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Sizing of Polystyrene Spheres Produced in Microgravity

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U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, *Secretary*
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director*

Abstract

The standard deviation of the size distribution was determined for a polystyrene latex produced in a space shuttle experiment and in an earth-bound control experiment. Values determined from direct measurement of transmission electron micrographs, corrected for magnification distortion, were 0.033 µm for the space grown material and 0.15 µm for the control. The standard deviations obtained from an aerodynamic particle-sizer were only slightly greater than those obtained by TEM; 0.042 µm and 0.20 µm for the shuttle and ground material respectively. However, these values were produced in a few hours versus the several weeks it took for the electron microscopy. Both of the techniques used here resulted in measured standard deviations significantly smaller than those previously reported for this material.

Keywords: aerodynamic particle sizing; particle counting; particle sizing; polystyrene latex; optical array sizing; size distribution; size resolution; transmission electron microscopy

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1. Introduction

The major effort of this investigation was to accurately determine the standard deviation, σ, of the central peak of the size distribution for polystyrene (PSL) spheres produced in a space shuttle experiment as well as in an earth bound control experiment. The space shuttle particles were prepared in an automated reactor apparatus on the third orbital mission of the "Columbia" begun on March 22, 1982. The analyzed particles were nominally 5 µm in diameter and were produced using a 2.5 µm seed latex and a 10:1 monomer-polymer ratio. We found, as did Vanderhoff _et al_ [1], that the size distribution of the space shuttle spheres was narrower than that of the ground experiment's. In fact, we found that σ of the central peak of the space shuttle spheres to be about half the value obtained by Vanderhoff _et al_. So the space grown spheres are in a sense twice as good as was previously thought. This result was obtained by two independent techniques, transmission electron microscopy and aerodynamic particle sizing. The second technique is of special interest because it allows the sizing of several thousand particles in minutes compared to several weeks using electron microscopy.

In addition to the measurement of the standard deviation, we determined the average particle diameter and the fraction of off-size particles for each specimen. The average diameter was measured by array sizing using a magnification calibrated optical microscope. Electrical sensing zone instrumentation and optical microscopy were used to estimate the percentage of particles outside the main peak of the size distribution.

In the following report we present our results for the standard deviation, σ, of the size distribution the number average diameter, D_n, ($D_n = \frac{1}{N} \sum_{i=1}^{N} D_i$), and the fraction of off-size particles. We find that the number average diameter, D_n, for the space shuttle spheres is 0.24 µm smaller than the ground based spheres. This finding disagrees with the result of Vanderhoff et al, who found the space shuttle spheres to be larger than the ground spheres.

2. Transmission Electron Microscopy

The sample was prepared for electron microscopy by evaporating a small drop of a diluted suspension of the spheres on a standard TEM grid. Three grids were prepared from each PSL specimen. The grids were coated with approximately 20 nm of carbon and then examined with a JEOL 200 CX[1] at an accelerating potential of 100 kV and at a nominal 1500X magnification. The magnification was carefully monitored for variation, but its absolute value was not accurately determined. About 15 micrographs were taken of each grid in order to obtain 300 particle images to size from each grid. The particle size was measured directly from the negative using a 7X magnifier with an accurate millimeter scale reticle. A series of concentric circles on the reticle enabled quick location of the diameter.

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[1] Materials and instruments are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or instrumentation is the best available for the purpose.

The value of σ determined from the individual diameter measurements of 300 particles will differ from the actual standard deviation of the particle size distribution due to systematic and random uncertainties in the measurement process. The systematic uncertainties are caused by the imprecision of the individual particle measurements and the inclusion of off-size particles in the central peak of the size distribution. The former can be further divided into the uncertainty in measurement of the particle image and the variation of the image size due to its position in the electron microscope's field of view (magnification distortion). The random uncertainty is due to the size of the measurement sample. We balanced measurement time with an acceptable accuracy level of ±10% by choosing to measure 300 particles. Each of the preceding error sources and the means by which we limited them will now be discussed in more detail in the following paragraphs.

We estimate the uncertainty in the measured diameter, U_e, associated with the use of the graduated magnifier to be 0.022 mm (corresponding to 0.016 µm). This uncertainty was determined by repeat measurements on one particle by one person and by measurements of the same set of spheres by two persons.

The magnification distortion was determined by taking micrographs of the same cluster of spheres as they were positioned in various regions of the field of view. This is illustrated in figure 1. The magnification increased by 4.1% for particle diameters measured in the radial direction from the center of the micrograph out toward the corners, at 1500X nominal magnification. The distortion was significantly less in the

Composite print showing the same spheres at two different locations in the field of view. The diagram shows magnification distortion for sphere 2.

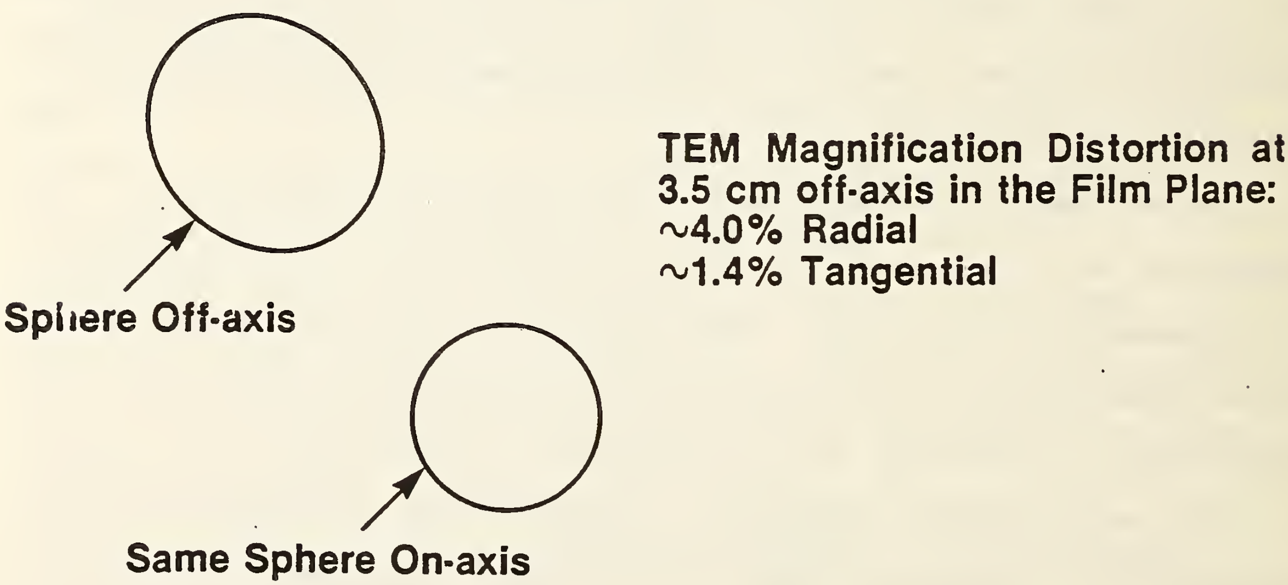

Fig. 1
Effect of Magnification Distortion Caused by TEM Imaging of Two Identical Spheres On- and Off-Axis

tangential direction; +1.4%. Consequently all measurements were made in this direction. The distortion was fairly constant for a fixed radius about the center of the micrograph. We made use of this property by locating the position of each sphere within one of four concentric zones. The diameter of each particle was then corrected for the average magnification distortion in each zone.

It is important to have a systematic procedure for excluding off-size particles when calculating the standard deviation, σ, of the size ditribution. We used a discordancy test [2] based on the sample kurtosis as the test statistic.

$$\text{sample kurtosis} = \frac{N \sum_{i=1}^{N} \left(D_i - D_n\right)^4}{\left[\sum_{i=1}^{N} \left(D_i - D_n\right)^2\right]^2} \qquad (1)$$

If the sample kurtosis exceeds a value of about 3.40 for a 300 sphere sample, then one or more spheres are off-size at the 5% level of discordancy. The spheres with diameters farthest from the average size would be eliminated consecutively until the sample kurtosis reaches the appropriate value. We typically found about 15 off-size particles out of a population of approximately 300. Slightly larger numbers of off-size particles were obtained for the spheres produced in space in two samples.

The size distributions of three grids prepared from the space shuttle spheres and three from the ground spheres were determined. The results are summarized in table 1. The σ for the space shuttle specimen was about 0.033 μm, while that for the ground specimen was four to five times larger at 0.151 μm. This large difference is not apparent from a visual inspection of the micrographs, as indicated by figure 2.

We were able to test the significance of the magnification distortion correction by repeating the statistical analysis without the correction for σ for the same particles. We find that σ is 9 to 21% greater than the corresponding value given in table 1; the percentage difference increases with an increasing fraction of the spheres in the outer zones. That our simple zone method has not accounted for all of the distortion is indicated

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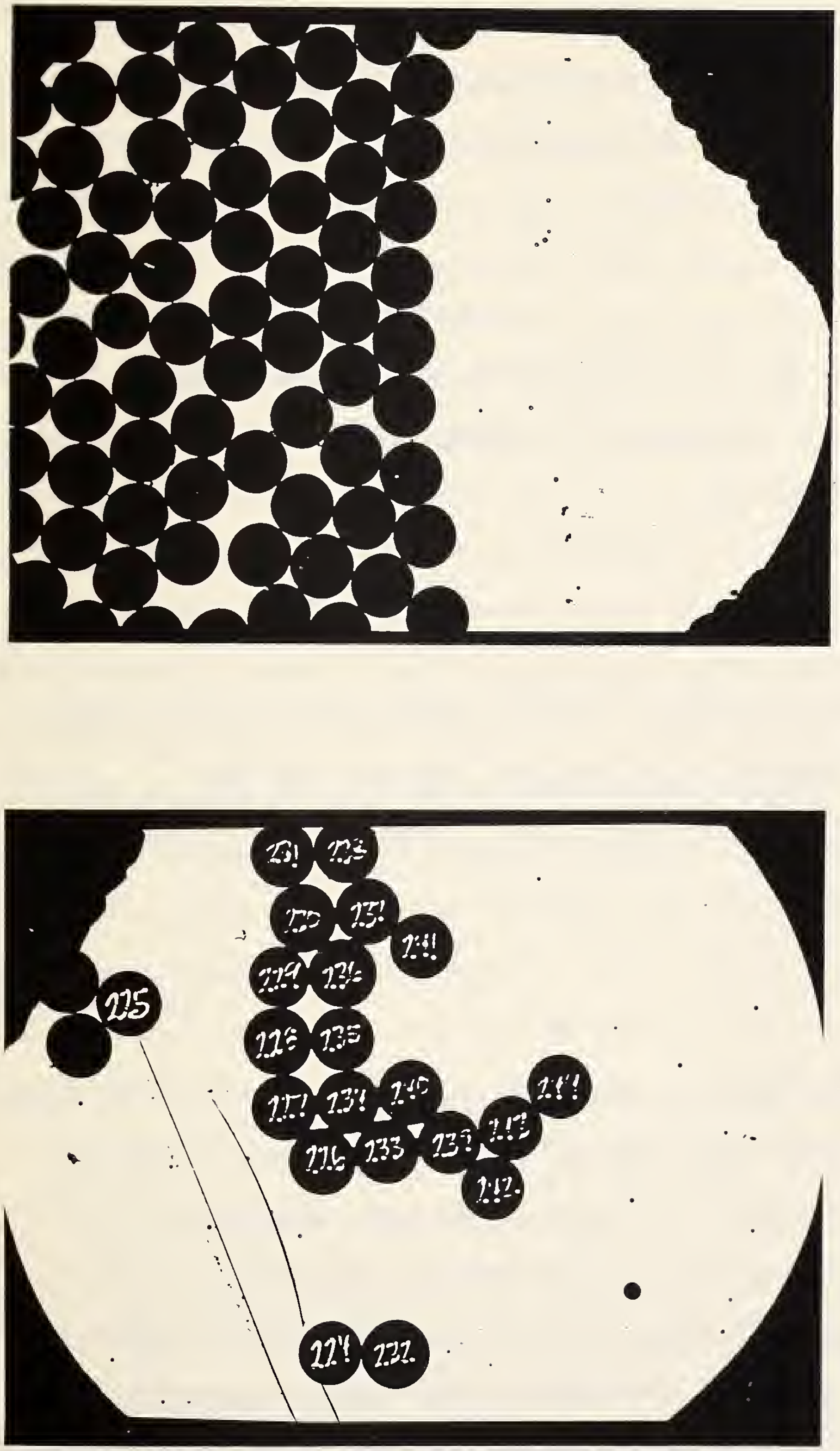
Table 1. Size Distribution Parameters

Measurement Techniques	Sample[a]	D_n (μm)	σ (μm)	$σ/D_n$ (%)	N	$\frac{n}{N}$ (%)[b]
Transmission	S1	5.033	0.036[c]	0.72	289	7.3
Electron	S2	5.033	0.034	0.67	293	6.8
Microscopy	S4	4.999	0.028	0.59	302	3.6
	G1	5.198	0.158	3.04	302	4.6
	G2	5.176	0.149	2.88	263	5.7
	G3	5.180	0.146	2.82	296	5.4
Aerodynamic	S2	5.340	0.043	0.81	3594	10.5
Particle Sizer	S3	5.327	0.042	0.80	3705	
	G9	5.552	0.205	3.69	4100	6.9
	G7	5.545	0.197	3.56	8143	
Optical Array	S	5.04[d]				
Sizing	G	5.27				

a S denotes space shuttle sample and G denotes ground sample.
b n is the number of off-size particles in the size range 4–6 μm outside the central peak.
c The estimated uncertainty in σ for the TEM measurements is given by a ±10% random component and a systematic component equal to −0.006 μm. See discussion on page 8.
d The uncertainty in D_n, including random and systematic errors, is ±0.12 μm for the shuttle spheres and ±0.19 μm for the ground spheres.



(A)
Space Shuttle
Material

(B)
Ground Run
Material

Fig. 2
TEM Micrographs of 5.0 μm Polystyrene Spheres Grown in Space (A), and on the Ground (B).

by the value of σ for sample S4 (28% of spheres in outer zones), 0.028 µm, being smaller than that of the other samples (about 50% of spheres in outer zones), 0.034 µm and 0.036 µm. Therefore, we estimate that the component of uncertainty in σ resulting from residual magnification distortion, U_m, to be about 0.01 µm for the case of 50% of the particles in the outer zones. The measured standard deviation of the size distribution, σ_m, is broadened from the true σ by the uncertainty in the diameter measurements, U_I. For statistically independent quantities the variances add; so we obtain

$$\sigma_m = \left(\sigma^2+U_I^2\right)^{1/2} \tag{2}$$

The quantity U_I itself results from the combination of the edge determination uncertainty (U_e=0.016 µm) and the residual magnification distortion (U_m=0.010 µm). Summing the variances of these quantities,

$$U_I = \left(U_e^2+U_m^2\right)^{1/2} \tag{3}$$

we obtain U_I equals 0.019 µm. Substituting for U_I in eq. (2) and setting σ_m equal to the value obtained for sample S2 (0.034 µm), we find σ equals 0.028 µm. In addition to this systematic uncertainty in σ there is also a statistical uncertainty resulting from the small number of particles measured on each grid. The quantity σ^2 has a χ^2 distribution and at the 95% confidence level the uncertainty in σ is about ±10% for 300 measurements [3]. Finally, we combine the random and systematic uncertainties in σ by adding 10% to σ_m and subtracting 10% from σ. This yields for the case σ_m=0.034 the limits: 0.025 μm<σ<0.037 μm. This is a first-order error analysis in which the various quantities are assumed to be statistically independent. It represents a first step in a detailed error analysis.

3. Aerodynamic Particle Sizer

The sample preparation is completely different for the Aerodynamic Particle Sizer (APS) [4] compared to the electron microscope, because the particles must be dispersed in air for the APS instrument. A pneumatic nebulizer filled with a suspension of PSL spheres in water was used to generate water droplets, some of which contained a PSL sphere. The water evaporated in seconds leaving the PSL spheres in aerosol form. By directing the aerosol spray vertically upward in a cylindrical tube (7 cm diameter, 30 cm high, closed at the top), we produced a suitable concentration for the APS, the inlet of which protruded through the open base of the cylinder. A clean air flow of about 20 l/min. was introduced in the same direction as the aerosol flow to insure that the water would evaporate.

The PSL spheres sampled by the APS flow through an accelerating nozzle. The speed of the spheres is measured at the exit of the accelerating nozzle with a two-spot laser velocimeter. The spheres will lag behind the air according to their aerodynamic size, and the measured velocity will be inversely related to the aerodynamic diameter of the sphere. The number-average diameter for the spheres determined by the APS is found to be about 6% larger than the value obtained by electron microscopy or by optical array sizing (discussed below). The APS is calibrated using liquid droplets of known size. A possible cause for the 6% discrepancy is the flattening of the liquid drops in the accelerating nozzle, which would cause them to be accelerated like a smaller spherical particle.

The standard deviation for the size distribution, as obtained by the APS, (0.042 µm) is slightly larger than the value obtained by electron microscopy (0.033 µm). The instrumental uncertainty is not known for the APS, although we obtained an instrument standard deviation equal to 0.032 µm for a 6.0 µm liquid aerosol generated by the Berglund Liu Vibrating Orifice Aerosol Generator, so the instrument σ is certainly less than this. It is surprising that the instrument uncertainty is so small, since one would expect some broadening depending on the initial position of the droplet in the accelerating nozzle.

The reduced number size distribution, $\Delta N/\Delta D$, for the space shuttle spheres and the ground spheres is plotted in figure 3 for both the TEM and APS results. The APS size scale has been shifted so that the number average diameter is close to the TEM result. The reduced size distribution in figure 3 must be divided by a scale factor of 0.026 µm to obtain $1/N\ \Delta N/\Delta D$ in units of μm^{-1}. The space-shuttle size distribution is seen to have a narrow peak. The rather spiky appearance of the TEM size distribution is a result of the relatively large statistical uncertainty resulting from the small number of particles in each channel. The population of each channel is typically ten times greater for the APS.

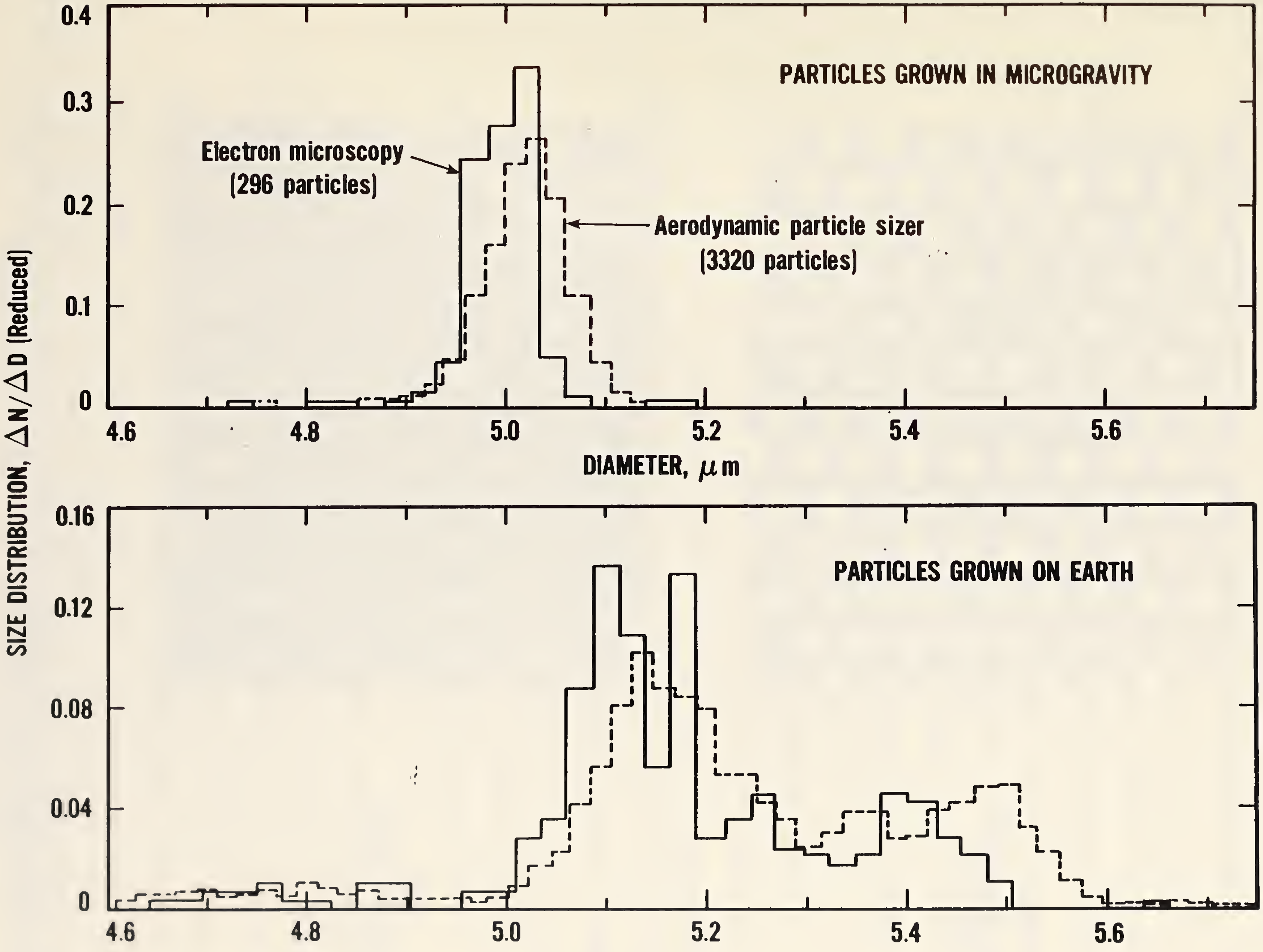


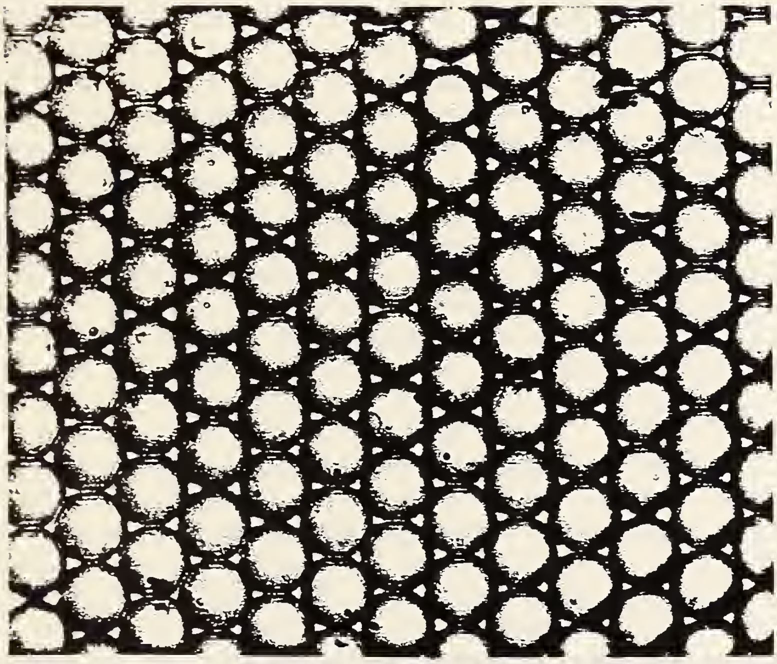
Fig. 3
Size Distribution of 5.0 μm Polystyrene Spheres Grown in Space and on the Ground.

The characterization of the size distribution by an average particle size and standard deviation is not adequate for the ground sample because of the complex structure in this histogram. The broad shoulder, which actually has one or two minor peaks, may provide a clue to the difference in the growth of the ground and space shuttle spheres. Also, one can detect a low amplitude shoulder of the main peak in the small particle region. This is more apparent in the APS results, although a suggestion of this structure is also seen in all three of the TEM ground samples.

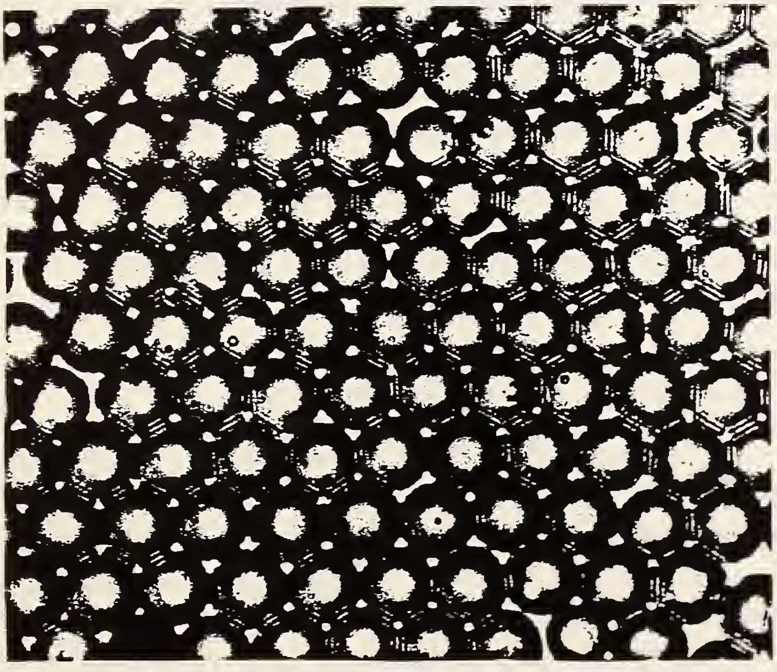
4. Average Particle Size and Analysis of Off-Size Spheres

Our most accurate measurement of the number-average sphere size is based on optical array-sizing. By smearing a drop of the PSL suspension over a microscope slide, one obtains a thin film of liquid which rapidly dries, leaving regions of hexagonally-close-packed 2-dimensional arrays. The regularity of the arrays depends in part on the monodispersity of the spheres. As seen in figure 4, the array made from the space shuttle spheres is clearly more regular than that made from the ground spheres.

To determine the number-average sphere size, the center-to-center distance for a row of particles is measured from a micrograph. While the edge of the particle cannot be accurately defined by optical microscopy, the position of its center can be determined to an accuracy of about 0.05 µm. The average diameter is then simply determined by dividing the length of the row by one less than the number of spheres in the row. The subtraction of one results from using the center-to-center row length rather than edge-to-edge row length. A grand average is obtained by analyzing several different rows. As indicated in table 1 the



(A)
Space Shuttle
Material



(B)
Ground Run
Material

Fig. 4
2-D Hexagonal Arrays of 5.0 μm Polystyrene Spheres, Grown in Space (A) and on the Ground (B).

space shuttle spheres have a number average diameter of 5.04 µm and the ground spheres, 5.28 µm. A careful error estimate for this technique has been made including magnification distortion, which is much smaller for optical microscopes than for electron microscopes, and the systematic error caused by small particles in the array not touching neighbors. The magnification of the microscope is accurately determined using an interferometrically-calibrated line scale standard. As indicated in table 1 the overall uncertainty is on the order of 0.1 to 0.2 µm.

We have estimated the percentage of off-size large spheres with diameters 30% greater than the average diameter by surveying almost 7,000 spheres by optical microscopy. The space-shuttle sample was found to have a slightly lower percentage of off-size large spheres than the ground sample; 1.2 to 1.6% respectively (see table 2). By observing the spheres in suspension with the optical microscope we found that less than 0.1% of the spheres were aggregated as doublets. Measurements with an electrical sensing zone instrument (ESZI) yielded the percentage of larger particles, but this technique does not distinguish between large

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Table 2. Number of Off-Size Particles

Sample	Large Particles[a]		Large Particles & Aggregated Doublets[b]		Aggregated Doublets[c]
Space	45/3612	1.2±0.2%		1.9±0.7%	<0.3%
Ground	48/3048	1.6±0.2%	810/49600	1.6±0.1%	<0.1%

a Large particles include all spherical particles with diameters 30% greater than the average size (approximately twice the volume) as determined by optical microscopy.
b Results based on electrical sensing zone instrument.
c Results based on optical microscopy of spheres in suspension.

spherical particles and aggregated doublets. The results obtained with the ESZI agree reasonably well with those for the optical microscope except that there appears to be slightly more large particles in the space shuttle sample. Because of the experimental uncertainties and because of the small differences in the percentage of off-size large spheres for the two samples, we can only say that both samples have about 1.5% (1 in 67 particles) off-size large spheres. For the optical case, the limitation is the qualitative "eyeball" estimate of large spheres from low magnification micrographs. Excellent statistics are obtained by the ESZI with close to 50,000 spheres sized, but the instrument uncertainty is much broader than the width of the size distribution and there is some possibility of aggregates being induced by the use of an electrolyte.

In addition to the off-size large spheres, we observe a large number of off-size small spheres with diameters in the range 0.2-0.4 µm on many of the TEM micrographs (see fig. 2). The relative percentage is not known. The particles seem to be concentrated in certain regions. In some micrographs there are as many off-size small spheres as average spheres.

5. Comparison with the Lehigh Results

The number-average size for the space shuttle sample, as determined by Vanderhoff et al. [1], agrees quite well with the NBS result (1.1% difference). However, the Vanderhoff et al. result for the ground sample is 10% low compared to our result. Furthermore, while we find the average size of the ground-produced spheres to be about 0.2-0.3 µm larger than the space shuttle spheres by three independent techniques, the Vanderhoff *et al*. results have the ground sample being smaller, not larger, by about 0.3 µm.

Another difference between the results of the two laboratories is in the value of the standard deviation for the size distribution of the space-shuttle sample. The size distribution obtained at NBS by TEM measurements is about two and a half times smaller than the value obtained at Lehigh (see table 3). We believe that one reason for the discrepancy is that no magnification distortion correction was made for the measurements at Lehigh. We estimate the magnification distortion to be about 0.5% for diameter measurements made in the tangential direction and 1.5% for measurements made in the radial direction. For an area measurement, which is the basis of the Lehigh measurements, we estimate the distortion to be the average, 1% or 0.050 µm. Assuming the true σ to be 0.028 µm and using Vanderhoff *et al*'s estimate of the uncertainty in measuring the sphere's image, 0.016 µm, we estimate sigma measured by the Lehigh method, σ_L,

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Table 3. Comparison with Lehigh Results

Laboratory/Method	Sample	D_n (µm)	σ (µm)	σ/D_n (%)
NBS/TEM	Space	(5.02)[c]	0.033	0.66
NBS/APS[a]	Space	(5.33)[c]	0.042	0.80
NBS/Optical[b]	Space	5.04		
Lehigh/TEM	Space	4.98	0.082	1.64
NBS/TEM	Ground	(5.18)[c]	0.151	2.90
NBS/APS	Ground	(5.55)[c]	0.201	3.62
NBS/Optical	Ground	5.28		
Lehigh/TEM	Ground	4.74	0.167	3.51

a Aerodynamic particle sizer
b Array sizing by optical microscopy
c Values for comparison purposes only

to be given by the following formula:

$$\sigma_L = [(0.050)^2+(0.028)^2+(0.016)^2]^{1/2} = 0.059\ \mu m\ .$$

So if the magnification distortion of the Lehigh microscope is similar to that of the NBS microscope, over half of the difference between the Lehigh result and the NBS result can be accounted for. We expect that part of the remaining discrepancy results from the different criteria for excluding off-size particles. We observed a decrease in σ when we started using a statistical discordancy test. The difference in σ between the two laboratories for the ground sample is slight. This is to be expected because the effect of the magnification distortion correction is not significant for the measurement of such a broad size distribution.

In regard to the off-size spheres, our results agree qualitatively with those of Lehigh. Both laboratories obtain about one large sphere per 70 average spheres for both samples. Vanderhoff et al at Lehigh find a slightly greater percentage of large particles in the ground sample. In our case the difference is not significant relative to our experimental errors. We also observe off-size small particles smaller than the seed particles. The presence of such particles is not discussed by Vanderhoff et al.

6. Conclusion

It is possible to determine the sigma of a size distribution of 5 µm spheres with an uncertainty of about 0.006 µm by TEM, but this requires expertise in the use of the TEM, careful magnification calibration, and careful diameter measurements. This is time consuming and expensive.

On the other hand, we have demonstrated that the Aerodynamic Particle Sizer (APS) can size about 4,000 spheres in two minutes, with the statistics and plotting completed in another two minutes. The resolution is almost as good as for electron microscopy for 5 µm spheres; in fact, it is twice as good as the electron microscopy sizing method being used at Lehigh. We show in Figure 5 the size distribution of nominal 10 and 15 µm PSL spheres manufactured by Dyno (distributed by Dow). The increase in noise is probably due to water droplets that have not evaporated. We believe that good results can be obtained for particles at least as large as 15 µm by the proper selection of nebulizer or sprayer together with an improved design of the drying tube.

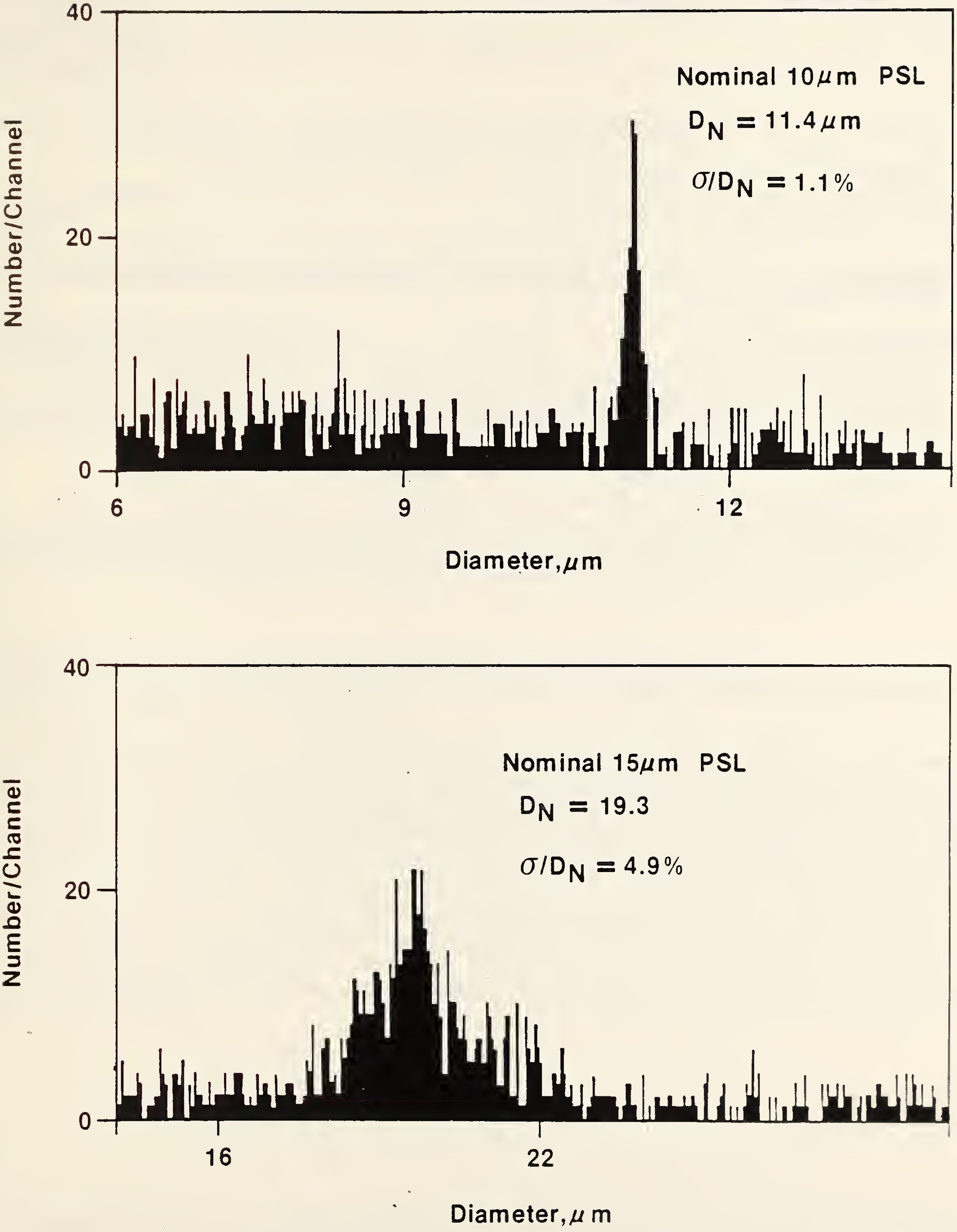

Figure 5.
APS Size Distribution of PSL Spheres

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The standard deviation of the size distribution was determined for a polystyrene latex produced in a space shuttle experiment and in an earth-bound control experiment. Values determined from direct measurement of transmission electron micrographs, corrected for magnification distortion, were 0.035 μm for the space grown material and 0.15 μm for the control. The standard deviations obtained from an aerodynamic particle sizer were only slightly greater than those obtained by TEM; 0.042 μm and 0.20 μm for the shuttle and ground material respectively. However these values were produced in a few hours versus the several weeks it took for the electron microscopy. Both of the techniques used here resulted in measured standard deviations significantly smaller than those previously reported for this material.

12. KEY WORDS (Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)

aerodynamic particle sizing; particle counting; particle sizing; polystyrene latex; optical array sizing; size distribution; size resolution; transmission electron microscopy

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