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# A TIME-OF-FLIGHT CALCULATION FOR PARAXIAL IONS FIELD-DESORBED FROM SHARP NEEDLE EMITTERS

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ABSTRACT

Paraxial travel times are calculated for positive ions accelerating between the surface of a field emitter and an opposite, grounded cathode. The electrode geometry is approximated by confocal paraboloids of revolution with the aperture in the ground electrode ignored in order to obtain an expression for the potential in closed form. By integrating the resulting velocity over the interelectrode distance, the travel time can be obtained in terms of the time required for the ion to drift the same distance with a constant velocity equal to its final velocity at the cathode. The resulting contribution to the measured travel time in associated time-of-flight mass spectrometers is evaluated, and shown to be important for species with small mass-to-charge ratios detected in spectrometers with short drift distances.



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In order to calculate the travel time of ions between the surface of a field-ion microscope specimen (tip) and grounded cathode, it is necessary to choose a potential model which realistically approximates the true electrode geometry. Approximating the tip and cathode as concentric spheres<sup>1</sup> results in a simple analytic expression for the travel time. Unfortunately, the model is unrealistic since it ignores the true shape of the specimen. A more satisfactory approximation is to choose the tip and ground electrode as two members of a family of confocal paraboloids of revolution. The resulting potential distribution, first obtained by Eyring et al.<sup>2</sup> and later used by Rose<sup>3</sup> and Russell<sup>4</sup> to calculate electron trajectories in an idealized field emission microscope, can be used to obtain an order of magnitude calculation for the travel time of ions in the field-desorption spectrometer and the atom-probe field ion microscope.<sup>5</sup> The specimen surface and shank will be approximated by a paraboloid of revolution having a vertex radius of curvature equal to the radius of the imaged portion of the specimen. This radius can be easily calculated once an analytical expression for the potential (and the corresponding electric field at the surface of the specimen) is obtained. The grounded cathode enclosing the tip assembly will be approximated by a second confocal paraboloid; the geometry forcing its vertex radius of curvature to be numerically equal to twice the actual tip to electrode distance. The aperture in the electrode, through which the ions pass, will be ignored in the calculation. The origin of coordinates will be chosen, for convenience, at the focus of the paraboloid representing the specimen. (Figure 1a).

Because of the geometry, the potential is most easily found by expressing Laplace's equation in confocal parabolic coordinates. Consider confocal paraboloids of revolution about the z-axis. The ordinary cartesian coordinates (x, y, z) are related to the confocal parabolic coordinates ( $\xi$ ,  $\eta$ ,  $\phi$ ) by the transformations:<sup>6</sup>

$$x = (\xi\eta)^{\frac{1}{2}} \cos\phi \quad (1)$$

$$y = (\xi\eta)^{\frac{1}{2}} \sin\phi \quad (2)$$

$$z = \frac{1}{2}(\eta - \xi) \quad (3)$$

From these transformations, the metric in the confocal paraboloidal system can be found. It is, in fact, for this orthogonal curvilinear coordinate system, just:

$$ds = \frac{1}{2} \left( \frac{\eta}{\xi} + 1 \right)^{\frac{1}{2}} d\xi + \frac{1}{2} \left( \frac{\xi}{\eta} + 1 \right)^{\frac{1}{2}} d\eta + (\xi\eta)^{\frac{1}{2}} d\phi \quad (4)$$

Now, consider only the family of confocal paraboloids of revolution described by  $\eta = \text{constant}$ . Since only  $\eta$  will enter into the boundary conditions, the potential must depend only upon this coordinate. In other words, Laplace's equation in curvilinear coordinates, for this special case, reduces to:

$$\nabla^2\phi = \frac{1}{h_\eta h_\xi h_\phi} \frac{\partial}{\partial \eta} \left[ \frac{h_\eta h_\xi}{h_\phi} \frac{\partial \phi}{\partial \eta} \right] = 0 \quad (5)$$

where the scale factors  $h_\eta$ ,  $h_\xi$ , and  $h_\phi$  are found from the metric to be:

$$h_\eta = \frac{1}{2} \left( \frac{\xi}{\eta} + 1 \right)^{\frac{1}{2}} \quad (6)$$

$$h_\xi = \frac{1}{2} \left( \frac{\eta}{\xi} + 1 \right)^{\frac{1}{2}} \quad (7)$$

and:

$$h_\phi = (\xi\eta)^{\frac{1}{2}} \quad (8)$$



Substitution of (6), (7), and (8) into (5) yields:

$$\frac{d}{d\eta} \left( \eta \frac{d\Phi}{d\eta} \right) = 0 \quad (9)$$

which can be integrated twice with respect to  $\eta$  to give, for the potential:

$$\Phi = C \ln \eta + B \quad (10)$$

It is now convenient to express  $\eta$  in terms of the cylindrical coordinates ( $r, z$ ) where  $z$  is measured as before, and  $r$ , the perpendicular distance from the  $z$ -axis to the point of interest is just:

$$r = (x^2 + y^2)^{\frac{1}{2}} \quad (11)$$

In terms of these new coordinates ( $r, z$ ) the potential,  $\Phi$ , becomes:

$$\Phi = C \ln \left[ z + (r^2 + z^2)^{\frac{1}{2}} \right] + B \quad (12)$$

where the equality:

$$\eta = z + (r^2 + z^2)^{\frac{1}{2}} \quad (13)$$

has been used, and can be verified from the transformation equations (1) - (3).

At the specimen surface,  $z = z_0$  and  $\Phi = V_0$ . At the other electrode where  $z = z_1$ ,  $\Phi = 0$ . Combining these boundary conditions with equation (10) gives, for the potential:

$$\Phi = \frac{V_0}{\ln (z_0/z_1)} \ln \left[ \frac{z + (r^2 + z^2)^{\frac{1}{2}}}{2z_1} \right] \quad (14)$$

which is equivalent to:

$$\Phi = \frac{V_0}{\ln (z_0/z_1)} \ln \left[ \frac{z + z (1 + r^2/z^2)^{\frac{1}{2}}}{2z_1} \right] \quad (15)$$

For the special case of paraxial ions  $r/z \ll 1$ , and the corresponding axial potential is just:

$$\phi = \frac{V_o}{\ln(z_o/z_1)} \ln \left[ \frac{2z}{2z_1} \right] \quad (16)$$

The electric field strength at the specimen surface is, from equation (16) just:

$$\left. \frac{\partial \phi}{\partial z} \right|_{z = z_o} \equiv F = \frac{V_o}{\ln(z_o/z_1)} \frac{1}{z_o} \quad (17)$$

But the vertex tip radius  $R$  is  $2z_o$ . This can be demonstrated by considering the parabola formed by the intersection of the paraboloid of revolution representing the tip, with, say, the  $y$ - $z$  plane, and recalling that at the tip for points near the  $z$ -axis,  $\eta = 2z_o$ . Combining this result with equation (13) and the general expression for the radius of curvature  $R$  of a section of arc gives:

$$R = 2z_o \quad (18)$$

Since the best image field,  $F$ , for helium is approximately  $4.5 \text{ V/\AA}$ , equation (17) can be used to predict the tip radius,  $R$ . Solving that equation for  $R$  and setting  $F = 4.5 \text{ V/\AA}$  gives:

$$R = \frac{V_o}{4.5 \left[ \frac{1}{2} \ln(R/2z_1) \right]} \quad (19)$$

For the field desorption spectrometer, with  $z_1 = .001 \text{ m}$ , equation (19) predicts that an 8 kV tip ( $V_o = 8 \text{ kV}$ ) will have a radius of  $322.2 \text{ \AA}$ , which is in good agreement with experimental data obtained by net plane ring counting.

The kinetic energy of a paraxial ion, at a position  $z$  in space where the potential  $\phi = V(z)$ , is just:

$$\frac{1}{2} mv(z)^2 = q \left( V_0 - V(z) \right) \quad (20)$$

Its travel time is obtained by integrating the velocity over the distance traveled. That is:

$$T = \int_{z_0}^{z_1} \frac{dz}{v(z)} \int_{z_0}^z \frac{dz}{\left[ \frac{2q}{m} \left( V_0 - V(z) \right) \right]^{\frac{1}{2}}} \quad (21)$$

Using equation (16) for the potential, the travel time becomes:

$$T = \left( \frac{m}{2qV_0} \right)^{\frac{1}{2}} \int_{z_0}^z \frac{dz}{\left[ 1 - \frac{\ln(z/z_1)}{\ln(z_0/z_1)} \right]^{\frac{1}{2}}} \quad (22)$$

This integral may be transformed into a more convenient form by defining: quantity,  $\mu$ , such that:

$$\mu \equiv \left[ \ln(z_0/z_1) \right]^{\frac{1}{2}} \left[ 1 - \frac{\ln(z/z_1)}{\ln(z_0/z_1)} \right]^{\frac{1}{2}} \quad (23)$$

Then, the travel time becomes:

$$T = -2T_t \frac{z_0}{d_0} \left[ \ln(z_0/d_0) \right]^{\frac{1}{2}} \int_0^{\left[ \ln(z_0/z) \right]^{\frac{1}{2}}} e^{-\mu^2} d\mu \quad (24)$$

where  $z_1 \approx d_0$ , the distance between electrodes, and  $T_t$  is the terminal travel time:

$$T_t = d_0 \left[ \frac{m}{2qV_0} \right]^{\frac{1}{2}} \quad q = ne \quad (25)$$

The terminal travel time is just the time required by an ion, having acquired its terminal velocity:

$$v_t = \left( \frac{2qV_o}{m} \right)^{\frac{1}{2}}, \quad q = ne \quad (26)$$

to drift through a field-free region equal in extent to the tip-to-ground electrode distance,  $d_o$ .

Plots of  $T_t / \left( \frac{m}{n} \right)^{\frac{1}{2}}$  as a function of total specimen potential,  $V_o$ , are given in Figure 1 for three values of  $d_o$ .

The integral in equation (24) is just the error integral defined by:

$$\frac{2}{\sqrt{\pi}} \int_0^x e^{-u^2} du = \text{erf}(x) = \frac{2}{\sqrt{\pi}} \left[ x - \frac{x^3}{3} + \frac{x^5}{5 \cdot 2!} - \frac{x^7}{7 \cdot 3!} + \dots \right] \quad (27)$$

so that equation (24) can be written:

$$T = -2T_t \frac{z_o}{d_o} \left[ \ln(z_o/d_o) \right]^{\frac{1}{2}} \left[ \ln(z_o/z) \right]^{\frac{1}{2}} \times \left[ 1 - \frac{x^2}{3} + \frac{x^4}{5 \cdot 2!} - \frac{x^6}{7 \cdot 3!} + \dots \right] \quad (28)$$

Where:

$$x = \left[ \ln(z_o/z) \right]^{\frac{1}{2}} \quad (29)$$

Defining:

$$y = \ln(z_o/z) \quad (30)$$

allows equation (28) to be written:

$$T = 2T_t \frac{z_o}{d_o} \left[ \ln\left(\frac{z_o}{d_o}\right) \ln\left(\frac{z_o}{z}\right) \right]^{\frac{1}{2}} \left[ 1 - \frac{y}{3} + \frac{y^2}{5 \cdot 2!} - \frac{y^3}{7 \cdot 3!} \right] \quad (31)$$

or equivalently:

$$T = 2T_t \frac{z_o}{d_o} \left[ \ln \left( \frac{z_o}{d_o} \right) \ln \left( \frac{z_o}{z} \right) \right]^{\frac{1}{2}} \left[ \sum_{v=1}^{\infty} \frac{[-\ln (z_o/z)]^v}{v!(2v+1)} \right] \quad (32)$$

Consider the special case  $z = d_o$ . Then  $T$  is just the tip-to-ground electrode travel time,  $T_o$ , and equation (32) becomes:

$$\frac{T_o}{T_t} = \frac{R}{d_o} \left[ \ln (R/2d_o) \right] \left[ \sum_{v=0}^{\infty} \frac{[-\ln (R/2d_o)]^v}{v!(2v+1)} \right] \quad (33)$$

Figure 2 is a graph of  $T_o/T_t$  for various values of  $R/d_o$ . To obtain the curve, 200 values of  $R/d_o$  were taken, and for each the series in equation (33) was evaluated. Sufficient terms were included (usually about 30) so that the sum of the series was always accurate to seven decimal places. For single atom mass spectrometers with  $z_1 \approx .001$  m, and  $R = 322.2 \text{ \AA}$  (8 kV tip) Figure 2 predicts that  $T_t / \left( \frac{m}{n} \right)^{\frac{1}{2}} = .81 \text{ nsec}/(\text{amu})^{\frac{1}{2}}$  and Figure 2 that:

$$T_o/T_t = 1.06 \quad (34)$$

Then  $T_o$ , the actual specimen-to-ground electrode travel time is, just:

$$T_o \text{ (nanoseconds)} = 0.859 \left( \frac{m}{n} \right)^{\frac{1}{2}} \quad (35)$$

To evaluate the effect of  $T_o$  on species identification in a time-of-flight, single-atom mass spectrometer, we will use the expression for the kinetic energy of an ion species after leaving the grounded cathode cap located at  $z = z_1$ ,

$$\frac{1}{2} m v_t^2 = qV_o = neV_o \quad (36)$$

and the drift distance,  $D$ , between this electrode and the detector:

$$d = v_t T_D \quad (37)$$

The actual time-of-flight,  $T_{\text{meas}}$ , of the ion is just the sum of its drift time,  $T_D$ , and the time taken,  $T_o$ , to tranverse the acceleration region:

$$T_{\text{meas}} = T_D + T_o = \frac{D}{v_t} + T_o \quad (38)$$

Combining equations (36) and (38) gives, for the identity of the unknown species:

$$\frac{m}{n} (\text{amv}) = \frac{2e}{D^2} V_o T_{\text{meas}}^2 \left[ 1 - \frac{T_o}{T_{\text{meas}}} \right]^2 \quad (39)$$

Equation (39) may be rewritten, to a first approximation, as:

$$\frac{m}{n} (\text{amv}) \cong \frac{2e}{D^2} V_o T_{\text{meas}}^2 \left[ 1 - \Delta \right] \quad (40)$$

where the first term in brackets is the usual expression<sup>6</sup> for the mass-to-charge ratio of the unknown species, and the second term is the acceleration correction

$$\Delta \equiv \frac{2T_o}{T_{\text{meas}}} \quad (41)$$

Using the first order approximation

$$T_{\text{meas}} \approx D \left( \frac{m}{2neV_o} \right)^{\frac{1}{2}},$$

and equations (25) and (33), the acceleration correction is obtained:

$$\Delta = 2G \left( \frac{R}{2do} \right) \frac{do}{D} \quad (42)$$

where:

$$G \left( \frac{R}{2do} \right) \equiv \frac{R}{2do} \left[ \sum_{\nu=0}^{\infty} \frac{[-\ln R/2do]^{\nu}}{\nu! (2\nu+1)} \right] \ln \left( \frac{R}{2d\delta} \right)$$

Practically,  $\Delta$ , varies slowly for  $10^{-8} \leq \frac{R}{2do} \leq 5 \times 10^{-5}$  and, therefore, can be treated as a constant for all specimen radii of interest. For  $do = .001$

$$\Delta \cong 1.8\% \quad (D = .118\text{m})$$

$$\Delta \cong 0.2\% \quad (D = 1.0 \text{ m}) .$$

Where  $\Delta$  has been calculated from the computer program of Appendix 1. The acceleration correction is negligible for long drift distances ( $D > 1\text{m}$ ), but must be considered for all short drift distance spectrometers. Specifically, for the 10-cm atom-probe<sup>7</sup> ( $D = .118\text{m}$ ), equation (40) becomes:

$$\frac{m}{n} = (.982) \frac{(.193)}{.118} V_o T_{\text{meas}}^2$$

## Appendix 1

```
PROGRAM CORR(TINPUT,OUTPUT)
C PROGRAM TO CALCULATE THE TRAVEL TIME CORRECTION DUE TO
C ACCELERATION NEAR THE SPECIMENT. R/2D0=Z, 2T0/ATMEAS=C1
C (1.0M DRIFT), C2(.118M DRIFT)
Z=0.5E-07
DO 1 K=1,100
SUM=0.0
TERM=1.0E-06
FAC= 1.
ZLOG= ALOG(Z)
DO 2 I=1,200
RI= I
FAC= FAC*RI
PTERM=TERM
RNUM= (-ZLOG)**I
DENOM= FAC*((2.*RI)+1.)
TFRM= RNUM/DENOM
SUM=SUM+TFRM
IF(ABS(TERM-PTERM).LT.1.0E-06) GO TO 3
2 CONTINUE
3 TO= 2.*Z*ABS(ZLOG)*(1.0+SUM)
C1= 2.*TO*.001
C2= C1/.118
C= 1.0 - C1
C3= 1.0 - C2
PRINT 4, Z,TO,I,C1,C2,C,C3
1 Z=Z+0.5E-06
4 FORMAT(5X,2(E12.6,5X),I3,4(5X,E12.6))
STOP
END
```



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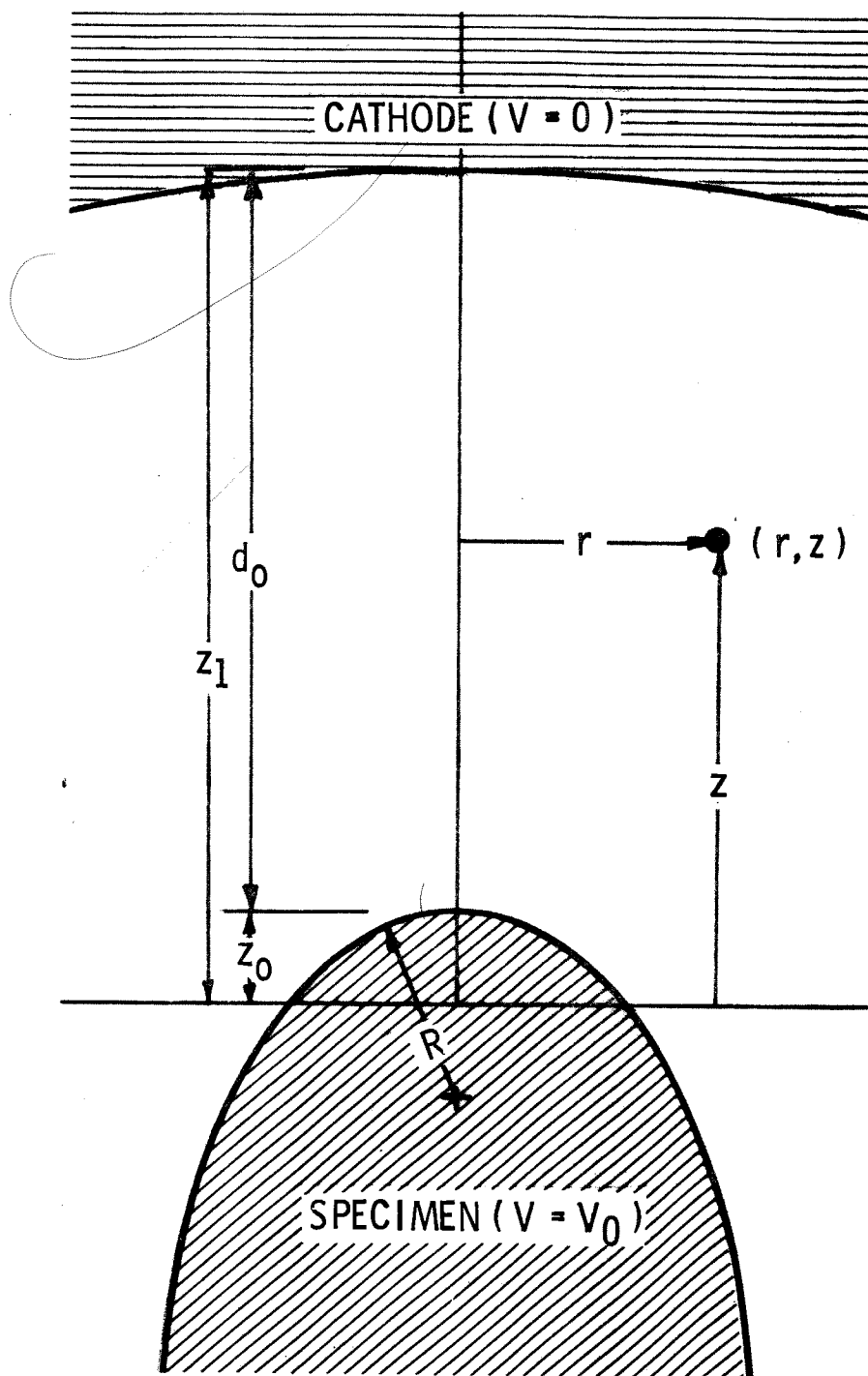


Figure 1a. Electrode Geometry

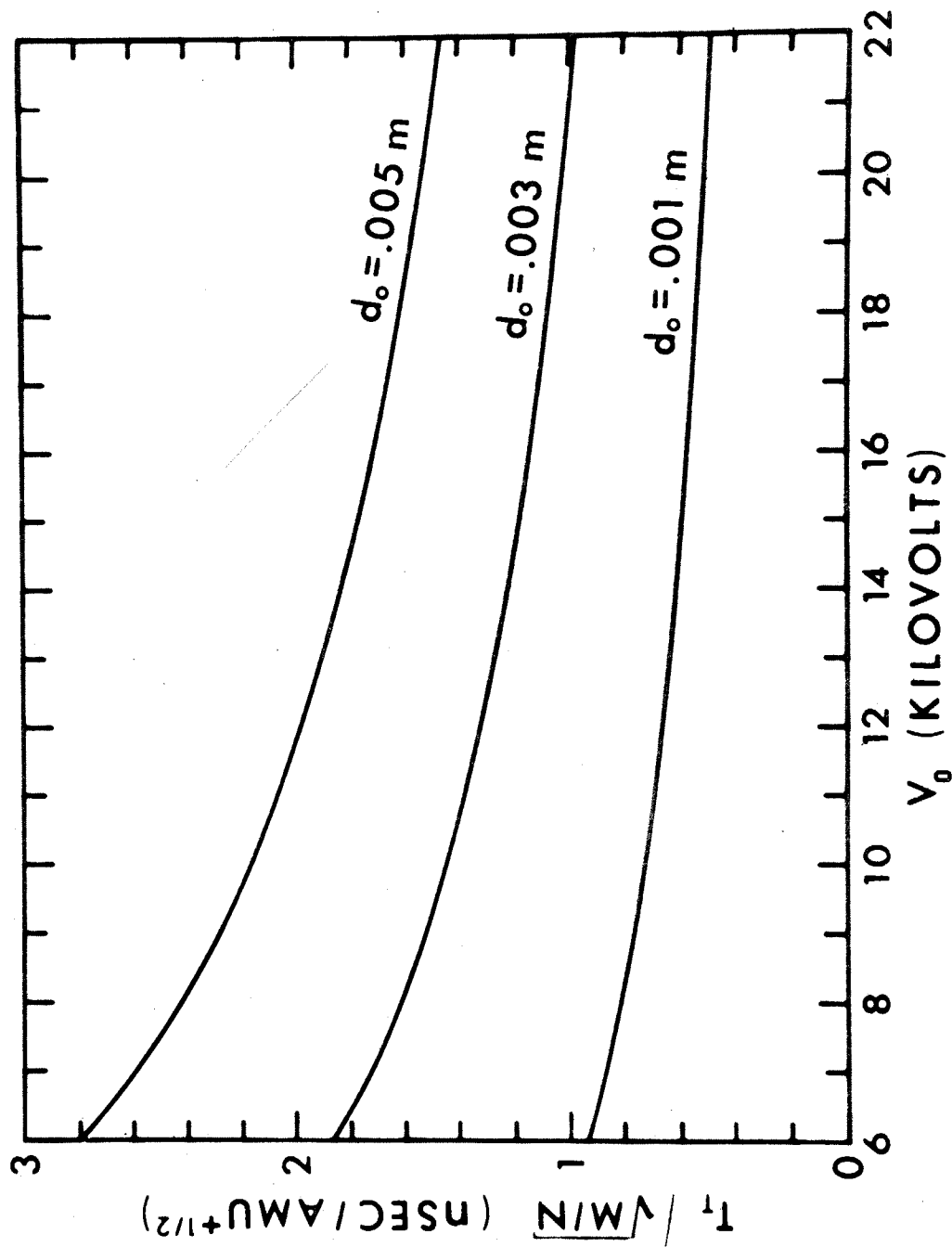


Figure 1. The terminal travel time  $T_T / (m/n)^{1/2}$  of paraxial ions for various specimen-to-cathode distances,  $d_0$  as a function of specimen bias,  $V_T$ .

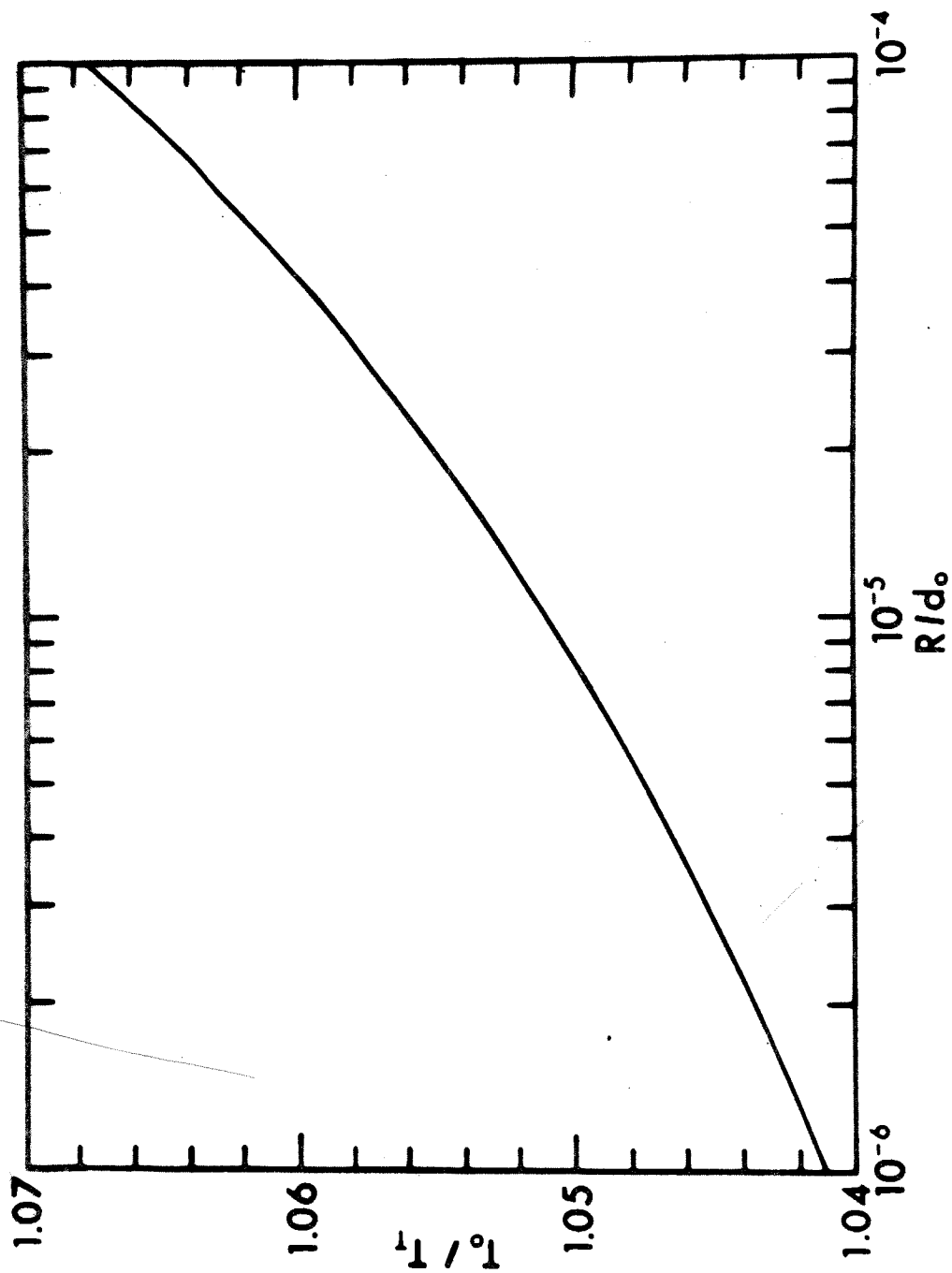


Figure 2. Ratio of actual to terminal travel time ( $T_o/T_t$ ) as a function of the specimen radius divided by the specimen to cathode distance ( $R/d_o$ ).

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