

"The Effect of Ultrasonic Waves on Emulsification"

Final Report to Branson Sonic Power Company

Submitted by

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SUMMARY

A new technique has been developed for producing small polymer particles with diameters in the micron and submicron region. The particles are produced by ultrasonically emulsifying a monomer in water to form droplets which are then polymerized. The particle size distribution obtained with this technique is believed to be the narrowest that has ever been reported.

Current results show that, over the range of irradiation times applied (from 0.1 min. to 5 min.) at a frequency of 20 KHz, the mean particle sizes approach to constant values for different intensity levels. Standard deviations, on the other hand, are generally inversely dependent on the total number of particles counted; and in most cases, the deviations are less than 1% of the corresponding mean diameters.

While the mechanism is not entirely understood, as well as how all variables will affect the particle size and particle size distribution, we have delineated certain operating variables and variable settings which will produce particles of a given size. Further studies could be conducted to elucidate the emulsification mechanism and identify other parameters which could influence the mean particle size and distribution.

INTRODUCTION

The method developed in this laboratory for producing small particles by acoustic emulsification has application not only in the uses of the particles themselves, but also as a definitive means of studying the mechanism and parameters which produce the emulsion. The technique involves ultrasonically emulsifying a monomer in water and then polymerizing the monomer droplets to form solid spheres. These spheres can be readily analyzed with the aid of a scanning electron microscope (SEM). Photomicrographs taken on the SEM at 30,000X magnification of two different runs are shown in Figure 1(a) along with the plots of particle size distributions for the other two runs (Figures 1 (b) and 1(c)). The mean particle size in the left hand photograph is 0.37 microns and the mean in the right is 0.32 microns. As evidenced by the photomicrographs and the plot, the distribution of particle sizes is believed to be the narrowest ever reported, for particles of this size produced by emulsification without the aid of a chemical emulsifier or additive of any type. One also notes that a number of particles as small as 0.07 microns have been observed. If the mean particle size could be made to fall in this range, it should be possible to affect the average molecular weight and molecular weight distribution by varying the particle size, when the amount of initiator added is chosen and controlled.

Although the mechanism by which ultrasonic emulsions are produced is not well understood, acoustic emulsification has been used successfully in a number of industrial applications (wax-sizing emulsions, food processing, paints).^{1,2,3} If the key parameters affecting the emulsion could be identified in a more quantitative manner, the efficiency of these and other potential applications should be greatly increased.

Perhaps one of the most exciting potential applications is the use of the technique to produce encapsulated enzymes or

immobilized enzymes attached to the particles. Owing to the small particle size and narrow distribution, the treated particles could be injected directly into the blood stream to act as a poison scavenger or in some other therapeutic means. This latter idea came about after a discussion of a technique in which perfluorochemical emulsions, produced by applying acoustic waves, were subsequently used as blood substitutes.⁴ The perfluorochemical droplets were small enough to readily pass through the blood capillaries. One of the major disadvantages of the technique these investigators reported was that the sonification broke down the perfluorochemicals releasing toxic quantities of fluoride ions. However, degradations of this type are usually a result of cavitation. Consequently, if the investigators had carried out the emulsification at higher frequencies or under pressure, where cavitation will not occur, it is highly unlikely that the degradation would have occurred. In applications of this type it is imperative that particles be small with a very narrow distribution so as not to block the smallest of the blood capillaries, thereby producing an embolism.

This technique may also find application in the ion-exchange and chromatographic field³⁰, where a mixture of monomers, (such as styrene-divinylbenzene with strong acidic sulfonic group, or neutral styrene-divinylbenzene copolymers) is emulsified in water. With subsequent removal of water, the resulting resin may be used for amino-acid analysis or chromatographic separations. Presently, commercial resin with narrow particle size distribution in the micron region are available; price ranges from \$3-10/gm of resin, depending on the size and distribution range of the resin³⁰.

Some of the basic advantages of acoustic emulsification are:⁵

1. Pure, concentrated, and highly monodispersive emulsions.

The emulsions formed by acoustic emulsification can have a mean particle size of 0.2 to 2 μ , with an extremely narrow particle size distribution. Pure emulsions of over 30% concentration have been obtained by acoustic emulsification. Higher concentrations of up to 70% have also been obtained with the aid of emulsifiers.

2. Stable emulsions. One of the most important properties of acoustic emulsification is that it yields extremely stable emulsions without the use of emulsifiers or stabilizers. This is believed to be due to the monodispersive nature of the emulsions and to the formation of an electric double layer around the suspended droplets.

3. Control of the type of emulsion. Under certain acoustic field conditions, both oil-in-water and water-in-oil types of emulsions can be produced. This is not possible by means of mechanical processes, where only the nature of the emulsifier controls the type of emulsions produced. Thus, toluene can be emulsified in water at low sonic intensities, and the continuous phase can be reversed at high intensities.⁶

Because of these many advantages, ultrasonic emulsification is becoming increasingly popular in dairy, petroleum, pharmaceutical, and similar industries and has potentially greater areas of application in a number of technological and medical processes. However, there is a lack of understanding not only of how to obtain optimum results, but also of the mechanisms of the formation of emulsions in an acoustic field.

PREVIOUS WORK

Bondy and Sollner⁷⁻¹⁰ were among the first to investigate the mechanism of emulsification of oil-in-water systems by ultrasonic waves. They concluded that cavitation, which is the nucleation, growth and subsequent collapse of bubbles or cavities in liquids¹⁰, was responsible for the emulsification process. They also reported the degree of dispersion, based on 300 counts of particles on a photograph magnified 1,000 times by a water-immersion microscope, in terms of relative (%) masses. If one converts their units to relative counts of particles in different size groups, one finds their mean diameter to be approximately 3 microns for the toluene-water system irradiated for 3 minutes at 50 milliamps. This particle diameter is similar to that which can be achieved in a colloid mill.

In the 1960's, Neduzhii^{6,11-14} carried out a series of studies on parameters, such as density, viscosity, intensity and frequency, to learn how they affect the dispersion process and the nature of the dispersion. In view of the facts that (1) the particle size at the onset of dispersion is independent of the sound intensity (2) the rate of emulsification increases with increasing intensity, which is believed to be due to an increase in number of cavities; and (3) the threshold of sound intensity required for the initiation of cavitation and dispersion is nearly the same, he reached the same conclusion as Bondy and Sollner.

Neduzhii's studies were in the frequency range of 22 kHz to 2,000 kHz. At frequencies above 500 kHz, the cavitation mechanism is essentially eliminated, consequently Neduzhii's general conclusion certainly does not apply to the whole frequency range of his study. His results relating particle-size to frequency and intensity need also be viewed with

reservation, as the optical microscope would be incapable of differentiating 1/3 micron from 1/2 micron, as was claimed by Neduzhii¹³. Some of the disparity of these results as well as those of other investigators^{15,16} may also have come about owing to the limitations of their optical equipment used to measure particle sizes.

In addition to cavitation, the interfacial instability mechanism is also believed to be involved in the emulsification process¹⁷⁻¹⁹. The classical Rayleigh-Taylor instability analysis of an interface subjected to vertical accelerations will yield an unstable mode of an interfacial wave which may grow when the acceleration is directed from the lighter liquid to the heavier liquid. The Kelvin-Helmholtz type of instability occurs when the viscosities of the two liquids subjected to an acoustic field, differ and become controlling. Here the growth rates of interfacial waves may differ owing to the different viscosities. This may give rise to a relative tangential velocity at the interface which could become unstable²⁰. In general, at low frequencies, cavitation should prevail; while at high frequencies, large differences in viscosity and small density differences, the cavitation mechanism should be less prominent and the interfacial instability mechanism should dominate²¹.

With the aid of scanning electron microscope, we have shown that, the particle size distribution for (monomer-styrene)*-water system after being irradiated by ultrasonic waves and subsequently polymerized in a water bath, is extremely narrow with a mean particle size in the vicinity of 0.3 microns (at exciting frequency of 20 kHz over the irradiation period ranging from 6 seconds to 5 minutes), which has not been previously observed. A question then arises as to whether the primary mechanisms are able to produce monodispersive particle size distribution in the

* Courtesy of the Dow Chemical Company, Midland, Michigan.

sub-micron region^{13,22}, or there could be a secondary break-up process occurring after the initial eruption of the interface.

EXPERIMENTAL PROCEDURE

The first stage of the work has been devoted to the formulation and familiarization of experimental technique, which is outlined in Figure 2, for measuring particle sizes and distribution of the ultrasonically-induced emulsions. Transducer tip was placed into the monomer-saturated water phase. After irradiation, the emulsion was transferred to a sample bottle with subsequent dilution to a desirable degree; the sample bottle was then introduced into a thermo-regulated tank and the monomer emulsion was polymerized at a constant temperature. A few drops of the polymer emulsion were air-dried on a metal stub and gold-plated in order to increase conductivity of the sample for the scanning electron microscopic analysis. Pictures at various magnifications were taken and particle sizes measured and interpreted accordingly. Monomer-styrene and water were chosen to be the immiscible two-phase system because of the readily-availability of their physical and chemical data^{23,24}.

One notes from Smoluchowski's flocculation rate expression, that (1) if one assumes the mutual diffusion coefficient of two nearby particles equal to the sum of their individual diffusivities, the rate of flocculation for uniform (particle-size) emulsion will always be slower than that of emulsion with non-uniform particle sizes^{25,26}; (2) the coalescence rate is also decreased as concentration of the emulsion is decreased.

The experimental technique described here eliminates the coalescence of particles during measurement of particle sizes, and minimizes coalescence after the formation of the droplets by the ultrasonic action. The following are responsible for this:

- (i) The monodispersive nature of the emulsion tends to greatly reduce the coalescence rate;
- (ii) Initially, 2 ml of styrene, containing 0.013 mole/liter of benzoyl peroxide, were emulsified in 50 ml of styrene-saturated water. The emulsion was further diluted by 75 ml styrene-saturated water after the irradiation was completed; this will greatly reduce the coalescence rate;
- (iii) The monomer emulsion was polymerized in a thermo-regulated 75 °C water-bath after the dilution. When the conversion of monomer rises above 30%²³, most particles were rigid and the tendency for their coalescence upon collision is practically eliminated²⁷. This differs from other methods in that here emulsion becomes more stable as time elapsed²⁶;
- (iv) Most of the particle-size distribution photomicrographs were taken by the scanning electron microscope within 15 hours from the start of the polymerization to avoid as much as possible the settlement of large and heavy particles while maintaining a uniform distribution of the particles in the emulsion.

One of the most critical points in the study of distributions at this size (sub-micron region) is that of resolution. The scanning electron microscope can produce a magnification of 50,000X or above while the resolution can be as small as 0.00001 mm as compared to an average light microscope of 500X and 0.0004 mm²⁸. Presently, all particle size distributions were analyzed with the aid of scanning electron microscope at magnification of 5,000X or 10,000X, with 30,000X pictures as size calibration for small particles, based on approximately 700 to 5,000 counts per picture. The smallest particles observed on some of the pictures has been determined to be 0.07 microns.

DISCUSSION

A few drops of the polymerized emulsion sample were dipped onto a well-polished metal stub, which was then air-dried, gold-plated and placed on a vacuumed sample-stand inside a scanning electron microscope. Photomicrographs were taken at random spots at various magnifications.

Photomicrographs of 5,000X and/or 10,000X were utilized to measure the particle size with the use of a micrometer. A large number of particles (~1000) were counted and the particle sizes were obtained and their particle size distributions plotted (see Figs. 1(a) and 1(c) for typical runs). As evidenced by the graph, the distribution is extremely narrow.

Figure 3 shows the plot of the most-frequently-occurred particle sizes as a function of the irradiation time at various intensities. The general trend seems to be that, as irradiation time increases, the particle sizes become smaller toward constant values at different intensities, namely, 0.28 microns, 0.34 microns and 0.30 microns for intensity levels 2, 4 and 7 respectively. One plausible explanation for this could be that, upon irradiation, the monomer phase was injected into the water phase, either due to the surface instability or cavitation mechanisms, in the forms of, presumably quite large, spherical particles. And these primary particles then went through the same action as before and further broke down into smaller particles. When a particle reached a critical small size, unless a very large amount of energy is supplied, it will not undergo any further self-splitting; the levelling-off of the particle sizes at long irradiation times seems to suggest the critical sizes for respective intensity levels.

Figure 4 is a plot of the ratio of the calculated deviation to the mean vs the irradiation time at various intensities. In general, the calculated deviation is indirectly proportional to the number of particles counted. Despite the fact that not very

many data points are available to yield significant interpretations, it may be suggested that the longer the irradiation time, the more disperse the emulsion will become. Figure 4(a) is another plot of calculated deviation vs irradiation time at various intensities, to show the general magnitude of the standard deviation, σ .

Figure 5 represents the log-normal distribution of various particle sizes in one of our samples (the corresponding normalized number-particle size distribution is shown in Figure 1(c)). It may be seen that despite the measured deviation from this graph differs from the calculated by a factor of 10, the sample that we have obtained approximates to a normal distribution with very small deviation. Since acoustic emulsification involves the action of dispersion and the counter-action of coalescence, some particles may coalesce and be dispersed again. It seems that, from our results, the net effect of these actions produces a batch of finely-distributed particles.

FURTHER RECOMMENDATIONS

Of the studies that have been undertaken on ultrasonic emulsifications there is a disparity of results between a number of investigators. No definitive trends or correlations currently exist to predict the variation of the mean particle size and particle size distribution with solution properties and acoustic parameters in ultrasonically formed emulsions. One of the primary reasons that this has not been accomplished is that the mean particle sizes produced by this technique are smaller than can be accurately measured with the optical microscope. However, by emulsifying a monomer in water, polymerizing the droplets, and then analyzing the solid polymer spheres with a scanning electron microscope, meaningful correlations and trends can be formed. Once the important parameters are identified it might be possible to change the particle size by varying either the acoustic or solution properties. Our results show the particle size does change with such variables as the ratio of the volume of monomer to the volume of water, irradiation time, and ultrasonic intensity.

The mean particle size and particle size distribution could be further studied as a function of the following variables, which are believed to be the most important:

Acoustic Parameters: (1) Frequency, (2) intensity, (3) Irradiation time.

System and Solution Variables: (1) Manner in which the two phases are irradiated, (2) Ratio of the volume of monomer to volume of water, (3) type of monomer used.

In addition one could attempt to measure the rate of emulsification and investigate ways of monitoring the oil-water interface prior to the onset of emulsification.

Transducers and generators available in the University of Michigan sonochemical laboratory are capable of producing ultrasonic waves over a frequency range of 10 kHz to 800 kHz. It is

believed at low frequencies, cavitation plays the dominant role in producing the emulsion. At frequencies above 400 kHz, it is highly unlikely that cavitation will occur. Consequently, at high frequencies it is believed that surface instability plays a major role in the emulsification. If the variables of irradiation time and dilution and re-irradiation affect the particle size, there is a strong possibility that the initial droplet formed from the eruption of the "oil-water" interface is broken into smaller droplets by the ultrasonic wave. We believe that further study of the parameters may not only allow one to develop useful correlations which will delineate how to produce a particle of a specified size, but also it will hopefully lend great insight into the underlying mechanism of ultrasonic emulsification.

Finally, as it is suspected that the molecular size, hence the molecular weight, will be affected by the particle size in the low sub-micron region, a brief investigation could be undertaken to study the molecular weight and molecular weight distribution via gel-permeation chromatography²⁹. With a refractive-index spectrophotometer attached to the outlet of the gel-column, the various molecular weights can be analyzed and plotted continuously on a X-Y plotter. This phase of investigation could have two additional variables: type and concentration of initiator.

BIBLIOGRAPHY

- 1) _____, Paper Trade Journal (June 3, 1968).
- 2) _____, Food Engineering (March 1967)
- 3) Shall, E.C. Am. Paint Journal (Nov. 28, 1966)
- 4) Maugh, T.H. Science 179 669, (1973).
- 5) Fogler, H.S. C.E.P. Symposium Series, 67, No. 109, 1, (1971).
- 6) Neduzhii, S.A. Sov. Physics Acoustics 7, No. 2, 209 (1962).
- 7) Bondy, C., and Sollner, K., Trans. Faraday Society, 31, 835 (1935).
- 8) Ibid., 843.
- 9) Ibid., 32, 556 (1936).
- 10) Ibid., 616.
- 11) Neduzhii, S.A., Soviet Phys.-Acoustic, 7, 79 (1962).
- 12) Ibid., 221
- 13) Ibid, 9, 195 (1964).
- 14) Ibid., 10, 390 (1965)
- 15) Rajagopal, E.S., Proc. Ind. Acad. Sci., 49(A), 333 (1959)
- 16) Beal, H.M. & Sakauen, D.M., J. Am. Pharm. Assoc. 44, 487 (1955).
- 17) Baram, A.A. Soviet Physics-Acoustics, 10, No. 4, 343 (1965)
- 18) Gershenzon, E.L., et. al., Sov. Phy. Acous., 10, No. 2, 127 (1964).
- 19) Marinesco, N., Chemie et Industrie, 55(2), 87 (1946).
- 20) Yih, C.S., "Fluid Mechanics", McGraw-Hill, N.Y. (1969).
- 21) Lo, C.L., Mischke, R.A., C.E.P. Symposium Series, 67, No. 109, 46 (1971).
- 22) E. Yeager, A. Patsis, and F. Hovorka, Proceedings of the Third International Congress on Acoustics, Amsterdam-London-N.Y., 2, 1276-1278.
- 23) Boundy, R.H., Boyer, R.F., "STYRENE-Its Polymers, Copolymers and Derivatives", Reinhold Publishing Corp. (1952).
- 24) Handbook of Physics and Chemistry.
- 25) Bernstein, D.F., Ph.D. Thesis (The University of Michigan, 1971).
- 26) Kitchener, J.A., Mussellwhite, P.R., "The Theory of Stability of Emulsions", Sherman, P., Ed., "Emulsion Science", Academic Press, N.Y. (1968).
- 27) Burnett, G.M., "Mechanisms of Polymer Reactions", Interscience Publishers (1954).
- 28) Research News, Vol. XXII, No. 11 & 12, Ann Arbor, The University of Michigan.

- 29) Bio-Rad Laboratories, "Gel Chromatography".
- 30) "Hamilton", Catalog H-73, p. 35. Hamilton Company, P.O. Box 7500, Reno, Nevada 89502.

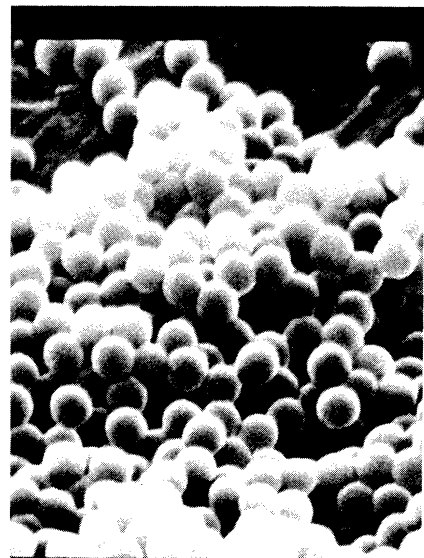
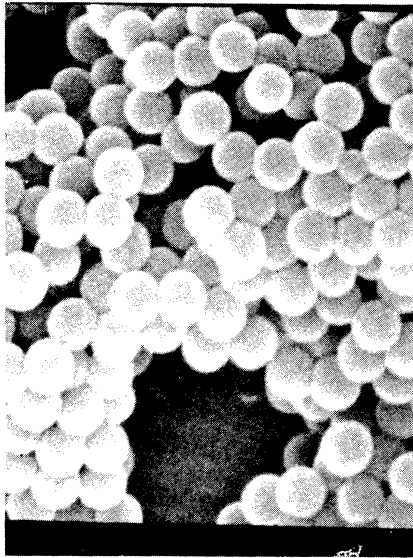


Figure 1(a). Typical Particle Sizes at 30,000X

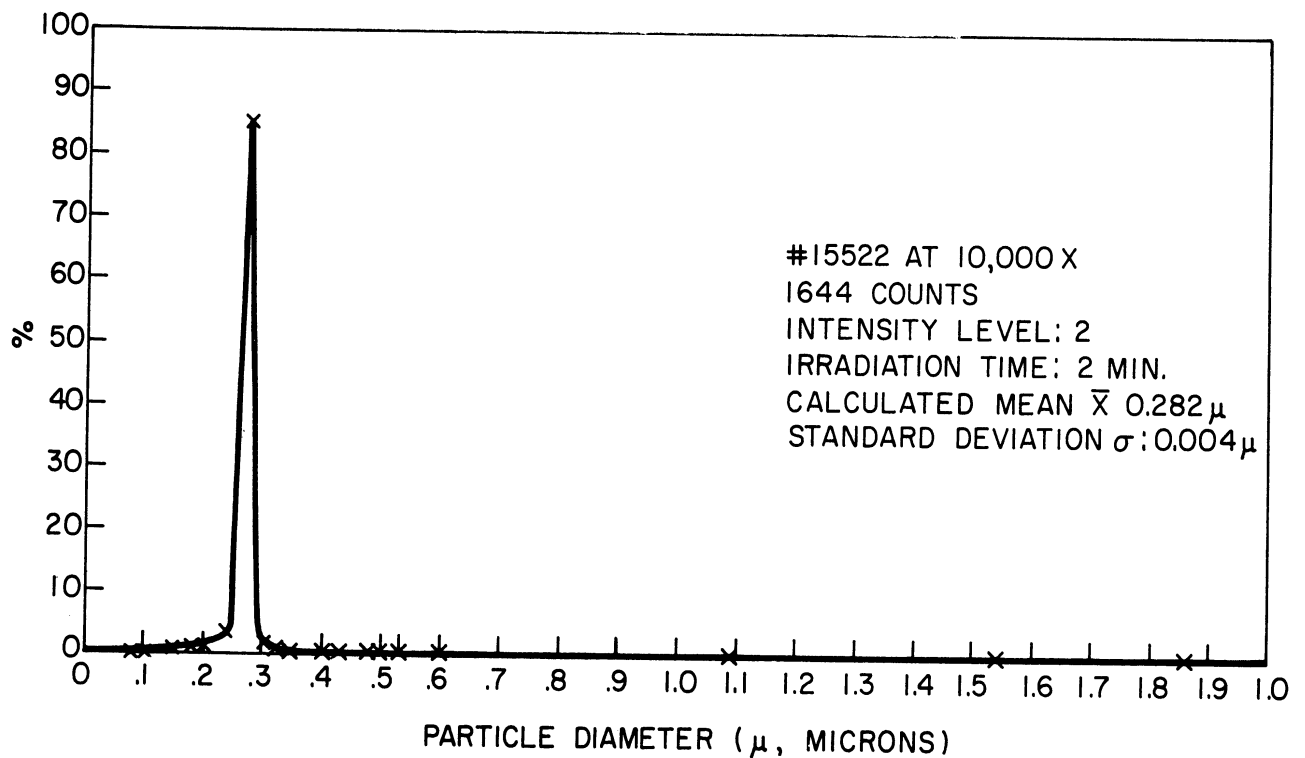


Figure 1(b). Normalized Plot--Number-Particle Size Distribution

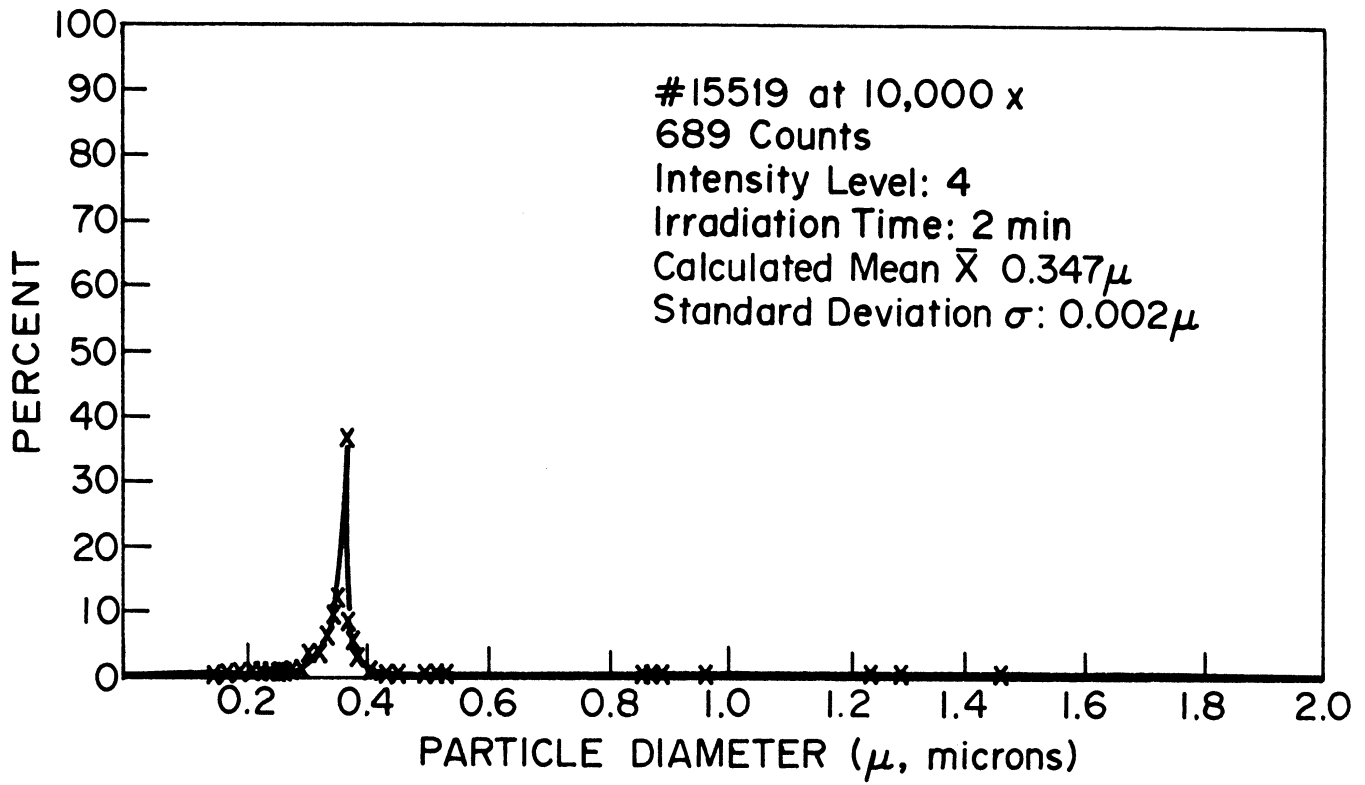


Figure 1(c).

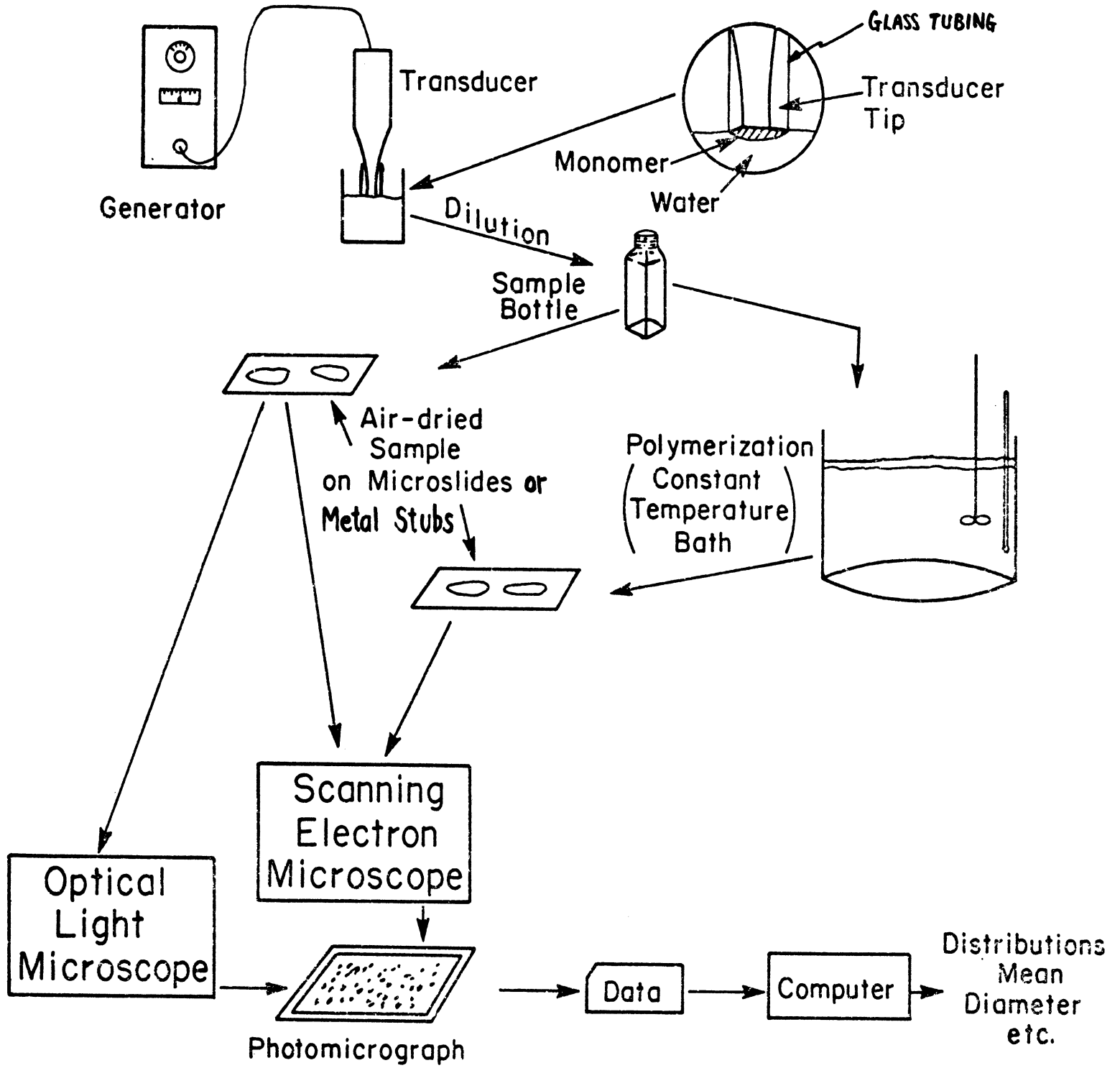


FIGURE 2

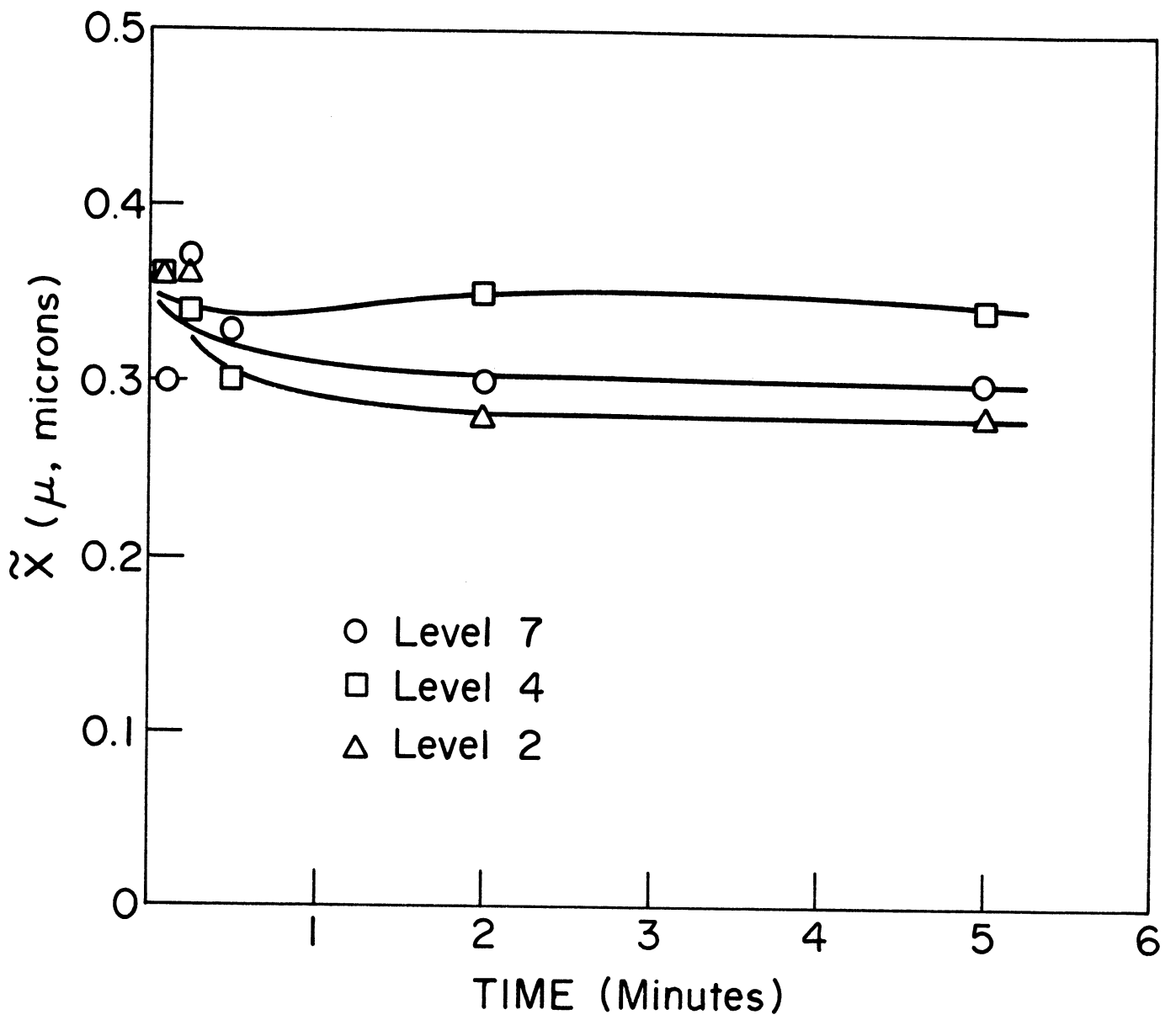


Figure 3. Most-Frequently-Occurred Particle Size vs Irradiation Time at Various Intensities

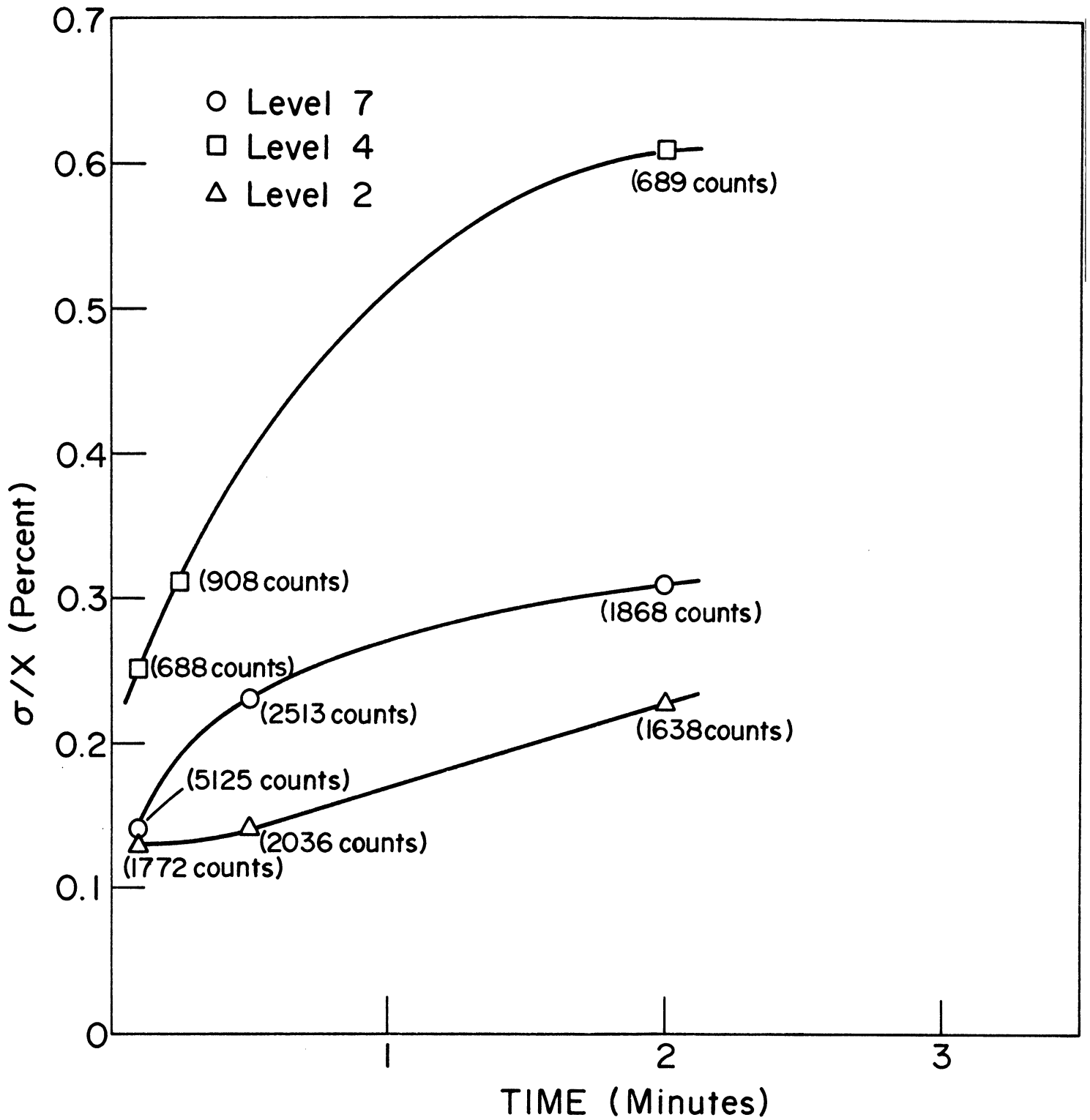


Figure 4. The Ratio of the Calculated Deviation to Mean vs Irradiation Time at Various Intensities

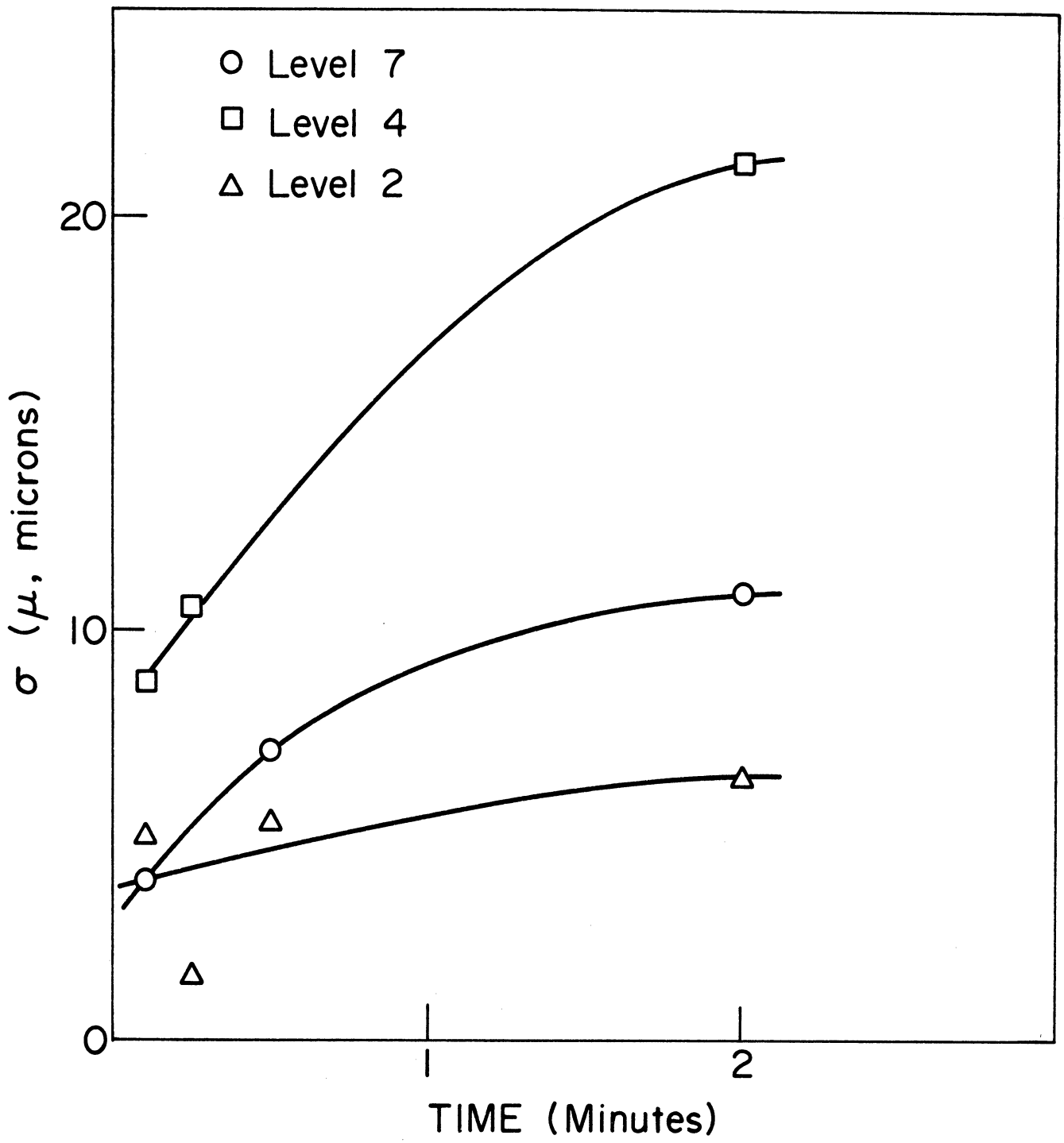


Figure 4(a). Calculated Derivation vs Irradiated Time

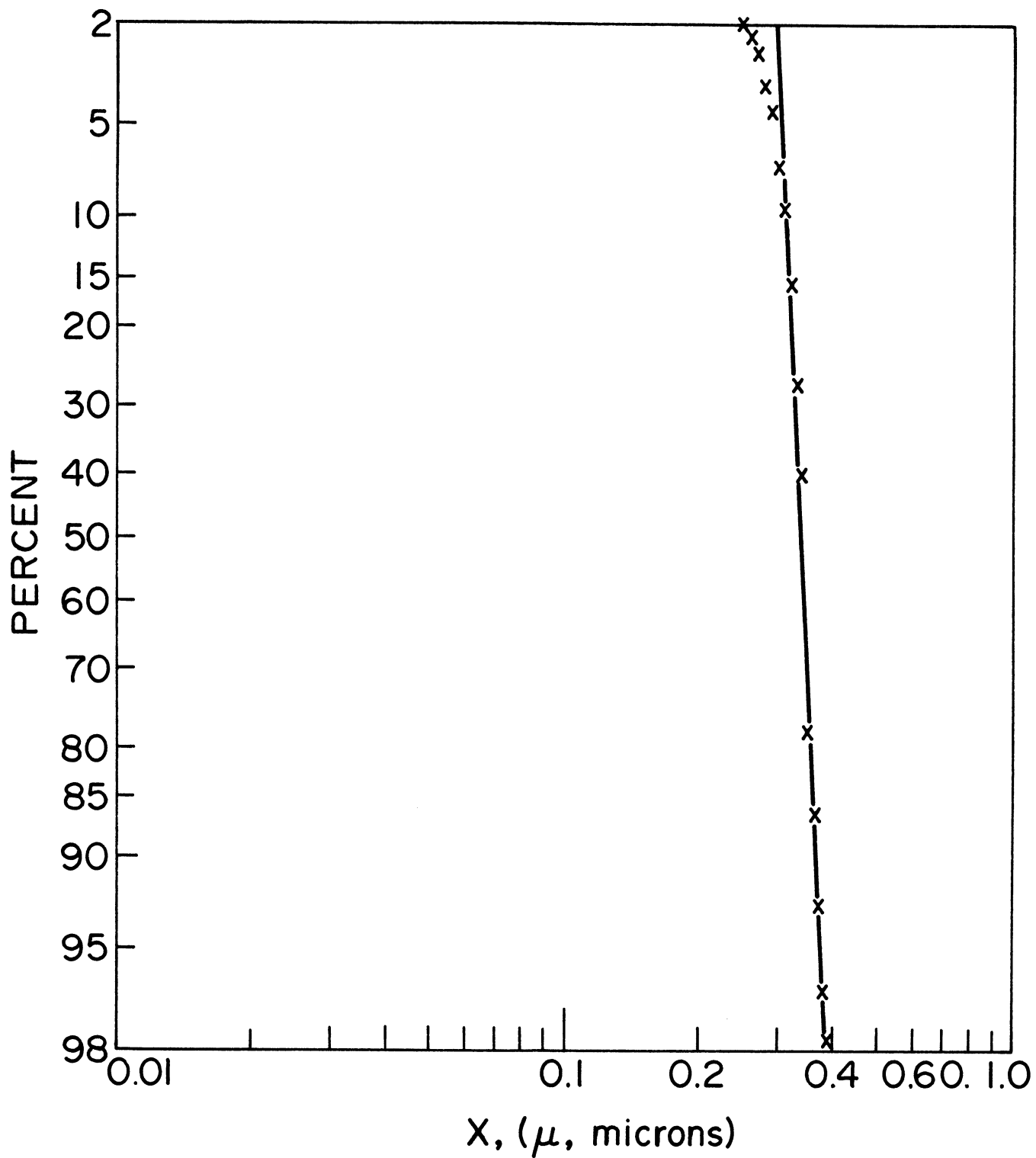


Figure 5. Lognormal Particle Size Distribution for #15519 at 10,000X. Measured mean \bar{X}_m : 0.339 microns, Measured Derivation σ_m : 0.019 microns.

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