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# Certification of NBS SRM 1691: 0.3- $\mu$ m-Diameter Polystyrene Spheres

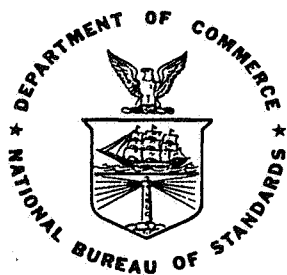
Thomas R. Lettieri  
Gary G. Hembree\*

U.S. DEPARTMENT OF COMMERCE  
National Bureau of Standards  
National Engineering Laboratory  
Center for Manufacturing Engineering  
Gaithersburg, MD 20899

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\*Now with the Department of Physics, Arizona State University.

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## Abstract

The mean diameter of submicrometer polystyrene spheres, to be used as a new Standard Reference Material (SRM) for particle sizing, was accurately measured using two independent micrometrology techniques. One technique, transmission electron microscopy, measured the particles dry and in a vacuum, and gave a result of  $0.269 \pm 0.007 \mu\text{m}$  for the certified mean diameter. The supporting method, quasi-elastic light scattering, yielded a value of  $0.276 \pm 0.007 \mu\text{m}$  for the diameter of the microspheres in liquid suspension. Descriptions of the experimental techniques, data analyses, and sources of uncertainty are discussed and, in addition, results from four cooperating laboratories are presented for comparative purposes. The calibrated microspheres are now available from the National Bureau of Standards as SRM 1691 for use as a primary length standard in the submicrometer size range. Applications include microcontamination measurement in semiconductor processing, atmospheric sampling, and electron-microscope calibration.

**Keywords:** electron microscopy; light scattering; micrometrology; microspheres; particle sizing; Standard Reference Materials

## Table of Contents

	page
1. Introduction .....	4
2. Transmission Electron Microscopy .....	4
3. Quasi-elastic Light Scattering .....	9
4. Conclusion .....	19
References .....	24

### Tables

Table 1. Results of the TEM Measurements .....	8
Table 2. Results of QELS Experiment 4Q .....	14
Table 3. Results of the QELS Measurements .....	15
Table 4. Uncertainties in the QELS Measurements .....	18
Table 5. Results from Cooperating Laboratories .....	23

### Figures

Figure 1. Schematic of bright-field TEM .....	5
Figure 2. TEM photomicrograph of SRM microspheres .....	6
Figure 3. Schematic of QELS apparatus .....	11
Figure 4. Correlation curve for $\theta = 40^\circ$ .....	13
Figure 5. Plot of $\eta\Gamma$ vs. $Tq^2$ for experiment 4Q .....	16
Figure 6. Optical photomicrograph of SRM 1691 spheres .....	21
Figure 7. Angular light scattering from SRM 1691 spheres .....	22

### Appendices

Appendix A. Certificate for SRM 1691 .....	20
Appendix B. NBS Results from Two Additional Techniques .....	21
Appendix C. Results from Cooperating Laboratories .....	23

## 1. Introduction

The National Bureau of Standards (NBS), in a cooperative program with ASTM Coordinating Committee S-21 on Standard Reference Materials for Particle Metrology, is currently certifying a series of Standard Reference Materials (SRMs) for use as primary calibration artifacts for microparticle sizing and for general use as micrometrology standards [1, 2, 3]. All of the SRMs will be monosized polystyrene spheres in liquid suspension, and the nominal mean diameters will be 0.1, 0.3, 1, 3, 10, 30, and 100  $\mu\text{m}$ .

In this report, the certification of SRM 1691, nominal 0.3- $\mu\text{m}$ -diameter polystyrene spheres, is discussed in detail. Two independent micrometrology methods were used, transmission electron microscopy (TEM) and quasi-elastic light scattering (QELS); both techniques have well-demonstrated accuracy for particles in this size range. The results for the mean diameter from both methods agreed within experimental uncertainty, with the QELS value being somewhat higher than the TEM value.

As stated on the calibration certificate (Appendix A), the certified mean diameter of SRM 1691, as determined by TEM, is  $0.269 \pm 0.007 \mu\text{m}$ . SRM 1691 is sold in 5-ml plastic vials of particles in aqueous suspension at a 0.5% weight concentration of microspheres. Both a surfactant and a biocide (50 ppm sodium azide) are added to the bottled material, the former to minimize particle agglomeration and the latter to retard the growth of algae and bacteria.

Details of the experimental apparatus and procedures used to calibrate the SRM 1691 microspheres, as well as experimental results and error analyses, are given in this report. In addition, the results from two other techniques used at NBS (Appendix B) and from four cooperating laboratories (Appendix C) are provided for completeness and comparison purposes.

## 2. Transmission Electron Microscopy

The basis for the certified measurement of SRM 1691 was the calibration of the magnification of a transmission electron microscope (TEM) using the nominal 1- $\mu\text{m}$  polystyrene microspheres, SRM 1690, to set the dimensional scale [4].

### 2.1 Experimental Procedure

Samples were prepared by evaporating a small drop of an aqueous mixture of the two SRM polystyrene latexes (PSLs) onto a thin carbon foil mounted on a 3-mm-diameter copper TEM grid. The ratio of 1- $\mu\text{m}$  calibration particles to 0.3- $\mu\text{m}$  unknowns was controlled by using different amounts of each suspension in the diluted mixture. A volume ratio of 10 (standard) to 1 (unknown) was found to provide the best balance between the number of each particle size.

# Parallel Illumination

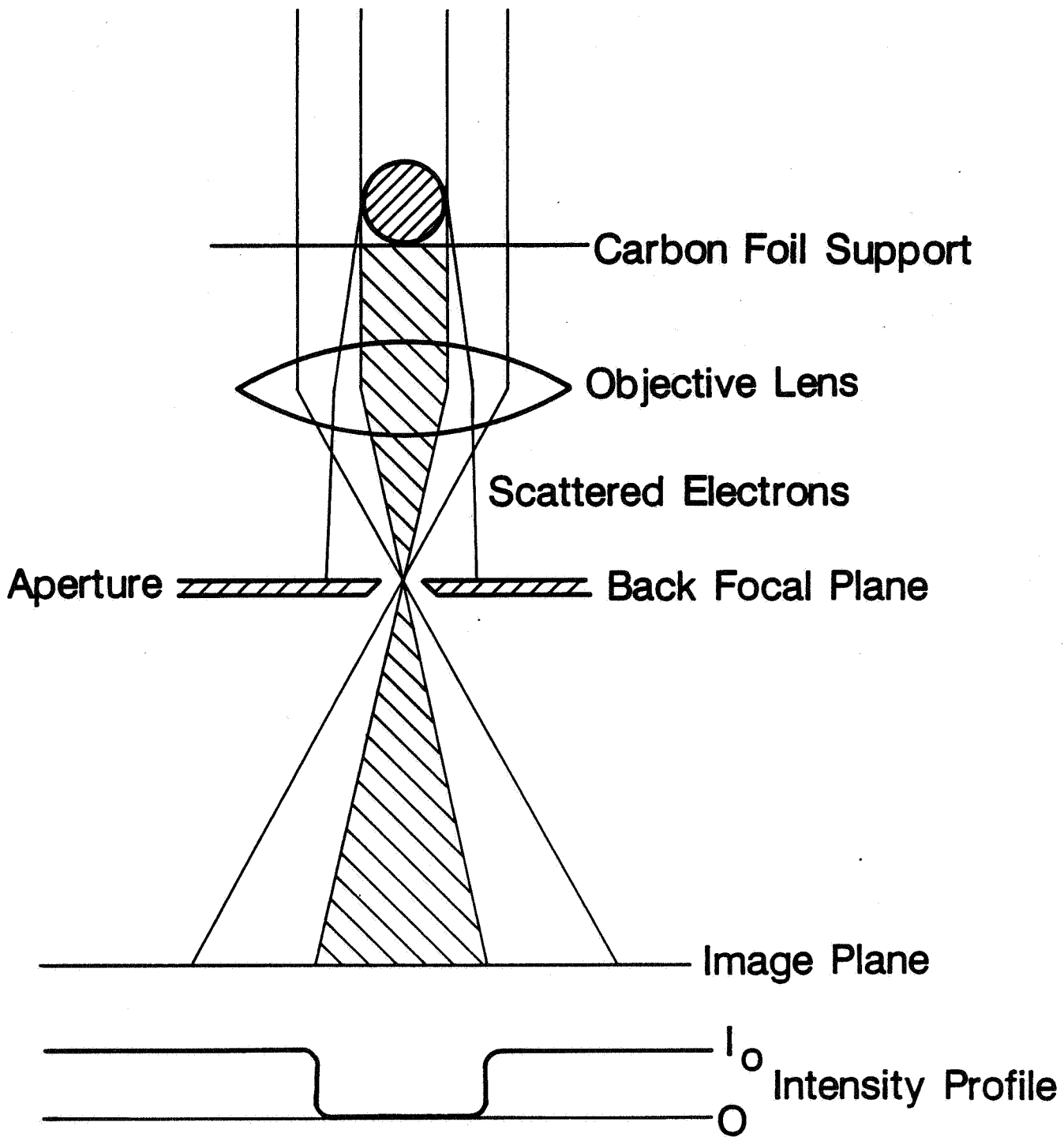


Fig. 1 Schematic representation of image formation in the bright-field, amplitude-contrast mode of the transmission electron microscope (TEM). The objective aperture blocks scattered electrons from reaching the image plane; therefore, the particle image will be a dark circle against a bright background.

Grids were made using samples from five different vials of SRM 1691 material (labelled 1T through 5T) and two vials of SRM 1690.

Photomicrographs were taken using a JEOL 200CX TEM at an accelerating voltage of 100 kV. The microscope was used in the bright-field, amplitude-contrast imaging mode, as shown schematically in Fig. 1. In this configuration, an objective aperture blocks the scattered electrons from reaching the image plate; therefore, the particles appear as dark disks against a bright background. Fig. 2 is a typical photomicrograph showing both standard and unknown particles. The nominal magnification used was 20,000X for all photomicrographs. Edge resolution under these conditions was less than 1 nm.

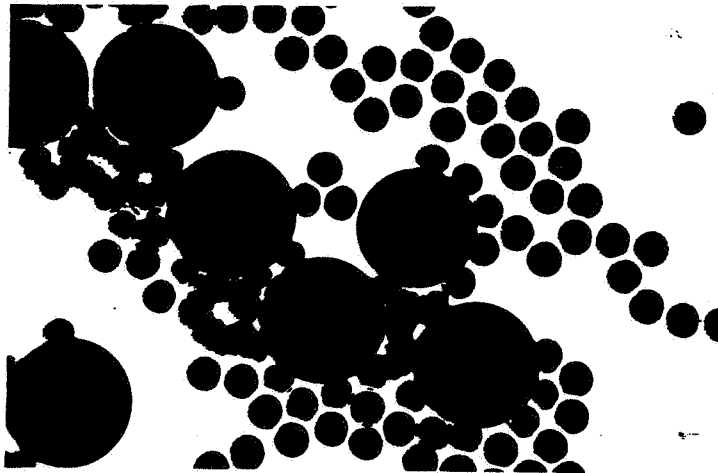


Fig. 2 TEM photomicrograph of the nominal 0.3- $\mu\text{m}$  spheres (SRM 1691) together with the nominal 0.9- $\mu\text{m}$  spheres (SRM 1690) that were used to set the dimensional scale.

The particle diameters were measured directly from the photographic negatives using a 7X optical magnifier with an accurate millimeter-scale reticle. A series of concentric circles on the reticle allowed the diameter to be located quickly. Previous particle measurements at NBS have shown the importance of avoiding, and correcting for, magnification distortion when the particle lies off the optical axis of the electron microscope [5]. Since the magnification used in the present measurements was relatively high, variations in magnification could be minimized by measuring the particle diameter perpendicular to the radial line from the center of the photomicrograph which passed through the center of the sphere [5].

Each data set consisted of approximately 100 image diameters of the standard particles (SRM 1690) and 50 from the unknown particles (SRM 1691); the measurements were performed on images taken of a small area on a single grid. Care was taken when the micrographs were obtained to avoid changing the focus of the microscope by more than very small amounts between micrographs so that the image size would remain constant for the same object size.

## 2.2 Data Analysis and Results

The number-average mean diameter of the SRM 1691 particles,  $d_o$ , was calculated for each set of measurements on the standard and unknown particle images. Given the known mean diameter of the standard,  $d_k = 0.895 \pm 0.008 \mu\text{m}$ , the mean magnification was determined from

$$M = X_k/d_k, \quad (1)$$

where  $X_k$  is the mean image diameter of the standard microspheres. The mean SRM 1691 particle diameter was then determined by dividing its mean image diameter by the magnification. The results for each data set, along with the numbers of particles measured and the mean image diameters, are given in Table 1.

To eliminate outlying TEM measurements, a discordancy test based on the sample kurtosis,  $K$ , was used at the 5% level [6] where:

$$K = \frac{N \sum (d_i - d_o)^4}{[\sum (d_i - d_o)^2]^2} \quad (2)$$

In this expression,  $N$  is the total number of particles measured,  $d_i$  is the measured diameter of the  $i$ th particle, and  $d_o$  is the mean particle diameter. Assuming a Gaussian distribution for the diameters, outlying measurements are eliminated until  $K \leq 3.5$  (for 250 measurements). For all of the measurements,  $K = 5.14$ ; only two outlying measurements on the small-diameter side had to be removed to lower this value to  $K = 3.5$ .

The final reported number-average diameter for SRM 1691 was determined by taking the mean value of the five independent measurements. This value is  $0.269 \mu\text{m}$ , when rounded to three significant figures.

Table 1  
Results of the TEM Measurements<sup>a, b</sup>

Grid	N(0.9)	X(0.9), mm	N(0.3)	X(0.3), mm	$d_o$ , $\mu\text{m}$	$\sigma$ , $\mu\text{m}$
1T	65	16.592	42	5.023	0.272	0.006
2T	80	16.656	52	4.958	0.266	0.005
3T	99	16.522	50	4.953	0.268	0.004
4T	109	16.666	50	4.930	0.265	0.007
5T	106	16.459	53	4.995	0.271	0.006

Mean 0.269 0.003

<sup>a</sup> N(0.9) and X(0.9) are, respectively, the number and the mean diameter of the TEM photomicrograph images of the known, 0.9- $\mu\text{m}$  particles.

<sup>b</sup> N(0.3) and X(0.3) are, respectively, the number and the mean diameter of the TEM photomicrograph images of the unknown, 0.3- $\mu\text{m}$  particles. Note that these numbers do not include the two outliers.



### 2.3 Error Analysis

The total uncertainty in the TEM-measured particle diameter contains both a random component and a systematic component:

$$|U_t| = |U_r| + |U_s| \quad (3)$$

The random uncertainty was calculated from the standard deviation,  $\sigma_t$ , of the mean value of the five independent TEM measurements. Note that since each measurement was performed on a sample from a different vial of SRM 1691, the random uncertainty includes vial-to-vial variability, as well as measurement uncertainty. The total random uncertainty is [4]:

$$\begin{aligned} U_r &= t_m(0.025)\sigma_t/\sqrt{N} \\ &\approx 3(0.003 \mu\text{m})/\sqrt{5} = 0.004 \mu\text{m} \end{aligned} \quad (4)$$

where  $t_m(0.025) \approx 3$  is the student t-value, at the 95% confidence level, for 4 degrees of freedom and  $N = 5$  is the number of measurements.

Systematic uncertainties in the measurement process arise from two sources. The first of these is caused by the uncertainty in assigning the point in the particle image which corresponds to the actual object edge (i.e., edge-location uncertainty). The magnitude of this uncertainty was estimated to be about  $0.001 \mu\text{m}$  for the instrumental conditions used in the measurements. The other source of systematic uncertainty, the mean size of the  $0.9\text{-}\mu\text{m}$  standard particles (SRM 1690), was the larger of the two. The total uncertainty in the certified mean diameter of the  $0.9\text{-}\mu\text{m}$  material is  $0.008 \mu\text{m}$  [4], which causes a fractional uncertainty of 0.9% or  $0.0024 \mu\text{m}$  in the SRM 1691 microspheres. The systematic uncertainties are added linearly to get  $U_s = 0.003 \mu\text{m}$ .

From Eq. 3, the total uncertainty for the TEM measurement is taken as the linear sum of the random and systematic uncertainties, which is  $0.007 \mu\text{m}$ , at the 95% confidence level.

### 3. Quasi-elastic Light Scattering

In addition to TEM, quasi-elastic light scattering (QELS), was used to get information about the mean particle size of SRM 1691 in aqueous suspension. This well-established micrometrology technique is based on measuring the time correlation function of the Brownian motion of the particles as a function of scattering angle. For additional information about the QELS technique, the reader is referred to Refs. 7 and 8. The utility of QELS in the certification of SRM 1691 lies in its applicability

with submicron particles and its independence of the optical properties of the particles [7,8].

### 3.1 Apparatus

The apparatus used in the QELS measurements, a homodyne (or self-beating) type system, is diagrammed schematically in Fig. 3 and described in further detail elsewhere [9,10]. The vertically polarized argon-ion laser beam, at a wavelength of 488.0 nm, was focussed into a dilute suspension of SRM 1691 microspheres contained in a glass sample tube surrounded by a temperature-controlled, index-matching bath of paraffin oil. The beam that passed through the tube was caught by a beam trap to prevent backscattering into the sample. Only the vertically polarized component of the scattered light was detected (i.e., the scattering was VV).

Light collection/detection optics, consisting of a periscope, an analyzer/polarizer, a variable diaphragm, and a photomultiplier tube (PMT), were mounted on a rotary table to allow a range of scattering angles: the acceptance angle of this optical system was 0.5 mrad. Detected photoelectrons from the PMT were amplified, discriminated, and sent to a commercial 128-channel digital correlator. After a QELS spectrum was collected, which took anywhere from 1000 to 3000 seconds depending on the intensity of the scattered light at a particular angle, the spectrum was transferred to a mainframe computer for data analysis and curve fitting.

The sample cell was a precision ground and polished glass tube of 12.5 mm diameter. To load the tube with particles, one drop from a vial of SRM 1691 was diluted by a factor of 20,000 in deionized and filtered water. The resulting particle weight concentration of  $2.5 \times 10^{-7}$  assured that multiple light scattering and particle interactions would be negligible [11].

Since the surfactant was diluted by several orders of magnitude, it was necessary to check for possible agglomeration of the particles. To this end, a study was conducted over a 2-day period to look for detectable changes in mean particle size as measured with the QELS apparatus. The change of  $\pm 0.002 \mu\text{m}$  over the 2-day period was within the experimental reproducibility, indicating that no appreciable agglomeration of particles had occurred. Thereafter, to assure that agglomeration would not be a problem in the QELS experiments, all of the spectra taken on the same sample were collected within a relatively short time period of about 4 hrs.

As discussed later in the error-analysis section, it is important to both control and accurately measure the temperature of the sample, primarily because of the strong dependence of the water viscosity on temperature. In the present experiments, the temperature at the sample was monitored with an accurately calibrated thermocouple having a temperature uncertainty better than  $\pm 0.05 \text{ }^\circ\text{K}$ .

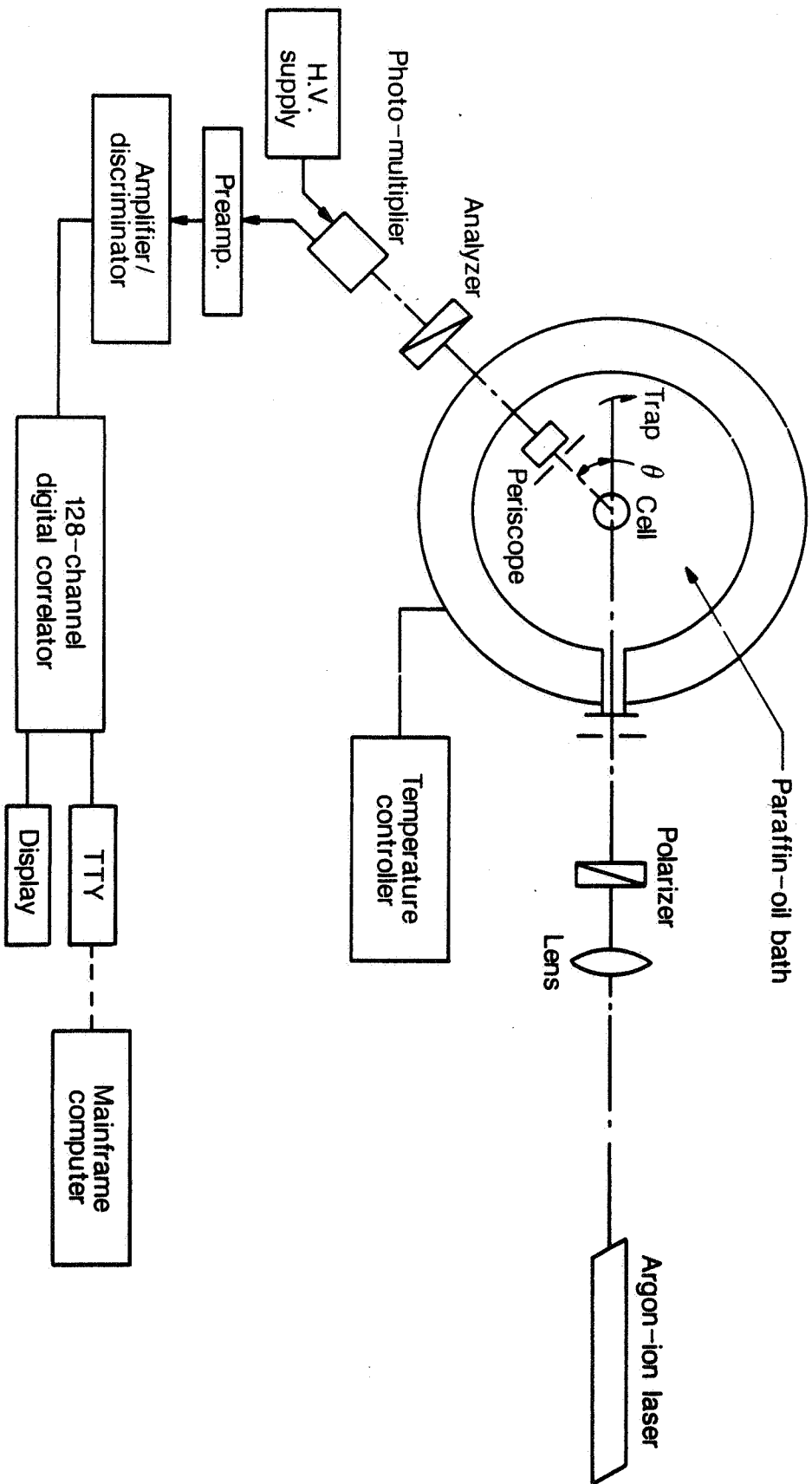


Fig. 3 Schematic diagram of the quasi-elastic light scattering (QELS) apparatus. After Ref. 9.

### 3.2 Data Analysis and Results

Five homodyne QELS experiments (labelled 1Q through 5Q) were conducted, each one consisting of correlation curves taken at nine scattering angles,  $\theta$ : 25°, 30°, 35°, 40°, 45°, 50°, 55°, 60°, and 70°. Each experiment used a droplet of particles from a different vial chosen at random from the complete lot of 1000 vials. A typical correlation curve at  $\theta = 40^\circ$  (for experiment 5Q) is presented in Fig. 4. To obtain the particle diffusion time  $\tau_D$  from each correlation curve, a least-squares fit to an exponential correlation function of the form [7,8]

$$g(\tau) = a + b \exp(-\tau/\tau_D) \quad (5)$$

was done, where  $\tau$  is the delay time and  $a$  and  $b$  are fit parameters. Particle diffusion times  $\tau_D$  ranged from about 6 msec at  $\theta = 25^\circ$  to about 0.8 msec at  $\theta = 70^\circ$ . From these diffusion times, a value for  $\Gamma = 1/2\tau_D$  (for homodyne QELS) was determined for each scattering angle (see Table 2). None of the exponential fits showed evidence for a finite width of the particle-size distribution, so it was ignored in the QELS data analysis. The effect on the mean diameter from neglecting a possible size-distribution width is discussed in the error-analysis section.

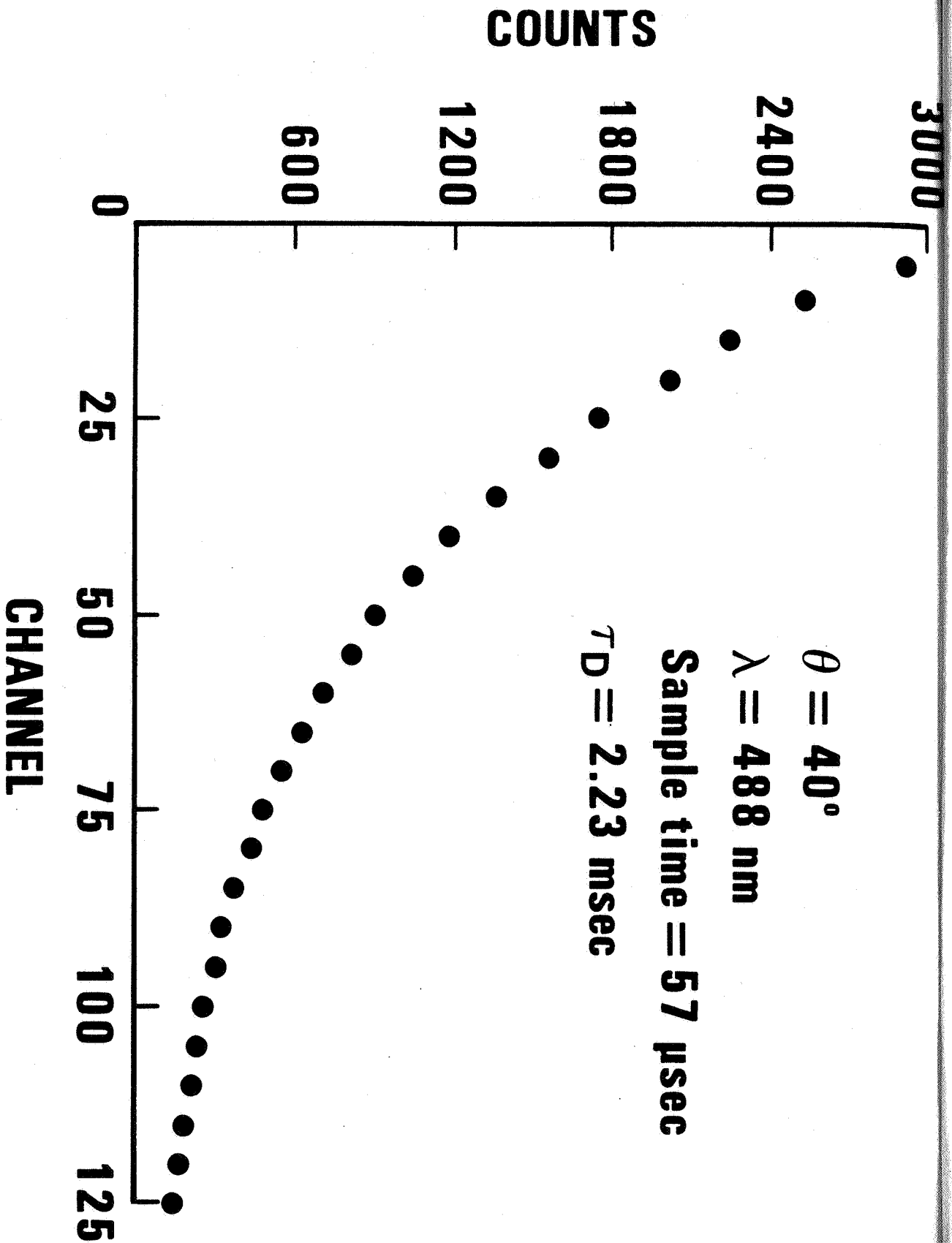


Fig. 4 Exponential QELS correlation curve for  $\theta = 40^\circ$ .

Table 2

Results of QELS Experiment 4Q

$\theta$	T °K	$q^2$ $\text{cm}^{-2}$	$Tq^2$ $10^{-3} \times \text{°K}/\text{cm}^2$	$\eta(T)$ cp	$\Gamma$ $\text{sec}^{-1}$	$\eta\Gamma$ cp/sec
25°	295.56	5.55	1.640	0.9457	88.6	83.8
30°	295.52	7.94	2.346	0.9465	129.3	122.4
35°	295.52	10.72	3.168	0.9465	175.2	165.8
40°	295.52	13.86	4.096	0.9465	228.8	216.5
45°	295.52	17.35	5.127	0.9465	292.0	276.4
50°	295.52	21.16	6.253	0.9465	345.7	327.2
55°	295.52	25.27	7.468	0.9465	424.0	401.3
60°	295.52	29.62	8.753	0.9465	493.3	466.9
70°	295.53	38.98	11.520	0.9464	656.3	621.1

For each of the five experiments, the values of  $\eta\Gamma$  (where  $\eta$  is the water viscosity) were plotted as a function of  $Tq^2$  where T is the temperature in °K. The parameter q is related to momentum transfer and is defined as:

$$q = (4\pi n/\lambda)\sin(\theta/2) \quad (6)$$

in which n is the refractive index of water,  $\lambda$  is the laser wavelength in air, and  $\theta$  is the scattering angle as measured from the forward direction. The refractive index of water was taken to be 1.3368 at 22 °C and 488.0 nm laser wavelength in air. Note that the viscosity  $\eta$  is itself a function of temperature; thus, each  $\eta$  was corrected for temperature using the equation [12]

$$\eta(T_c) = 1.002 \text{ antilog}_{10} \frac{1.327(20-T_c) - 0.001(T_c-20)^2}{T_c + 105} \quad (7)$$

in which  $T_c$  is the temperature in °C and  $\eta$  is measured in centipoise.

An example of a plot of  $\eta\Gamma$  vs.  $Tq^2$ , for experiment 4Q, is given in Fig. 5. Straight-line fits of the form

$$\eta\Gamma = m (Tq^2) \quad (8)$$

where  $m$  is the best-fit slope, were then calculated from the data for each of the five QELS experiments.

Since the particle diffusion coefficient  $D$  is equal to  $\Gamma/q^2$ ,  $m$  is related to  $D$  through the Stokes-Einstein equation [7,8]

$$D = kT/6\pi\eta r \quad (9)$$

where  $k$  is the Boltzman constant and  $r$  is the particle radius. Thus, the particle diameter is given as

$$d_0 = kTq^2/3\pi\eta\Gamma = k/3\pi m \quad (10)$$

where the latter expression results from the straight-line fit.

The diameters obtained in this manner for each of the five experiments 1Q through 5Q are listed in Table 3. The diameter for the QELS measurement is taken to be the mean of these values, which is 0.276  $\mu\text{m}$ .

**Table 3**  
Results of the QELS Measurements

Exp.	$d, \mu\text{m}$	$\sigma, \mu\text{m}$
1Q	0.276	-
2Q	0.279	-
3Q	0.277	-
4Q	0.274	-
5Q	0.275	-
Mean	0.276	0.002

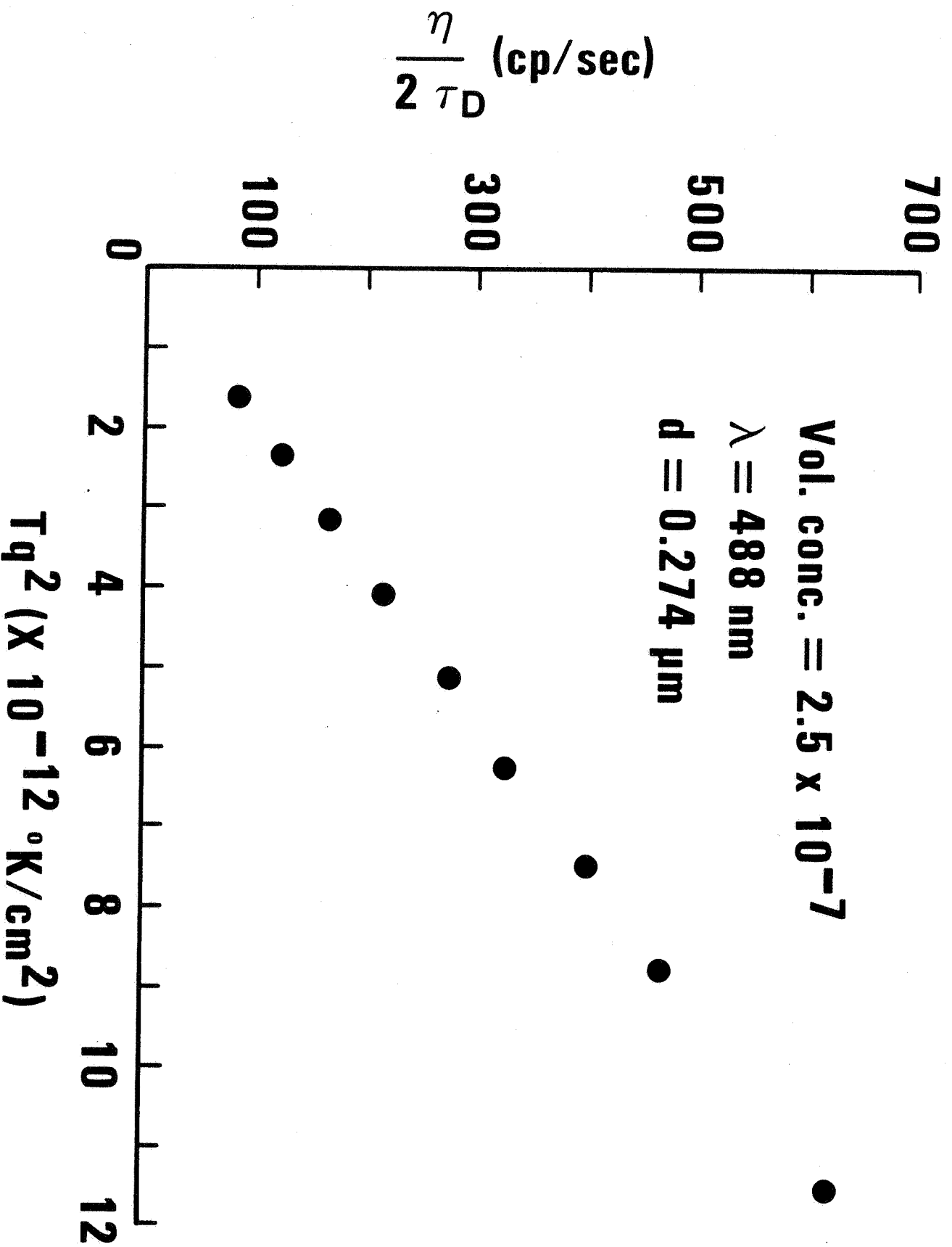


Fig. 5 Plot of  $\eta\Gamma$  vs.  $Tq^2$  for QELS experiment 4Q.



### 3.3 Error Analysis

As with the TEM measurements, the total uncertainty in the QELS-measured particle diameter contains a random component and a systematic component (Eq. 3).

The random component of the uncertainty,  $U_r$ , is mainly due to the small number of measurements (five) and is given by Eq. 4. For  $\sigma = 0.002 \mu\text{m}$ , the random uncertainty due to sampling is  $0.0025 \mu\text{m}$ , at the 95% confidence level. Note that this random uncertainty also contains a component due to vial-to-vial variability since each QELS experiment used a droplet from a different vial. However, it is expected that the vial-to-vial variability is negligible [4].

The systematic uncertainties are primarily a result of uncertainties in the scattering parameter  $q$ , the viscosity, and the relaxation time. A possible systematic uncertainty due to undissolved surfactant on the particles is expected to be small and is, therefore, neglected [4].

To estimate the systematic uncertainty,  $U_s$ , for a single measurement, Eq. 10 is differentiated to give [13]

$$\Delta d/d = \Delta T/T \pm 2\Delta q/q \pm \Delta \eta/\eta \pm \Delta \Gamma/\Gamma \quad (11)$$

Each of these systematic uncertainty components is discussed separately:

**3.3.1 Temperature** The temperature uncertainty was  $0.05 \text{ }^\circ\text{K}$ . For the  $295 \text{ }^\circ\text{K}$  temperatures of the present experiment, this results in a negligible diameter uncertainty of  $0.00005 \mu\text{m}$ .

**3.3.2 Uncertainty in  $q$**  The uncertainty in  $q$  is the biggest component of systematic uncertainty, due largely to the inaccuracy in scattering angle,  $\theta$ . Differentiating the expression for  $q$  (Eq. 6) yields

$$\Delta q/q = \Delta n/n \pm \Delta \lambda/\lambda \pm \Delta \theta/[2 \tan(\theta/2)] \quad (12)$$

The first term, the uncertainty in the refractive index of the water, is about 0.1%; the second term, the laser wavelength uncertainty, is negligible (less than 0.002%); and the third term, the angular uncertainty of  $0.25^\circ$  gives an uncertainty in  $q$  of 0.5% at  $\theta = 45^\circ$ . [Note that the angular uncertainty contains a component due to the finite acceptance angle of  $0.008^\circ$ .] Thus, the total systematic uncertainty in  $q$  is 1.2% or  $0.0032 \mu\text{m}$ , because of the factor of 2 in Eq. 12.

3.3.3 **Viscosity** The viscosity uncertainty results, primarily, from uncertainty in the temperature of the sample. At 22 °C, the temperature variation in water viscosity is about 2% per °C (see Eq. 7). Thus, for a 0.05 °C temperature uncertainty, the viscosity uncertainty is 0.1%, which results in a diameter uncertainty of 0.0003  $\mu\text{m}$ .

3.3.4 **Relaxation Time** The uncertainty in  $\Gamma$  (or  $\tau$ ) has two components, one due to neglecting the finite standard deviation,  $\sigma_d$ , of the size distribution and another due to the uncertainty in baseline subtraction in Eq. 5. The correlator-timebase uncertainty is less than 1 ppm, so its effect on  $\Gamma$  is negligible. The size-distribution uncertainty can be estimated with the cumulant method, in which the measured diffusion coefficient  $D$  is a z-average of diffusion coefficients resulting from the distribution of particle volumes [14]. For a narrow Gaussian distribution of diameters, this uncertainty is about  $\sigma_D/3$  [14]. From measurements from the four cooperating laboratories (see Appendix C),  $\sigma_d$  is at most 0.003  $\mu\text{m}$ , resulting in at most a 0.001  $\mu\text{m}$  uncertainty on  $d$ . The baseline-subtraction uncertainty is estimated to be 0.2% (or 0.0006  $\mu\text{m}$  on  $d_0$ ), from the reproducibility in repeated measurements of  $\Gamma$ . Thus, the total systematic uncertainty on  $d_0$  due to  $\Gamma$  uncertainty is 0.0012  $\mu\text{m}$ .

3.3.5 **Total Uncertainty** All of the random and systematic uncertainties in the QELS measurements are summarized in Table 4. Combining them linearly gives a total uncertainty of 0.007  $\mu\text{m}$ , at the 95% confidence level, for the QELS measurement of the mean diameter of the SRM 1691 particles.

Table 4

Uncertainties in the QELS Measurements

	Source	$\Delta d$ , $\mu\text{m}$
Random	sampling	0.0025
Systematic	q	0.0032
	viscosity	0.0003
	$\Gamma$	0.0012
Total Uncertainty		0.007

#### 4. Conclusion

The work reported here is evidence that an accurate mean diameter can be obtained for submicrometer particles, if they are nominally spherical and monosized. The two micrometrology techniques used in the certification, transmission electron microscopy and quasi-elastic light scattering, measured the particles in radically different environments, using significantly different physical principles to get the mean size. Even so, the closeness of the results indicates that the major systematic uncertainties have been accounted for and that the polystyrene microspheres are essentially unaffected by changes in environment, at least for those of the present study (i.e., vacuum and water). Within experimental uncertainty, there was no evidence for particle degradation due to either electron-beam damage or outgassing in the vacuum.

It is expected that SRM 1691 will have many industrial applications in particle sizing, as well as some in basic research involving small particles. Examples of the former include the monitoring and sizing of microcontamination in semiconductor processing; dimensional calibration of electron microscopes; sampling and analysis of atmospheric aerosols; and calibration of various instruments which size submicrometer particles [15, 16, 17].

#### Acknowledgements

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# National Bureau of Standards

## Certificate

### Standard Reference Material 1691

#### Nominal 0.3 $\mu\text{m}$ Diameter Polystyrene Spheres

(In Cooperation with the American Society for Testing and Materials)

This Standard Reference Material (SRM) is intended for use as a primary particle size reference standard for the calibration of particle size measuring instruments including electron microscopes. The SRM is a suspension of polystyrene spheres in water at a weight concentration of about 0.5%.

The number average particle diameter was determined by transmission electron microscopy (TEM) using SRM 1690 (nominal one- $\mu\text{m}$  polystyrene spheres) to set the dimensional scale. The value reported is the mean of five independent data sets each consisting of over 100 measurements of 1- $\mu\text{m}$  standard spheres and over 30 measurements of nominal 0.3- $\mu\text{m}$  spheres.

<u>Number Average Diameter, <math>\mu\text{m}</math></u>	<u>Uncertainty, <math>\mu\text{m}</math></u>
0.269	$\pm 0.007$

The uncertainty consists of both random and systematic errors, and includes sample-to-sample variability.

The value certified for the number average diameter was confirmed by one additional technique, quasielastic light scattering (QELS). In this technique, the average lifetime of the Brownian motion of the particles suspended in water is measured as a function of scattering angle. This gives a diffusion coefficient which can be used with the Stokes-Einstein relationship to yield the hydrodynamic particle diameter. The result from QELS was:  $0.276 \pm 0.007 \mu\text{m}$ .

The size distribution of the polystyrene spheres, as determined by TEM, is narrow with a standard deviation less than 2% excluding outliers (particles with diameters not on the main peak). The number of small outliers is less than 1% and the number of large outliers is less than 0.5%.

The material is expected to have at least a four-year shelf life when stored at room temperature provided the cap on the vial is not removed. Care should be exercised once the cap has been removed to prevent contamination. Fifty ppm of sodium azide was added as a biocide before the material was packaged.

Before sampling, manually shake and/or expose SRM to ultrasonics until the spheres are uniformly distributed. Then take a sample by squeezing a drop from the vial. Use filtered (0.1- $\mu\text{m}$  pore size filter) distilled water for dilution. When electrolytes are used for electrical sensing zone counter measurements, first dilute the sample with water to prevent agglomeration.

The technical direction and physical measurements leading to certification were provided by T. Lettieri, G. Hembree, D. Gilsinn, and E. Marx of the Mechanical Production Metrology Division.

The overall coordination of the measurements by the cooperating laboratories was performed under the direction of R. Obbink, Research Associate, ASTM-NBS Research Associate Program.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by L.J. Kieffer.

## APPENDIX B

### NBS Results from Two Additional Techniques

As supplementary information, mean diameters for SRM 1691, as measured at NBS using two other micrometrology techniques, are given in this Appendix. These results have not been certified, nor have their accuracies been determined. However, this additional information may be useful to other experimenters using either of the techniques.

**Optical array sizing** This micrometrology technique was pushed to its limits by the small size of the SRM 1691 microspheres [18]. To resolve particles as small as  $0.3 \mu\text{m}$ , off-axis illumination with near-UV light had to be used in the optical microscope. Although hexagonal arrays of the particles were made successfully (Fig. 6), they could only be resolved along one axis due of the nature of the illumination. The measured diameter of  $0.29 \mu\text{m}$  is not expected to be accurate because of the limited resolution of the optical microscope.

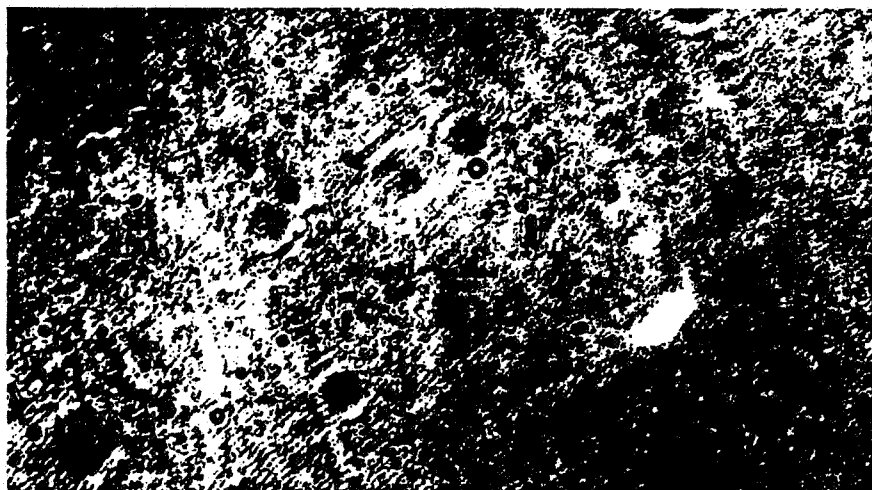


Fig. 6 Optical photomicrograph of hexagonal array of SRM 1691 microspheres.

**Mie angular-intensity light scattering (AILS)** The angular-intensity light scattering patterns for microspheres are featureless for particles this small (Fig. 7). Because of this, it was difficult to get precise values for  $d_0$  using angular light scattering, without first making some assumptions about the standard deviation of the size distribution,  $\sigma_d$ . If both  $d_0$  and  $\sigma_d$  were used as free parameters in the Mie-scattering computer calculations, then the resulting best-fit measurements for these parameters were clearly incorrect and had large associated uncertainties. However, if  $\sigma_d$  was fixed at 0 (i.e., monosized particles), then the resulting computer fit was very good, and the mean diameter of  $0.262 \mu\text{m}$  was reasonably close to the certified value of  $0.269 \mu\text{m}$ . An even closer value resulted when  $\sigma_d$  was assumed to be  $0.003 \mu\text{m}$  (as measured by several outside collaborators); in this case, the measured diameter was  $0.266 \mu\text{m}$  (Fig. 7).

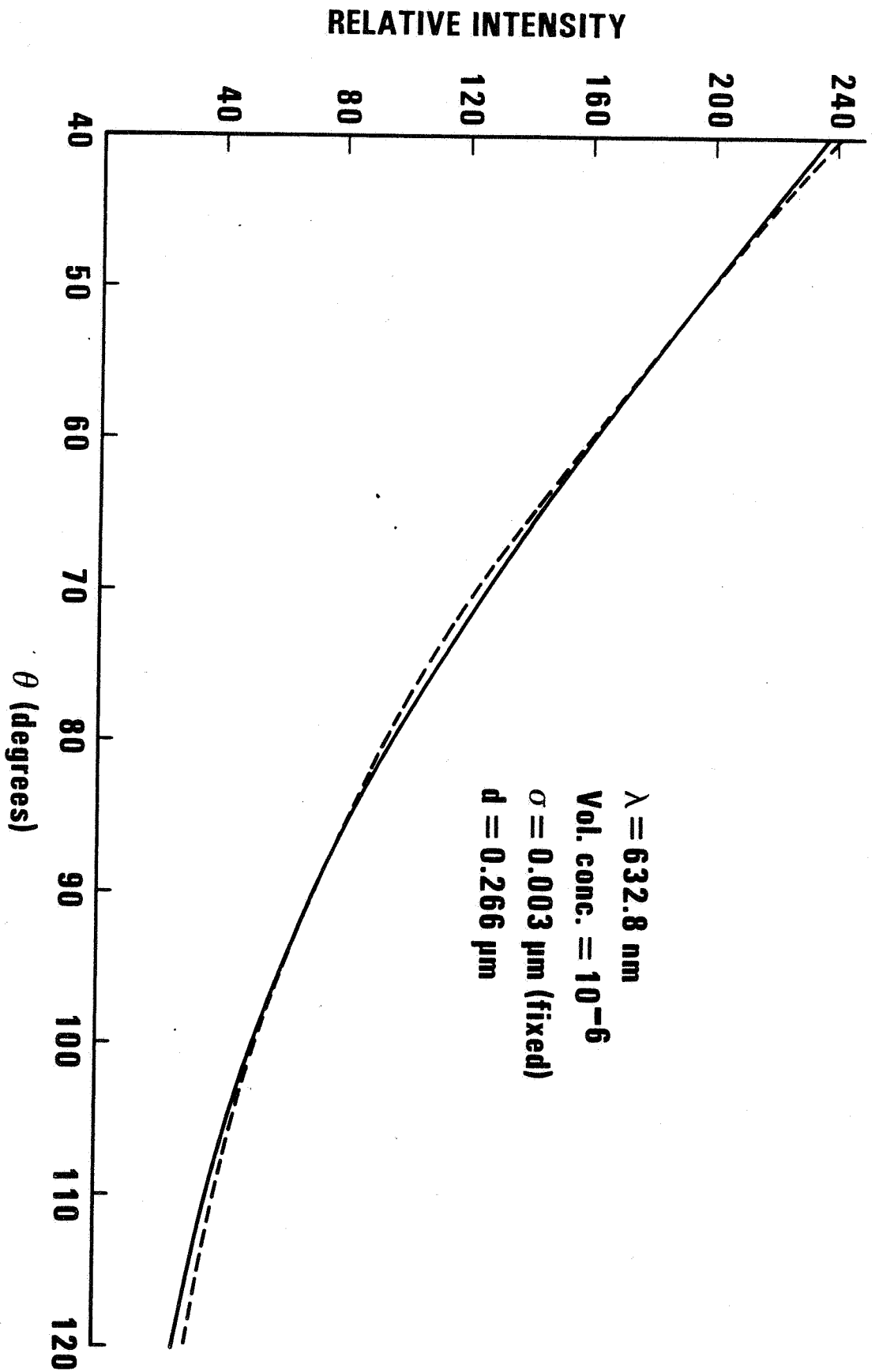


Fig. 7 Experimental (solid) and calculated (dashed) curves for angular light scattering from liquid suspension of SRM 1691 microspheres.

## APPENDIX C

### Results from Cooperating Laboratories

Four other laboratories participated in the certification of SRM 1691: Brookhaven Instruments, Eastman Kodak Co., Malvern Instruments, and G. D. Searle and Co.. Most of the techniques used by these labs involved some type of light scattering, primarily QELS. In addition, one measurement was made with each of the following methods: polarization-ratio light scattering, TEM, disc centrifuge, and ultracentrifuge.

The mean diameters determined by the cooperating laboratories are summarized in Table 5. Although these results are given for informational and comparative purposes only, it is interesting to note that the arithmetic mean of all these diameters is  $0.275 \mu\text{m}$  (excluding three outlying measurements). This value is within the experimental uncertainties of the two NBS results. Also note that several of the measurements indicated a finite standard deviation of about  $0.003 \mu\text{m}$  for the particle size distribution of SRM 1691.

Table 5

Method	Laboratory	d, $\mu\text{m}$	$\sigma$ , $\mu\text{m}$
TEM	Kodak	0.248	0.0026
Light Scattering:			
Polarization Ratio	Kodak	0.273	0.003
QELS	Kodak	0.272	
QELS	Kodak	0.293	
QELS	Brookhaven	0.273	
QELS	Searle	0.282	0.0032
QELS	Malvern	0.273	
Disc Centrifuge	Kodak	0.25	0.0027
Ultracentrifuge	Kodak	0.28	0.0029

## References

1. T. Lettieri, A. Hartman, G. Hembree, and E. Marx in "Proceedings of the 1985 International Symposium/Workshop on Particulate and Multi-phase Processes," T. Ariman and T. Veziroglu, Eds. (Fine Particle Society, Tulsa, OK, 1985), p. 416.
2. K. Kirby in "Methods and Standards for Particle Measurement," J. Beddow, Ed. (NSF, Washington, DC, 1983), p.42.
3. G. Porter, NBS Research Reports, p. 16 (Oct. 1984).
4. G. Mulholland, A. Hartman, G. Hembree, E. Marx, and T. Lettieri, J. Research NBS 90, 3 (1985).
5. G. Mulholland, G. Hembree, G., and A. Hartman, "Sizing of Polystyrene Spheres Produced in Microgravity," NBSIR 84-2914, U.S. Department of Commerce, National Bureau of Standards, Gaithersburg, MD, 1985.
6. V. Barnett and T. Lewis, "Outliers in Statistical Data" (John Wiley and Sons, New York, 1978).
7. B. Chu, "Laser Light Scattering" (Academic Press, New York, 1974).
8. B. Berne, B. and R. Pecora, "Dynamic Light Scattering" (John Wiley and Sons, New York, 1976).
9. C. Han, Rev. Sci. Instrum. 49, 31 (1978).
10. S. Shaya, C. Han, and H. Yu, Rev. Sci. Instrum. 45, 280 (1974).
11. D. Napper and R. Ottewill, J. Coll. Int. Sci. 19, 72 (1964).
12. "CRC Handbook of Chemistry and Physics (60th Edition)," R. Weast, Ed., (CRC Press, Boca Raton, FL, 1979), p. F-51.
13. P. Bevington, "Data Reduction and Error Analysis for the Physical Sciences," (McGraw-Hill, New York, 1969).
14. D. Koppel, J. Chem. Phys. 57, 4814 (1972).
15. B. Weiner and W. Tscharnuter in "Particle Size Distribution: Assessment and Characterization," T. Provder, Ed. (American Chemical Society, Washington, DC, 1987), p. 48.
16. D. Alliet, R. Freitag, and L. Switzer in "Proceedings of the 17th Annual Fine Particle Society Meeting," T. Ariman, Ed. (Fine Particle Society, Tulsa, OK, 1986).



17. D. Pitt and P. McGibney in "Proceedings of the 17th Annual Fine Particle Society Meeting," T. Ariman, Ed. (Fine Particle Society, Tulsa, OK, 1986).
18. A. Hartman, Powder Tech. 39, 49 (1984).

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<b>10. SUPPLEMENTARY NOTES</b>  <input type="checkbox"/> Document describes a computer program; SF-185, FIPS Software Summary, is attached.			
<b>11. ABSTRACT</b> <i>(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)</i> <p>The mean diameter of submicrometer polystyrene spheres, to be used as a new Standard Reference Material (SRM) for particle sizing, was accurately measured using two independent micrometrology techniques. One technique, transmission electron microscopy, measured the particles dried and in a vacuum, and gave a result of <math>0.269 \pm 0.007 \mu\text{m}</math> for the certified mean diameter. The supporting method, quasi-elastic light scattering, yielded a value of <math>0.276 \pm 0.007 \mu\text{m}</math> for the diameter of the microspheres in liquid suspension. Descriptions of the experimental techniques, data analyses, and sources of error are discussed and, in addition, results from four cooperating laboratories are presented for comparative purposes. The microspheres are now available from the National Bureau of Standards as SRM 1691 for use as a primary length standard in the submicrometer size range. Applications include microcontamination measurement in semiconductor processing, atmospheric sampling, and electron-microscope calibration.</p>			
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