and conductivity. Responsiveness to actual mass change in a liquid is shown by an experiment in which aluminum was etched from the probe. Finally, because we have interest in monitoring mass changes during electrochemical deposition and oxidation/reduction reactions, the DQCM probe is demonstrated as the working electrode of an electrochemical cell.

Dual QCM configurations have been reported recently by other researchers.[8] We share with them the concept of using the heterodyned frequency as the measured parameter. The major difference in our approach is the dipstick probe design. With chemical sensing as a goal, our intent is to make the probe independent of any particular experimental arrangement. It may be operated in laboratory environments such as an electrochemical cell, industrial applications such as tanks or pipelines, or environmental gas or liquid sensing such as in a cone penetrometer for soil testing. This adaptability results from our design, which combines configurational advantages with electronic autonormalization to a reference crystal exposed to the same environment as the sensor crystal. One significant configurational feature is the isolation of the excited electrode on each crystal from the solution by placing it in the air gap of the probe. By preventing electrical leakage, the probe's operating range is extended into very conductive solutions. Another feature is our choice of an outer (ground) electrode larger than the inner (excited) electrode. This prevents acoustoelectric coupling to the solution which might otherwise cause frequency changes with changing solution conductivity. The consequence of this structure, however, is that the piezoelectrically sampled area is smaller than the total area of the outer electrode and nonuniform mass changes (very possible in electrochemical deposition where diffusion effects might cause a thicker perimeter band) may be measured incorrectly.

EXPERIMENTAL APPROACH

The crystals supplied by ICM (Oklahoma City, OK) oscillate at the fundamental resonant frequencies of 10.004 and 9.996 MHz, respectively. The electrode pattern is shown in Figure 2. Metalization is 135-Å chromium plus $\sim$1400-Å gold. The quartz is polished to nominally 0.1-μm roughness. Polishing and metalization was performed by ICM, but the sandwich structure is fabricated at PNL by successively laminating five rings of 0.003-in. Vacrel (DuPont photosensitive acrylic epoxy) to one side of each crystal and then laminating the crystals together. A Western Magnum XRL 120A circuit board laminator was used, at 111 °C, 6 f min^{-1}, and 32 psi. After wiring and testing, the sandwich is epoxied to a glass tube, which serves as a handle and a protective channel for the wires. For applications where the gold surface must be clean, such as electrochemical depositions, the surface layer of Cr_2O_3 (resulting from chromium diffusing through the gold) can be removed by electrochemical cleaning in phosphate-buffered potassium chloride.[9]

The two oscillator circuits and the countercircuit were built from standard parts. Each crystal is the resonator in a Colpitts

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(8) Bruckenstein, S.; Michalski, M.; Fensore, A.; Zhufen, L.; Hillman, A. R. *Anal. Chem.* **1994,** *66,* 1847.

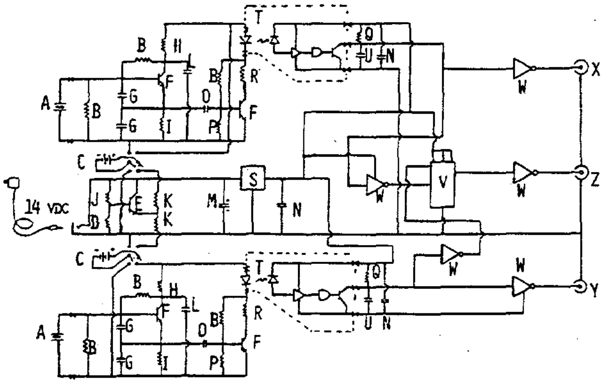

Figure 3. Circuit diagram for the Colpitts oscillator. A-QCM crystals; B, 100 kΩ; C, 9-V battery; D, 68 kΩ; E, D40K1; F, 2N3904; G, 160 pF; H, 220 Ω; I, 385 Ω; J, 60 kΩ; K, 150 Ω; L, 100 μF; M, 1 μF; N, 0.1 μF; O, 47 pF; P, 22 kΩ; Q, 1 kΩ; R, 915 Ω; S, 78M05; T, 6N137; U, 15 pF; V, 74LS74; W, 74LS14; X, channel 1; Y, channel 2; Z, channel 1 minus channel 2.

transistor oscillator, with one electrode held at circuit ground. The two resonant frequencies are transmitted through optical isolators to a digital mixer circuit which outputs the heterodyned frequency. To maximize isolation between the two resonators, each is separately battery powered. The circuit diagram is presented in Figure 3.

Frequency measurements at 0.1-s gate times were taken from three Hewlett Packard (HP) 53131A universal counters by a GPIB connection to an HP 382 computer running VEETEST, HP's graphical virtual instrument program. The frequency counters can achieve resolution of 0.1 Hz on a 10-MHz signal with a 0.1-s gate. By measuring the heterodyne frequency, this same resolution, 0.1 Hz, is acquired with a gate less than 0.1 ms. Thus, a 1000-Hz sample rate is possible (although the maximum GPIB transmission rate is 200 Hz). An additional advantage of measuring the heterodyned frequency, which ranges from 4000 to 100 000 Hz, is that unsophisticated and economical single-chip or plug-in card counters may be used to measure these low frequencies without compromising performance. Temperature and conductivity were acquired over GPIB via an HP 34401A multimeter, with the appropriate sensor-to-voltage interface on the multimeter. Impedance measurements were performed with an HP 4194A impedance analyzer.

The electrochemical study utilized a Princeton Applied Research 273 potentiostat/galvanostat operating in the galvanostatic mode. All chemicals were ACS reagent grade, mixed into semiconductor quality 18-MΩ deionized water. The counterelectrode was platinum.

RESULTS

Cross-talk between the Two Crystals. One concern with the DQCM structure was that the crystals might interfere with each other physically by transmitting vibrations through the mounting material or electrically due to the proximity of the leads and circuit components. To test this possibility we connected one crystal at a time to the impedance analyzer, leaving the other crystal connected to its driver, and with all three circuits (the two oscillators plus the heterodyne counter) operational. This experiment was performed with all crystal/driver combinations and with the probe operating in air and in water. A representative impedance plot for air is shown in Figure 4. The strong series resonance at 10.011 250 MHz is the oscillation frequency for the test crystal. A weak local resonance appears at 9.989 875 MHz when the second crystal is powered and disappears when the second driver is switched off. This is the resonant frequency of the second crystal. The impedance of this potentially interfering peak reaches down to only 700 Ω, while the impedance of the primary resonance peak is 50 Ω. Therefore, there is no expectation that operating the second crystal will shift the resonance of the first crystal. Similar results were obtained in water.

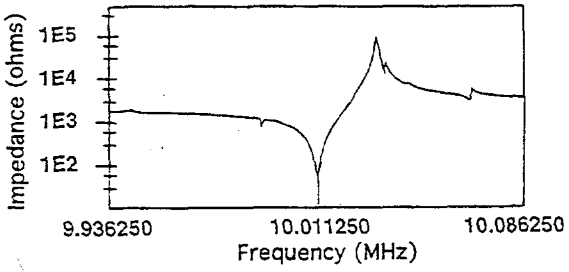

Figure 4. Impedance spectrum of the reference crystal (higher frequency of the pair) while the sensor crystal is also oscillating. The reference resonance is at 10.011 250 MHz, and the sensor resonance appears at 9.989 875 MHz. This impedance measurement was performed in air.

Small-signal high-frequency electronic measurements are often vulnerable to interference from environmental electrical noise and the proximity of charged or grounded surfaces. A Faraday cage can be used to isolate the sensitive device from these influences. We have observed no such interference with the DQCM probe, and its signal is unchanged when a Faraday cage is placed around the probe.

Immunity to Liquid Temperature Changes. The temperature dependence of the AT crystals themselves is small, but temperature effects from changing fluid properties can be large. The viscosity of water is related to temperature by[10]

$$\eta/\eta_{20} \approx 10^{[1.3(20\text{-}T)-0.001(T\text{-}20)2/T+105]} \qquad (5)$$

where η_{20} is the viscosity at 20 °C and T is temperature in degrees celsius. Obviously, by eq 4, a similar exponential dependence applies to a QCM oscillating in water. Bruckenstein reported a dependence of 30 Hz/°C.[8]

A DQCM probe was immersed in 60 °C water, and the individual crystal frequencies along with the heterodyned frequency were recorded as the water was cooled to 7 °C. Warm-to-cool ramping was chosen to prevent bubble formation. Deionized 18-MΩ (at the tap) water was used. Frequencies were measured as described above. Results are shown in Figure 5. The overall change for each crystal was greater than 200 Hz; the heterodyned frequency changed by 60 Hz, or 1.1 Hz/°C.

Immunity to Viscosity Changes. Referring again to eq 4, the change in resonant frequency with respect to change in viscosity is predicted to have a square-root dependence. For a 9-MHz crystal, Yang and Thompson[11] showed a frequency change of 1400 Hz for a change of $(\eta_L \varrho_L)^{1/2}$ from 1.6 to 2.4. Because of

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(9) Guiseppi-Elie, A.; Pradhan, S. R.; Wilson, A. M.; Allara, D. L.; Zhang, P.; Collins, R. W.; Kim, Y.-T. *Chem. Mater.* **1993**, *5*, 1474.

(10) *Handbook of Chemistry and Physics*, 63rd ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1980; p F40.

(11) Yang, M.; Thompson, M. *Langmuir* **1993**, *9*, 1990.

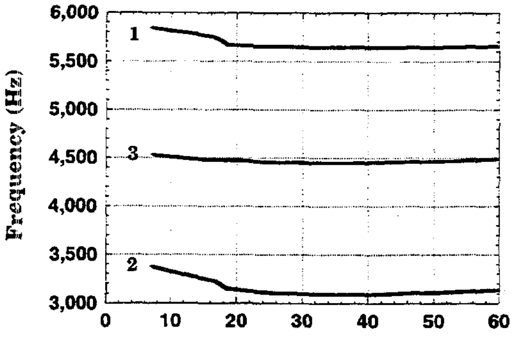

Figure 5. DQCM performance vs water temperature. The two individual frequencies have been scaled by the subtraction of suitable constants to allow the display of all three curves on one plot: (1) reference (higher) frequency minus 9.989 MHz; (2) sensor frequency minus 9.996 MHz; (3) heterodyned frequency.

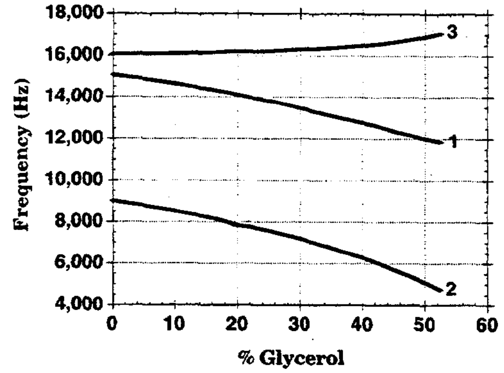

Figure 6. DQCM performance as viscosity is varied by adding glycerol to water. As before, constants have been subtracted from the two individual frequencies to allow presentation on the same plot as the heterodyned frequency: (1) reference frequency minus 10.000 MHz; (2) sensor frequency minus 9.990 MHz; (3) heterodyned frequency.

the $f_0^{3/2}$ term in eq 4, our 10-MHz crystals are expected to exhibit slightly greater viscosity dependence than these 9-MHz crystals.

A DQCM probe was operated in 25 °C water as glycerol was added to increase viscosity. All three frequencies were recorded and are presented in Figure 6. As expected, the individual crystals respond similarly to increasing viscosity by a reduction in resonant frequency of ~4000 Hz; the heterodyned frequency falls by 1000 Hz with the addition of glycerol to 52% by volume. Over the range given above, $1.6 \leq (\eta_L \varrho_L)^{1/2} \leq 2.4$, the individual frequencies changed by ~1200 Hz and the heterodyned frequency changed by 292 Hz.

Immunity to Solution Conductivity Changes. Two problems arise when a standard QCM is immersed in a conducting solution. First, ionic conductivity may shunt the electrodes, precluding piezoelectric excitation. Second, acoustoelectric effects may couple the excitation field to polarizable molecules or mobile ions in the solution, causing spurious frequency changes related to conductivity. DQCM probes rely on configuration to minimize these effects. The air-gap structure and the careful electrical isolation between the two oscillators and their circuits minimize shunting or cross-talk through the fluid. The electrode configuration, with the outer electrode grounded, larger area than the inner electrode on each crystal, and entirely overlapping the inner electrode, minimizes acoustoelectric coupling.

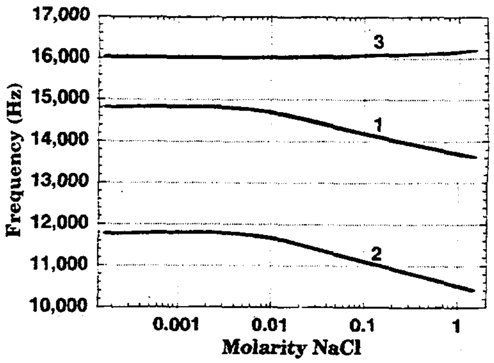

Figure 7. DQCM performance in an electrolyte solution as conductivity is increased by adding sodium chloride to water: (1) reference frequency minus 10.000 MHz; (2) sensor frequency minus 9.987 MHz; (3) heterodyned frequency.

Table 1. Probe Sensitivities

	sensitivity		
probe	temperature (Hz/°C)	viscosity (Hz/cP)	conductivity (Hz/M)
1	1.1	62	79
2	3.1		68
3	2.5	132	88
4	0.3		80
5	0.6	115	263
6	1.3		68

To characterize DQCM response to changing fluid conductivity, a probe was operated in 25 °C water, beginning with pure deionized water, as a 3.4 M NaCl solution was added to the stirred beaker. As shown in Figure 7, the individual resonant frequencies fell ~1500 Hz while the heterodyned frequency increased by only 158 Hz, over the concentration range of 0–1.4 M NaCl. The large decrease of the individual resonant frequencies in concentrated NaCl solution is probably due to the mass added by adsorption of chloride ions at the surface of the gold electrodes.

Summary of Insensitivity to Interfering Effects. The preceding experiments were conducted with six DQCM probes. The results presented in the figures were chosen as the most representative both in magnitude and in curve shape. Table 1 lists all the results. The values listed in the conclusion are averages of these table entries.

Response to Mass Change during Etching. To demonstrate mass sensitivity in liquid, an etching experiment was performed in which the DQCM monitored metal dissolution in an acidic solution. One of the electrodes of a DQCM was vacuum coated with 2000 Å of aluminum, with the reference face remaining uncoated gold. Figure 8 shows the three probe frequencies, of each crystal separately (refer to left ordinate), and the heterodyned frequency converted to aluminum thickness using eq 6 (refer to right ordinate). The first point was recorded with the probe operating in air with the 2000-Å aluminum coating. Next it was immersed in water, causing large changes (1200 Hz) in the individual frequencies but only a 200-Hz change in the heterodyned frequency. The water was then exchanged for 0.24 M hydrochloric acid, and aluminum etching commenced as indicated by the sloping line on the plot. After 20 min the acid was exchanged for pure water and etching ceased. In fact, the increase of the heterodyned frequency suggests a mass increase at this point due to the growth of a hydrated oxide, ~40 Å thick. Return

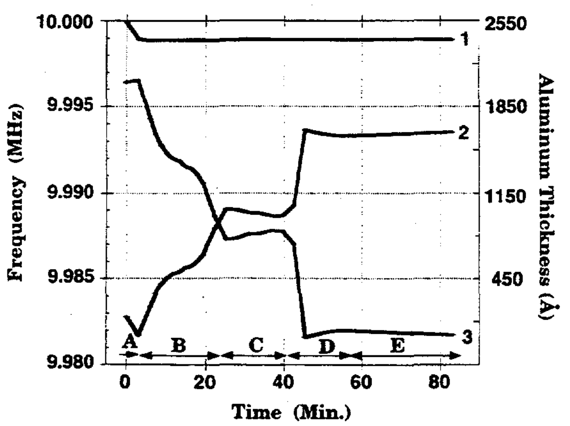

Figure 8. DQCM response during aluminum etching in hydrochloric acid at room temperature. This plot is divided into zones according to the process occurring at the probe. The starting condition was a DQCM probe with 2000-Å aluminum vacuum deposited on the sensor crystal: (1) reference frequency; (2) sensor frequency (both read at left ordinate); (3) aluminum thickness obtained from the heterodyned frequency (right ordinate). Zone A, frequency change with immersion from air to water; zone B, etching in 0.24 M hydrochloric acid; zone C, immersion in water; zone D, etching in 0.24 M hydrochloric acid; zone E, etching in 0.46 M hydrochloric acid.

to the acid solution quickly removed most of the remaining aluminum, and more concentrated hydrochloric acid continued the etching only marginally.

From eq 3, assuming rigid coupling of the additional film to the 10-MHz quartz crystal, a simple relationship between frequency and mass is obtained, normalized to 1 cm^2.

$$\Delta m \text{ (g)} = \Delta f \text{ (Hz)}/2.27 \times 10^8 \qquad (6)$$

The overall change in heterodyned frequency is 12 000 Hz, so the change in mass is 53 μm cm^{-2}. Dividing by the density of aluminum, the thickness etched is 1960 Å, consistent with the original thickness. In air before aluminum deposition the heterodyned frequency was 4267 Hz and after aluminum deposition and etching the frequency in air was 4510 Hz, indicating an unetched residue of 39 Å or a small difference in surface roughness. Thus the dry before-and-after results are consistent with the liquid results. Note that the Sauerbrey relationship cannot be directly applied to a crystal oscillating in solution because the liquid does not couple rigidly to the crystal. The environmental compensation inherent in the DQCM largely removes this difficulty, assuming the limiting case of perfectly matched crystals such that viscous effects on the two crystals are identical. In practice, using crystals from the same fabrication batch but not specifically matched, these effects are reduced by a factor of at least 5 relative to a single QCM. Also significant is the sensitivity demonstrated in this experiment. The change of the heterodyned frequency can be reproducibly measured to ±1 Hz, so the minimum detectable mass change is (conservatively) that associated with a 2-Hz frequency change, or 9 ng cm^{-2}. Assuming typical (for polymers) film densities of 1 g cm^{-3}, the minimum detectable thickness change is 0.9 Å, or less than one atomic monolayer.

Electrochemical DQCM. Monitoring electrochemical deposition, dissolution, or oxidation/reduction is an ideal application for the DQCM probe because these processes typically occur in fluids possessing various viscosities and conductivities, often at elevated temperature. Sometimes these properties may even change during an experiment. However, to utilize the DQCM requires wiring one electrode of one crystal to the potentiostat as the working electrode, through which current must flow, an additional challenge to the oscillator circuit. Our oscillator accepts this configuration. Because no direct current path is provided through the electrodes on the other crystal, no deposition occurs on that crystal. We galvanostatically deposited silver from a 0.044 M silver nitrate solution at a current density of 0.2 mA cm^{-2}, with a platinum counterelectrode, at 25 °C. VEETEST's internal timing was used to integrate the current to obtain the accumulated charge. The calculations needed to express frequency change as a mass change were also programmed in VEETEST, yielding a rectilinear plot with a slope of 0.91 corresponding to deposition of 0.91 atoms of silver per electron. Others have reported unity efficiency for this deposition.[12,13] Microscopic inspection of the electrode after deposition suggests the reason for the observed deviation from Faraday's law: there is a slightly enhanced deposition rate around the perimeter of the electrode, outside the piezoelectrically active (mass sensitive) area. Thus, with this electrode configuration, quantitative electrochemical processing requires an independent assessment of film uniformity.

CONCLUSIONS

We have constructed and characterized a number of DQCM probes which, when driven by our heterodyning oscillator circuitry, are stable and largely self-compensating for changing environments. In aqueous solutions these DQCM probes are typified by the following coefficients:

temperature:

$$df/dT = 1.5 \text{ Hz/°C}$$

viscosity:

$$df/d\eta_L = 103 \text{ Hz/cP}$$

conductivity:

$$df/dM = 108 \text{ Hz/M}$$

where conductivity is expressed as molarity of NaCl.

Furthermore, we have demonstrated that DQCM probes operating in conducting liquid maintain good sensitivity to added mass, according to the expected relationship

$$df/dm = 0.23 \text{ Hz cm}^2\text{/ng}$$

Therefore, while preserving the theoretical QCM sensitivity to mass changes, we have created a DQCM probe for use in liquids with less than 20% of the typical dependence on viscosity and conductivity and only 5% of the ordinary dependence on temperature. This significantly relaxes the degree of experimental control required in laboratory applications and makes possible sensor applications where control of the environment is impossible. The DQCM probe can easily be customized for a specific

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chemical-sensing task by applying a chemically selective film to one face. The major bonus is its dipstick configuration, which obviates the need for a special chamber or other experimental arrangement. The probe also operates reliably without electrical shielding from environmental electrical noise.

It should be explicitly stated that the fundamental premise of this work is that the mass-independent forces acting on the two exposed crystal faces can be made and kept nearly identical. In liquid this is the viscous loading, which depends partly on surface finish. No effort was made to match crystals with respect to polish as we had no way to measure roughness. Recently we acquired a profilometer that will allow such matching in future work and we believe further insensitivity to liquid influences will ensue. Also an issue in the etching and deposition experiments reported here is the possibility of changing surface roughness during the experiment, which could cause viscous effects to be misinterpreted as mass changes. This is an inherent limitation of our DQCM design, though the careful electrochemist may compensate by predepositing on the reference electrode a film very similar to the one intended for the sensor electrode.

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