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AN ACCURATE MODEL FOR SAMPLE DROPLET ACCELERATION IN ANALYTICAL--ETC(U)

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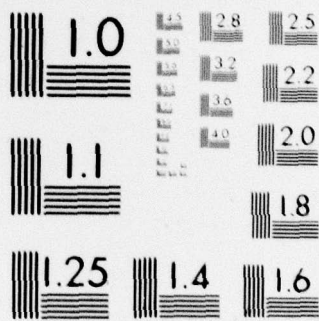
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AN ACCURATE MODEL FOR SAMPLE DROPLET ACCELERATION  
IN ANALYTICAL FLAMES

by

Richard E. Russo and Gary M. Hieftj.

Prepared for Publication

in

ANALYTICAL CHEMISTRY

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Department of Chemistry

Bloomington, Indiana 47405

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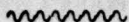
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BRIEF

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A revised model for droplet acceleration in an analytical flame or plasma accurately predicts experimentally observed behavior in an air-acetylene flame. The principal modification involves a spatially changing flame rise velocity.

## ABSTRACT



The experimentally observed velocity of an aerosol droplet in an air-acetylene flame is compared to the velocity calculated through a new mathematical model. The experimental droplet velocity is measured by means of stroboscopic photography of a stream of individual droplets sent into a flame at a known frequency and traveling very reproducible trajectories. Because the temporal spacing between these droplets is known, a measure of the instantaneous droplet location enables their velocity to be calculated. The droplet acceleration model was modified by incorporating into it a spatially changing flame rise velocity, which was assumed constant in earlier treatments. Excellent agreement has been found between calculated and measured droplet acceleration in the flame.

## INTRODUCTION

An aerosol droplet of sample solution, directed into an analytical flame or plasma, will rapidly accelerate toward the moving gas velocity. The rate and degree of approach of the droplet to the flame gas velocity is important both fundamentally and practically in analytical spectrometry. For example, the differential velocity between the droplet and the flame (or resulting particle and the flame) governs whether or not convective mass transport is significant in desolvation and vaporization. Also, droplet acceleration affects the eventual distribution of analyte atoms throughout the flame, which in turn influences analytical sensitivity, precision and working curve linearity.

In particular, the horizontal acceleration of droplets as they enter a flame has been shown to be responsible for some of the lateral spread of atom populations (1). More importantly, the vertical acceleration of aerosol droplets determines the distribution of analyte atoms above the burner, and therefore contributes to the optimal viewing height in the flame. It is also this vertical acceleration which determines the amount of time before a droplet (or particle) reaches the flame gas velocity, at which time convective mass transport becomes negligible in its influence on the atomization processes.

A mathematical expression has been formulated to model the vertical acceleration of aerosol droplets in a flame or plasma (2). However, the time-dependent droplet velocity calculated through this expression does not accurately predict the velocity actually observed. The

apparent oversight in this previous work (2,3) is that flame rise velocity was assumed to be constant across the burner. Unfortunately, this assumption leads to greater theoretical than observed droplet acceleration; in the experimental test of the model, droplets were injected into the flame in a direction perpendicular to its flowing axis, so they experienced a spatially changing flame velocity. Moreover, in the present study it was found that the measured droplet velocity in the flame is affected significantly by the droplet introduction rate. At droplet introduction rates greater than 2KHz, the droplets bunch together, forming a quasi-continuous stream of solution. The flame then must accelerate the entire stream instead of individual entities, thereby leading to different behavior than expected for acceleration of single droplets. In the present paper, the agreement between theoretical and experimental results is improved by incorporating a measured, spatially changing flame rise velocity into the acceleration expression, and by controlling carefully the droplet introduction rate. Significantly, theoretical results are shown to compare quite favorably with the measured droplet velocity over the entire droplet lifetime in the flame.

#### THEORY

The droplet acceleration expression is derived from Newton's Second Law,  $a=F/m$ , where  $a$  is the acceleration of the droplets,  $m$  is their mass, and  $F$  is the algebraic sum of forces acting on the droplets in the flame. There are two such forces: the viscous drag of the rising flame gases which serve

to accelerate the droplets, and gravitational attraction, which tends to retard them. For a laminar flame and spherical droplets, viscous drag can be expressed by Stoke's Law as:  $3\pi\eta d(V - V_d)$ , where  $\eta$  is the average viscosity of the flame gases,  $d$  is the diameter of the droplets, and  $V$  and  $V_d$  are the velocities of the flame and droplet, respectively. Gravitational attraction is  $mg$ , where  $g$  is the gravitational constant.

Unfortunately, droplet diameter and mass are not constant in the flame because of ongoing desolvation. Therefore, time-dependent relations for droplet mass and diameter must be incorporated into the foregoing treatment. The time dependence of droplet size during desolvation has been determined (4) to be,  $d^2 = d_0^2 - kt$ , where  $d$  is the droplet diameter at time  $t$  after its entry into the flame,  $d_0$  is the initial droplet diameter, and  $k$  is the desolvation rate constant. Upon substitution of the two time-dependent forces into Newton's Second Law, the droplet acceleration expression becomes:

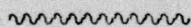
$$a = \frac{18\eta(V - V_d)}{\rho(d_0^2 - kt)} - g$$

where  $\rho$  is the density of the aerosol droplet.

In an earlier treatment (2), this expression was integrated to calculate the droplet velocity in the flame. However, direct integration is valid only if one assumes the flame velocity to be constant over the entire lifetime of the droplet. We have found that this assumption is not valid, especially when a droplet generator (4) is used to inject the aerosol droplets into the flame. In this situation, used to test the proposed model, droplets are introduced into the flame in a direction perpendicular to the flame

flow and therefore experience a parabolic flame rise velocity gradient as they penetrate into the flame. Consequently, to obtain agreement between the proposed model and results obtained using the droplet generator, one should determine experimentally the flame velocity profile, relate this profile to the time-dependent horizontal droplet position, and then integrate the acceleration expression. Unfortunately, such a procedure leads to a fourth-order dependence of acceleration on flame rise velocity, making integration difficult and laborious. Instead, a numerical approach was chosen in the present study. In this approach, the acceleration expression is directly evaluated at very small time intervals using an experimentally mapped flame rise velocity.

#### EXPERIMENTAL



In the measurement of droplet velocities, a droplet generator is used to inject into the flame uniform-sized aerosol droplets with reproducible, isochronal spacing (4,5). Because of this reproducibility, a single high-intensity flash photograph reveals the trajectory and spatial relationship of droplets in the flame, from which their instantaneous and spatially dependent velocities can be deduced. Figure 1 of reference 4 shows such a single-flash photograph, with a droplet introduction rate of 1000 droplets per second.

In the present study, droplets were introduced into the flame in a slightly downward direction in order to establish a zero-vertical-velocity droplet location. Experimentally, vertical droplet positions were obtained

by direct measurements above this reference droplet. Of course, small variations in individual droplet positions exist because of air currents about the apparatus. Therefore, droplet positions from several photographs were averaged to obtain an experimental curve of droplet position versus droplet residence time in the flame (Figure 1). Each droplet position in Figure 1 represents the average of five different photographs in which all droplet generator and flame conditions were the same. Error bars in Figure 1 represent 95% confidence limits, indicating that less than 6% error exists in assigning droplet positions. If necessary, the magnitude of this error could be decreased by averaging additional photographs or by shielding the experimental apparatus from ambient air currents.

The time-dependent horizontal position of the droplets in the flame was also measured from the single-flash photographs. Coupled with knowledge of the rise velocity of the flame as a function of position across the burner (horizontal flame rise-velocity profile), this measurement enables one to calculate the flame velocity that each droplet experiences as it traverses the flame. The method of obtaining flame rise-velocity profiles is described elsewhere (6). The rise-velocity profile for the air-acetylene flame used in this study is shown in Figure 2. Asterisks in Figure 2 represent the flame rise velocity values measured at a particular burner location. Again, error bars show the 95% confidence limits. Not surprisingly, the relationship between rise velocity and position across the flame was found to fit a second-order polynomial expression with a correlation coefficient of 0.98. The smooth parabolic curve (dotted), obtained from this polynomial expression, is what one would expect from Poiseuille's

equation for a laminar flow system. The velocity of the flame that each droplet experiences with respect to spatial position can be easily found from this polynomial (or from Fig. 2), and direct evaluation of the acceleration expression at short time intervals then becomes possible.

A 100ppm barium chloride solution (density = 1.0 g/mL) was used in the droplet generator reservoir. The initial droplet diameter was measured to be  $68 \pm 2 \mu\text{m}$ , using the MgO technique (7). Droplet introduction rates were kept below 2KHz in order to minimize the slip-stream effect (8). Flame gas viscosity was calculated to be 660 micropoise, using statistical mechanics, for a flame temperature of 2450K (9). This average flame temperature was measured over the flame region of study using the sodium line-reversal technique (10).

#### RESULTS AND DISCUSSION

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The random spatial distribution of droplets produced by a conventional nebulizer makes it unlikely that one droplet will strongly affect the acceleration or velocity of another. However, with the droplet generator used in the present study, droplets follow identical trajectories through the flame and can affect each other by developing a slip-stream (8). Understandably, this slip-stream effect is most marked when droplets are closely spaced; visual changes in droplet velocity (spacing) are evident at droplet introduction frequencies greater than 2KHz. Because this slip-stream effect, if pronounced, tends to shield each droplet somewhat from the viscous forces of the flowing flame gases, upward droplet acceleration is somewhat lowered at high droplet introduction rates.

This reduction in acceleration is evident by examination of Figure 3, in which all experimental conditions were the same except for the droplet introduction rate. At an introduction rate of 2.8KHz, droplets approach the flame velocity more slowly than at 1.6KHz. To obtain a measure of droplet velocity consistent with the developed theoretical model, a low droplet introduction rate (1.6KHz) was employed in the present study. At this rate, the slip-stream effect should be negligible (8).

Figure 4 compares droplet velocity curves calculated through the acceleration expression with one obtained experimentally at a droplet introduction rate of 1.6KHz. The upper theoretical curve (dot-dash) represents the droplet velocity calculated assuming a constant flame rise velocity of 10.0 m/s. The lower curve (dotted) was calculated by incorporating the spatially changing flame rise velocity (ca. Fig. 2) into the acceleration expression and evaluating it as small, discrete time intervals. As expected, the predicted acceleration is too great when a constant average flame rise velocity is assumed. In contrast, the curve incorporating a spatially changing flame rise velocity (dotted) agrees within experimental error with observed velocities over the entire lifetime of a desolvating droplet. Clearly, a spatially changing flame rise velocity must be considered in order to accurately model droplet acceleration when a droplet generator is used for nebulization. In conventional nebulizer systems, however, droplets usually enter the flame vertically and a constant flame rise velocity in the acceleration expression should provide close agreement with observed behavior.

Additional but small improvement in the droplet acceleration model is possible. For example, the existing expression does not take into account

the change in density which occurs as droplets desolvate and become more concentrated. Also, a changing flame viscosity could be incorporated into the model. Such a change probably occurs as a result of changing flame temperature and water vapor concentration in the vicinity of the droplets. Inspection of the acceleration expression reveals that both of these modifications would improve agreement with experiment. Finally, it is not yet certain that the effect of one droplet on another is completely removed at the droplet introduction rate employed in this work. In order to measure the true droplet trajectory (velocity) in the flame, one would have to inject a single droplet and monitor its path with a high-speed motion camera.

In our view, the improved agreement between experiment and theory which the above three modifications would yield does not justify the substantial complications which they would introduce into both the existing model and its verification. In most cases, the agreement obtained in this study would be sufficient to predict both the spatial distribution of atoms in an analytical flame and the amount of time required for introduced droplets (or particles) to reach the flame rise velocity.

CREDIT

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FIGURE LEGENDS

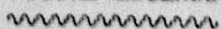


Figure 1. Droplet trajectory in the flame. Initial droplet diameter =  $68 \mu\text{m}$ . Introduction rate =  $1.6\text{KHz}$ . Error bars indicate  $\pm 95\%$  confidence limits.

Figure 2. Spatial velocity profile in stoichiometric (fuel/oxidant = 0.13) air/acetylene flame. Asterisks represent measured velocities; dotted line is curve obtained from second-order fit (correlation coefficient = 0.98).

Figure 3. Measured droplet velocity in the air-acetylene flame. All droplet generator and flame conditions are the same, except for the droplet introduction rate.

0  $\equiv$  introduction rate =  $2.8\text{KHz}$

\*  $\equiv$  introduction rate =  $1.6\text{KHz}$

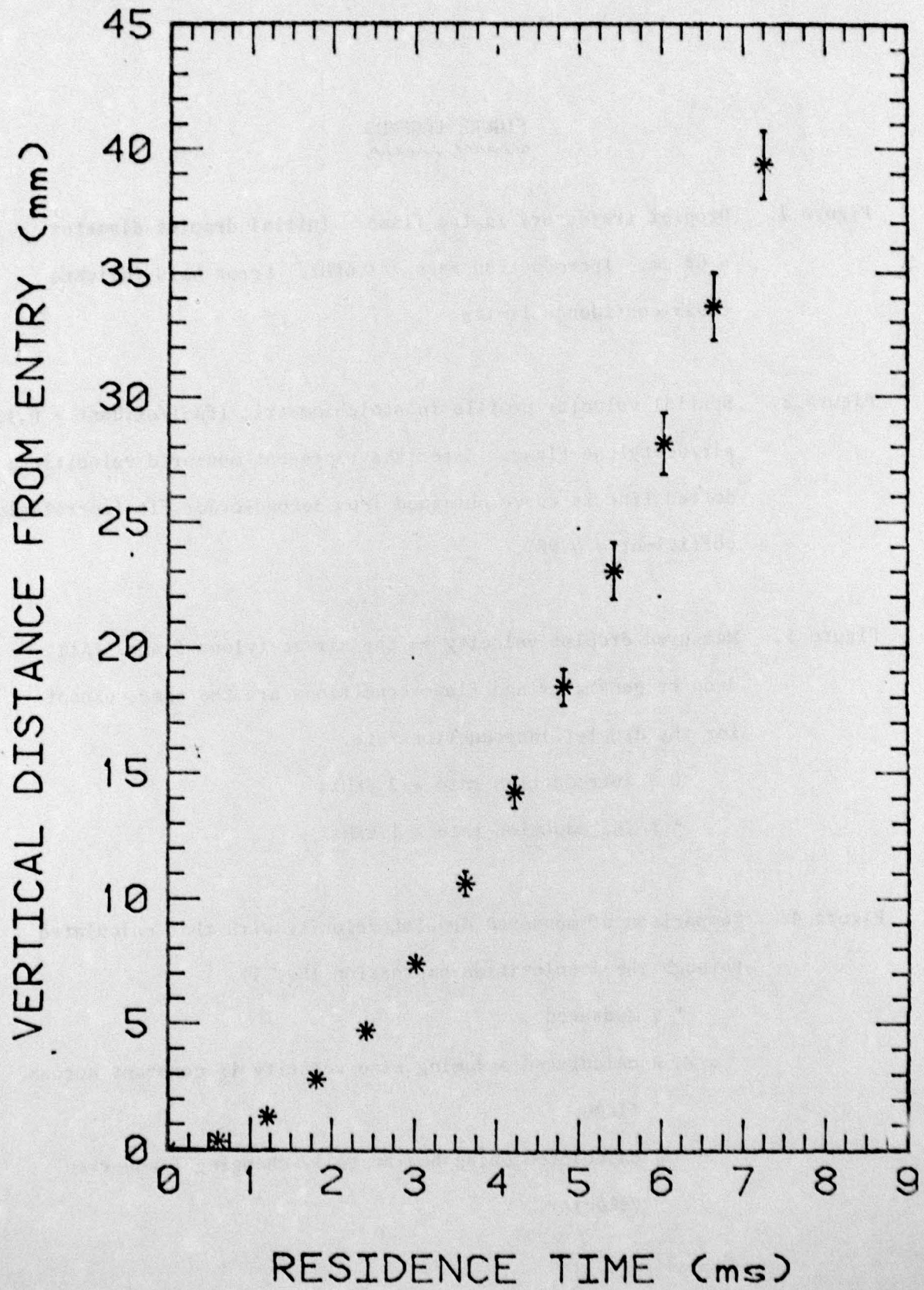
Figure 4. Comparison of measured droplet velocity with that calculated through the acceleration expression (Eq. 1).

\*  $\equiv$  measured

---  $\equiv$  calculated assuming rise velocity is constant across flame.

....  $\equiv$  calculated using horizontally changing flame rise velocity.

Figure 1



FLAME VELOCITY (m/s)

Figure 2

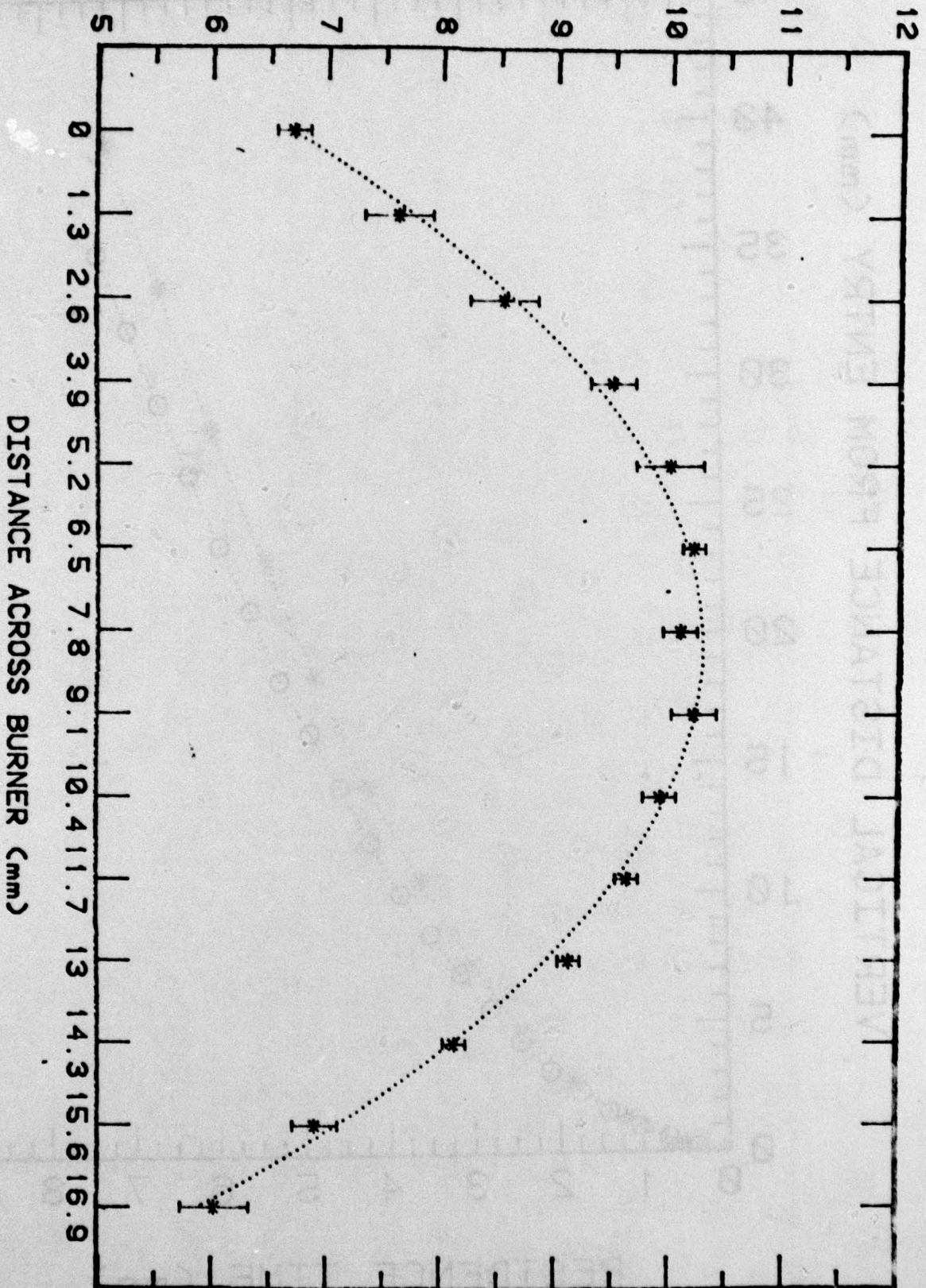


Figure 3

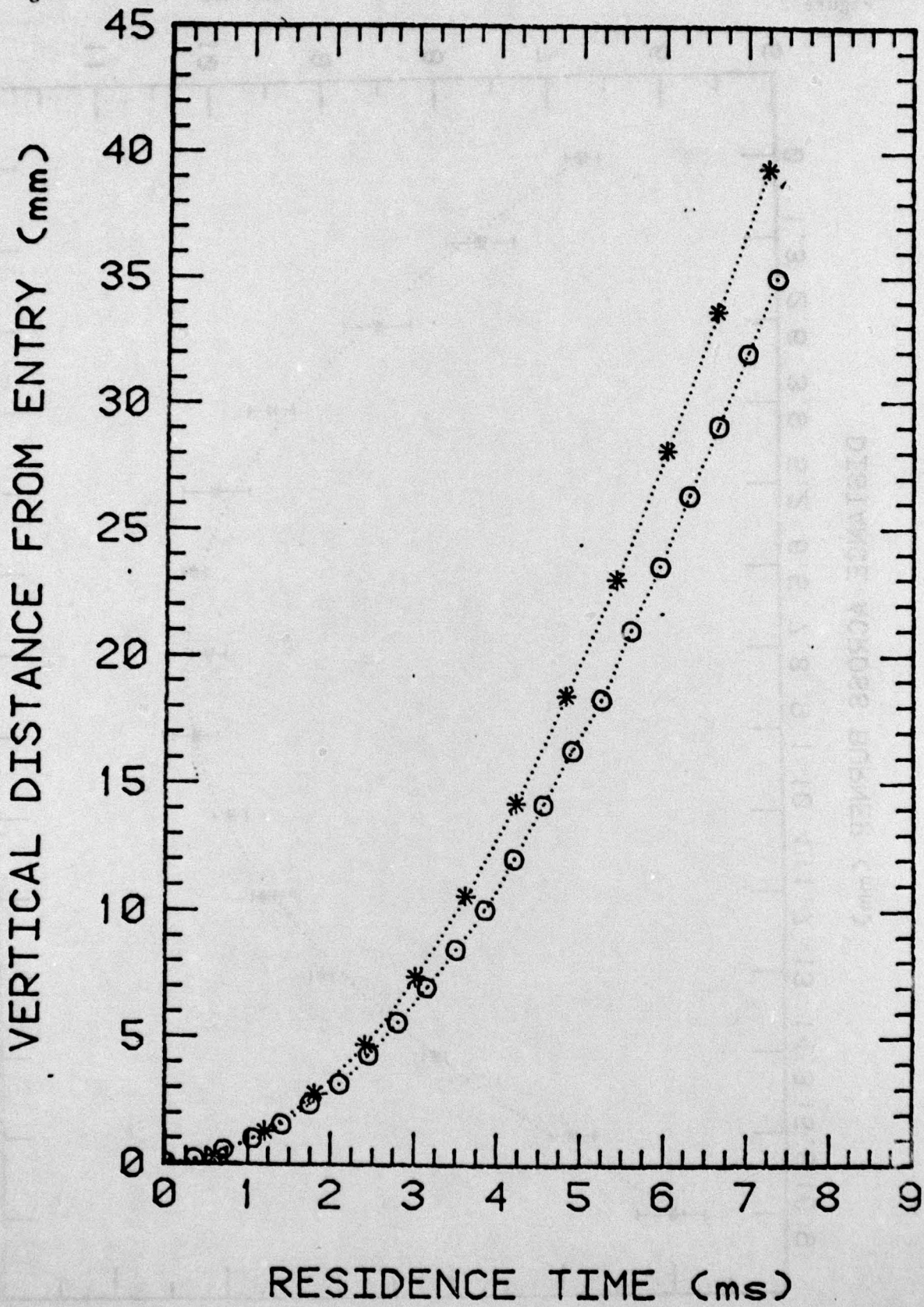
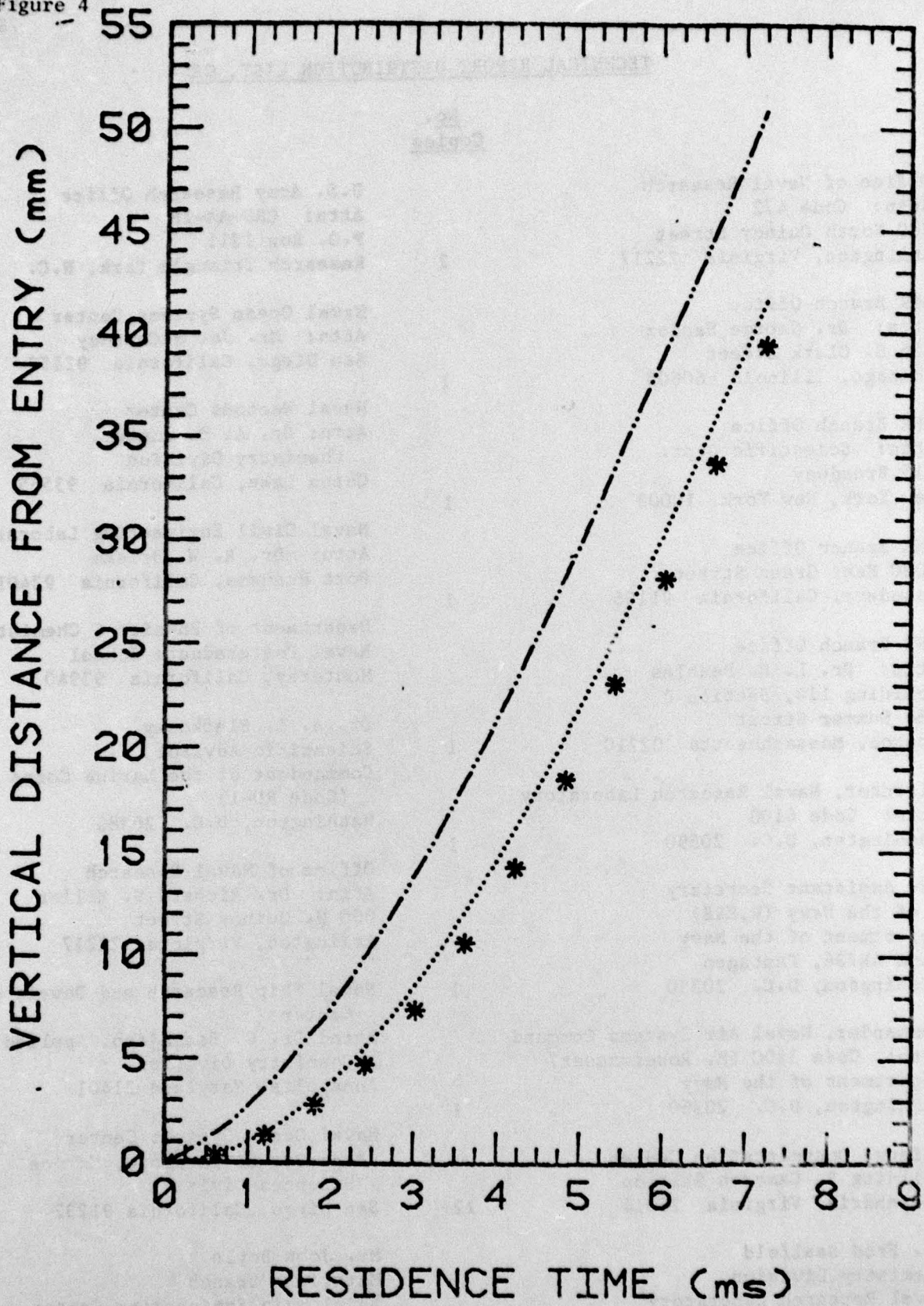


Figure 4



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