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Quartz Crystal Microbalances

A refined technique for determining changes in mass loading from frequency shifts

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QUARTZ CRYSTAL MICROBALANCES

A refined technique for determining changes in mass loading from frequency shifts.

by

Malcolm M. Fowler

and

William A. Sedlacek

ABSTRACT

Current methods of converting quartz crystal microbalance frequency shifts to mass are frequently quite inaccurate. An improved method is presented which reduces the error to a fraction of a per cent. The algorithm requires a knowledge of the crystal response function and the mass loading distribution.

I. INTRODUCTION

The quartz crystal microbalance (QCM) currently is used in several commercial instruments that measure concentrations of atmospheric aerosols. The QCM is based on the principle that the frequency of a crystal-controlled oscillator varies inversely proportional to mass deposited on the crystal. In the past, observed frequency shifts have been converted to corresponding changes in mass loading by using the average sensitivity of the crystal over the electrode area. This approach can introduce error when using some of the existing commercial instruments in which the deposited aerosol either does not cover the entire electrode or is located on several small spots.

Normally an AT-cut crystal operating in the shear mode at a frequency in the 5- to 15-MHz range is used. A typical 10-MHz crystal is pictured in Fig. 1.

This crystal, with a 0.3175-cm electrode radius, has an average sensitivity of 717 Hz/μg for a uniform deposit over the entire electrode area. The sensitivity at the center of the crystal is 1355 Hz/μg and decreases to near zero at the edge of the electrode.

Because the sensitivity of a QCM is not the same for all areas of the crystal, it is necessary to have an algorithm for relating the observed frequency shift produced by a particular distribution of deposited material to mass.

In our use of QCMs as the collection plates of a multistage cascade impactor, the deposition pattern is different on each stage. The first stage covers nearly the entire electrode area, whereas on the eighth stage the deposit is only on the central 0.5 mm of the crystal. Stage nine has two deposits and stage ten has four deposits. Thus, the computed mass distribution will be badly "skewed" if the same simple average response function to convert frequency shift to mass is sued for all stages of the cascade. The error in the case of the last stage can be greater than a factor of two.

We have modeled the response of a QCM to mass deposition in a uniform layer over a circular area covering only a part of the electrode. This model enables one to correctly convert observed frequency shifts to mass.

II. DERIVATION OF THE TECHNIQUE

The QCM frequency shift mass deposited on the crystal is caused by the average effect of the distribution of mass on the crystal, weighted by the sensitivity of the crystal for each infinitesimal area where mass is deposited. The observed frequency shift can be modeled by applying the mean value theorem to the sensitivity function over the area on which mass is deposited. To solve this model mathematically one must know the sensitivity function and the distribution of the deposited mass.

Measurements of the sensitivity function of circular quartz crystals resonating in the shear mode have been made by Daly[1] and Sauerbrey.[2] Each of these measured functions is well described by Gaussian distribution. Therefore, we assume the sensitivity function is of the form

$$S(r) = Ke^{-Br^2} .$$

B is a function of the electrode-radius r_e of the crystal and relates the σ of the Gaussian fit to the measured sensitivity function.

$$B = \frac{1}{2(\sigma)^2} \qquad \sigma = \frac{FWHM}{2.355} .$$

K is the sensitivity of the QCM to mass located at the center of the crystal and is a function of the electrode radius and oscillating frequency. We shall also assume that the mass distribution, M(r), is uniform, of radius r_1, centered r_2 from the center of the crystal electrode as shown in Fig. 2.

We now apply the mean value theorem, where $dA = r\, dr\, d\Theta$.

$$\frac{\partial f_o}{\partial m} = \frac{\int_0^{2\pi}\int_0^{r_1} M(r)S(r_3)\, r\, dr\, d\Theta}{\int_0^{2\pi}\int_0^{r_1} r\, dr\, d\Theta} \tag{1}$$

where f_o = the crystal fundamental frequency.

$$\frac{\partial f_o}{\partial m} = \frac{\int_0^{2\pi}\int_0^{r_1} Ke^{-B(r_3)^2}\, r\, dr\, d\Theta}{\pi(r_1)^2} \tag{2}$$

M(r) is assumed to be 1.

$$\frac{\partial f_o}{\partial m} = \frac{K}{\pi(r_1)^2}\int_0^{2\pi}\int_0^{r_1} r\, e^{-B[(r)^2 + (r_2)^2 - 2r\, r_2\cos\Theta]}\, dr\, d\Theta. \tag{3}$$

The constants K and B can be evaluated from the simple case where mass is distributed evenly across the electrode area, i.e., $r_1 = r_e$ and $r_2 = 0$.

Then Eq. (3) becomes

$$\frac{\partial f_o}{\partial m} = \frac{K}{\pi(r_e)^2}\int_0^{2\pi}\int_0^{r_e} r\, e^{-B(r)^2}\, dr\, d\Theta. \tag{4}$$

$$\frac{\partial f_o}{\partial m} = \frac{2K}{(r_e)^2} \int_o^{r_e} r\, e^{-Br^2}\, dr. \qquad (5)$$

$$\frac{\partial f_o}{\partial m} = \frac{2K}{(r_e)^2} \left[\frac{1 - e^{-B(r_e)^2}}{2B}\right] = \frac{K}{B(r_e)^2} \left(1 - e^{-B(r_e)^2}\right). \qquad (6)$$

Let $\frac{K}{(r_e)^2} = A.$

$$\frac{\partial f_o}{\partial m} = \frac{A}{B} \left(1 - e^{-B(r_e)^2}\right) \quad . \qquad (7)$$

Starting with the physical properties of quartz, it is also possible to derive an expression for $\partial f/\partial m$ for uniform layers as given in Ref. 2.

(1) From the acoustic impedance of quartz and the density, one can calculate the velocity of sound for transverse waves to be 3.325×10^5 cm/s and this agrees well with experimental data for quartz.

(2) AT-cut crystals oscillate in the shear mode and are $\lambda/2$ thick. Where λ is the wavelength calculated from the aforementioned speed of sound,

$t = \lambda/2, \quad \lambda = v/f_o, \quad \lambda = \text{cm}, \quad v = 3.325 \times 10^5$ cm/s .

(3) Then for quartz, $f_o = \frac{1.6625 \times 10^5}{t}$ $\qquad f_o$ = Hz, t = cm .

Let m = mass of active part of crystal, g

ρ = density of SiO_2 = 2.65 g/cm^3

a = area of active part of crystal, cm^2 (assumed to be the electrode area)

t = thickness of crystal, cm.

Then, $t = \frac{m}{a\rho}$ and from above

$$f_o = \frac{1.662 \times 10^5}{t} = \frac{1.662 \times 10^5\, a\rho}{m}$$

and $\frac{\partial f_o}{\partial m} = \frac{-1.662 \times 10^5 \ a\rho}{m^2} = \frac{-f_o}{m}$.

Furthermore; $m = \frac{1.662 \times 10^5 \ a\rho}{f_o}$,

so that $\frac{\partial f_o}{\partial m} = \frac{f_o^2}{1.662 \times 10^5 \ a\rho} = (-2.27 \times 10^{-6}) \frac{f_o^2}{a} \quad \frac{cm^2}{Hz \cdot g}$.

B is evaluated from experimental data.

For a response function of the form $S_r = A\ e^{-Br^2}$, the full width at half maximum (FWHM) is defined.

$$FWHM = 2\ r \text{ for which } S_r = \frac{S_o}{2} = \frac{A}{2}$$

$$\frac{A}{2} = A\ e^{-BR^2(FWHM)} \quad \text{or} \quad \frac{1}{2} = e^{-B(\frac{FWHM}{2})^2}$$

or $\ln 2 = \frac{B(FWHM)^2}{4}$

finally, $B = \frac{4 \ln 2}{(FWHM)^2} \qquad (cm^{-2})$.

The measured response curve of the quartz crystal in question is used to obtain the FWHM and calculate B. Equation (7), using B, is equated to the theoretically calculated $\partial f_o/\partial m$ to evaluate A. For this to be valid, one must assume that the modulus of elasticity of the deposited material is the same as that of quartz.

The values determined for some of our crystals, along with those of Refs. 1 and 2, are given in Table I.

TABLE I

CALCULATED DATA USING THERMAL SYSTEMS INC. (TSI) RELATIVE RESPONSE DATA FOR A 5-MHz CRYSTAL AND SCALING TO 10-MHz CRYSTALS

Crystal	f_o,MHz	r_e,cm	FWHM,cm	$\partial f_o/\partial m$,Hz/μg	K,Hz/μg	B,cm^{-2}
TSI[2]	5.0	0.3175	0.44	-179	339	14.33
Celesco	10.0	0.3175	0.44	-717	1355	14.33
Intl Xtal	10.0	0.2380	0.33	-1275	2410	25.49
Sauerbray[2]	14.0	0.3175	0.44	-1405	2656	14.33

Of course, the more general case of Eq. (3) is much more difficult to integrate. A numerical integration can be accomplished if we split the deposit area up into a series of annular ring segments about the center of the electrode as shown in Fig. 3, instead of doing the circular integration over the deposit. The $\partial f_o/\partial m$ for each ring segment is found by integrating from r_{4i} to r_{5i}.

$$\left(\frac{\partial f_o}{\partial m}\right)_i = \frac{K \int_{-\Theta}^{\Theta} \int_{\theta_{4i}}^{r_{5i}} e^{-Br^2} \, r \, dr \, d\Theta}{\int_{-\Theta}^{\Theta} \int_{r_{4i}}^{r_{5i}} r \, dr \, d\Theta} \tag{8}$$

$$\left(\frac{\Theta f_o}{\Theta m}\right)_i = \frac{K}{B} \; \frac{e^{-B(r_{4i})^2} - e^{-B(r_{5i})^2}}{(r_{5i})^2 - (r_{4i})^2} \quad \text{for the ring between } r_{4i} \text{ and } r_{5i}. \tag{9}$$

The mean value of $\partial f_o/\partial m$ for the entire deposit is found by weighting the $\partial f_o/\partial m$ of each ring proportional to its fraction of the total deposit area;

$$\text{i.e.,} \quad \sum_{i=1}^{N} \left(\frac{\partial f_o}{\partial m}\right)_i \times \frac{2\Theta_i(r_{5i}^2 - r_{4i}^2)}{\sum_{i=1}^{n} 2\Theta_i(r_{5i}^2 - r_{4i}^2)} = \frac{\partial f_o}{\partial m}$$

for division into N rings, where Θ_i is the angle subtended by the deposit at $r_{3i} = \frac{r_{4i} + r_{5i}}{2}$. (See the Appendix for a simple program to do this approximation.) Figure 4 shows the calculated results for 0.001-mm-radius spot at various distances from the center of the electrode. To study the sensitivity of this calculation method to various combinations of input parameters, Figs. 5 and 6 were constructed. In each case, the number of annuli used to divide up the deposit area is plotted vs per cent deviation from the results obtained using 100 annuli. Figure 5 shows the results for a deposit one-half millimeter in radius located tangent to the center, approximately halfway between the center and the edge of the electrode, and at the edge of the electrode. Figure 6 is a similar plot for different sizes of deposits located approximately halfway between the center and edge of the electrode. The oscillation shown by some of the cases for the first few numbers of annuli appears because of variations in compensating errors as 1, 2, or 3 annuli are used.

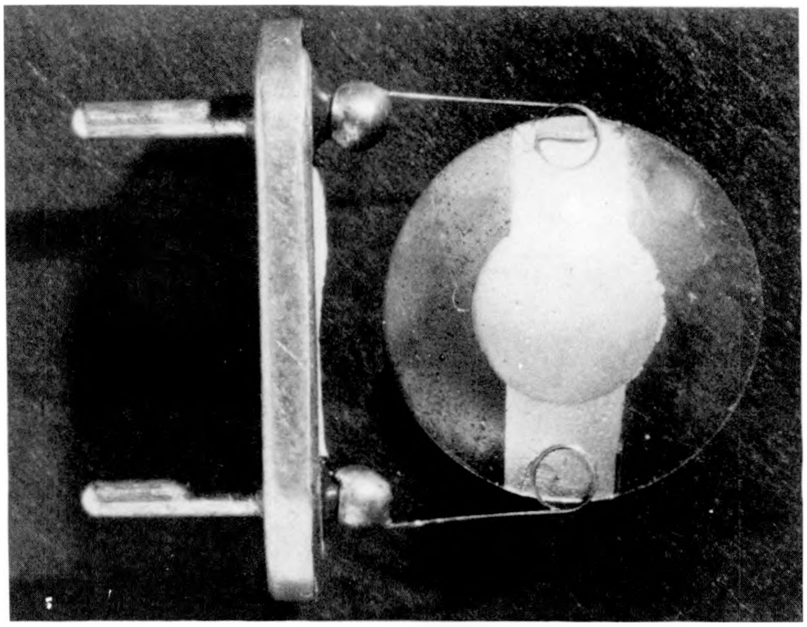

Fig. 1. 10-MHz quartz crystal.

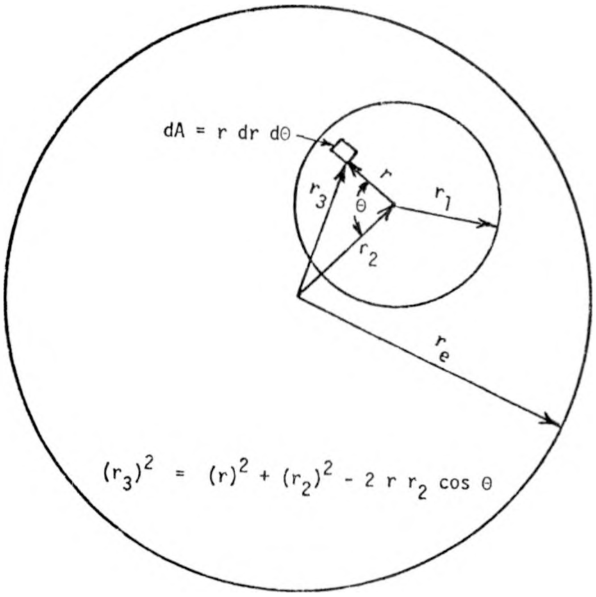

Fig. 2. Relationship of deposit coordinates to those of the crystal electrode.

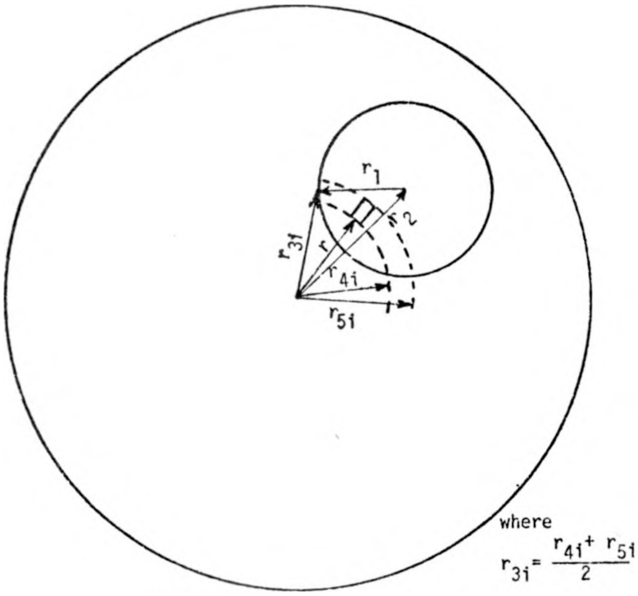

Fig. 3. Relationship of parameters used for numerical integration.

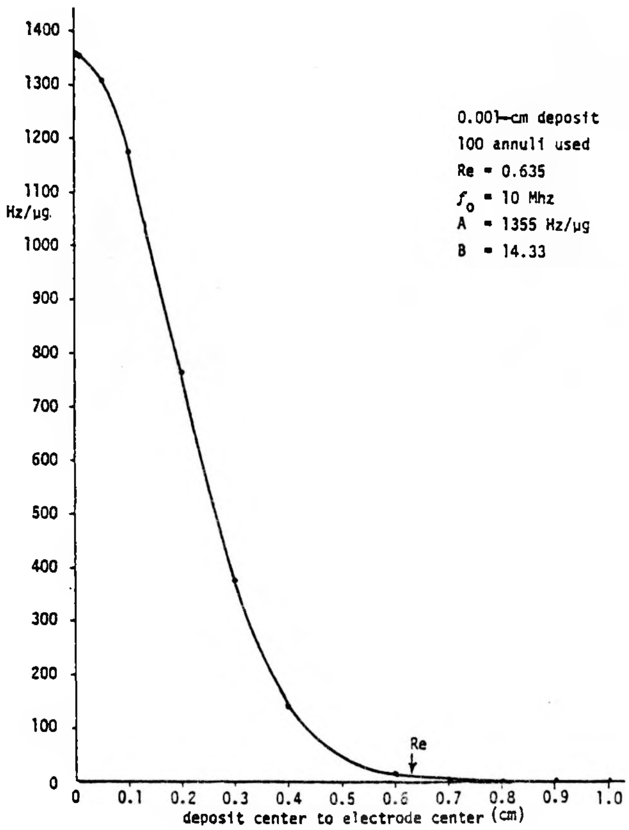

Fig. 4. Sensitivity of a quartz crystal as a function of distance from center of electrodes.

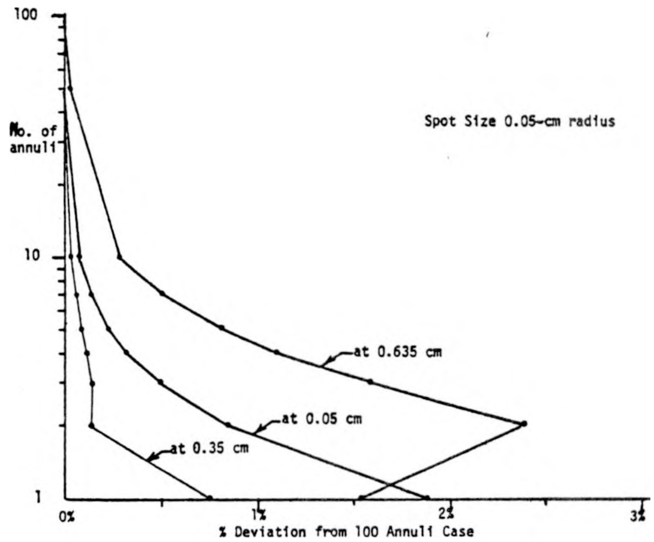

Fig. 5. Relative errors of the numerical solution as a function of the number of annuli used for various deposit distances from the electrode center.

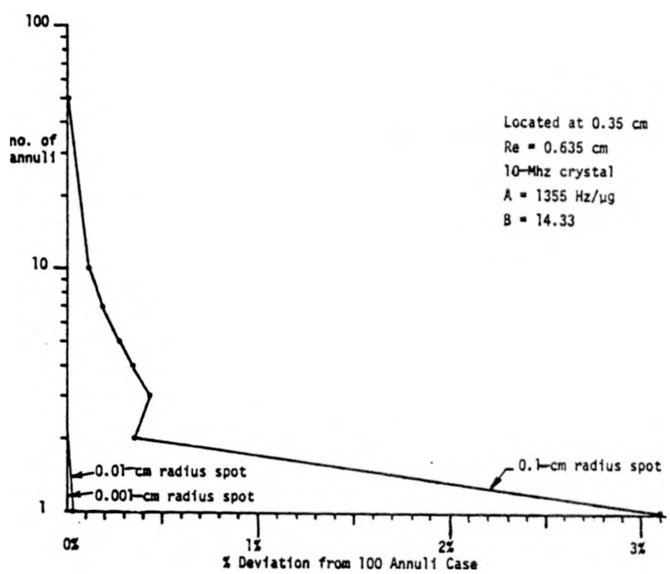

Fig. 6. Relative errors of the numerical solution as a function of the number of annuli used for various deposit sizes located 0.35 cm from the electrode center.

Even "bad" cases such as a large spot or location near the edge of the crystal give only a few per cent deviation with only one annulus being used. By the time 10 annuli are used, deviations much less than 1% are achieved.

In general, uncertainties in atmospheric measurements are such that the few per cent deviation is quite acceptable. Therefore, using the equation

$$\frac{\partial f_o}{\partial m} = \frac{A}{B}\,\frac{\left(e^{-Br_4^2} - e^{-Br_5^2}\right)}{(r_5^2 - r_4^2)}$$

gives a very good answer. It is certainly a great improvement over the factor of two error which would result from using the average response for a small deposit near the center of the electrode.

III. SUMMARY

A technique has been developed whereby the mass measured by a quartz-crystal microbalance can be corrected for the variation in the microbalance sensitivity as a function of the location of the deposit on the crystal. Two cases are considered --

1. a circular deposit at the center of the quartz crystal electrode,
2. a circular deposit not including the center of the electrode.

A circular deposit not centered on the electrode, but including the electrode center, can be treated by a combination of the two techniques. A similar technique could be employed for noncircular deposits. Calculations using the method developed in this report indicate that the data-reduction techniques previously used can be in error by as much as a factor of two.

IV. DISCUSSION OF THE ASSUMPTIONS USED IN THIS TREATMENT

We assume the sensitivity function of the crystal has a Gaussian shape. Experimental data indicate that this is a good assumption for circular AT crystals.

We also assume the deposited mass is uniform in thickness. In our application this is usually true for a large area. For a small area, when this is not true, the error becomes quite small.

Finally we assume the deposited material has the same modulus of elasticity as quartz. This has been treated for uniform layers by Miller and Bolef.[3]

However, the effects of varying the modulus in nonuniform layers that do not cover the entire electrode has not been treated as yet and may be a substantial source of error.

REFERENCES

1. P. S. Daley, "The Use of Piezoelectric Crystals in the Determination of Particulate Mass Concentrations in Air." Ph.D. Thesis, University of Florida, Gainesville, FL (1974).

2. G. Sauerbrey, Use of Oscillator Quartz Crystals for Weighing Thin Layers and Micro-weighing, (Z Physik 155 206-222(1959) in German, Translation by Technical Information and Library Services, Ministry of Aviation, Feb. 1962, TIL/T.5282).

3. J. G. Miller and D. I. Bolef, "Acoustic Wave Analysis of the Operation of Quartz-Crystal Film-Thickness Monitors," Appl. Phys. 39, 5815(1968).

APPENDIX

COMPUTER CODE TO CALCULATE SENSITIVITIES FOR VARIOUS DEPOSITS

The following computer program to do the numerical integration is operational on the Los Alamos Scientific Laboratory (LASL) NOS interactive computer terminals. It prompts the user for input data through an unformatted read, outputs the results, and then asks if the operator desires to do any more.

A typical interactive session follows the program listing.

LASL Identification Code: LP-0881

```
 77/11/15. 16.07.02.
PROGRAM   FPM

          PROGRAM RRPM(INPUT,OUTPUT)
          PRINT 300
    300   FORMAT(*  RE = ELECTRODE RADIUS CM., A = AMPLITUDE CONSTANT, B = WI
+DTH CONSTANT*//* RD = DEPOSIT RADIUS CM., RX = ELECTRODE CENTER TO DEPOSIT
+ CENTER CM.*/* DNR = NO. ANNULI USED IN APPROXIMATION*)
          PRINT 400
    400   FORMAT(*  FE     A     B?*)
          READ, RE,A,B
     10   PRINT 100
    100   FORMAT(*  RD     RX     DNR?*)
           READ, RD,RX,DNR
          DR = (2.*RD)/DNR
          R4 = RX - RD
          SRPM = 0.0
          STHETA = 0.0
          NDR = DNR
          DO 20 I=1,NDR
          R5 = R4 + DR
          R3 = (R4 + R5)/2.0
```

```
      THETA=ACOS((R3*R3+RX*RX-RD*RD)/(2.*R3*RX))*(R5*R5-R4*R4)
       STHETA = STHETA + THETA
        R4 = R5
   20  CONTINUE
       R4 = RX - RD
       DO 30 I=1,NDR
       R5 = R4 + DR
        R3 = (R4+R5)/2.
      RPM = (A/B)*(EXP(-B*R4*R4)-EXP(-B*R5*R5))/(R5*R5-R4*R4)
      THETA=ACOS((R3*R3+RX*RX-RD*RD)/(2.*R3*RX))*(R5*R5-R4*R4)
       R4 = R5
   30 SRPM = SRPM + (THETA*RPM)/STHETA
             PRINT 500
  500   FORMAT(*  *)
       PRINT 200,SRPM,RD,RX,RE,DNR
  200  FORMAT(*  FR/M =*F10.3* RD =*F7.4* RX =*F7.4* RE =*F7.4,
+* DNR =*F5.0//*  ANY MORE?  Y OR N?*)
        READ, Y
       IF(Y.EQ.1HY) GO TO 10
       STOP
       END
READY.
```

```
 77/11/15. 16.08.28.
PROGRAM   FPM

  RE = ELECTRODE RADIUS CM., A = AMPLITUDE CONSTANT, B = WIDTH CONSTANT

 RD = DEPOSIT RADIUS CM., RX = ELECTRODE CENTER TO DEPOSIT CENTER CM.
 DNR = NO. ANNULI USED IN APPROXIMATION
  RE     A     B?
? .635 1355 14,33
  RD     RX     DNR?
? .001 .35 10

  FR/M =    234.191 RD =  .0010 RX =  .3500 RE =  .6350 DNR =   10

  ANY MORE?  Y OR N?
? Y
  RD     RX     DNR?
? .05 .1 100

  FR/M =  1156.243 RD =  .0500 RX =  .1000 RE =  .6350 DNR =  100

  ANY MORE?  Y OR N?
? Y
  RD     RX     DNR?
? .01 .635 1

  FR/M =      4.210 RD =  .0100 RX =  .6350 RE =  .6350 DNR =    1

  ANY MORE?  Y OR N?
? Y
  RD     RX     DNR?
? .01 .9 75

  FR/M =       .012 RD =  .0100 RX =  .9000 RE =  .6350 DNR =   75

  ANY MORE?  Y OR N?
? Y
  RD     RX     DNR?
? .1 .5 10

  FR/M =     44.915 RD =  .1000 RX =  .5000 RE =  .6350 DNR =   10
```

```
  ANY MORE?  Y OR N?
? .1 .1 4
ON OR ABOUT LINE NUMBER 00350, MORE DATA THAN LIST-REENTER DATA.
? Y
  RD     RX     DNR?
? .1 .1 4

  FR/M =  1092.176 RD =  .1000 RX =  .1000 RE =  .6350 DNR =    4

  ANY MORE?  Y OR N?
? N
    STOP

SRU      1.989 UNTS.

RUN COMPLETE.
```