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Citation: [Review of Scientific Instruments](#) **39**, 291 (1968); doi: 10.1063/1.1683352

View online: <http://dx.doi.org/10.1063/1.1683352>

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# THE REVIEW OF SCIENTIFIC INSTRUMENTS

VOLUME 39, NUMBER 3

MARCH 1968

## Direct Gravimetric Calibration of a Quartz Crystal Microbalance

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(Received 12 October 1967; and in final form, 13 November 1967)

A commercial quartz crystal microbalance has been calibrated via simultaneous comparison with a reference vacuum electrobalance. Aluminum, copper, and gold thermally deposited on 10 MHz AT-cut oscillators gave a composite linear calibration to a precision of  $\pm 0.2\%$ . For a uniformly distributed deposition, the ratio  $K$  of the fractional change of mass  $\Delta m/m$  to the fractional change of frequency  $\Delta f/f$  is shown to be 0.991 with a probable error of 0.6% for a configuration having peripheral contact restraints of the oscillators. The response function  $\delta f/\delta m$  (sensitivity variation over the face of the crystal) was determined to exhibit asymmetries about the central axes.

### INTRODUCTION

QUARTZ crystal microbalances are widely used as thickness monitors for thin film depositions, since such balances are simple, compact, and capable of good precision and high sensitivity. However, there have been few direct calibrations, the number of materials deposited has been small, and the number of calibrations successfully employing a wide range of densities has been limited.<sup>1,2</sup> Much of the published data relates to crystals with electrical contacts soldered to plated metal electrodes. While this arrangement is desirable for frequency stability, it is often impractical in situations where the crystals must be replaced easily and often. This latter situation is the usual one, since the total loading of the crystals should be limited to 1% of the mass of the crystal. Thus for ease of operation, most commercial units use springs to provide mechanical support and electrical contact. For these balances it is desirable that the calibration be unaffected by crystal replacement. In this work the reliability and precision attainable for one such configuration, that of the Westinghouse model 701A quartz crystal microbalance, was investigated. The experimental calibration is in close agreement with theoretical expectations. Thus the results are applicable to morphologically similar balances.

A method of simultaneous comparison with a reference

balance was used and appears satisfactory despite possible limitations due to geometry and variation of vapor density. For thermally deposited aluminum, copper, and gold in the range 5 to 75  $\mu\text{g}/\text{cm}^2$  per deposition, simple vacuum evaporation techniques are shown to be sufficient. The thickness range investigated is one of general interest, since it encompasses the range where many thin films become continuous on smooth substrates. A measurement of the variation of sensitivity over the surface of several crystals showed marked asymmetry, which is likely due to mechanical constraints. The response, however, is sufficiently peaked near the center of the crystal so that even fairly large peripheral masking of the crystals has only a slight effect on the calibration.

This work was carried out over a period of 1 yr in conjunction with other programs.<sup>3</sup> The conditions then are representative of actual operating experience and give a realistic estimate of reliability and precision.

### THEORY

For a quartz crystal plate of mass  $m$ , the change in frequency  $\Delta f$  of the resonant frequency  $f$  due to the addition of a small mass  $\Delta m$  is given by<sup>4</sup>

$$\Delta f/f = -K\Delta m/m,$$

<sup>3</sup> W. White and R. M. Mueller, *J. Appl. Phys.* **38**, 3660 (1967).

<sup>1</sup> G. Sauerbrey, *Z. Physik* **155**, 206 (1959).  
<sup>2</sup> See the collected works and references of *Vacuum Microbalance Techniques*, K. H. Behrndt, Ed. (Plenum Press, Inc., New York, 1966), Vol. 5.

<sup>4</sup> C. D. Stockbridge, in *Vacuum Microbalance Techniques*, K. H. Behrndt, Ed. (Plenum Press, Inc., New York, 1966), Vol. 5, p. 193. The relation  $K = \Delta f_{\text{observed}}/\Delta f_{\text{calculated}}$  requires definition as above in contrast to the definition  $K\Delta f/f = -\Delta m/m$  used by Stockbridge.

where  $K$  is a constant dependent on the mechanical configuration.

This equation may be rewritten as

$$\Delta f = -K(f/\rho d)(\Delta m/A),$$

where  $\rho$ ,  $d$  and  $A$  are respectively the density (2.648 g/cm<sup>3</sup>),<sup>5</sup> thickness, and area of the quartz plate.

The frequency constant

$$N = fd = 1668 \text{ kHz-mm}$$

may be calculated from the measured values of the elastic moduli of quartz<sup>6</sup> using the assumptions of Stockbridge.<sup>7</sup> Introducing  $N$  into the equation, the frequency change of the crystal is then related to the areal density of the deposit  $\Delta m/A$  by

$$\Delta f = -K(f^2/N\rho)(\Delta m/A) = -C_t \Delta m/A,$$

where  $C_t = K(f^2/N\rho)$  is the sensitivity or calibration constant of the microbalance. For an AT-cut crystal, the induced frequency change is independent of all properties of the added material except its mass. The quantity  $K$ , however, has been introduced to account for frequency dependence on the *exact* mode shape of vibration, and the distribution of the added mass. Stockbridge<sup>4</sup> has discussed the variability of  $K$  and shows that  $K$  may be expected to be close to unity for a uniform deposition over the entire electrode area in a system with small mechanical constraint. However, mechanical asymmetries such as varying surface curvatures (introduced in grinding), and mounting assembly constraints can cause  $K$  to deviate from unity. Further, since the response function<sup>8</sup>

$$c_t = \delta f / \delta m,$$

where

$$C_t = \int_A c_t dA$$

is markedly dependent on the position of the added mass on the surface, being greatest near the center, the use of masks may be expected to change  $K$ .

It should be emphasized that  $C_t$  and  $c_t$  are not, strictly speaking, constants, since they depend upon the resonant frequency which in turn changes during deposition.<sup>9</sup> However, deviations from linearity for this reason are either correctable or negligible for frequency excursions limited to 1% of the resonant frequency.

<sup>5</sup> R. B. Sosman, *The Properties of Silica* (Chemical Catalog Company, Inc., New York, 1927).

<sup>6</sup> H. J. McSkimin, P. Andreatch, Jr., and R. N. Thurston, *J. Appl. Phys.* **36**, 1624 (1965).

<sup>7</sup> C. D. Stockbridge, in *Vacuum Microbalance Techniques*, K. H. Behrndt, Ed. (Plenum Press, Inc., New York, 1966), Vol. 5, p. 179.

<sup>8</sup> "Response function" is used here in preference to "differentielle Schicktwägeempfindlichkeit" as given in Ref. 1, since all sensitivities are differential ratios.

<sup>9</sup> K. Behrndt and R. W. Love, *Transactions of the 7th National Vacuum Symposium* (Pergamon Press, Inc., London, 1961), p. 87.

## APPARATUS AND METHOD

The microbalance used in this work was the Westinghouse model 701A, which is the commercial version of the unit described by Langer and Patton.<sup>10</sup> This balance employs two 13.5 mm diam, 10 MHz fundamental mode crystals of the low temperature coefficient AT-cut (IEEE rotation angle  $\Phi = 35^\circ 17' \pm 3'$ ). The exposed sides only of the crystals were plated with approximately 500 Å of gold. By means of an Inconel spring of approximately 5 N thrust, this electrode was held in mechanical and electrical contact with a 0.4 mm rim. Thus only the central 1.27 cm<sup>2</sup> of the crystal was exposed to the evaporant. Contact to the rear face of the crystal was established by a full-width, coin-silver electrode. Two different arrangements were used. In one, the crystal was separated from the electrode by three equally spaced feet 0.4 mm square by 0.1 mm high, located at the edge of the crystal. This type of capacitive contact, however, requires crystals of high activity, and accordingly the feet were removed for some of the work. This probably lowers the stability by a small amount, but since stability is a function of many variables, the data were not sufficient to distinguish this effect alone. All data for the two arrangements were simply lumped together.

In normal operation, one of two crystals in the balance head is shielded from the evaporant and thus serves as a (partially) temperature-compensated frequency reference. The output frequency of the balance is the difference of the oscillator frequencies as derived from a beat circuit. Thermistors bonded to the body of the balance and to one mounted crystal indicated that temperature rise was not a serious problem. Less than 4 C° total rise was noted after

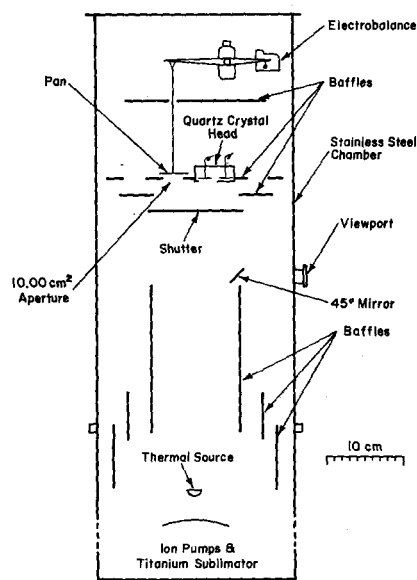


FIG. 1. Vacuum evaporator.

<sup>10</sup> A. Langer and J. T. Patton, in *Vacuum Microbalance Techniques*, K. H. Behrndt, Ed. (Plenum Press, Inc., New York, 1966), Vol. 5, p. 231.

repeated evaporations at  $\frac{1}{2}$  h intervals. The temperatures of the holder and crystals were found to equilibrate within a few minutes. Although the unit was designed to allow baking, this precaution was not found necessary.

The vacuum evaporator is shown schematically in Fig. 1. Ultimate vacua of  $5 \times 10^{-8}$  Torr were achieved in the 75 liter volume by an Ultek model TNB unit comprised of two 25 liter/sec ion pumps and a titanium sublimator rated at 3600 liter/sec. With deposition rates of 0.1 to 2  $\mu\text{g}/\text{cm}^2$  sec at a distance of 45 cm from the source, the vacua during evaporations were maintained in the range of  $2 \times 10^{-7}$  to  $2 \times 10^{-6}$  Torr as measured by the ion pump current. These pressures were found to be within a factor of 4 of those indicated by a nude ionization gauge located behind the baffles shielding the electrobalance.

The aluminum was evaporated from stranded tungsten helices, the copper from 13 mm tantalum dimples, and the gold from 13 mm dimples of both tungsten and molybdenum. Rate control was established manually. In all cases the shutter shielded the balances during a melting and pre-evaporation period. Before deposition of the layers for comparative weighings, a liberal prelayer was deposited on the electrobalance pan and the quartz crystal in order to establish identical substrates and so eliminate errors due to variation of sticking probability. High purity materials were used, the gold and copper having impurity content less than 0.01% and the aluminum better than 0.1%.

The reference balance was a Cahn RG electrobalance. This is a beam balance with restoring torque provided by a d'Arsonval-type movement located at the beam fulcrum. A voltage output is obtained which is linearly related to the weight change of a single pan. The balance was calibrated with class M weights (Natl. Bur. Std. circular 547) accurate to within 5.4  $\mu\text{g}$  of the marked values. A balance pan of 1.7  $\text{mg}/\text{cm}^2$  clean aluminum foil was suspended a few millimeters above, and totally covering, a 10.00  $\text{cm}^2$  aperture in a baffle plate, by approximately 15 cm of 25  $\mu$  tungsten wire. The foil was stiffened by crimping a vertical rim of about 1 mm in height around a 40 mm diam disk by means of a die. The pan rested on a planar spiral formed from 3 cm of a 6 cm length of 100  $\mu$  Nichrome wire (nonmagnetic). The remainder of the wire extended from the center of the spiral, normal to its plane, passing through the center of the pan and terminating in a small hook. The tungsten suspension wire was attached directly to this hook. It was found important to use nonmagnetic materials for the pan and suspension to avoid possible interaction with magnetized materials near the evaporator. The total mass of the pan and suspension was about 30 mg. A secondary calibration weight of a value close to that of the pan and suspension was manipulated in the vacuum system by means of simple manual controls, thus providing substitution weighings of the weight change of the pan after evaporation. In this manner a probable

error of weighing of  $\pm 0.15 \mu\text{g}/\text{cm}^2$  was achieved. Experiments with pans of accurately known area located either below the baffle or flush with the baffle indicated that no detectable amount of reflected evaporant material was weighed by the method adopted.

Since much of the work was carried out as part of another experimental program,<sup>3</sup> many, though not all, of the depositions formed part of a "sandwich" structure of different metals. For example, most of the aluminum data were obtained from experiments where the weighed aluminum layer was "sandwiched" between two layers of gold of about 2  $\mu\text{g}/\text{cm}^2$ . This structure was laid down on a freshly deposited prelayer of aluminum. Despite the fact that the quartz crystal and the aluminum pan were identically exposed so that sticking probabilities for the weighed, or comparison central layer of aluminum (or copper), should be the same, the assumption was checked, since the difference in surface roughness of the aluminum pan and the quartz crystals might conceivably cause an error in sticking probabilities. The method of Ref. 3 formed a convenient means to check this supposition. In this method a beam of protons in the 100 keV energy range was scattered from the identically prepared substrates and detected by means of a low-noise solid state detector. The large difference in the Rutherford-scattering cross section of gold relative to aluminum (or copper) gives rise to pronounced peaks in the spectrum of backscattered particles. The energy difference between the peaks is then closely proportional to thickness of the central layer and forms the basis for a thickness comparison technique. Representative data are shown in Fig. 2 for a gold-aluminum-gold film simultaneously deposited on a balance pan and a quartz crystal located in closely adjacent positions. Because of the rough-

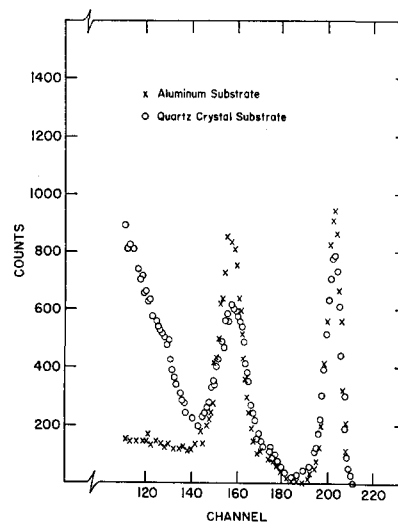


FIG. 2. Solid state detector spectra of 131 keV  $^1\text{H}$  backscattered  $157.5^\circ$  from thin films consisting of a prelayer of 20  $\mu\text{g}/\text{cm}^2$  aluminum covered with a sandwich structure of 35  $\mu\text{g}/\text{cm}^2$  aluminum between two 10  $\mu\text{g}/\text{cm}^2$  gold (marker) layers. The substrates were the aluminum foil of the electrobalance pan, and a 10 MHz quartz crystal.

ness of the surface of the quartz as compared to the aluminum foil, the peak widths for the quartz substrate are larger than those for the aluminum substrate. This fact limits the accuracy of the determination to about 1.5%. However, to this accuracy, the deposited layers are identical in thickness. Since no differences in calibration were noted between new crystals and those with a thick layer of about  $500 \mu\text{g}/\text{cm}^2$ , (the latter presumably smooth), it was concluded that no error was involved due to weighings performed using the "sandwich" technique. Moreover, all gold evaporations were on predeposited gold, thus not subject to the above criticism, and gave a calibration consistent with those for aluminum and copper.

The same method proved suitable for checking the geometry factor for the evaporator. Glass microscope slides and aluminum foil substrates located both in the electrobalance pan and quartz crystal positions showed a 2.0% difference in the deposited thicknesses as determined by proton scattering. Since the calculated difference based on the inverse square and a small cosine correction was 1.5%, a final geometry correction of 1.5% was adopted with an assigned error of  $\pm 0.5\%$ .

The response function  $c_f$  was obtained by placing small collimators (of two sizes, 1.5 and 3.0  $\text{mm}^2$ ) at various locations over the face of the crystals and depositing approximately  $25 \mu\text{g}/\text{cm}^2$  of gold. All readings were normalized by the electrobalance. Since the frequency changes (as measured directly to about 1 Hz by a frequency counter attached directly to the oscillator circuit rather than the difference circuit) were typically several hundred hertz, an extreme demand was placed upon stability of the system. As many as 30 evaporations were required to map one crystal surface adequately, thus requiring the experiment to be run over several days. By trial-and-error mounting of various crystals, stabilities of the order of  $\pm 5 \text{ Hz/h}$  were attained. By staggering the sensitivity determinations over the surface of the crystal, any long-term drifts could be detected; none were apparent. Reproducibility checks spaced 16 h apart, for identical points on the surface, showed the experiment to be accurate to within  $\pm 10\%$  in a given determination of response function. The positions of the points on the surface of the crystal were accurately measured after the experiment by mounting in a movable microscope stage.

## RESULTS AND DISCUSSION

Plots of response function are given in Fig. 3. These differ from those reported by Sauerbrey<sup>1</sup> in that they are markedly asymmetric for the two cases tested, i.e., rear electrode with and without feet. Without a much more elaborate determination, it is difficult to state unequivocally whether the asymmetries are due to imperfections of the crystal, or of the mechanical mount. However, the

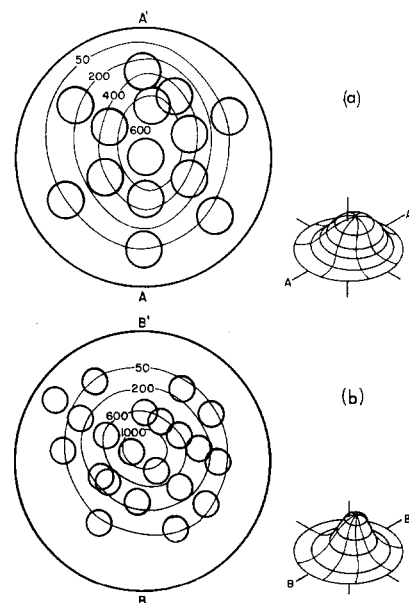


FIG. 3. Response function contours for the 10 MHz quartz oscillators in two different mounts—(a) rear electrode without feet, test spot  $3.0 \text{ mm}^2$ ; (b) rear electrode with feet, test spot  $1.5 \text{ mm}^2$ . The small heavy circles indicate the test spots. The contour units are in hertz per microgram. The insets are isometric drawings of the response function.

data were reproduced for two other crystals tested in mounts with and without feet. The broadening of the response function in the case of a flat or nearly flat rear electrode is indicative of a restraint lowering the mechanical  $Q$  of the oscillator. From the viewpoint of the calibration constant, the point is established, however, that the combination of peripheral masking and asymmetric response function does not appreciably affect calibration. For an electrode with feet, the 0.4 mm wide peripheral mask reduces the sensitivity by less than 0.1%. Without feet the correction is less than 0.4%. Since the data for the two cases were lumped in this work, a correction due to masking of 0.2% was adopted with an error of  $\pm 0.2\%$  assigned.<sup>11</sup>

The calibration results for the microbalance are shown in Table I and Fig. 4. These results were obtained from least squares fits to the data for each of the metals and for the composite data. In each case, error was assumed to lie only in the frequency determinations. The calibration constants and the associated probable errors were obtained from the slopes of lines constrained to go through the origin.<sup>12</sup> It is evident from the consistent results that no significant difference in calibration may be attributed to the use of these metals. The above least squares analysis assumes constant frequency error independent of added mass up to the imposed upper limit of 1% of the mass of

<sup>11</sup> The manual of the Westinghouse model 701A balance assumes a masking correction of 10%, since the mask shields 10% of the area of the crystal. Since as shown above the sensitivity is not proportional to the exposed area, the calibration constant given by Westinghouse is 10% low.

<sup>12</sup> *Experimental Statistics. National Bureau of Standards Handbook 91* (U. S. Government Printing Office, Washington 25, D. C., 1963).

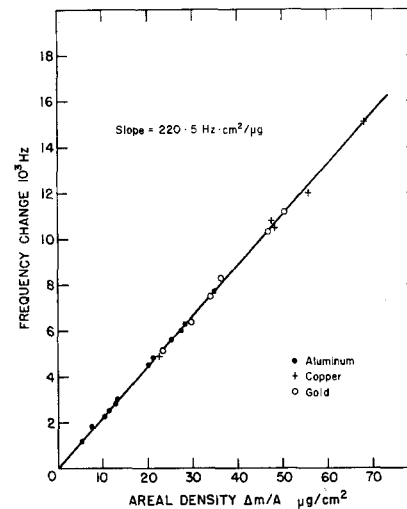
the crystal. This appears reasonable for this situation as long as a small correction ( $<1\%$ ) is included (as was done) to correct all results to a base resonant frequency of 10 MHz. In all, six different crystals were used for the calibration data. The stability (stated in terms of the probable error of a frequency) to be expected from the balance may be inferred from Table I. The difference stability refers to an actual weighing where a difference of two frequencies must be obtained.<sup>13</sup> The single reading stability is calculated as  $0.707 \times$  difference stability assuming random independent variations of frequencies. These values actually refer to the experimental situation where frequency readings were monitored several minutes before and after a weighing. However, experience has shown that these single reading values are applicable to variations over a period as long as one day. In some few cases variations as small as  $\pm 5$  Hz were noted over a period of several days. However, the nature of the crystal mounting made the balance somewhat sensitive to shock. For example, a sharp rap on the side of the evaporator would change the frequency by  $\pm 20$  Hz typically. The variations appear to be related to electrical and mechanical conditions which could not be easily reproduced. The calibration constants of Table I show the precision attainable for the given

TABLE I. Calibration constants and stabilities of a 10 MHz quartz crystal oscillator.

	Calibration constant	Probable error	Stability (probable error) Single Difference <sup>13</sup> reading	
Aluminum	220.8 Hz·cm <sup>2</sup> /μg	$\pm 0.6$ Hz·cm <sup>2</sup> /μg	$\pm 65$ Hz	$\pm 46$ Hz
Copper	219.8	$\pm 0.8$	$\pm 135$	$\pm 95$
Gold	221.3	$\pm 0.7$	$\pm 91$	$\pm 65$
Composite	220.5	$\pm 0.4$	$\pm 91$	$\pm 65$

<sup>13</sup> For the particular balance used, a difference of difference frequencies is intended, since all frequency readings are taken as the difference between the resonant frequency in question and a reference 10 MHz frequency.

FIG. 4. Composite least squares plot of quartz crystal microbalance calibration data.



evaporator configuration. Corrections of  $+(1.5 \pm 0.5)\%$  for geometry and  $+(0.2 \pm 0.2)\%$  for masking were applied to the composite value to obtain an absolute calibration which may be compared to the response predicted by theory. It may be seen that the uncertainties of geometry and masking exceed the statistical uncertainty of the calibration. With the corrections, the absolute sensitivity for a uniform deposition over one entire side of a 10 MHz plate was determined to be  $224.3 \pm 1.3$  Hz·cm<sup>2</sup>/μg as compared with a theoretical value of 226.4 Hz·cm<sup>2</sup>/μg. Thus the *K*-value referred to the unmasked crystal is given to be  $0.991 \pm 0.006$  PE.

#### ACKNOWLEDGMENTS

The authors would like to express their appreciation to G. O. Engelmohr for his valuable contribution in the design and construction of the vacuum evaporator, and to J. A. Brooks for assistance in collecting and evaluating the data.

## Production of Quiescent Discharge with High Electron Temperatures

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(Received 6 October 1967; and in final form, 8 November 1967)

Collision-free quiescent plasmas are produced in a magnetic mirror geometry by applying  $\sim 50$  W uhf power to a novel coupling structure which surrounds one section of the plasma. The plasma characteristics are favorable for studies of waves, diffusion, stability, and turbulence.

**C**OLLISIONLESS steady state plasmas showing a remarkably low level of fluctuations have been generated in a mirror-geometry magnetic field by applying

radio-frequency power to a coupling structure of new design. This mode of plasma generation has been carried out with modest power levels ( $\sim 50$  W), frequencies from