National Institute of Standards & Technology

Certificate

Standard Reference Material® 1690

Polystyrene Spheres

(Nominal Diameter 1 µm)

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. A unit of SRM 1690 consists of one bottle containing approximately 5 mL of a suspension of polystyrene spheres in water at a mass concentration of approximately 0.5 %.

Certified Value: The certified value is given below. The certified value and uncertainty were calculated according to the method described in the ISO/JCGM Guide [1]. The measurand is the number average diameter. Metrological traceability is to the SI unit for length, expressed as micrometers.

Certified Number Average Diameter: 0.895 µm ± 0.005 µm

Information Values: Information values from the original certification of SRM 1690 are provided in Tables 1 and 2. An information value is considered a value that will be of interest to the SRM user, but insufficient information is available to assess the uncertainty associated with the value. Information values cannot be used to establish metrological traceability.

Expiration of Certification: The certification of **SRM 1690** is valid, within the measurement uncertainty specified, until **20 March 2023**, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see "Instructions for Storage and Use"). This certification is nullified if the SRM is damaged, contaminated, or modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification, NIST will notify the purchaser. Registration (see attached sheet or register online) will facilitate notification.

Overall technical direction and physical measurements leading to the original certification were provided by G. Mulholland, T. Lettieri, G. Hembree, A. Hartman, and E. Marx of the former NIST Mechanical Production Metrology Division with guidance on statistical analysis provided by K. Eberhardt formerly of NIST. Coordination of the measurements by the cooperating laboratories was performed under the direction of R. Obbink, formerly of NIST.

Overall updated results for this material were provided by J. Dagata, N. Farkas, M. Stocker, P. Kavuri, A. Vladar, and T.V. Vorburger of the NIST Engineering Physics Division and G. Mulholland of the NIST Chemical Sciences Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Office of Reference Materials.

David G. Seiler, Chief
Engineering Physics Division

Gaithersburg, MD 20899
Certificate Issue Date: 09 August 2016
Certificate Revision History on Last Page

Steven J. Choquette, Acting Director
Office of Reference Materials

INSTRUCTIONS FOR STORAGE AND USE

Storage: Store SRM 1690 at room temperature. Care should be exercised once the cap has been removed to prevent contamination. Fifty parts per million of sodium azide, was added as a biocide before the material was packaged.

Use: Before sampling, manually shake and/or expose the SRM to ultrasonics until the spheres are uniformly distributed. Then take a sample by squeezing a drop from the vial. Use filtered (0.2 µm 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. When this SRM was first certified, light scattering, as described below, was used as part of the certification design. The material has since developed a small fraction of agglomerates, which makes this particular approach unsuitable for measuring the number average particle diameter. **Consequently, this SRM is not suitable for use on light scattering instrumentation, such as Dynamic Light Scattering (DLS).**

ANALYSIS AND CERTIFICATION[(1)]

The original number average particle diameter was determined by measuring the light scattered by the polystyrene spheres suspended in water. The value used for the refractive index of polystyrene was n = 1.6121 at a wavelength of 441.6 nm [2]. The value reported is the mean of ten one-drop samples drawn randomly from 1000 SRM 1690 vials. The diameter was determined from the best fit of Mie light scattering theory to the measured intensity versus angle. SRM 1690 was originally calibrated and certified in 1984 [3], before NIST had adopted its current policy on the determination of measurement uncertainty [1]. The original data were reanalyzed [4] in order to produce an uncertainty budget compliant with the current NIST policy. Seven uncertainty components are considered here:

u_A – standard deviation of the means for the set of 1.0 µm particle samples measured

u_R – uncertainty due to errors in determining refractive index of polystyrene spheres

u_D – uncertainty arising from the presence of particle doublets

u_S – uncertainty due to multiple scattering in higher concentration particle solutions

u_C – uncertainty caused by secondary sample cell reflections

u_F – uncertainty introduced by the finite acceptance angle of the photometer

u_M – uncertainty resulting from error in the zero angle of the light scattering photometer

The first component, u_A, is a Type A component estimated by statistical methods. The remaining components (u_R, u_D, u_S, u_C, u_F and u_M) are Type B, estimated by other means. These seven components are combined in quadrature sum to arrive at the combined uncertainty of 0.0026 µm for the 1.0 µm particle measurements. Using the Welch-Satterthwaite formula [4], the effective number of degrees of freedom is determined to be 1.47×10^5, giving a coverage factor of 1.96 for a 95 % confidence interval. The final expanded uncertainty for the 1.0 µm (SRM 1690) particle measurements is the combined uncertainty (0.0026 µm) multiplied by coverage factor of 1.96. The calibrated diameter and its associated expanded uncertainty are shown on page 1. The uncertainty is approximately 30 % smaller than the uncertainty given on the original certificate.

The value certified for the number average diameter was confirmed by two other measurement techniques. The first of these was by measuring the light scattered by eight individual spheres levitated in air. In this technique both the diameter and refractive index are determined by the best fit to light scattering theory. In the second technique the average diameter was determined by optically measuring the row length of particles in two dimensional arrays formed by air drying. The uncertainty budgets for these two methods were also recalculated to make them compliant with current NIST policy on measurement uncertainty. The results obtained by these methods are shown on Table 1.

Table 1. Information Values for SRM 1690

Technique	Average Diameter (µm)		
Scattering by individual particles	0.900	±	0.010
Optical array sizing	0.898	±	0.017

[(1)]Certain commercial equipment, instruments, or materials are identified in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

The particle size distribution of the polystyrene spheres (as determined by measurements with a transmission electron microscope) is narrow with a standard deviation of about 0.0095 µm, excluding small particles with diameters less than 0.6 µ (about 0.5 %) and large single particles with diameters in the range of 2 µm to 6 µm (about 0.1 %). A discordancy test based on the sample kurtosis was used at the 5 % level for rejecting these particles [5]. The particles are spherical with an average deviation from sphericity, $(D_{max} - D_{min})/D_{ave}$, of about 0.006.

During the original certification, cooperative determinations were performed in the following laboratories:

Air Products and Chemicals (Allentown, PA) by D.J. Nagy
Coulter Electronics Co. (Hialeah, FL) by R.T. Rodewald
Dow Chemical Co. (Midland, MI) by M.A. Langhorst
Duke Scientific Corp. (Palo Alto, CA) by S.D. Duke
Eastman Kodak Co. (Rochester, NY) by B.C. Wood
General Electric Co. (Worthington, OH) by E.J. Connors
Pacific Scientific (Menlo Park, CA) by L.D. Carver

Table 2. Original Information Values for SRM 1690

Method	Laboratory	Average Diameter (µm)	Standard Deviation of Distribution (µm)
Transmission Electron Microscope	Kodak	0.875	0.018
Optical Microscope Array Sizing	Kodak	0.895	
Light Scattering			
Polarization Ratio	Kodak	0.900	0.067
Quasielastic	Kodak	0.930[a]	
Quasielastic	Coulter	0.896[a]	
Light Absorption	Pacific Scientific	0.870	0.030
Electrical Sensing Zone	Kodak	0.890[b]	0.023
Electrical Sensing Zone	Duke	0.900[b]	0.058
Electrical Sensing Zone	Coulter	0.870[b]	
Electrical Sensing Zone	G.E.	0.890[b]	0.017
Disc Centrifuge	Kodak	0.910	0.046
Disc Centrifuge	Air Products	0.880	0.260
Hydrodynamic Chromatography	Dow	0.880[c]	

[a] Type of average not specified.
[b] Number median diameter.
[c] Volume median diameter.

REFERENCES

[1] JCGM 100:2008; *Evaluation of Measurement Data — Guide to the Expression of Uncertainty in Measurement*; (GUM 1995 with Minor Corrections), Joint Committee for Guides in Metrology (JCGM) (2008); available at http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed Aug 2016); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297; U.S. Government Printing Office: Washington, DC (1994); available at http://www.nist.gov/pml/pubs/index.cfm (accessed Aug 2016).

[2] Marx, E.; Mulholland, G.W.; *Size and Refractive Index Determination of Single Polystyrene Spheres*, J. Res. Natl. Bur. Stand. Vol. 88, pp. 321–338 (1983).

[3] Mulholland, G.W.; Hartman, A.W.; Hembree, G.G.; Marx, E.; Lettieri, T.R.; *Development of a One-Micrometer-Diameter Particle Size Standard Reference Material*; J. Res. Natl. Bur. Stand. Vol. 90, pp. 3–26 (1984).

[4] Mulholland, G. W.; *Re-Analysis of the Uncertainty of the 0.895 µm Diameter (NIST SRM 1690) and the 0.269 µm Diameter (NIST SRM 1691) Sphere Standards*; J. Res. Natl. Inst. Stand. Technol., Vol. 110, pp. 27–30 (2005).

[5] Barnett, V; Lewis, T.; *Outliers in Statistical Data*, Third Edition; Wiley: New York, (1994).

Certificate Revision History: 09 August 2016 (Update of certified value and instructions for use; change of expiration date; editorial changes); **13 May 1996** (Editorial Changes); **22 December 1982** (Original certificate date).

Users of this SRM should ensure that the Certificate in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 948-3730; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.