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Traceability of frequency based mass measurements using a quartz crystal microbalance

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Abstract. The quartz crystal microbalance provides critical measurement capability for a wide variety of \textit{in situ} and \textit{in vivo} applications. However, it suffers from an underdeveloped connection to the SI (International System of Units). Here, a vacuum metal deposition system is used to deposit films of various masses on to the quartz crystals. The frequency change, which is proportional to the mass shift through the Sauerbrey equation, is compared to gravimetric based mass measurements using SI traceable mass artifacts.

1. Introduction
The commercial availability and low cost of the quartz crystal microbalance or QCM makes it highly attractive for a wide range of uses. Thin film deposition monitoring is a common industrial use, but functionalized QCM’s are also used for a variety of biomedical applications [1]. The QCM is easily integrated into microelectronics making it ideal for embedded applications [1] and has been deployed as a research tool for liquid based applications [2].

The use of the QCM for thin film monitoring makes it an intriguing tool for studying sorption effects on mass artifacts. While the coming redefinition of the unit of mass, the kilogram, will move from a primary realization based on a physical artifact to one based on a fixed value of Planck’s constant, the continued dissemination will rely on physical artifacts [3, 4]. Furthermore, the realization will be performed in vacuum and reliable methods to move from vacuum to air are required [5] because the sorption process that occurs when moving between environments can shift the mass of the artifact from its calibrated value to a new, unknown value. A large focus in recent years has been on understanding the sorption processes that occur when moving from vacuum to air [6]. Among these studies, the most common approach is to move artifacts, that nearly replicate the common masses used in mass metrology, back and forth between vacuum and air to characterize the sorption process.

In this paper, we consider a simple question regarding the QCM: how accurately does the change in frequency using the Sauerbrey equation [7] predict the actual change in mass? Most work in the past has focused on the areal mass (mass per unit area), often ignoring the difficulty of accurately measuring the area of deposition, and have not made comparisons to mass standards that are directly traceable to the SI. Here we measure the QCMs mass using a double-substitution technique with OIML E1-class mass standards that were calibrated at NIST. The mass is...
quantified before and after the deposition of gold films of varying thicknesses. Through this experiment we pursue two goals: first, we can validate the use of the QCM for accurate small mass measurements; second, we can study the QCM’s efficacy for quantifying the sorption process with the hope of focused studies on both vacuum to air transfer and long term mass tracking of artifacts.

2. Theory

The link between the change in resonance frequency of the QCM ($\Delta f$) and its change in mass ($\Delta m$) resulting from the addition of a thin film onto its surface was first attributed to Sauerbrey, in what is commonly known as the Sauerbrey equation [7]:

$$\Delta f = -\frac{2f_0^2}{A\sqrt{\rho_q\mu_q}}\Delta m.$$  

Here $f_0$ is the resonant frequency of the shear mode of a quartz crystal and the area of the deposition is noted as $A$. The constant $\rho_q$ and $\mu_q$ refer to the density and shear modulus of the quartz crystal; values for AT-cut crystals are $\rho_q = 2.648 \text{ g} \cdot \text{cm}^{-3}$ and $\mu_q = 2.947 \times 10^{11} \text{ g} \cdot \text{cm}^{-1} \cdot \text{s}^{-2}$ [8]. Fig. 1 shows images of a commercial QCM used in our experiments. The resonant mode of interest, as noted in Fig. 1c, is the thickness shear mode. The addition of mass leads to an effectively thicker crystal which lowers its frequency; see caption of Fig. 1.

The nominal starting frequency for the QCM’s used here was $(5.9868 \pm 0.0023)$ MHz. By collecting the other constants in the experiment and defining $S_T = \frac{2f_0^2}{\sqrt{\rho_q\mu_q}}$ as the sensitivity [9] we can simplify Eq. 1:

$$\Delta f = -S_T \frac{\Delta m}{A},$$  

where $S_T = 81.1 \text{ Hz} \cdot \text{cm}^2/\mu g$ is the expected sensitivity for the QMC’s used in our studies. The validity of Eq. 2 depends on the material that is deposited and the overall thickness of the deposition. Viscoelastic materials, for example, require a modified version of Eq. 2 [10]. For frequency shifts beyond 2 %, the $Z$-match technique is better suited [11]. Additionally, mounting assembly constraints and surface curvature can also lead to small deviations.

3. Experimental Procedure

The experimental setup is shown in Fig. 2a. The QCM is mounted, facing downward, in a vacuum chamber. Positioned approximately a half-meter below the QCM, but still within the

Figure 1. (A) Top and (B) bottom views of QCM. The film is deposited onto the top surface of image A. (C) The QCM resonates in the thickness shear mode. The resonant frequency for the quartz crystal is $f_q = v_q/2t_q$, where $v_q$ is the shear wave velocity along the thickness direction and $t_q$ is the thickness of the crystal. In general, the deposited film can be viewed as increasing $t_q' = t_q + t_d$, where $t_d$ is the thickness of the deposited film.
Figure 2. (A) Cartoon image of basic experimental apparatus. The QCM is placed at the top of a vacuum chamber. The top side (Fig. 1a) is directed downward. (B) Change in frequency as gold is added onto QCM surface. (C) The measured frequency shifts versus the measured mass changes divided by the measured area for several different QCM’s. The slope, $S_E$, is the experimental sensitivity and can be compared to $S_T$ from Sec. 2.

chamber, is a furnace. Just above the furnace is a manual shutter used to control when the deposition starts and stops. A frequency counter is used to monitor the frequency of the QCM before, during and after the deposition process. The gravimetric based mass comparisons are performed using a mass comparator with 0.1 µg resolution and a set of masses that are NIST traceable to the SI. A substitution based weighing scheme is used for the mass comparison of the QCM before and after deposition.

The following procedure is used to measure the mass and frequency change of all tested QCM’s:

(i) Weigh QCM by performing a mass comparison to masses that are NIST traceable.
(ii) Place QCM into vacuum chamber, but measure its resonant frequency at atmospheric conditions.
(iii) Evacuate the vacuum chamber and measure the frequency at low pressure $< 1 \times 10^{-6} \text{ Pa}$.
(iv) Deposit a thin layer of gold onto the QCM, while monitoring the QCM frequency.
(v) Vent the vacuum chamber to atmospheric pressure and measure the QCM resonant frequency again.
(vi) Repeat step 1 to determine the final mass and determine the gravimetric mass change.

This procedure provides a change in frequency over the course of the deposition, Fig. 2b, that can be associated with a change in mass from the deposition film through Eq. 2.

3.1. Area of Deposition

While the initial frequency is known, and the values of the crystal’s density and shear modulus can be found in the literature, accurately identifying the area of deposition is challenging. This is one reason most QCM mass readings are given in mass per unit area. Here we outline an approach to measure the deposition area through an optical imaging method. The nominal deposition area is 0.540 cm$^2$. To keep the contribution to the mass uncertainty below 0.25 %, the uncertainty in the area must be below 0.0015 cm$^2$. This means we need to resolve length differences of less than 10 microns in the diameter. Imaging a large area with small features requires utilizing the stitching capability of modern image software. A set of 9 images are taken
Figure 3. (a) Stitched microscope image (false color) of QCM. Because of back-lighting, the image of the underside electrode can be seen. The gold circle is the area of interest. (b) Result of extracting edge points from image and fitting an ellipse to the data. The fitted area is $A = (0.544 \pm 0.003) \text{ cm}^2$

and overlaid to produce the final image. The translation of the image between acquisitions is done using an X-Y stage with an optical encoder. This provides a reference for the overall size of the image. To verify the validity of this approach, a slide with calibrated shapes will be used in the future. Once the image is acquired, an algorithm is used to extract a set of points from around the image edge. The set of points can be fitted to an ellipse to determine the overall area. This procedure can be carried out on a set of QCM’s to acquire an average deposition area with a known uncertainty.

4. Conclusion
We have laid out a method for checking the accurate mass measurement capability of the QCM using the Sauerbrey equation by comparing to SI traceable masses. A comparison between the theoretical value of $S$ and the experimental value $S_E$ from Fig. 2c can be made [9]. Our preliminary percent difference, $(S_T - S_E)/S_T \times 100$, is 1.9 %. While the accuracy falls in line with other experiments that have attempted similar type measurements [9, 12], this result only represents our initial effort to quantify the absolute accuracy of the QCM when used for frequency based mass measurements. We are currently upgrading elements of the experiment, checking for possible sources of error, and taking additional measurements.

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