# *Certification of 10 μm Diameter Polystryrene Spheres ("Space Beads")*

There are numerous examples in trade and commerce in which small particles play an important role, either as the commodity of trade itself, as unwanted contaminants in a product or an environment, or as a basis for comparison between a "normal" particle and an "abnormal" one. Many of the products we buy come in the form of small particles, powders, or particle suspensions, including medicines, cosmetics, food products, paints, talcum powder, cements, photocopier toners, and milk (which is essentially a suspension of microdroplets of fat in water). In other cases, small particles are unwanted, for example in cleanrooms for microelectronics or pharmaceutical manufacturing, in lubricating oils in motor vehicles, and in the air we breathe and the water we drink. There are also situations where one would like to compare a known, standard particle to an unknown, test particle as in the case of blood-cell testing. In all of these instances, particle standards play a key role, enabling quality control, product uniformity, conformance to standards, traceability to NIST, interchangeability of instrumentation, uniformity of measurement, or some combination of these goals.

With these benefits in mind, the National Bureau of Standards set out, in the early 1980's, to develop a range of particle-sizing Standard Reference Materials (SRMs) for use in calibrating and certifying instruments that measure particle size, whether as products, by-products, or contaminants. In cooperation with ASTM Committee E-29 on Particle Size Measurement, researchers in the Precision Engineering Division (PED) at NBS developed a series of five SRM's consisting of monosized polystyrene microspheres with diameters of 0.3, 1, 3, 10, and 30 μm [1-4]. The three smallest particles, donated by commercial vendors, were certified first, since such small microspheres were comparatively easy to grow using conventional polymer emulsion techniques. However, for the two larger diameters, 10 μm and 30 μm, the techniques that existed at the time did not yield rigid particles of the required sphericity because of the detrimental effects of gravity on the microsphere growth process. (At the time, there were techniques to make large microspheres, but these were relatively soft and unsuitable for use as SRMs, which must be rigid and stable.)

At about the same time that NBS was certifying its series of particle-sizing SRMs, a group of researchers led by John Vanderhoff of Lehigh University and Dale Kornfeld of NASA Marshall Space Flight Center was conducting experiments aboard the space shuttle to determine the effect of microgravity on chemical reaction rates of emulsion polymerization, as well as on the morphology (shape) of polymer microspheres grown in microgravity [5]. The first experiments of the Monodisperse Latex Reactor (MLR) were conducted in 1982 aboard space shuttle flight STS-3 and resulted in microspheres as large as 5 μm in mean diameter. A subsequent experiment on a later shuttle flight, STS-6, produced particles of 10 μm mean diameter. In 1984, the NBS group obtained samples of the 5 μm and the 10 μm materials and did a detailed intercomparison between the space-made particles and earth-made particles of similar composition [1,2]. In both cases, the space-made materials were found to be superior in terms of individual particle sphericity, narrowness of size distribution, and, importantly, in particle rigidity. An agreement was then made between NASA and NBS for NASA to provide a sufficient quantity of the 10 μm material to make up 600 5 mL vials containing liquid suspensions of the polystyrene microspheres for use as an SRM. The agreement also called for NBS to receive the 30 μm polystyrene spheres to be grown on a subsequent shuttle flight.

To certify SRM 1960, the so-called "space beads" (Figs. 1 and 2), researchers at NBS, led by Tom Lettieri of the PED, developed three new particle-sizing techniques, which are described in the publication *Certification of SRM 1960: Nominal 10 μm Diameter Polystyrene Spheres ("Space Beads")* [1]. These techniques were center distance finding (CDF), resonance light scattering (RLS) from a liquid suspension of microspheres, and metrology electron microscopy (MEM). The primary certification technique for SRM 1960, center distance finding, was developed by Ike Hartman of the PED. CDF uses a conventional optical microscope and relies on the fact that the microspheres act like tiny lenses when placed on a glass slide in the microscope. The microspheres were spread onto a slide such that they formed long chains of contacting spheres, rather than the regular hexagonal arrays formed in conventional array sizing. This ensured that the particles were in close contact, compared to conventional array sizing where the non-zero diameter distribution of the microspheres leads to voids, cracks, gaps, and other flaws in the arrays. These flaws lead to uncertainties in

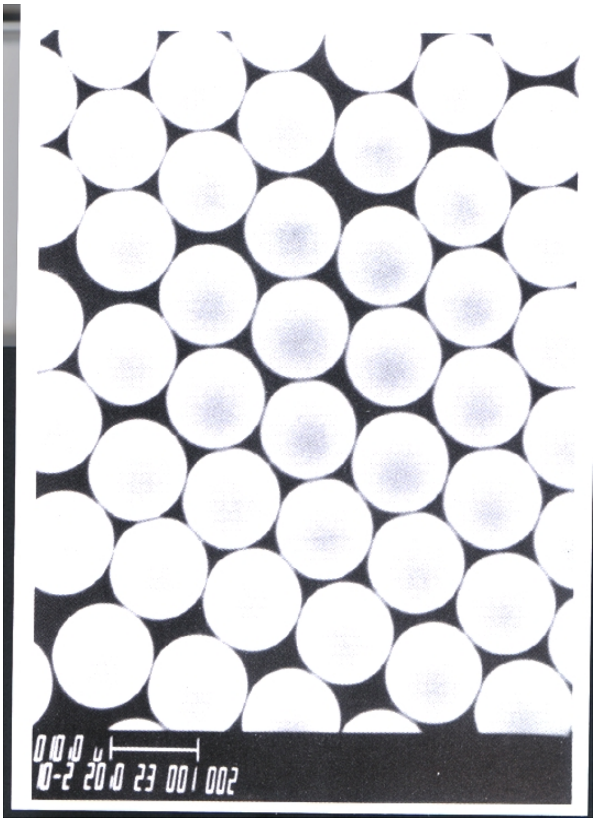

**Fig. 1.** Scanning electron photomicrograph of Standard Reference Material 1960 microspheres.

the mean sphere diameter measured with conventional array sizing, uncertainties that are avoided when particle chains are used. If the microspheres are illuminated from below and the microscope is focused just above them, then the tiny focal spots can be photographed and the distance between the spots determined very accurately. Using CDF, the mean sphere diameter for SRM 1960 was determined to be $9.89 \pm 0.04$ mm: this was the certified mean diameter for the SRM.

Supporting measurements were made using RLS and MEM. In the RLS technique, developed by Tom Lettieri, a tunable dye laser was used to generate resonance light-scattering intensity patterns from the microspheres as they were suspended in water. As the laser was tuned through its wavelength range, relatively sharp peaks in the light-scattering intensity appeared at certain wavelengths. Although this technique had been used before by others to investigate sharp resonances from single microspheres, this was the first time that such resonances were detected in a suspension of many microspheres: this could be done because the spheres had a very narrow size distribution (<1 % standard deviation). By comparing the experimental resonance wavelengths with those calculated by Egon Marx of the PED using Mie scattering theory, the NBS researchers were able to use RLS to arrive at a mean diameter of $9.90 \pm 0.03$ μm for the SRM 1960 microspheres. This result was in excellent agreement with those from both CDF and MEM.

The other supporting metrology technique was MEM. Gary Hembree of the PED used MEM to measure the microspheres in a scanning electron microscope (SEM). With MEM, the spheres are mounted onto the microscope stage as in a conventional SEM. However, in a conventional SEM the electron beam is raster-scanned past the stationary spheres, whereas in the MEM technique developed at NBS, the electron beam is held stationary while an individual particle is moved through the beam via a piezoelectric scanning stage. The scattered electron intensity is measured versus stage position and, from this, a particle profile is generated. These profiles could then be used to determine the diameter of the individual particles. Using MEM, a mean diameter of $9.89 \pm 0.06$ μm was obtained for the SRM 1960 spheres, in excellent agreement with the other two metrology techniques. Indeed, the remarkable agreement among the three metrology techniques, and the relatively small uncertainty in the diameter, likely made SRM 1960 the best characterized particle-size standard in the world at the time. An important point in these measurements was that the three metrology techniques were independent of each other, in that none of the measurements relied in any way on measurements from the other techniques. This is always good practice when certifying an SRM.

In 1985, SRM 1960 was first offered for sale to the public through the NBS Office of Standard Reference Materials (OSRM), making the SRM the first commercial product to be manufactured in space (SRM-1961, the nominal 30 μm spheres, was the second space-made product). The sale of the space beads was reported in hundreds of newspapers, magazines, and television/radio news stories around the world, from the *New York Times* to the CBS *Nightly News* to ABC's *Good Morning America.* The work was also featured on a National Public Radio program and on an Australian science show, *Beyond 2000.* Later on, SRM 1960 won an IR-100 award from *Research & Development* magazine for being among the top 100 products of 1985.

Over the years, SRM 1960 has proven to be a valuable tool for the calibration of particle-sizing instruments in the United States and around the world. Samples have been purchased by dozens of U.S. and foreign companies for use as primary particle-sizing standards. These companies include not only the makers of particle-sizing standards and instrumentation, but also "every day" users who need to maintain accuracy and traceability of their measurements. Among the primary users are

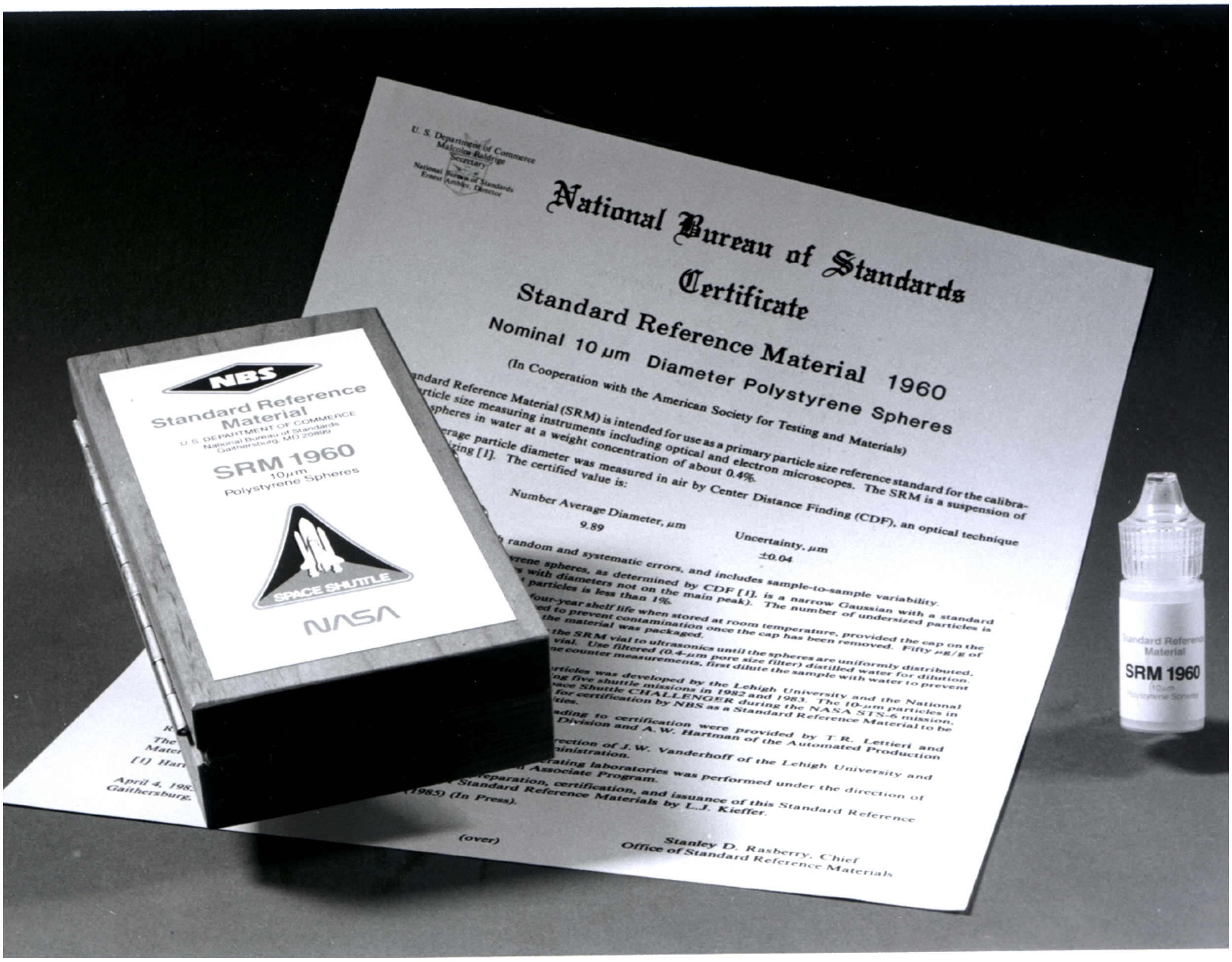


**Fig. 2.** Photograph of SRM 1960 showing a vial of the SRM, the certificate, and the package.

major pharmaceutical companies, Fortune 500 petrochemical and chemical companies, small-to-mid-sized biomedical instrumentation companies, particle standard supply houses, and numerous firms, of all sizes, involved in the measurement of particle size. Several U.S. Government and non-profit labs, including NASA Ames, Battelle Northwest, EPA, FDA, Los Alamos, Sandia, and the USGS have also purchased SRM 1960. In the international arena, the material has been used by research laboratories in Australia, Austria, Brazil, Canada, England, France, Germany, India, Italy, Japan, Korea, Mexico, Norway, Spain, Switzerland, and Thailand. Sales of SRM 1960 average about 25 vials per year through the NIST OSRM. The OSRM also offers for sale another version of the space beads, SRM 1965, which are standard microscope slides with small patches of particles in both regular arrays and microsphere chains. These have been used throughout the world for educational and training purposes, as well as to satisfy the needs of those who wish to own something "made in space." In addition to OSRM, the microspheres are also sold through the European Community's Bureau Communautaire de Reference (BCR).

The demand for SRM 1960 is spurred, in part, by its incorporation into several document standards in the United States. For example, the U.S. Pharmacopeia, in its test entitled "Particulate Matter in Injections," specifies the use of SRM 1960 for calibrating the liquid-borne particle counters used in the test. As a water-quality standard, SRM 1960 is listed by the National Oceanic and Atmospheric Administration (NOAA) in its compilation of *Standard and Reference Materials for Marine Science* as a physical standard for the assessment of water and sediment quality. The particles have also found application in the monitoring and assessment of air quality, especially with regard to the Environmental Protection Agency (EPA) $PM_{10}$ standard that specifies a cutoff of 10 $\mu$m for the aerodynamic diameter of particulate emissions from motor vehicles, smokestacks, and other industrial emission sources. In the medical field, SRM 1960 has been valuable as a calibration standard for blood-cell counting and sorting, as the mean diameter of the SRM is very near that of human red blood cells. Thousands of hospitals and medical testing laboratories throughout the U.S. use blood-cell counters to check for sickle cell anemia, Tay-Sachs disease, and other blood abnormalities, and SRM 1960 helps to ensure the quality and accuracy of such tests. SRM 1960 will, undoubtedly, find more applications in the medical field as biotechnology and medical diagnostics become more pervasive in our daily lives.

In addition to the above applications of SRM 1960, other areas of scientific research where the material has found use include: electron microscopy; chemical chromatography; powder metallurgy; ceramics; food processing; photographic films; and basic particle research, among many others. The rigid demands of ISO9000 will likely increase the importance of particle-sizing standards such as SRM 1960, as companies become more concerned with quality control, conformance assessment, and reliability issues.

Of the four authors of the space beads paper, two, Tom Lettieri and Egon Marx, are still at NIST. Tom started at NBS in 1978 after graduate school at the University of Rochester, joining the Pressure Group to do high-pressure optical studies of liquids. Less than two years later, he joined the PED to conduct optical metrology studies of small particles, rough surfaces, and noncontact methods for dimensional measurement. Tom is now a Program Manager with the NIST Advanced Technology Program, where he helps select and manage industrial technology projects in the area of optics/photonics. Egon Marx did his graduate studies in nuclear physics under the direction of Murray Gell-Mann at the California Institute of Technology. After a few years of teaching at Drexel University, Egon went to work at Harry Diamond Laboratories, conducting theoretical investigations in electromagnetic (EM) interference. His interests at NIST have included EM scattering, surface roughness, linewidth metrology, and quantum electrodynamics. Two authors, Gary Hembree and Ike Hartman, left NIST not long after the space beads project was finished. Gary came to NBS after completing graduate studies in electron microscopy at Arizona State University (ASU). After several years at NBS, he returned to ASU to work with the world-renowned electron microscopy group there. Ike Hartman came to NBS after spending a number of years at General Electric doing optics and imaging research. At NBS, he worked in various areas of optical metrology, including microscopy, particle sizing, electro-zone particle counting, and linewidth metrology. He retired from NIST after a long and satisfying career in optics, both in his native Netherlands and in the United States.

*Prepared by Tom Lettieri.*

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