Small mass measurements for tuning fork-based atomic force microscope cantilever spring constant calibration

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Abstract

Cutting edge mass sensors are capable of discriminating mass changes as small as several dozens of atoms, however the smallest mass commercially available from NIST with a calibration traceable to the International System of Units (SI) is 0.5 mg. To bridge this gap, new metrological techniques are being developed. A mass change from the electrochemical dissolution of tungsten wire has been measured using a commercial microbalance, and applied to a dynamic calibration of the spring constant of a tuning fork oscillator designed for use in frequency modulated atomic force microscopy (FMAFM). The spring constant measured using the dynamic method agreed within experimental uncertainty with that determined using an instrumented indenter, however an improved model for the indenter's contact mechanics will be necessary to validate the assumptions used in the dynamic method to less than 10 %.

Introduction

Currently, the smallest mass artifact available that is traceable to the international system of units (SI) has a mass value of 0.5 mg. A wide variety of manufactured products require the use of materials with mass values less than 500 μg, however. For example, a 10 nm titanium adhesion layer deposited on a 100 mm wafer in the semiconductor industry has a mass of less than half a microgram. All traceable mass measurements are based on the International Prototype Kilogram (IPK) stored at the Bureau International des Poids et Mesures (BIPM), although the definition of the kilogram may soon change to one based on fundamental quantum invariants [1]. The IPK is compared against a set of replica kilograms stored at various National Measurement Institutes, including the U.S. National Institute of Standards and Technology (NIST). To obtain smaller traceable mass values, the kilogram must be subdivided [2], and this process introduces additional uncertainty in the mass value. The total relative expanded uncertainty of mass for a 1 mg artifact is approximately 3×10^{-4}, and by linear extrapolation as shown in Figure 1, for a 1 μg artifact this uncertainty could increase to 1×10^{-2}. In practice, the minimum mass of commercially available ultramicrobalances is approximately half a microgram, leading to possible uncertainties approaching 50 % for 1 μg mass measurements.

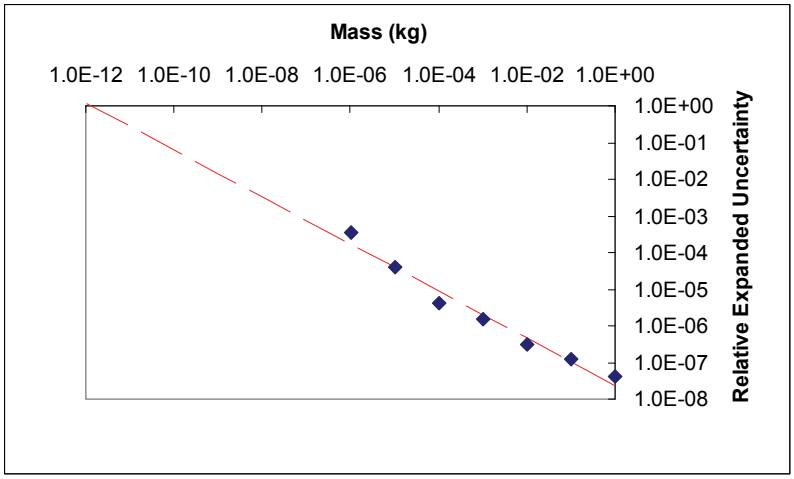

Figure 1. Projected uncertainties in small mass metrology. Points indicate current uncertainty at various mass levels, and the dashed line is a linear fit to these data points.

Two approaches can be followed to extend the range of traceable mass measurement. The first is to develop new traceability paths for mass. This type of work is already underway through the electronic kilogram [1] and small force [3,4] metrology programs at NIST. Another approach is to examine how currently available mass metrology techniques scale to smaller values of mass. This approach has been followed in previous studies [5] and shown the feasibility of mass metrology down to 100 micrograms with a combined standard uncertainty of 0.38 micrograms limited primarily by the statistical uncertainties associated with the balance used for measurement. This is still impractical for mass metrology in the microgram range. The development of a mass sensing method better suited to the small mass range could improve resolution, repeatability, and reproducibility in the mass measurement process, and decrease the uncertainty associated with small mass values.

Dynamic methods offer an attractive option for mass measurement, provided that mass can be correlated with a frequency measurement, since frequency measurements can be performed with very small uncertainty. For this study, a small quartz tuning fork resonator was chosen for examination as a mass sensor. These oscillators are inexpensive, readily available, and designed as frequency reference devices. They have also been used extensively in FMAFM, producing sub-atomic imaging resolution [6], and atomic-scale force measurements [7]. The quantitative measurement of forces and potentials at this scale requires the evaluation of the tuning fork spring constant, k. Although methods have been described for the measurement of k for the tuning fork systems [8-10], no method yet exists that provides SI-traceability. The following study provides a possible method for the calibration of this spring constant based on SI-traceable mass metrology similar to the Cleveland method [11]. This method is then compared against the result from an instrumented indentation method previously described, and the values from the two methods are shown to agree within experimental uncertainty.

Experimental Methods

Tuning fork sensors were obtained from Omicron [12] pre-mounted on a ceramic chip attached to a metal tripod base such that one tine of the tuning fork was firmly affixed to the ceramic. This creates a rectangular cantilever beam out of the other tine. A tungsten wire tip had been mounted at the end of the free tine with conductive epoxy, creating a conductive pathway from one leg of the tripod base to the tungsten wire tip(i.e., a “qPlus” sensor [13].)

The tuning fork was then placed on a piezo stack under an inspection microscope equipped with a Polytech laser Doppler vibrometer (LDV) as shown in Figure 2. The sensor was shaken by the piezo, which was attached to the oscillator output of an Agilent 35670A dynamic signal analyzer. The oscillator frequency was swept through the sensor's resonance at constant excitation voltage amplitude of 20 mV, and the output of the LDV simultaneously monitored. From this data, a frequency response function was generated by dividing the LDV RMS output amplitude by the oscillator amplitude and plotting against oscillator frequency. A natural frequency, $f_{n,}$ was extracted from this data using the following algorithm

$$f_n = f_{\max} - 2\xi \tag{1}$$

where f_{max} is the frequency corresponding to the maximum amplitude in the frequency response function, and ξ is the damping calculated using the resonance's full width at half maximum. This process was repeated five times, and the tuning fork was removed from and replaced onto the piezo stack between each trial to randomize systematic boundary effects at the contact between the piezo shaker and the tuning fork's tripod mount.

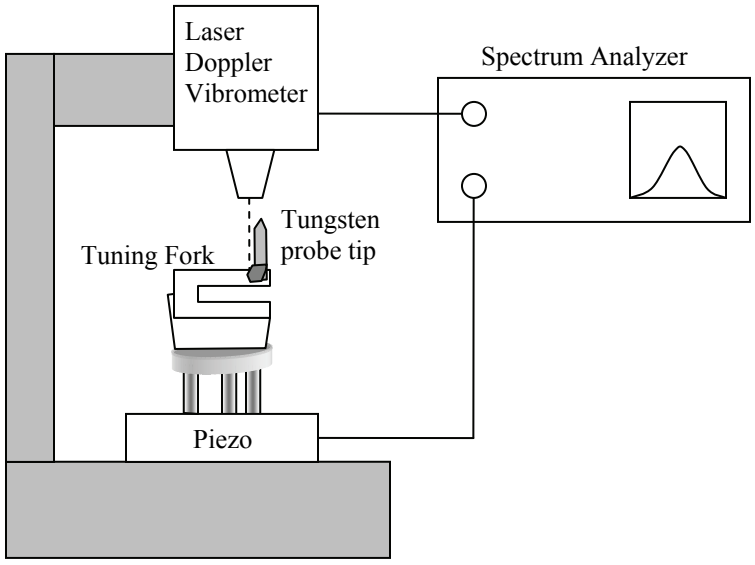

Figure 2. Experimental apparatus for determining sensor resonant frequency. The qPlus sensor is shaken by the piezo, which is excited using the sine wave oscillator from the dynamic signal analyzer. The motion of the tip is measured using the laser Doppler vibrometer, and used to construct a frequency response function.

Subsequently, the mass of the tuning fork, and its attached mount were determined using a Mettler XP2U microbalance. Prior to all measurements, an internal self-calibration procedure was used to calibrate the balance. The balance's mass measurements after this internal calibration were then checked against two NIST-calibrated wire masses bracketing the mass of the tuning fork and mount. A mass reading was taken before placing any objects on the balance pan, then the object to be tested was placed approximately at the center of the balance pan and another mass reading was taken. This process was repeated five times, and then a final mass reading was taken with no object on the balance pan. The mass of the object was then calculated calculating the difference between the balance reading when the object was on the pan and the average of the two baseline measurements before and after that reading. The average of these five mass measurements agreed with the mass value provided by NIST for the wire masses tested within the standard deviation of the five measurements described above, although the standard deviation of the five measurements was greater than the uncertainty of the NIST values.

After determining the mass and $f_{n,}$ of the tuning fork sensor, the tungsten wire tip was partially etched away using 1 mol/L potassium hydroxide solution by immersing the tip in the solution and applying a 0.5 V potential between the tip and a platinum mesh counter electrode for a period of 8 minutes. The mass and f_n of the tuning fork sensor were then remeasured, and the etch and weigh cycle repeated once more.

Instrumented indentation testing of the tuning fork stiffness was carried out in a Hysitron Triboscope indenter. A Berkovich indenter tip was positioned near the center of the tuning fork next to the area occupied by the conductive epoxy holding the tip onto the free end of the cantilevered tuning fork tine. The indenter tip was preloaded to 250 μN, then a series of 5 linear load and unload cycles from 265 μN to 350 μN were carried out while applied force and displacement of the indenter tip were monitored. These force and displacements can be used to provide a stiffness measurement, and the use of this apparatus to provide traceable spring constant measurements has been discussed elsewhere [14].

Results and Discussion

Previous work has shown that a microfabricated atomic force microscope (AFM) cantilever's spring constant can be determined by placing micromasses near the cantilever tip [12]. Resonant frequency of a mass-loaded cantilever in the case of a single degree of freedom harmonic oscillator scales with added mass according to

$$M = k\omega^{-2} - m^* \tag{2}$$

where M is the value of the mass change from the micromass positioned at the cantilever's free end, $\omega = 2\pi f_{n,}$, and m^* is the effective mass of the cantilever. Figure 3 shows a graph of the mass changes resulting from the tip etch process vs. the resonant circular frequency of the tuning fork. According to Equation 3, the slope of this line provides a value for the static spring constant of the cantilevered tuning fork tine. However, in contrast to the previous implementations of the technique, this approach eliminates the uncertainty associated with the position of the mass relative to the tip, since it is the mass of the tip itself that is changing. The method also contrasts with the destructive process of gluing spheres onto cantilever tips, in that the tip etch process enhances the tip's usefulness for scanning probe applications. Equation 2 is based upon a simplified representation of the cantilevered tuning fork, however.

In order to test the validity of the assumptions of the dynamic model mentioned above, the spring constant determined using Equation 3 can be compared to one determined using the quasi-static indentation method described previously. A portion of the instrumented indentation data is shown in Figure 4. The slope of the force displacement curve is the static spring constant of the cantilever at the point of contact with the indenter. The dynamic stiffness measurement described above defines stiffness at the point where the mass is varied. As a result, the stiffness from the instrumented indenter must be corrected to collocate it with the mass of the tip according to

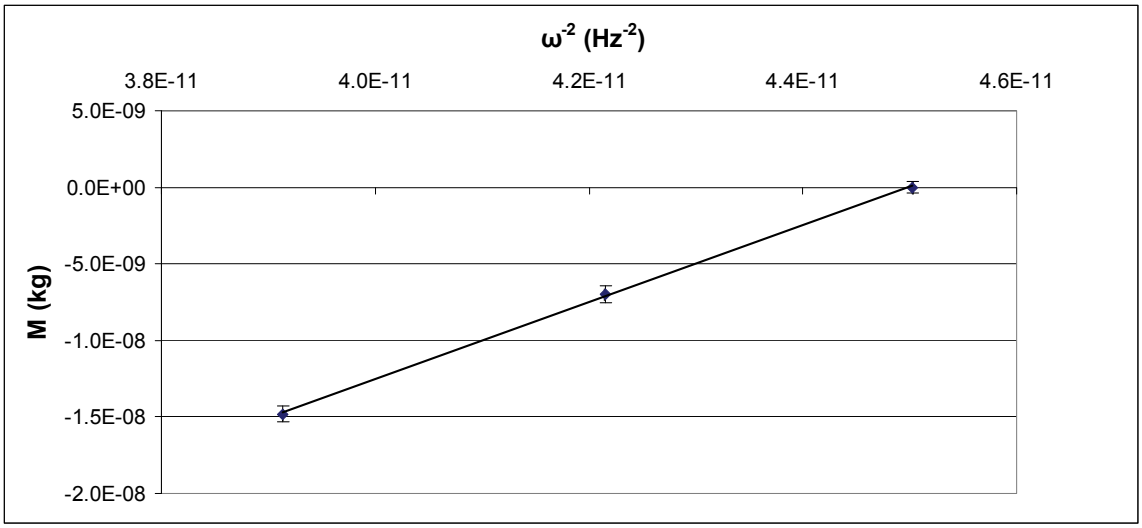

Figure 3. Sensor resonant frequency as a function of mass change of the tungsten probe tip. Error bars indicate the root-sum-of-squares from the standard deviation of five measurements of mass and frequency before and after etching part of the tungsten tip off. Note that frequency error bars are very small on this scale.

$$k_T = k_{ind}\left(\frac{L-\Delta L}{L}\right)^3, \tag{3}$$

where k_T is total system compliance, as discussed further below, k_{ind} is the spring constant determined using indentation, L is the distance from the tuning fork cantilever base to the tungsten wire tip, and ΔL is the distance between the tip and the point of contact between the cantilever and indenter tip. An additional correction must be made for the effects of contact compliance, c_c, machine compliance, c_m, and the angle of repose of the tuning fork sensor, θ, such that

$$k = \cos^2\theta\left(k_T^{-1} - c_c - c_m\right)^{-1}. \tag{4}$$

Machine compliance was measured by indenting a fused quartz reference sample [15], and contact compliance was estimated by assuming the contact area could be calculated from the hardness of the gold surface, using

$$c_c = \frac{\sqrt{\pi}}{\beta E_r\sqrt{F_m/H}}, \tag{5}$$

where β is a geometric factor equal to 1.034 for a Berkovich indenter, F_m is the maximum force applied to the indenter, H is the indentation hardness of gold, E_r is reduced modulus calculated using

$$\frac{1}{Er} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i}, \tag{6}$$

where E and E_i are the Young's modulus of the gold film coating the end of the tuning fork sensor at the contact point, and diamond indenter tip, respectively. Likewise v and v_i are the Poisson's ratios of the film and indenter materials [16].

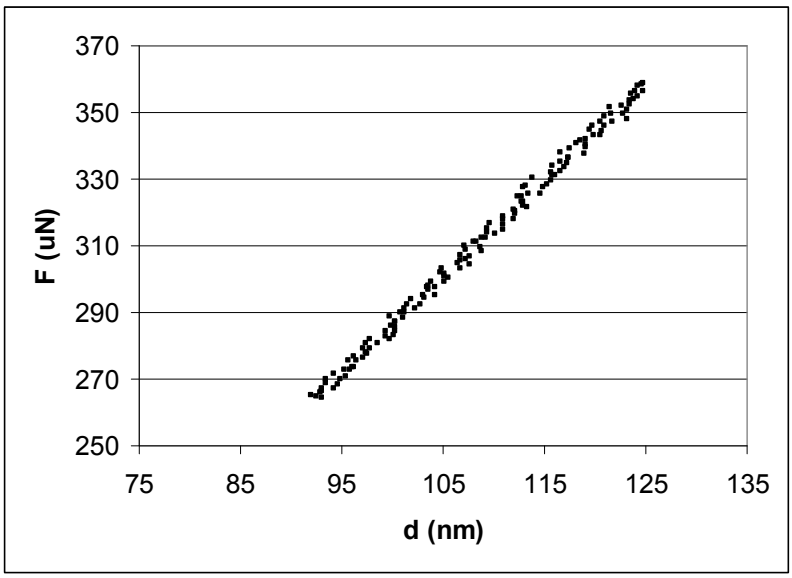

Figure 4. Indentation measurement of sensor spring constant. This data represent the combined qPlus sensor, contact, and machine compliance.

The values and uncertainties of the measured sensor spring constants are shown in Table 1 for the dynamic and indentation methods. Combined standard uncertainty is reported as the root sum of squares of all uncertainty components [17]. For the dynamic method, the curve linearity was evaluated using the methods of Taylor [18] from an analysis of the linear least squares fit to the data shown in figure 4, and is a type A uncertainty. The type A uncertainty in frequency is calculated by first determining the standard deviation of f_n from the sets of five measurements performed as described above, and then calculating the average of these standard deviations for all the tests performed. The type A uncertainty in mass was likewise calculated from the standard deviation of the weighing results. The mass correction for buoyancy of the tip mass in air is also a small contributing uncertainty [2]. For the Indentation method, uncertainties due to indenter force, displacement, cantilever length and indenter linearity have been previously described [14]. Repeatability is the standard deviation of the slopes of the force displacement curves such as that shown in Figure 4. The type B uncertainty in machine compliance was evaluated by conservatively assuming a 100 % uncertainty in the determined value of 2 nm/mN. Type B uncertainties from Hardness and Young's modulus values were determined by propagation through equations Equations 4-6. It was assumed that the contact sampled only the mechanical properties of the gold film on the surface of the tuning fork sensor. There is a substantial range of literature values available for Hardness and Young's modulus. The bulk value of Young's modulus for gold is 80 GPa, however low-force indentation experiments have reported values as high as 119 GPa for E [19]. To calculate k, the average of these two numbers was used. The uncertainty was estimated from the difference between the mean and either of these values. There is similar spread in the value of Hardness determined for gold thin films [20], and therefore the same approach is followed in determining uncertainty.

In order for the dynamic sensor described here to be used for mass metrology, the assumption that the tuning fork oscillator behaves as a single degree of freedom harmonic oscillator must be tested in a more precise fashion than described above. With a better procedure for determining contact stiffness, the uncertainty in the indentation measurement of *k* can be decreased substantially. The dynamic method is primarily limited by the uncertainty of the mass measured using the microbalance, since the values of the masses measured are close to the balance's resolution. The uncertainty in this measurement can be decreased by examining larger mass changes, by performing more experimental repetitions, or by using an alternate SI-traceable method for determining the mass [4]. The continued development of small mass metrology will help ensure SI traceable standards are available as the ultimate physical limits of measurement are probed [21,22].

Table 1. Measurement results and uncertainty components for qPlus sensor spring constant.

Dynamic		**Indenter**	
k (N/m)	$2.5\text{x}10^{3} \pm 0.2\text{x}10^{3}$	k (N/m)	$2.5\text{x}10^{3} \pm 0.2\text{x}10^{3}$
Source of uncertainty	**Magnitude of uncertainty**	**Source of uncertainty**	**Magnitude of uncertainty**
Curve linearity	$3.4\text{x}10^{-2}$	Force	$1\text{x}10^{-2}$
Frequency	$7\text{x}10^{-5}$	Displacement	$1\text{x}10^{-2}$
Mass change	$8.1\text{x}10^{-2}$	Repeatability	$7\text{x}10^{-4}$
Buoyancy	$1\text{x}10^{-4}$	Indenter linearity	$1\text{x}10^{-3}$
		Machine compliance	$2\text{x}10^{-3}$
		Young's modulus	$3.3\text{x}10^{-2}$
		Hardness	$9.0\text{x}10^{-2}$
		Cantilever length correction	$6.9\text{x}10^{-2}$
Combined Standard Uncertainty	$8.7\text{x}10^{-2}$	Combined Standard Uncertainty	$9.7\text{x}10^{-2}$

Conclusion

In order to determine the accuracy of the assumption that a cantilevered quartz tuning fork mechanical resonator (i.e. a qPlus sensor) behaves as a simple harmonic oscillator, a comparison of the values of its spring constant were determined with a dynamic and a quasi-static method. The spring constant values determined agreed within the experimental uncertainties of approximately 10 %. There is, however, substantial potential to reduce this uncertainty with further development of the measurement procedures described above.

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