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U.S. DEPARTMENT OF COMMERCE/National Bureau of Standards

Standard Reference Materials:

A Look at Techniques for the Dimensional Calibration of Standard Microscopic Particles

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Standard Reference Materials:



A Look at Techniques for the Dimensional # 2 Calibration of Standard Microscopic Particles

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PREFACE

Standard Reference Materials (SRM's) as defined by the National Bureau of Standards are well-characterized materials produced in quantity and certified for one or more physical or chemical properties. They are used to assure the accuracy and compatibility of measurements throughout the Nation. SRM's are widely used as primary standards in many diverse fields in science, industry, and technology, both within the United States and throughout the world. They are also used extensively in the fields of environmental and clinical analysis. In many applications, traceability of quality control and measurement processes to the national measurement system are carried out through the mechanism and use of SRM's. For many of the Nation's scientists and technologists it is therefore of more than passing interest to know the details of the measurements made at NBS in arriving at the certified values of the SRM's produced. An NBS series of papers, of which this publication is a member, called the NBS Special Publication - 260 Series, is reserved for this purpose.

This 260 Series is dedicated to the dissemination of information on different phases of the preparation, measurement, certification and use of NBS-SRM's. In general, much more detail will be found in these papers than is generally allowed, or desirable, in scientific journal articles. This enables the user to assess the validity and accuracy of the measurement processes employed, to judge the statistical analysis, and to learn details of techniques and methods utilized for work entailing the greatest care and accuracy. These papers also should provide sufficient additional information not found on the certificate so that new applications in diverse fields not foreseen at the time the SRM was originally issued will be sought and found.

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Executive Summary

The purpose of this report is to examine the metrological capabilities of various generic techniques suitable for use at NBS for the dimensional calibration of future NBS particle size Standard Reference Materials (SRMs). At present, within the overall range of sizes from 100 μ m to 0.1 μ m, some sized glass beads, spherical polymers, pollens, and test dusts are commercially available as reference materials. Currently, NBS provides as SRMs only some wide-size-distribution glass beads. The intent is to develop other particle-size SRMs: initially, narrow-distribution spherical polymers and, finally, stable particulate matter of arbitrary shape and size distributions.

At the present level of development of calibration technology, the spherical polymers are most suitable for an initial SRM. They are highly spherical, and have narrow size distributions, thus providing for minimal ambiguity in measurements and maximal separation of object and instrument variables. Batch-manufactured spherical polymers range in size from less than 80 nm to over 100 μ m with size distributions characterized by standard deviations which range in a complex manner from about 5 nm for the smallest particles to 1-10 μ m for the largest.

The report explicitly looks at various size-dependent phenomena which are the basis for measurement techniques. It examines the way an individual particle is given one characteristic dimension, and how a collection of particles is given an average dimension. Of the variety of techniques examined, three generic ones have been singled out from those with individual characteristics which contribute to a comprehensive calibration approach.

<u>Microscopy</u> which gives direct-imaging includes both optical which is limited by depth of focus and electron which has high resolution and great depth of focus. Electron microscopy can provide direct-imaging, shape-verifying definitive measurements of limited numbers of particles <u>in vacuo</u>. For polystyrene, a glassy polymer, there is evidence that the required evacuation and electron-irradiation can be used without producing significant dimensional changes. Transmission electron microscope measurements on polymer spheres by the manufacturer over nearly three decades show consistency at 5 to 10 nm level with some indication of a systematic difference of 15 nm from an average of light-scatter and other electron microscopy values.

Light-scattering techniques vary considerably in detail but generally are one of two fundamentally different types: the first determines size from the intensity characteristics of scattered light with analysis based on Mie calculations for scattering of a plane wave from a uniform dielectric sphere; the second determines size from the frequency characteristics of scattered light with analysis based on hydrodynamic calculations for objects moving in fluids. The former, angular-intensity type, is of specific interest as a means to obtain first-principle measurements potentially accurate at the 1% level on highlyspherical, narrow-distribution particles. The calculations assume particles are spheres with a known index of refraction. Briefly noted in the report are other light-scattering techniques with demonstrated capability for calibration quality particle size measurements such as Rayleigh spectrometry, laser Doppler, and single-particle levitation; from among the suitable techniques, the angular-intensity one has been chosed for initial calibrations and for description here for reasons of directness in implementation, use, and interpretation.

Automatic liquid-borne particle counters measure some characteristic dimension of individual particles passing sequentially past a detector. There are two fundamentally different types: (1) the electrical-resistivity type measures the volume of electrolyte displaced by a particle; and (2) the optical type which can be of two kinds: (a) one measures a projected shadow area; and (b) the other measures a Fraunhofer-diffraction pattern dimension. The optical types measure dimensions down to about 2 μ m while the electrical-resistivity types measure down to about 0.5 μ m. All three devices can give explicit histograms of size distributions but are comparators which require particles of known size for calibration. Reproducibility of comparisons of mean diameters are of the order of 1% to 3%.

Within the body and seven appendices, this report contains 50 tables of data, 250

literature references, and lists of 10 domestic commercial suppliers of sized particles, 30 principal and 40 secondary documentary standards on particles, 22 industry and university contacts, and 125 domestic and foreign suppliers of particle-sizing equipment.

The report concludes that the definitive calibration of narrow-distribution polymer spheres, a prerequisite first step toward size-calibration of irregularly-shaped matter, can be obtained by a three-element, self-consistent approach involving the three techniques named: electron microscopy to provide direct-view shape-verification and direct measurement of a limited sample of particles <u>in vacuo</u>; liquid-borne counting to provide an explicit histogram verification of the broad size distribution in a sample liquid; and angularintensity light scattering to provide a nondestructive mean-size measurement of the original population in the delivery vial. Under these conditions, an overall uncertainty in calibration of 0.005 µm or 1%, whichever is greater, is anticipated as achievable.

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A LOOK AT TECHNIQUES FOR THE DIMENSIONAL CALIBRATION OF STANDARD MICROSCOPIC PARTICLES

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This report surveys generic techniques for the dimensional calibration of microscopic particle size standards. It notes some user needs and available instrumentation, documentary standards, and commercial, sized particles. It discusses the elements of the measurement process, including the particle and medium, size-dependent phenomena, shape factors, singlenumber indices of average size, and means of length calibration. The report examines systematic differences among published results of electron microscopy, light scattering, particle counter, and other measurements on widely-used commercial polymer spheres. It concludes that the definitive calibration of narrow-distribution polymer spheres, a prerequisite first step toward calibration of irregularly-shaped matter, would best involve a three-element approach involving the techniques named.

Key Words: Dimensional measurement; electron microscopy, flow-through particle counters; latex spheres; light scatter; micrometrology; microscopic spheres; Mie scattering; particle standards; optical microscopy; particle size calibration; polymer spheres; scanning electron microscope; transmission electron microscope.

1. INTRODUCTION

Particle-size measurement is an inclusive term that encompasses a diversity of measurements by a spectrum of techniques on a host of different particulate substances. To calibrate particle-size measuring devices, particles of "certified size" are available from commercial sources. At the same time, requests for NBS-certified, particle-size Standard Reference Materials (SRM's) have been insistent and recurrent (for example, Refs. Cl, K5, W10).

As part of an investigative-developmental project at NBS on such SRMs, this report has been prepared. Its purpose is to look at those techniques which can potentially be used as (1) reference methods for the definitive, primary dimensional-calibration of particle standards and (2) comparison methods for convenient transfer calibration from the reference method to bulk calibration method.

Guided by experience at NBS and the preponderance of work of a more fundamental nature reported in the scientific literature, this report has of necessity focussed on the basic techniques of electron microscopy and light scattering and the comparison techniques of automatic particle counting. An underlying premise of the report is that in order to understand and manage the basic measurement techniques, the object-to-be-measured should be as simple and lacking ambiguity as possible. Hence, because of their unique metrological properties, latex spheres play a central role in the examination of individual techniques and their intercomparisons.

In its structure, this report follows the topical outline given in the Table of Contents. Part I is introductory background on particles and their size-measurement as generally practiced. Part II outlines some of the basic metrological factors of measurement systems to be taken into explicit account. In Part III, candidate instruments are looked at individually, and in Part IV their measurement results are intercompared. Part V summarizes the general conclusions of the report, and Part VI lists references. Part VII includes appendices on domestic suppliers of particle reference materials, equipment suppliers, documentary standards, bibliographic sources used, and contacts at universities and in industry. Also included is a note on how some quoted statistical uncertainties are computed.

A. Sample of Users' Needs

A vast spectrum of end-products, by-products, and waste-products or contaminants of modern industrial technology are microscopic particles which require dimensional measurement. As end-products, particles can be constituents of anything from plastics to cement to metal ores to photographic emulsions. As end products or by-products particles can be the result of manufacturing processes as varied as milling, mining, refining, grinding, spraying, or chemical precipitation. As contaminants, particles can occur in drugs and intravenous fluids for medical use, in lithographic chemicals for microelectronics manufacture, in hydraulic fluids for aerospace systems, and in the atmospheres industrial workers and the general population breathe.

Particles which require dimensional measurement vary greatly in range of size, chemical composition, and uniformity of size and shape. What various workers refer to as particles range in characteristic dimension over as many as six orders of magnitude: from 10,000 to 0.01 micrometers (μ m) [A14]. They vary in physical make-up from complex-but-stable, naturally-occurring minerals (asbestos) or biological material (cotton dust), to mixed and dynamically changing smoke and combustion products, to pure and stable synthesized materials such as polymers. Individual particles vary in shape from jagged irregular road dusts, to fibrous (actually rolled-plates) asbestos, to disc-like blood platelets, to spheroidal bacteria or pollens, to spherical polymer resins. Populations of particles range from

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.

heterogenous mixtures of irregularly shaped debris of widely different average size to collections of nearly perfect spheres of nearly identical sizes.

B. Current Techniques

1.B.1. Available Instrumentation: Reviews

The instrumentation developed to dimensionally measure these diverse particles apart from the equipment to collect and separate them - is as varied as the particles themselves. The instruments vary in fundamental principle of operation, the size-dependent attribute of the particle measured, range of sizes measurable, resolution, precision and accuracy. Physical phenomena used as bases for dimensional measurements include: direct imaging by light and electron optics; light scattering of a multitude of types; X ray, Y ray, ultrasonic and acoustic attenuation; pressure, flow, magnetic, electrostatic, or resistivity variations; and settling, sieving, separation, diffusion, and other properties.

Over the last few years, reviews of particle-size measurement instrumentation have been published in archival journals, trade magazines, monographs, and engineering text books. For example:

A comprehensive survey of instrumentation was reported by Davies in 1974-75 [D11, D12, D13]. It was further updated and revised in 1978 [D8]. A popularized view of some commercial instruments and related techniques was given by Austin [A14] and Carver [C1]. Stockham and Fochtman [S10] discussed, among other aspects of particle size analysis, a range of instruments and techniques [S10]. Collins, et al., [C21] reviewed the common methods of measurement while other reviewers such as Kratohvil [K13] considered a general technique, such as light scattering, as it applied to particle-size measurement. Others, who will be referenced later in this report, compared specific techniques with each other. Finally, Allen [A3], in his textbook on particle-size measurement, provided a detailed and referenced discussion of phenomena, instruments, and techniques. Taken with the articles of Davies, Allen's compilation of commercial suppliers of instruments [Appendix B] provides a comprehensive list of available equipment and their sources.

1.B.2. Documentary Standards

Faced with a broad array of instruments and techniques which (after measuring different dimensional attributes of collections of irregularly shaped and compositionally varied particles) yield numbers called "particle size", industry takes the normal recourse and seeks suitable documentary and physical standards. Documentary standards are written descriptions of methods, procedures or specifications, for example, how to specify or test the performance of an instrument. Physical standards are artifacts, e.g., a particle of known size, by which one calibrates or tests an instrument or process.

The American National Standards Institute (ANSI) and the American Society for Testing and Materials (ASTM) as well as the National Fluid Power Association (NFPA) and the Society of Automotive Engineers (SAE) have documentary standards relating to particle size measurement. Appendix C lists seventeen ANSI, thirteen ASTM (existing or in draft), and three NFPA standards, as well as an SAE and an ISO (International Organization for Standardization) standard. It also gives the identification numbers of thirty-seven other ASTM standards, twenty-two of which are on material characterization and fifteen on system characterization.

1.B.3. Standard Reference Particles

Some of the documentary standards refer to physical reference materials; that is, sized, standard, and uniform particles or test dusts. Ten organizations have been identified as commercial domestic sources of sized particles [Appendix A]. These include: particle supply firms who make and/or handle standard reference particles as their primary business; manufacturers of particle-measuring instruments who make and/or supply reference particles for instrument calibration; and manufacturers of other products who produce sized-standard reference particles or dusts as a sideline.

There are four major types of commercially available, sized-standard reference particles suitable for calibration of particle-size measuring instruments. These include: test dusts; naturally occurring, spherical pollens; uniform glass beads or microspheres; and various polymer "latex" spheres. Examples of the characteristic dimensions of these various types of reference materials are given in Table 1. Commercial test dust is a collection of coarse, irregularly shaped particles primarily used to simulate the matter removed by filtration from hydraulic systems. Pollen, glass, and latex-type polymer particles are used as spherical particles to calibrate, for example, various flow-through particle counters, light scattering, and other particle-sizing instruments. Latex-type polymer spheres of small diameters are used as electron-microscope calibration standards.

Latex-like polymers and glass beads are most widely used as sized, spherical calibration reference materials, and each has physical properties which are advantageous in some applications, and drawbacks in others. The following sketches of their properties are drawn from a technical article by NBS workers on glass beads for calibrations [H18], glass bead and latex supplier's literature [Appendix C], and undocumented accounts by NBS workers and particle manufacturers.

Glass beads have the following properties: appear fairly spherical in direct observation; are transparent with a high index of refraction; are rigid solids without cleavage planes; are somewhat surface-tempered; and have impact strength. In addition, the glass beads can have voids and/or an onion-like layer structure, can shatter or fragment, can agglomerate in the presence of atmospheric moisture, have a broad distribution of sizes within a sample and mean sizes for the population typically which range from about $5\,\mu$ m (or as low as l μ m) to 100 μ m.

Latex-like spheres (polystyrene, polyvinyl toluene, etc.) appear highly spherical, have low-or-moderate specific gravity, are translucent-to-opaque, are glassy-to plastic solids, and can distort in shape when dried or irradiated. Further, the latex-like spheres can have dimensions and properties dependent on surface-active and dispersal agents, cannot be airborne above about 3 µm in size, and can agglomerate in pairs, triads, or clumps. Mass-produced, batch-grown spheres can have a single, relatively narrow distribution of sizes while limited-production, droplet-grown spheres can have a very narrow "main-mode" size with "satellite modes," one below and one above the main-mode. Latexes cover the range 0.01 to 100 µm with distribution of size within populations strongly dependent on mean size. Batch-produced latex spheres have population standard deviations (σ) characterized as in Fig. 1 (drawn from a manufacturer's technical data sheets): below 1 µm mean size, is of the order of 0.005 $\mu\text{m};$ it rises at 1 μm to about 0.01 μm and remains at 1% or so up to 2 μ m, rising to 5% or 0.15 μ m at 3 μ m, 10% at 5 μ m, and 20% at 10-20 μ m. Dropletproduced latex spheres are reported by another manufacturer to have a "main-mode" distribution of less than 1.5% over the range of 5 to 100 μ m. ("Satellite-modes" are not counted in the computation of this narrow width.)

At present, NBS provides, as standard reference materials, the sized glass beads and spheres described in Table 2, as well as a stage-micrometer also described. The basic method of calibration of the glass spheres and beads is described in Ref. H18 and in the certificates of calibration (example in Appendix G) which accompany the materials.

Also reported to be available from other sources are: encapsulated, graduated rows of individually selected particles [T4]; dyed latexes and ones to whose surface chemicals can be atomically bonded [B2, B3]; and specially sieved, narrow-distribution glass beads [C22]. Potentially available sometime after 1982 [E2] are narrow-distribution, large-diameter latex spheres batch grown in the gravity-free environment of the space shuttle [K8].

Among particle reference materials, latex-like polymer spheres play a central metrological role; and among the suppliers of latex-like spheres, the metrological role of the Dow-Diagnostic Division of Dow-Chemical Company* is unique. For over 25 years, latex spheres with individual particle diameters measured by electron microscopy and with mean diameters covering at close intervals the range from sub-0.1 μ m to over 1 μ m, have been distributed by Dow [B2, B3]. From 1954 until 1979, published values of latex diameters

*Please note disclaimer at beginning of Introduction.

have been measured at Dow by the same basic technique and often by the same individual [B16, R10]. Within the industrial and scientific communities, these latex particles have been measured by numerous other workers and techniques, and published accounts and results of these measurements provide a systematic and comprehensive body of metrological data and form a major portion of this report. Various aspects of the measurement techniques and instruments will be discussed in Parts II and III of the report while Part IV will present an examination of some of that data.



Figure 1. The width of the particle size distribution (σ) as a function of mean particle diameter of the distribution for batch grown polymer spheres produced by one manufacturer [Ref. B3].

Table l

Examples of Commercially Available Sized Standard Particles

Material	Mean Size (µm)	Range About Mean (µm)
Polymer Spheres		
Polystyrene (PS) Polyvinyl-Toluene (PVT) Polystyrene-Divinyl Benzene (DVB) Polystyrene-Butadiene (PSB)	(Great variety with see figure l	n size-dependent range; for typical values)*
Uniform Glass Microspheres**		
	- 7 1.8 8.0 10 100	1-3 1-5 1-30 0.5-6 4-14 5-15 90-115
Spherical Pollens**		
Paper Mulberry Ragweed Bermuda Grass Walnut Corn		13-14 19-21 22-30 40-50 65-75
Test Dust**		
AC Fine AC Fine		1-45 45-80

*Suppliers Bulletin (Dow Diagnostics; see note below).
**Suppliers Bulletin (Duke Standards Inc.; for identified suppliers of
standard particles see Appendix A.)

Ta	Ьl	е	2

NBS Standard Reference Materials Used in Particle Size Measurement			
Standard Reference Material Number	Туре	Dimensions (µm)	
SRM 1003	glass spheres	5-30	
SRM 1004	glass beads	34-120	
SRM 1017a	glass beads	100-310	
SRM 1018a	glass beads	225-780	
SRM 484a	SEM stage micrometer	1,2,3,5,50*	

*Spacings calibrated to \pm 0.04 μ m in 1-5 μ m range and 0.48 for 50 μ m.

2. SUMMARY OVERVIEW OF ELEMENTS OF PARTICLE SIZE MEASUREMENT SYSTEMS

The purpose of particle-size measurement is to associate with the particles a number, that is, a "size," which characterizes some important dimensional property of the particles. The measurement process involves the particles as an object, the measuring instrument and a conceptual model of how it interacts with the object, and the mathematical manipulations done with the data collected on the particles.

This section will look at some of the combinations of object-instrument-mathematical models which give rise to different operational definitions of particle size. Specifically, the section briefly examines various kinds of particles and their environments, some measuring instruments and the size-dependent phenomena they exploit, conceptual definitions of particle size.

A. The Object: State of Matter

Particles to be sized can be any one of the three states of matter as can the medium in which the particles exist. In aerosols, the medium is gaseous and the particles can be liquid drops or solids. In hydrosols, the medium is liquid and the particles are most often solids, although they may be drops of other liquids or air bubbles. When not suspended in a gaseous or liquid medium, solid particles can be in the form of a dry powder or dry individual particles. And finally, both liquid drops and solid particles can exist in an extremely low-pressure gaseous or vacuum medium.

As candidates for sized particle reference materials, solids have the attribute that they may be used in liquid, gaseous, or vacuum media with some degree of mechanical size and shape stability. For example, polymer spheres in water solution may be measured in that solution by (1) laser-light scattering, (2) in an electrolyte solution by a resistivetype, flow-through counter, (3) air-dried and on a substrate by an optical microscope, and (4) evacuated and irradiated in an electron microscope. By comparing sizes measured by different techniques, the effect on the size and shape of the particle by the change of medium can and should be considered explicitly.

B. The Measuring Instruments

At the heart of each operational definition of a particle size is a device which responds to some size-dependent property of the particles. The size-dependent phenomena may involve one or more particles at a time or may involve a physical separation of particles by size. Thus, some calibration by which the basic unit of length is associated with that phenomena is required. This section examines some of these phenomena, the number of particles involved, any separation process used, and the types of calibrations possible and useful.

2.B.1. Size-Dependent Phenomena

Initially, particle-size measuring instruments detect some signal which is assumed to be related to the size-property of the particle. For imaging-instruments, the intensity distribution in the directly viewable, magnified image of the microscopic particle is the signal. For non-imaging instruments, the nature of the signal depends on the phenomena exploited.

a. Imaging: Optical and Electron

Microscopes, both light-optical or electron-optical, are valuable for particle-size analysis because they present a direct-image of the particles to the investigator for visual examination. The visual image can contain information on shape, surface features, and debris present, as well as dimensional information. The reliability of the dimensional information obtained from microscopy depends, among other things, upon specifics of the instrument and technique. These specifics include the familiar matters of magnification, resolution limit, and depth of focus, and the less familiar matter of edge-location, with its dependence on a selection criterion and its variation with focus and other system variables. In optical microscopy, the magnification in the image plane can be up to 1000 or 1500 X so that particles as small as 0.5 μ m or so can be imaged. In reflected light, the surface features of the object and the shape of the plane section of the object perpendicular to the optical axis of the microscope are viewed, while in transmitted light, only the plane section can be seen.

In electron microscopy, the maximum magnification in the image plane depends on the type of microscope: for the scanning electron microscope (SEM), which forms images of the surface of solid objects, the magnification can be up to about 100,000 X while for the transmission electron microscope (TEM), which forms images from electrons which pass through thin specimens, the maximum magnification is typically 300,000 X but can reach 800,000 X. SEM's can image particles as small as 0.015 μ m, while the TEM's can image those as small as 0.001 μ m. As with the optical microscope with reflected light, the SEM images the surface and the plane section, while like the optical microscope with transmitted light, the TEM images the plane section only.

In addition to surpassing the optical microscope in maximum magnification by orders of magnitude, electron microscopes have the major advantage of sharper focus and greater depth of focus. Microscope images, whether optical or electron, do not have sharp, discontinuous edges, but are bounded by blurred transition regions. The width of the blur-region is a variable which depends on the instrument resolution and depth of focus capabilities as well as a subjective judgment of best focus.

In a dimensional measurement of an extended object, such as a particle or a planar feature, the apparent width depends on where in the blur region one decides the edge lies. The location of the edge therefore changes with the subjective criterion of edge location within the blur region and the location of the blur region varies with focus settings. There is clear evidence that filar-eyepieces, image-shearing (i.e. split image) eyepieces, and automatic-image analyzers, such as TV-microscope systems, locate the edges of optical images on different levels within the blur region [S11,12].

For an ideal object with square edges, the width of the blur region for an optical microscope is determined by the object and by diffraction phenomena modulated by the performance characteristics and focus setting of the microscope; for a real optical microscope and real object, the blur region will be greater than that for an ideal laminar object imaged by a diffraction-limited lens system. As a rule of thumb, the smallest blur attainable will be wider than about 0.25 μ m [N5]. The location of each of two edges which define the width of an object's image (e.g., the diameter of a particle) is ambiguous by an amount twice as great or up to the full-diffraction spot, i.e., 0.5 μ m or more, depending on edge-location criteria, focus choice, and instrument operating conditions.

It has been demonstrated that the apparent size of microscopic objects as measured by optical microscopy depends systematically on lens and diaphragm apertures [C8, N5, S3], illumination levels [C9], focus conditions [N5, S3] and image-measurement device type [S12]. It has been demonstrated experimentally that automatic-TV-microscope systems, filar-eyepiece visual microscopes, and image-shearing visual microscopes can yield size-measurements on identical 1 to 10 μ m planar objects that differ systematically from -0.25 to +0.25 μ m, depending on image polarity [S12]. Further, a related study [S11] showed systematic differences among measurement results from several industrial laboratories on a 3 μ m planar object of up to 0.6 μ m. In these cases, the thickness of the object (0.1 μ m) was advantageously small compared to the depth of focus of the optical microscope. In particle size measurement, this is not the case.

Classically, the depth of focus of an optical microscope is on the order of $0.5 \ \mu$ m at 1000 X (and, for example, 10 μ m at 100 X). In such a situation, the depth of focus is a significant fraction of the large particles in a field of view (and can exceed the size of small ones in the same field). Attainment of an acceptable, albeit arbitrary, "best focus" is a major limitation on particle size measurement by optical microscopy, although it is not the only limitation on dimensional accuracy.

Electron microscopes surpass optical microscopes not only in overall magnification but also in greater depth of focus, while at the same time, on a different scale of dimensions, are more susceptible to edge-location difficulties. As a rule of thumb, the depth of focus of an electron microscope is equal to the width of the field of view. At 1000 X, this corresponds to about 100 μ m (compared to 0.5 μ m for the optical microscope). At a typical magnification for particle size, e.g., 20,000 X, the depth of focus is on the order of 5 μ m. The width of the blur-region in electron microscope imaging is correspondingly smaller but still significant in proportion to the size of the objects measured. For an SEM, the blur-region width is of the order of the electron-beam spot size, and can be as small as 5 nm in high-resolution systems or as large as 50 nm. The lower limit applies only in the case of transmission electron detectors. Edge location uncertainties of 10 nm and larger can be anticipated for secondary and backscattered electron detection. For a TEM, the blur-region width is on the order of 1-2 nm for ordinary instruments. Thus, while the optical microscope as described above has an edge-location ambiguity in width measurements of up to 0.5 μ m for an ordinary SEM and about 2 nm for a not-unusual TEM.

The significance of edge-location ambiguity is this: similar objects measured with similar microscopes can have apparent sizes which differ systematically by as much as double the width of the blur region depending on the arbitrary choice of edge-location and focus setting alone. In an optical microscope, systematic differences of the order of 0.5 μ m in size measurements could be attributed to just these effects. These are not errors inherent to the instrument but rather are systematic errors which are not removed by line-scale calibration. Other calibration techniques, involving either comparison to extended objects of known size or theoretical modeling of the image process, can reduce or eliminate these effects. This topic will be discussed more thoroughly in another section of the report.

As a note, for a number of reasons, including attempts to eliminate changes in polymer particle dimensions for certain PVC latexes due to evacuation and irradiation in electron microscopy [C20, D5] and also to reduce depth of focus problems in optical microscopy [C9], metal vapor deposition has been used to produce shadows of polymer spheres, where measurements are subsequently made on the circular openings in the deposited film rather than on the original polymer sphere [C9, C20, D5].

b. Non-imaging size phenomena

Apart from instruments which produce direct images, there are instruments which exploit other size-dependent phenomena for particle measurements. Most of these other phenomena involve the particles' radiation scattering properties, velocity, or volume displacement.

The volume-displacement type of particle-size instrument is the one which has been variously described as an electrical-sensing-zone [A3] or electrical-resistance [D11] particle counter. Such an instrument scales and counts the current pulses produced as individual particles pass sequentially through an aperture, on either side of which is an electrode, and thereby displace a volume of electrolyte through which current flows. Versions of the basic device were patented and first marketed by Coulter Electronics Inc. over two decades ago and have been available from at least six manufacturers in the U.S., West Germany, Japan, and Eastern Europe [A3, Appendix B].

In principle, the measured change in current due to the particles' presence between the electrodes is directly proportional to the volume of the fluid displaced which is identical to the volume which the material of the particle occupies. Allen devotes a textbook chapter to the instrument, reviewing the equation form $\Delta i \sim v(1 - a/A)^{-1}$, where v is the volume of of fluid displaced, Δi is a change in current, and a and A are crosssectional areas of the particle and aperture, respectively.

Allen reports that for spherical particles which are large compared to the aperture (particle diameter about 0.4 times aperture diameter), "the error involved in assuming a linear relationship is about 5.5%." He also reports "discrepancies of unspecified degrees between computed weight of particles counted and weight in suspension as being usually explained by differences between the envelope of the particle being measured, as opposed to the true volume."

Coincidence effects, which affect flow-through counters of both the light-blockage [W10] as well as the electrical-sensing-zone types, have been studied extensively as

indicated by the citations in, for example, Coulter's Industrial Bibliography* and Allen's text [A3]. Two types of coincidence errors are postulated: primary or horizontal coincidence due to two particles which give rise to two overlapping pulses; and secondary or vertical coincidence due to two particles below threshold which give rise to one pulse of a single large particle. Besides these error sources in counting, Allen (A3) covers the work of others and his own work on factors which distort the basic volume displacement proportionality [A3]. These factors include: the conductivities of the particle and electrolyte; the effective volumes of the aperture and the particle; the particle shape and its orientation during passage through the aperture; the presence of more than one particle in the sensing zone (coincidence); pulse shape dependence on wall effects and hydrodynamic focusing; and means of end-point determination.

Apparently, in practice, instrument response is independent of the resistivity of the particle and Berg, quoted in Ref. A3, suggest that this is due to the Helmholtz electrical double layer and associated solvent molecules at the surface of the particle.

While instruments involving electromagnetic scattering include examples such as x-ray, Y-ray, or ultrasound [see, for example, Refs. D8, D11-14], light scattering and specifically visible-light scattering are the most common instruments currently in use.

Similarly to the term particle-size, <u>light scattering</u> is an inclusive one that encompasses a broad range of instrumentation, techniques, and physical phenomena. In general, there is an incoming light beam incident on one or a collection of particles and a measurement of some property of the scattered outgoing light. The outgoing light, like the incident light, is characterized by amplitude or intensity, phase, frequency, direction of propagation and state of polarization. A theoretical model is used to relate some combination of these parameters of the scattered light to the size of the particle or particles doing the scattering. In some instruments, the relevant theory is explicit and detailed enough to provide a direct measurement of particle size, i.e., one in which the size is calculated directly from the basic mode; in other light-scattering instruments, the model is sufficient only to allow comparisons of particles of unknown size to those of known sizes. Because of their significance as potential candidate instruments for the calibration of particle reference materials, the function and theory of light-scattering instruments will be examined in more detail below in Section 3.B.

Instruments which determine particle-size via the measurement of size-dependent velocity of motion do so by various means. The means differ according to the cause of the motion and how the velocity is measured. The size-dependent velocity can be due to, for example: settling with buoyancy under gravity [C4, C5]; centrifugation or flow under pressure [D8, D11-13]; Brownian motion [R7, L13]; or forced-vibration of sinusoidal [S2] or non-sinusoidal types [S1]. The size-dependent velocity can be measured, for example, by: transit-times or separation due to velocity differences [D8, D11-13], doppler-frequencyshift [C4, C5], or time-correlation [L13, G10].

While some of these techniques and their variations use light, even scattered light, for the particle velocity determination, these techniques are distinguished from what is here called angular-intensity light-scattering because the size-dependent phenomena is principally described by aerodynamic or hydrodynamic equations for objects moving in fluids rather than by equations for electromagnetic waves scattered from spheres.

Velocity-dependent light-scattering as a means of particle size measurement, especially applied to liquid-drop aerosols, is well-established with a literature of its own. It includes the doppler-shift instruments and techniques variously described, for example, as: laser doppler velocimetry [F5], doppler shift spectroscopy [C4, C5, F4, H12, H13], or simply laser doppler systems [S1, S2, D22]. For the most part, these systems, with the exception of those of Refs. S1 and S2, deal with flow or settling. Where the particle velocity is due to Brownian motion, a related family of techniques includes those variously described, for example, as: photon correlation [C11, G10], homodyne [H14], optical self-beating [L13]; or Rayleigh-linewidth [R10] spectroscopy.

*Available from Coulter Electronics, Inc., Hialeah, Fla.

2.B.2. Number of Particles Involved

The number of scatterings involved in most light scattering techniques is usually a single one; that is, the light which reaches the detector has been scattered only once. Single-scattering is the basis of techniques which look at one isolated particle at a time in a single event [e.g., W15-W16], at one isolated particle at a time in a rapid series [e.g., W12], or at many particles at one time for single-scattering from multiple particles in parallel [e.g., R7].

2.B.3. Separation of Particles By Size

Another factor about particle-size instruments which bears on their performance as measuring devices is whether they involve intentional separation of particles by size. Such separation can be achieved in a number of ways, for example, mechanically, aerodynamically, or hydrodynamically.

Sieving is a technique for mechanically separating particulate matter into size intervals and is used both for mass-handling of tons of large particle materials and micro-handling of fine particle materials as small as $1 \mu m$ in size. For sieves with openings of known dimensions, the sieving operation is one of successive separations into groups smaller and larger than those which just fit through the openings. It is a conventional way of sizing standard glass beads and microspheres [H18, C22]. It gives a name to those particles smaller than those which can be satisfactorily sized by sieving; particles in the "subsieve" category [01], however, can be larger than the smallest sized by sieving.

Impactor-sizing is a technique for aerodynamically separating particulate matter into size intervals; impactors are used most often for the characterization of airborne contaminants such as dusts and smokes. In such devices particulate matter is deposited on collectors according to the aerodynamic momentum associated with the particles. For a fixed velocity, separation by momentum corresponds to separation by mass, which for a known density corresponds to separation by volume, which for an assumed spherical shape corresponds to separation by diameter. Relatively recent designs for variable-slit [C24] and low-pressure [H7] impactors have provided a means to measure aerodynamic particle sizes over continuous or discrete ranges down to diameters of $0.05 \ \mu m$ or less.

Sedimentation and centrifugation are techniques for hydrodynamically separating particulate matter into size intervals and, most often in laboratories, are used for the smaller, <1 μ m, particles [01, D11-14]. In such devices the concentration of particles suspended at various depths is determined as a function of settling time. Concentrations are determined, for examples, by light [D12], x-ray [01] or γ -ray [D12] attenuation at various depths or times.

2.B.4. Types of Dimensional Calibration

Instruments which measure particle-size do so by a comparison, indirect or direct, with the basic dimensional unit of length. This comparison requires explicitly or implicitly the use of some practical length standard, which can be a particle of known size, a linescale or a wavelength of light. Direct-imaging instruments can use any of the three; non-imaging instruments can use only the first and last.

a. Direct-imaging instruments

Electron and optical microscopes are usually calibrated for dimensional measurements by a ratio technique either using a linescale such as a stage micrometer or replica grating [e.g., in Refs. B16, R11, H4], or using particles of a known size [e.g., in Ref. H4, C8]. While each of the two approaches, linescale or particles of known size, follows the same procedure, there is a consequential if subtle difference in them which results in differences and varying degrees of dimensional errors. Where the magnification M_s of a microscope is calibrated by means of a linescale of known spacing S_0 , the measured dimension of the unknown, D_x , is given in terms of the dimensions of the images of the known spacing and the unknown particles, s_0 and d_x respectively:

(1a)
$$D_{\chi}(\mu m) = \frac{d_{\chi}(mm)}{s_{0}(mm)} S_{0}(\mu m)$$
, or

(1b)
$$D_{\chi}$$
 (µm) = $M_{S}^{-1} d_{\chi}$ (µm), where

(1c)
$$M_{S} = \frac{S_{O}(mm)}{S_{O}(\mu m)}$$

Where the magnification M_p of a microscope is calibrated by means of particles of known dimension D_0 , the measured dimension of the unknown, D_χ , is given in terms of the dimensions of the images of the known and unknown particles, d_0 and d_χ respectively:

(2a)
$$D_{x} (\mu m) = \frac{d_{x} (mm)}{d_{0}(mm)} D_{0}(\mu m)$$
, or
(2b) $D_{x} (\mu m) = M_{p}^{-1} d_{x} (\mu m)$, where
(2c) $M_{p} = \frac{d_{0} (mm)}{D_{0} (\mu m)}$.

The analogous equations for the measurement of unknown line spacings in terms of known ones are:

(3a)
$$S_{x}(\mu m) = \frac{s(mm)}{s_{o}(mm)} S_{o}(\mu m)$$
, or

(3b)
$$S_x(\mu m) = M_s^{-1} s_x(mm)$$
, where

(3c)
$$M_{s} = \frac{s (mm)}{S_{o} (\mu m)}$$
.

Equations la and 2a are usually implicitly and erroneously assumed to yield results identical to each other and to Eq. 3a. But because of the edge location phenomena described earlier, they can and do give greatly different results. Rearrangement of Eqs. la, 2a, and 3a into explicit ratios begins to show the basis for the differences which occur:

(4a)
$$\frac{D}{D_0} = \frac{d}{d_0}$$

$$(4b) \qquad \frac{D}{S_0} = \frac{d}{s_0}$$

$$(4c) \qquad \frac{S}{S_0} = \frac{s}{s_0}$$

Here it is at least formally explicit that calibration with particles of known size, as in Eq. 4a, consists of comparing widths-to-widths while calibration for particle measurements with a linescale as in Eq. 4b consists of comparing widths-to-spacings in dissimilar objects.

Calibration for spacing measurements with a linescale as in Eq. 4c consists of comparing spacings-to-spacings.

It has been demonstrated that in an optical microscope, the apparent width of an object's image depends on the edge location criterion, focussing, and instrument operating conditions [C9, N5, S11-12]. Further, it has been demonstrated, for both spherical particles [C9] and planar objects [S12], that the apparent width d' can differ from the geometrical-optical width d by an increment Δ which depends on edge-location criteria, etc., but is relatively constant over a range of object sizes (e.g., from 0.2 to 2 μ m [Ref. C9] and similarly 1 to 10 μ m [S12]). Thus,

(5a)
$$d' = d + \Delta$$
.

In the same imaging systems, the apparent spacings of a linescale are in practice to a very high degree free of these effects and in principle are independent of them [S11, S12]. Thus,

(6) s' = s.

Substitution of Eqs. 5a and 6 as appropriate into Eqs. 4a-4c results in expressions for the ratios of object and image dimensions.

(7a)
$$\frac{D_{x}}{D_{0}} = \frac{d_{x} + \Delta}{d_{0} + \Delta}$$

(7b)
$$\frac{D}{S_0} = \frac{d + \Delta}{S_0}$$

(7c)
$$\frac{S}{S_0} = \frac{S}{S_0}$$

For a difference in size between the known and unknown particles of Eq. 7a given by $d_x = d_0 + \delta$ and for a geometrical-optical magnification M given by Eqs. 1c through 3c, the difference in the object size corresponding to the difference between the apparent and the geometrical-optics image size, becomes for the three cases shown in Eqs. 7a-7c:

Case I. Particles of unknown size measured by ratio to particles of known size.

(8a)
$$\varepsilon = D_{x} - \frac{d}{M} = \frac{\Delta}{M} \cdot \frac{\delta}{d_{0}}$$

Case II. Particles of unknown size measured by ratio to lines of known spacings.

(8b) $\varepsilon = \frac{D}{x} - \frac{d}{M} = \frac{\Delta}{M} \cdot (1) = \frac{\delta}{M}$.

Case III. Lines of unknown spacing measured by ratio to lines of known spacing.

(8c)
$$\varepsilon = S_{X} - \frac{S_{X}}{M} = \frac{\Delta}{M} \cdot (0) = 0$$
.

Eqs. 8a, b, and c can be used to examine how systematic error which can arise in microscope measurements of dimensions due to ambiguities in image edge location is affected by various calibration techniques. The basis for such errors is the distance $\Delta/2$ between the apparent edge of an object's image and that determined by geometrical (electron or light) optics; the corresponding ambiguity for the object edge is $\Delta/2M$ and for the object width Δ/M . Based on the discussion earlier, Δ/M can be of the order of 0.25 μ m or more for an optical microscope [e.g., in Refs. C4, S11, and 12] while for an electron microscope, the author would anticipate Δ/M to be of the order of one-tenth that amount or 0.01 μ m or so for an ideal object.

Given a non-zero Δ/M then, in a measurement of an unknown linespacing against a known one, the error due to edge location as represented by Eq. 8c is zero. In a measurement of an extended object, either against a similar extended object or against a linespacing, the error due to edge location as represented by Eqs. 8a and 8b is non-zero. For calibration with a linescale, the error in the dimensions of a particle could be on the order of 0.25 μ m for an optical microscope measurement and on the order of 0.02 μ m for a scanning electron microscope measurement independent of particle size (based just on considerations of what goes on in the image plane; other effects can mitigate or compound these errors). For calibration with particles of known size, the error depends also on the difference in size between the unknown and known particles. For example, in the measurement of an (unknown) 15 μ m particle against a (known) 10 μ m particle, the error in size according to Eq. 8a for an optical microscope measurement might be:

(9)
$$\varepsilon = 0.25 \left(\frac{10-15}{10}\right) = 0.125 \ \mu m$$

and for an electron microscope measurement:

(10)
$$\varepsilon = 0.02 \left(\frac{10-15}{10}\right) = 0.01 \ \mu m$$

while for a measurement of a 10.1 μm (unknown) against a 10 μm (known) the respective errors might be:

(11)
$$\varepsilon = 0.25 \left(\frac{10.1-10}{10}\right) = 0.025 \ \mu m$$
.

Both the formal relationships of Eq. 8a, b, and c and the numerical examples just given illustrate some major points about the calibration of microscopes for dimensional measurements. First, there is sound evidence that edge-location ambiguities should lead one to anticipate systematic errors on the order of many tenths of a μ m in optical microscope measurements and on the order of a hundredth of a μ m in electron microscope measurements of the dimensions of extended objects such as particles. Second, these errors can be reduced, but not eliminated, by calibration against known spheres and only if the knowns and unknowns are close in size. Since these errors depend on the specific means by which an imaged apparent edge is located with respect to the geometric edge, one further way to deal with them is via a theoretical model of the microscope and its interaction with the object. In formal terms such a model mathematically describes, for example, the (light or electron) intensity distribution within the image as a function of position x and variables of the instrument, e.g.

(13)
$$I = I(x, \alpha, \beta).$$

Such a model and a linear displacement measuring device allow scanning of a microscope image and the location of the intensities, Ig, corresponding to those determined by geometric optics. The measured width of an object corresponds then to the distance between the points on the image at those intensities:

(14)
$$w = x(I_1) - x(I_2).$$

The displacement measuring device for such a measurement can be a calibrated transducer [N5] or an interferometer which can relate the measurements directly to the wavelength of light [S13].

b. Non-imaging instruments

While imaging instruments can be dimensionally calibrated by linescales (or displacement-measuring devices), non-imaging are usually calibrated by one or the other of the two remaining methods: explicit comparison of particles against other particles of known size or implicit comparison against a wavelength of light.

Commercial flow-through counters of the volume-displacement type [C25], the light shadow-projection type [W10], or other light-ratio types [W12] are calibrated using particles of known mean size and size distributions. Some commercial single-particle light scatter instruments of the levitation [W15] or flow-through type [W18] compare against the wavelength of the light source. Most laser light-scattering instruments, including those which scatter light from suspensions [D11-14, W12, G1] as well as the single-particle types just mentioned, make implicit comparison against the light wavelength which appears as an input parameter to a theoretical-analytical calculation of instrument response.

For angular-intensity light-scattering instruments, the calculation involves complex equations requiring computer numerical evaluation techniques. As such, no simple descriptive form of the dependence of intensity I vs. angles θ and ϕ , particle size d, and light wavelength λ and complex index of refraction m can be given. Formally, however,

(15) $I = I(\theta, \phi, x, m...)$

where the size parameter $x = \pi d/\lambda$ and d is the diameter of the spherical particle. Here the comparison of particle size vs wavelength is calculationally direct.

In particle-velocity light-scattering instruments, the calculation, in special cases, can be independent of angular-intensity theory and involve only hydrodynamic motion theories: for example, in first-order calculations, measurements on collections of particles of

nearly identical size [C4]. The most analytically simple case will demonstrate a point about dimensional calibration against the wavelength of light in velocity systems. For example, for particles following Stokes behavior, the viscous force F is given by

(16)
$$F = 6_{\pi\pi}av$$

where a is particle radius, η is the viscosity, and v is the particle velocity. A more specific example is for spherical particles of density, ρ , settling under gravity g, at terminal velocity in air, where the viscous and gravitational forces are equal and

(17)
$$6\pi\eta Rv = \frac{4}{3}\pi R^3\rho g$$

and

(

$$18) \qquad v = \frac{2\rho g R^2}{9} \qquad .$$

For a Doppler shift given in terms of the vector velocity v and the light propagation vector k:

(19)
$$f = \frac{1}{2\pi} v \cdot k$$

where

(20)
$$|\mathbf{k}| = \frac{4\pi\eta}{1} \sin \frac{\theta}{2}$$
.

Combination of the Stokes and Doppler equations gives the measurable frequency shift of the scattered light as a function of the particle size r and the wavelength of the light λ , as well as other system variables:

(21)
$$\Delta f = \frac{1}{2\pi} \left(\frac{2\rho g}{9}\right) \left(4\pi \eta_{air}\right) \sin \frac{\theta}{2} \frac{r^2}{\lambda}$$

or

(22)
$$f \sim \frac{r^2}{\lambda}$$

The most significant point to be made concerns dimensional calibration, and is that while the particle size in aerodynamic or hydrodynamic velocity measurements is determined in terms of the wavelength of light, it is done in a way different than in angular-intensity light scattering where the size information and dimensional calibration is in the scaling parameter $x = 2 \pi r/\lambda$.

Calibration of flow-through counters against particles of known size can be accomplished in at least two ways: a single-point (one ratio) technique and a multiple-point (two or more ratio) technique. A single-point technique can accomodate scale-factor (i.e. multiplicative) effects if no off-set (i.e. additive) effects are present. In the presence of off-set effects, at least a two-point calibration is required. Some models of commercial flow-through counters of both light-blockage and electrical-sensing-zone types can be adjusted in at least two-point calibrations. Further, there is a technique for determining the fraction of the total particles in a sample which are smaller in size than that which can be detected, sized, and counted [A3].

2.C. Single-Number Index to Characterize Particle Dimensions

Individual particles of matter are three-dimensional objects and dusts, powders, and suspensions are collections of vast numbers of individual particles. The determination of a characteristic particle size for a collection of particles therefore involves defining and measuring a size of one particle and defining and measuring a size of a population of particles.

2.C.l. Characterizing a Single Particle

An individual particle is a real three-dimensional object which has no one unique dimension which to call its size. As a geometrical object it is complex and irregular. As an object-to-be-measured, it is the receiver of action in one of many operational definitions where other operational definitions yield other sizes because they treat other geometrical representations of the particle. Most often the geometry is described in terms of the diameter of an equivalent circle or sphere; a sample of twelve such diameters with their definitions is listed in Table 3.

Microscopes, both optical and electron, and one type of flow-through counter [W10], measure particle size by scaling a two-dimensional plane projection of the three-dimensional particle. In a microscope, a non-circular image can be characterized in various ways: Feret's diameter d_F which is the distance between parallel tangents to the outline of the projected image; Martin's diameter, a mean chord length; or, one not shown in Table 3, a shear diameter, d_S , which is obtained with an image splitting eyepiece and is the Feret's diameter parallel to the eyepiece axis independent of the particle orientation [S10]. In the light-blockage type of particle counter, the particle size is given as the diameter d_{pMAX} of the circle equal in area to the maximum projected area of a tumbling particle [W10]. Note that maximum projected area diameters d_{pMAX} differs from the random-orientation projected area diameters, d_pr , the latter being for a particle lying on a substrate in a microscope. Besides being characterized in terms of a straight line chord-type dimension or an area-type dimension, projected plane images can be characterized by their perimeter.

Electrical-sensing-zone particle counters and one special-type of light scattering instrument measure particle size in terms of the individual particle's volume. For the former, the effect is the volume of liquid electrolyte displaced [C25]; for the latter, the effect is the Rayliegh scattering in which an electronic polarizability gives rise to a dipole moment proportional in strength to the volume of the particle [A3].

Hydrodynamic and aerodynamic velocity-dependent particle-size measuring devices, ranging from Doppler-shift spectrometers [C4] to precipitation impactors [C24, A7], measure particle size via Stokes'-type equations which involve volume-surface phenomena. The linear dimension in a Stokes-equation of the form: force = (shape factor) x (dimension) x (velocity) appears as the result of evaluation of complex-boundary conditions integrated over the surface of the object moving in the fluid [A3]. Further, where terminal velocities such as those due to gravity are measured, the Stokes force is equated to a buoyant force which is proportional to volume displacement:

(gravity) x (density) x (volume) = (shape) x (dimension) x (velocity).

Solution of this form of equation for a specific object shape yields the size vs velocity equation upon which size measurements are based. Other size-dependent phenomena which involve surface effects, such as gas adsorption, are used in commercial and laboratory-prototype devices [D11-14, D8, A3].

In almost all particle measurements, and independent of the physical phenomena and geometrical effects involved, the resulting single-number characterization of the non-ideal irregular, three-dimensional particle is given as the diameter of a(n) (equivalent) sphere. Where the particle is perfectly spherical, many of the geometrical effects would in form be the same - for example, the plane projection of a sphere is a circle whose diameters, whether

Table 3

Symbol	Name	Definition
d _v	Volume diameter	Diameter of a sphere having the same volume as the particle
d _s	Surface diameter	Diameter of a sphere having the same surface as the particle
d _{sv}	Surface volume diameter	Diameter of a sphere having the same external surface to volume ratio as a sphere
dd	Drag diameter	Diameter of a sphere having the same resistance to motion as the particle in a fluid of the same viscosity and at the same velocity (d _d approximates to D _S when R _e is small)
d _f	Free-falling diameter	Diameter of a sphere having the same density and the same free-falling speed as the particle in a fluid of the same density and viscosity
d _{st}	Stokes' diameter	The free-falling diameter of a particle in the laminar flow region (R _o <0.2)
d _a	Projected area diameter	Diameter of a circle having the same area as the projected area of the particle resting in a stable position
dp	Projected area diameter	Diameter of a circle having the same area as the projected area of the particle in random orientation
dc	Perimeter diameter	Diameter of a circle having the same perimeter as the projected outline of the particle
d _A	Sieve diameter	The width of the minimum square aperture through which the particle will pass
dF	Feret's diameter	The mean value of the distance between pairs of parallel tangents to the projected outline of the particle
dМ	Martin's diameter	The mean chord length of the projected outline of the particle

Feret or Martin's or image-shear, is the equatorial diameter. The diameter of the projected area in a maximum, random or stable orientation is the same diameter, as is the diameter of the sphere of equivalent surface area.

Two points are worth keeping in mind in the evaluation and intercomparison of experimental measurements on real particles, especially nearly-spherical real particles. One point is that particles are spherical only in relation to an individual technique's ability to detect deviations from sphericity. The second point is that even highly spherical particles have different equivalent spherical diameters according to the physical phenomenon and operational definition by which the various diameters are measured. A particle does not have a simple "true size" or an "absolute diameter" but rather these operationally defined sizes. Increases in precision can reveal systematic differences between variouslydefined sizes while at the same time refinement and sophistication in theoretical modelling can produce convergence. Later in Section 4 on the intercomparison of particle sizes measured by various techniques, both the presence of systematic differences and the possibility of obtaining convergence will be apparent.

While this report is concerned primarily with spherical particles which can potentially serve as sized standard reference particles, Table 4 is given to illustrate some shape factors or coefficients and their definitions [A3, S10]. The factors have practical importance, especially in dealing with industrial powders, suspensions, dusts and atmospheres which are made up of irregularly-shaped particles. For spherical particles, the factors and coefficients reduce to unity or appropriate multiples of π .

As a practical matter, deviations from sphericity at even a low-level have a consequence on the precise determination of the mean size and population standard deviation (monodispersity) of highly spherical standard particles. Some observations that have been made about shape effects are worth keeping in mind in the evaluation of systematic error effects in the calibration of standard particles. In electron microscopy, the shape of the equatorial plane of the particle in a stable rest position on a substrate is viewed; and apparent particle shape can be changed by pin-cushion, barrel distortion, and related astigmatic effects on the two-dimensional imagery. Further, some evidence has been given that latex particles may distort in shape upon electron irradiation [T1]. In light scattering, the basic Mie theory only describes scattering from perfectly spherical objects [Bll, K7, V4]. Techniques for dealing with light-scattering from nearly spherical particles such as oblate and prolate spheroids [A6, L3] and ellipsoids [L5] treat deviations from sphericity as perturbations on complex mathematical formulations [B11, K7, V4]. In flow-through particle counting of either the light-obscuration [C1, W10] or electrical sensing zone types [C25], particle shape determines the apparent size, changing the form and location of the size distribution curve for non-spherical particles relative to that for spherical ones [A3, W10]. The probable effect of a particle's asphericity on a measurement, whether by electron microscopy, light scattering, or flow-through counting, is to increase the apparent width of the size distribution, increase the uncertainty in the mean size, and shift the apparent mean size to some degree as well.

2.C.2. Giving an Average Size to a Group

Commercially and environmentally important microscopic particles occur seldom, if ever, individually or in small numbers having practically equal sizes, but instead occur in groups of great numbers having measurably different sizes. The common practical requirement that such a complex system be describable by a single index is reflected in the wish to characterize that population of a large number of irregularly-shaped, three-dimensional particles by one number, that is, by some average particle size. While the problem of defining a size of an individual particle is geometrical-physical, the problem of defining an average size for a population is statistical-physical.

A conventional manner of describing, with one number, a population of particles having different sizes is by means of a particle size distribution function. In tabular, graphical, or equation form, the size distribution describes the amount of particulate matter which occurs for a given size or size interval. The amount can be given in terms of mass; thus there is a number size distribution and a mass size distribution. Either distribution, by mass or number, can be characterized by an arithmetic average (or arithmetic mean) size d_a , by a geometric mean (or geometric average) size d_q , by a median size d_m , or by other
Table 4

Shape Factors	Definition	Coefficients
Sphericity	The ratio of the surface area of a sphere having the same volume as the particle to its actual area; the reciprocal is known a the coefficient of rugosity or angularity	$s \qquad \psi = \frac{\frac{d^2}{v}}{\frac{d_s}{d_s}}$ $\psi < 1$
Circularity	The ratio of the perimeter of a circle having the same area as the projected area of the particle to its actual perimet	$\chi = \frac{d}{d_{c}}$ er $\chi < 1$
Surface-shape coefficient	Coefficient of proportionality relating the surface area of the particle with the square of its measured diameter	$S = \alpha_{s,A} d_a^2$
Volume-shape coefficient	Coefficient of proportionality relating the volume of the particle with the cube of its measured diameter	$V = \alpha_{v,A} d_A^3$
Surface- volume shape coefficient	Ratio of surface to volume shape coefficient	α s,v,A = $\frac{\alpha}{\alpha}$ s,A

Table of Shape Factors and Shape Coefficients [A3]

Mathematical Expressions of Various Mean Diameters of a Distribution ΣdL ΣxdN Number-length mean diameter x_{NL} = ____ = ____ ΣdN ΣdN $x_{NS} = \sqrt{\left(\frac{\Sigma dS}{\Sigma dN}\right)} = \sqrt{\left(\frac{\Sigma x^2 dN}{\Sigma dN}\right)}$ Number-surface mean diameter $x_{NV} = \sqrt[3]{\left(\frac{\Sigma dV}{\Sigma dN}\right)} = \sqrt[3]{\left(\frac{\Sigma x^3 dN}{\Sigma dN}\right)}$ Number-volume mean diameter $x_{LS} = \frac{\Sigma dS}{\Sigma dL} = \frac{\Sigma x^2 dN}{\Sigma x dN}$ Length-surface mean diameter $x_{LV} = \sqrt{\left(\frac{\Sigma dV}{\Sigma dL}\right)} = \sqrt{\left(\frac{\Sigma x^3 dN}{\Sigma x dN}\right)}$ Length-volume mean diameter $x_{SV} = \frac{\Sigma dV}{\Sigma dS} = \frac{\Sigma x^{3} dN}{\Sigma x^{2} dN}$ Surface-volume mean diameter $x_{VM} = \frac{\Sigma dM}{M} = \frac{\Sigma x^4 dN}{M}$ Volume-moment mean diameter $\Sigma x^3 dN$ ΣdV ΣxdW Σx⁴dN ΣdM Weight, moment mean diameter ____ = ____ = ХХМ $\Sigma dW \Sigma x^3 dN$ ΣdW

types of averages or means based on either number or mass, as will be discussed later. In some cases, the distribution is characterized by a mode size.

The differences among mean, median, and mode values of particle size are of practical metrological importance. Most measurement processes and calculations yield one of many types of mean size, as will be discussed shortly; a recommended way of calibrating flow-through counters employs a median size; and at least one manufacturer of standard reference particles characterizes them in terms of a main-mode size. The use of a median or a mode requires an explicit graphical representation of the size distribution, such as a histogram.

If the distribution of sizes shows a peak, that is, if some size d₁ has more particles occurring at it than at nearby sizes above and below it, the size with more particles is a mode and the distribution is modal. Some processes produce particles which have a dominant single mode as, for example, batch grown latex particles. In contrast, other processes, such as vibrating-orifice generators, have been observed to produce particle distributions with two, three, or more modes [C4]; droplet-grown latex particles with tri-modal distributions have even been reported by manufacturers.

Some natural and industrial processes result in well-behaved single mode distributions which are symmetric and monotonically and asymptotically approach zero at sizes well above and below the modal size. For narrow-distribution particles such as polymer spheres, the distribution is symmetric in the linear dimension and can be described well for most applications by the Gaussian or normal distribution [A3]; for many ground or milled powders and glass beads, the distribution is symmetric in the log of the dimension and can be described by the log normal distribution [G2]; certain sub-0.1 μ m polymer sphere distributions have been best described in hydrodynamic studies by symmetric but non-Gaussian distribution functions [C11].

The most commonly used mathematical distribution function is the Gaussian or normal distribution and its explicit use or implicit applicability is conveyed by the term "standard deviation" as the index of the width of the distribution. The standard deviation is the limiting value of the root-meansquare (RMS) average deviation of an infinitely large, normally distributed population. In metrology the standard deviation is a measure of the random scatter in measurement data, while in common usage in particle-size measurement, the standard deviation is a measure of the distribution of sizes in a population. Failure to clearly distinguish the variations associated with the measurements from the variations associated with the particle population can be troublesome and misleading.

In a measurement process statistical control is a must to yield valid results, and the variations in measurements are random and characterizable by a standard deviation $\sigma_{\rm m}$. In a particle population with a normal distribution of sizes, that variation among sizes is characterized by a standard deviation $\sigma_{\rm p}$. In a first order model of the results of applying the in-control measurement process to the normally-distributed particle population, the standard deviation $\sigma_{\rm t}$ of measurements on the population will be the quadrature combination of the two:

(23)
$$\sigma_t^2 = (\sigma_p^2 + \sigma_m^2)^{1/2}$$

for measurements on N particles, the standard deviation on the mean of the measurements will be:

(24)
$$\sigma_{\rm m} = \frac{1}{N} \sigma_{\rm i}^2 = \frac{1}{N} \left(\frac{1}{N-T} \sum (x-\overline{x})^2 \right)^2$$
.

Given that σ_t is an observed scatter in measurement results, σ_m is the component of that scatter due to variations in size among the particles in the distribution, and σ_p is the component due to variations in the measurement process itself, some caution in interpreting results is required. For example, if one measures the apparent diameters of a

great number of particles as images on TEM plates and computes an RMS average deviation from the mean diameter, one obtains an estimate of σ_t . Without moving, refocusing, reimaging, and remeasuring one single unvarying particle to obtain an estimate of σ_p , one cannot determine σ_m , the quantity of interest.

The two equations above formally illustrate two points about measurements of particle size distributions. First, Eq. 23 shows that a standard deviation σ_t computed from measurement data for a distribution of particles is equal to the particle distribution standard deviation σ_p only in the limit of small measurement uncertainty, or:

(25)
$$\sigma_t \simeq \sigma_p$$
 if and only if $\sigma_p \gg \sigma_m$.

Since σ_m can be determined only by a separate determination, such as by repeated measurements on one particle, the assumption that $\sigma_p >> \sigma_m$ should be questioned. However, given the absence from the literature of data upon which estimates of the variability σ_p for the different measurement techniques, one can only keep the difference between σ_t and σ_m in mind and treat σ_t as an upper limit for σ_m . As a second point, since the effective number of particles N involved in multiple-particle phenomena (such as that seen in many forms of light-scattering) is not known, the uncertainty in mean particle size cannot be easily reduced without separate redeterminations. Further, the assumption of a normal distribution of particle sizes for real populations of particles should be made with reserve.

Caution and special mathematical techniques are also required to deal with multi-mode or unsymmetric, skewed distributions [A3]. An expediency is to treat the dominant mode as a single mode, ignoring parts of the distribution. Number averages are most susceptible to the biasing effect of small particles which can occur in large numbers and would be counted in one technique and would go undetected or intentionally uncounted in another technique; mass averages are most susceptible to the biasing effect of large particles which carry proportionally so much more mass than many small particles.

While number-average and mass-average mean diameter are most commonly used, they are only two of the many moments of a distribution which can be computed and which find use.

Table 5 shows eight such moment-mean diameters, with their general and specific expressions for spherical particles. In general these moment-means are of the form:

(26) $w_{mean} = \frac{sum (number x weighting factor #1 x size)}{sum (number x weighting factor #2)}$

where the sum is over the sizes or intervals, the number is the number of particles for a given size or interval, and the weighting factors are geometrical factors such as length, area, volume, or weight. The physical and formal differences among these various mean diameters is of metrological consequence since different particle-size measurement techniques, either inherently or by convention or convenience, determine different types of mean diameters; for example, microscope measurements of diameters lead directly to a number-length mean diameter; certain light-scattering techniques including extinction and laser-Doppler velocimetry yield a number-area mean diameter; and mass-deposition devices, such as impactors yield a number-mass (or weight) mean diameter.

Part II of this report, now concluded, has been an overview of those elements of particle-size measurement systems which contribute significantly to the measurement process and produce a number called a particle size. The particles of central interest to this report are those which are spherical and monosize. The measurement techniques of central interest are the three techniques by which such particles can be dimensionally calibrated in a consistent and compatible scheme.

3. CANDIDATE INSTRUMENTS FOR STANDARDS CALIBRATION

A. Needs of Calibration Scheme

The needs and capabilities of industry and science with regard to sized particle reference materials place stringent demands on the method of calibration in regard to the dimensional measurements by which the particles are calibrated and their size is certified. The measurements must be definitive in the sense that they are accurate to a degree commensurate with users present and near-future capabilities. In more specific terms, this means that a calibration technique must yield high-resolution measurements of some defined particle size, and still, to a high degree, be independent of time and technique. Besides being accurate, the techniques also need to be reasonably fast and economical.

No single current measurement technique meets all these general requirements. Electron microscopy can provide high-resolution, unambiguous imaging and dimensional measurement of even sub-0.1 µm individual particles. It can provide direct-image information on particle shape and surface features and on the presence of agglomeration or debris. It can provide via image-analysis of either manual or automatic form, an explicit histogram of particle size distribution. However, it has the disadvantages that it is slow, necessarily involves limited sampling of the population, and subjects the particles to vacuum and electron irradiation.

Light-scattering from a suspension can provide high-resolution, dimensional information averaged over a large number of particles in their normal environment. The method is fast, non-intrusive, and can provide mean size and population standard deviation. It is advantageous in that it is based on a well-established theory. But the method is model-dependent and requires prior knowledge or assumptions, usually that the particles are spherical, homogenous, normally-distributed in size, and have a certain index of refraction. Also scattering from a suspension cannot well distinguish agglomeration or debris or deviations from sphericity.

Flow-through liquid-borne particle counters can provide moderately high resolution, and fast, sequential measurements of individual particles in a sample of a liquid suspension. They can provide an explicit, built-up histogram and so distinguish normal distributions from skewed or multimodal ones. They also are comparators which require particles of known size for their calibration, with the lower limit of the range of commercial devices at about 0.5 µm. The electrical-sensing zone type requires that particles be in an electrolyte solution. This type and the optical type involve consumption of the sample, and although they cannot distinguish debris, they do give evidence when agglomeration occurs.

While other particle-size measurement techniques are available, the three aforementioned complement each other in a scheme which promises to provide measurements which are accurate, fast, economical, and independent of method to a degree sufficient to meet the needs of today's seekers of sized standard reference particles.

Because both electron microscopy and certain forms of light-scattering are direct-measurement techniques (that is, they yield dimensional measurements of particle size without requiring particles of known size for comparison), each could be a primary calibration technique in its own right. However, because the two techniques involve independent operational definitions of particle size which do not necessarily yield corresponding results, intercomparison and refinement of the techniques, theoretical models, mathematical algorithms, and formal definitions to achieve such correspondence may be required. Flow-through counters could then provide more information for the refinement process and be used for a rapid, convenient, secondary calibration in which particles of unknown sizes are calibrated by comparison against particles of known sizes from a primary calibration. In this context, these three generic techniques will now be examined in more detail.

B. Interrelationships of Three Candidate Measurement Methods

3.B.1. Electron Microscopy

In electron microscope measurement of particle size, electrons from a source are focused via electron optics onto the particle and either electrons transmitted and attenuated

by the particle (as in a TEM) or "reflected" (actually either backscattered electrons or different secondary emission electrons) by the particle as in an SEM are imaged. In a TEM the imaging is usually done directly onto an electron-sensitive photographic plate; in an SEM the imaging is done by detecting the electrons and forming an image on a cathrode-ray tube where intensity is proportional to the current detected. TEM requires a measurement of the directly-exposed image on the plate, usually done visually with a reticle or with some form of semi- or fully-automated image analyzer. SEM requires a measurement of either an image on a photograph of the CRT screen or some form of scaling of the electron intensity profile. In general, analytical models of the imaging process are not used and apparently not thought to be required.

Early innovative work on electron microscope measurements of polymer sphere diameters was done by Bradford and Vanderhoff at Dow in 1954 [B16]. Bradford has continued to the present [R11] work which is the basis for the mean particle sizes attributed to the more than sixty Dow latexes marketed since 1947 [B2].

The basic technique, apart from some changes in instruments and calibration materials, has been unchanged [R11]. At the heart of the technique is the measurement of the apparent diameter of the TEM image of a particle against the apparent spacings of the TEM image of the lines of a replica grating upon which the particle rests. In the 1954 paper, the authors report using a shadowed silicon monoxide replica grating with 1134 lines per mm mounted on a stainless steel grid. The choice of the silicon monoxide stainless steel combination was made after they observed that collodion shrank 5% after five minutes of irradiation and that in a similar period 0.34 μ m polystyrene spheres on collodion replica on a copper grid could grow in size by 15% (0.007 μ m). In that report the effects and levels of beam current, contamination growth, and pumping rate were not known.

In the 1979 paper, the author reports using a new instrument with a shadowed carbon replica grating of 2160 lines/mm. By private communication he reports that particles to be measured are air-dried on the replica grating, evacuated to 10^{-5} Torr, and irradiated with 50 Kev electrons at magnifications of 7000X - 20,000X; the resulting photographic plate shows particle images 1-4 mm in diameter against a background showing about nine lines of the grating replica. The apparent diameters of the particle images and apparent spacings of the grating are measured visually with an eyepiece magnifier to a precision of about +0.02 mm. A range of from 70 to 300 particles are measured and the mean and standard deviation are calculated directly from the data. A typical standard deviation is +0.005 μ m for particles in the range 0.1 to 1.0 μ m, independent of mean size, and the standard deviation is attributed wholly to the distribution in particle sizes, on the apparent premise that the standard deviation of the measurement is much smaller than that of the particle size distribution. In 1979, the mean diameter of the Dow LS-1028-E latex, previously measured by Dow and found to be 1.099 μ m, was remeasured by them and reported without comment to be 1.192 μ m [R11].

In the last few years, independent and sometimes very thorough electron microscope measurements on polystyrene spheres and Dow latexes in particular have been reported by various workers [A4, C11, C20, C23, D3, D6, D20, H4]. Of these, some data from comparisons by Davidson and Haller [D3], Heard [H4], Dobbins [D21] and Davidson, et al. [D6] will be examined in some detail later in this report. For the moment, two of the reports of work, which like that of Bradford [B16], systematically investigated error effects in TEM measurements of particle-size, will be described in brief.

Heard, et al., measured mean particle sizes of nine Dow latexes and reported results in a paper entitled "A Redetermination of the Diameters of Dow Polystyrene Latices" [H4]. They reported that they used a carbon replica grating, 300 A° thick, gold-palladium shadowed, having 30,000 lines per inch (1181 lines per mm), and mounted on copper 200 mesh grids. To minimize radiation damage to the spheres, measurements were made at 100 Kev accelerating voltage at the lowest beam current giving acceptable images with three second exposures. To minimize contamination, a cold-finger stage was used. For 0.5 to 1 μ m spheres, the TEM magnification was 10,000 to 20,000X while for 0.3 to 0.8 μ m spheres the magnification was 30,000 to 50,000X. A measurement at 12,500X on the screen gave 25,000X on the photographic print, and on such a print the apparent diameters of images of latex spheres was 17 to 28 mm against an apparent spacing of 20 mm for six grating lines on the print. Diameters and spacings for images on print were measured with a reticle to precisions of +0.2 mm. Among other effects, Heard reported that fidelity of reproduction of the replica grid was demonstrated by direct measurement $(29,900 \pm 100 \text{ lines/inch measured for replica compared to 30,000 quoted for the master by the manufacturer). In addition, there was no detectable change in replica grating spacing on irradiation (<0.2% change in 10 min.), and no detectable change in sphere size on irradiation at normal beam currents. However, <math display="inline">l \ \mu m$ spheres decreased in size by 2% in the first minute and 5% in 10 minutes at beam currents of four times normal, corresponding to magnifications of twice normal; the decrease was about half as much for 0.1 μm spheres.

In Heard's measurements of particles against replica gratings and against other particles in a ratio technique, it was quoted that there were estimated total uncertainties (1 σ) of $\pm 0.008 \ \mu$ m for 0.365 μ m particles up to $\pm 0.016 \ \mu$ m for 1.16 μ m particles. These variations were attributed wholly to the measurements and not at all to the particle population.

Davidson and various co-workers, in allied papers [D2-7], performed measurements on various polystyrene latexes (including Dow latexes) using various techniques, including light-scattering and electron microscopy. One paper by Davidson and Haller, entitled "Latex Particle Size Analysis: V. Analysis of Errors in Electron Microscopy", deals systematically with the subject [D3]. Among the effects experimentally measured were those due to grid material, ion exchange of the latex, vacuum conditions, magnification variation over time, method of measuring the photographic images including filar eyepiece and spot-projecting image analyzer, and image reproduction by contact print and enlargement.

Among other conclusions, Davidson and Haller decided the following: neither grid type nor ion exchange "had much effect" on measured diameters; the effects of irradiation and pumping rate were negligible if micrographs were made within one minute of initial beam exposure; changes in pumping rate could cause apparent particle diameter to increase, decrease, or remain constant with beam exposure; sizing of images by means of a filar micrometer eyepiece gave diameters "very close to those from other methods"; the projectedspot image analyzer (Zeiss TGZ-3) gave results comparable to the filar if enlarged transparencies were counted which showed the latex particles as black dots against a white background; and if negatives were counted directly (white dots against black background), the diameters so obtained were often lower than those obtained by filar counting. Finally, it was concluded that "the magnitude of the various errors in electron microscopy of polystyrene latex for sharp negatives" is at the 90% confidence level $\pm 3\%$ in magnification, $\pm 3\%$ on average diameter of sample, $\pm 3\%$ for filar micrometer sizing, $\pm 5\%$ for Zeiss TGZ-3 sizing of 5 mm black spots, and the combined total error is approximately 5% for filar counting and 7% for the projected-spot counting.

On the important issue of changes in the diameter of polymer latex spheres during exposure to the electron beam in an electron microscope, the evidence is not overwhelming but seems to indicate that polystyrene latex spheres can be measured with a negligible (but unspecified) change in size if the exposure is at a low beam current and brief. Early on, Davidson and Haller [D3] reported that the apparent size could increase, decrease, or remain the same depending on pumping rates; they speculated that a no-change situation corresponded to a balance between diameter decrease due to mass loss and diameter increase due to contamination deposition. Talmon and Miller [T1] reported that while "soft" latexes, such as benzene-plasticized polystyrene, required special techniques such as an 85 °K cold stage and embedding between polyimide sheets, "glassy" latexes such as unplasticized polystyrene could be measured well just by spraying, drying, and normal handling. Similarly, Claver and Farnham [C20], while reporting decreases in diameters of polystyrene spheres of from 2 to 9% upon intense exposure for many minutes, conclude that "a maximum (mass) loss from polystyrene is negligibly small for all but the most precise measurements". Finally, Heard, <u>et al</u>. [H4], in the most explicit statement of the magnitude of the effect for normal exposures lasting up to ten minutes, report a "negligibly small" decrease in size with an upper limit of 0.2% for 1 μ m spheres and 0.1% for smaller ones.

Five potential sources of significant systematic error are apparent in the reports of electron microscope measurements of latex spheres drawn from liquid suspension as described above. First, there is the change in particle diameter due to drying in air and subsequent evacuation. Second, there is the decrease in particle diameter due to loss of mass due to irradiation by high energy electrons. Third, there is the increase in particle diameter due to deposition of contamination by the electron beam. Fourth, there is the determination of the point-to-point magnification of the electron image. And finally, there is the matter of properly measuring the image corresponding to that determined by geometrical-optics. Each of these potential sources of error would need to be investigated and managed in order to obtain definitive measurements from the technique.

3.B.2. Light-Scattering

As a candidate technique for direct measurement of particle sizes, especially highly spherical monosize particles in liquid or aerosol suspension, light-scattering in one or more of its many forms has conspicuous advantages. For example, it can measure such particles in their own environment, can average instantaneously over a great number of particles, and via a well-developed theory, can yield dimensional information without requiring comparison to particles of known size. Light-scattering, however, is not one thing. Rather, in contrast to the technique of electron microscope measurements of particle size, light-scattering measurements encompass a wide array of seemingly unrelated techniques and a complex of theoretical-analytical models. This report will only touch on some of the instruments and theoretical treatments in order to provide some context for the intercomparison of results and a discussion of the potential calibration techniques.

a. Light-scattering instrument systems

A major reason for the diversity of techniques and theoretical treatments of lightscattering as applied to particle size measurement is the nature of light and the number of its properties capable of carrying dimensional information about the particle which scattered it. These properties include amplitude (or intensity or photon count), phase, frequency (or wavelength), direction of polarization, and direction of propagation. In general the technique is to deduce particle size from the dependence of one of these properties upon a second one which varies as the remaining are held fixed or ignored. Some of the major types of light-scattering techniques for particle size measurements based on this type of independent-dependent variable categorization include:

° intensity-vs-direction of propagation measurements (referred to as angular scattering); some variations of this classic technique and their capabilities will be discussed shortly.

° intensity-vs-phase type measurements, which includes laser interferometry [R], R2]; holography with one-wavelength [H16, K9] or two-wavelength [M8] illumination in normal wide-angle or forward-scatter [S9] or with computer-synthesized holographs [T6]; and array-diffraction [F3, P2].

° frequency-vs-direction type measurements, which includes various Doppler shift techniques [C3].

° photon count-vs-time measurements, which includes various photon correlation techniques [C12, G10, H14, L13].

° intensity-vs-presence/absence of particles, which includes the optical extinction and turbidity techniques [D15, 18, 19, 21]; this technique involves measurement in the forward-direction with scattering as one of the attenuation mechanisms for the change in intensity, but it is distinguished from forward (or near-forward or low-angle) scattering [B12, D15, L11, S6] since the unscattered beam carries the information;

° intensity-vs-microscope quasi-imaging, including interference contrast microscopy [S8], dark-field microscopy [D2], and array-counting [K15, R3] techniques.

Among these various light-scattering techniques with demonstrated capabilities for measurement of particle size to uncertainties in the range 100 down to 3 nm, there are, for example, angular-intensity techniques to be discussed below, laser-Doppler techniques (with reported uncertainties of about 1% for 5-15 μ m particles [eg. B17], photon-counting Rayleigh-spectrometer techniques (with reported uncertainties of 0.003 μ m particles [H3a]), and, for measurements of single particles, deviation techniques [eg. C24, M1, W17]. Of these, angular intensity scattering is most interesting since it: (1) can be applied to collections of particles in suspension; (2) is suited to dimensional measurement of highly spherical, homogenous particles in the range 1-10 μ m as chosen for initial standard reference particles; (3) can be implemented and theoretically treated in a straight-forward convenient way; and (4) can also add to fundamental understanding of electromagnetic scattering phenomena.

Angular scattering, which is the classic technique of light scattering for particle size measurements involving intensity-versus-angle, is applied with various ways of extracting dimensional information from the angular intensity distribution, that is, from the scattering pattern. For example, early work on latex spheres used 90° scatter, polarization ratio, extremum location, dissymmetry ratio, and spectral transmittance to obtain dimensional information [D19]. This pre-laser work achieved agreement among mean diameters as measured by the various techniques which could often be considered to be good (each within, for example, 0.01 or 0.02 μ m of an average) and was occasionally strikingly good (for examples, mean diameters of a latex by the four methods of 0.808, 0.802, 0.803, and 0.805 μ m) [D19].

The technique of angular scattering has been applied continually with refinements of sources (from mercury lamps [D19] to HeNe CW lasers [G1] to wavelength-tunable dye lasers [A7]), detection, and data processing techniques [K1, K2]. Kratohvil, who has published continually over the period and maintained contact with the literature, reviewed light-scattering measurements in general in 1964 [K13] and, along with original measurements [K11, K12, K14, W6, W7, W8], has compared the results of some latex sphere diameter measurements by the variety of light-scattering techniques [K10]. Gebhart, et al. have discussed the various light-scattering instruments capable of high-resolution, direct measurement of particle size which they describe as particle-size spectrometers [G1], while Willeke and Liv discussed various light-scattering instruments which are usually limited to comparison measurements, and they describe as optical particle counters [W12]. Most of the particle counters are fixed angle, intensity-ratioing devices in which the design choice is to gain simplicity and speed by trading-off angle-scanning.

Angular-scattering measurements on standard spherical particles have been made using commercial and laboratory prototype instruments which scan various segments of the angular distribution. More or less full circle devices are referred to by Marshall, et al. [M1] and Powell, et al. [R10]. That reported by Marshall has been used to scan continuously over the angular ranges 5°-175° and 185°-355° with a 2° angular acceptance at the detector [M1], while that reported on by Powell has been used to scan over an assumedly large part of the full circle at 1° intervals with a 5° acceptance [R10]. Angular-scattering instruments which scan more-or-less the half circle are those used or described by Wyatt [W15, 16], Kerker, and Powell [R10]. In the devices of Wyatt and Kerker, which are from the same manufacturer and differ only in that the former measures electrostatically-levitated individual particles [W15, 16] while the latter measures. Particles in suspension, the scanning range is typically 8° to 172° with a 2° acceptance. Powell's instrument was used in a modified form to scan from 45° to 115° at 5° intervals with a 5° acceptance [R10].

For each of these five angular-scattering instruments, the size of the particle doing the scattering is determined from a comparison of the observed intensity-vs-angle distribution with a theoretical distribution calculated for a specific particle size-index of refraction combination. In essence, it is a two-parameter fit of observed-vs-calculated curves. As an example of a fast measurement and achievable results, the Gucker instrument [M1, R10] uses an ellipsoidal mirror for collecting the light-scattering by a particle at its focus and a second moving mirror to scan 360° in 20 msec; uncertainties in the measurement of the diameters of individual particles ranging from 0.3 to 11 μ m in size are given as 0.5 to <1%; the resulting mean diameter for a Dow (LS-1028-E) latex is given as D = 1.189 μ m with σ = 0.008 μ m and an index of m = 1.588.

Both types of angular intensity light scattering techniques, i.e., scattering from single levitated particles and scattering from collections of particles in suspension, can yield values for the distributions of particle size about a mean diameter. In singleparticle scattering methods such as in Ref. C24, particles are measured serially and a mean diameter and distribution about the mean calculated from individual measured diameters. In scattering-from-suspensions methods: (1) a mean diameter alone can be determined by a single best-fit match between an observed angular intensity pattern and one calculated for one diameter of sphere, or (2) a mean diameter and a distribution can be determined by a fit between an observed pattern and a pattern calculated as the average of a number of individual patterns for different size spheres [see, for example, Ref. K11, K12].

Potential sources of measurement uncertainty in angular intensity light scattering determinations of particle size include the effects of

- (1) deviations from sphericity of individual particles;
- (2) deviations of the index of refractions of individual microscopic particles from the known value for the bulk material;
- (3) deviations in the wavelength of the light used from the assumed value;
- (4) errors in angle measurement;
- (5) errors in intensity measurement;
- (6) finite acceptance angles detector;
- (7) deviations from planarity of incident light;
- (8) deviations from monochromaticity of incident light; and
- (9) fundamental light and limitations of Mie theory.

Quantitative determination of the systematic effects of these factors require extensive analysis which is beyond the scope of this work. Estimates of variability in results have been made, however, by numerous authors; estimates of the magnitude of systematic effects can be made, for example, by intercomparisons of results from various laboratories, such as in Ref. R10 and in this work. By inference, it appears that systematic errors of the order of 1-3% for the 1 µm particles can be encountered, while overall uncertainties of 1% (including observed variability with estimates of systematic errors) appear to be attainable.

b. Applicable theories of light-scattering

The interaction of light with real microscopic particles is a complex physical phenomenon which can be described mathematically only in restricted, approximate forms. As applied to particle size measurement, basic theory usually treats light which is elastically scattered from, at most, one homogenous dielectric sphere. Different theoretical models are used to quantitatively describe the behavior of the light scattered from such a spherical particle and to extract the dimensional information about the particle. The choice of models depends on the dimensions of the real particle relative to the wavelength of the light (x = 2 $\pi a/\lambda$) and on the effective index of refraction of the particle relative to the medium (m = n_{particle}/nmedium).

In the limit of very small particle diameters $(D << \lambda)$ and the limit of very large particle diameters $(D >> \lambda)$, the relevant models treat them as geometrical objects which do not interact with the electromagnetic wave. Within each of these limits, the next order approximations, for particles nearer in dimension to λ , add phase-shifts which depend on the index of refraction. For intermediate size particles, the most accurate theory treats the complex interaction of the dielectric sphere with the electromagnetic wave which describes the light.

Various elements of the five basic models have been described by, among others, Allen [A3], Born and Wolf [B11], Chu [C12], Deirmendjian [D16], Gebhart [G1], Kerker [K7], Van de Hulst [V4], and Willeke [W12], from whom this discussion is drawn. The names associated with these various models vary according to the vagaries of history and the inclinations of workers reporting (see Kerker [K7] for a discussion).

Rayleigh-scattering applies to very small particles such as air molecules. In terms of the size parameter x and the relative index m, the approximation applies for

(27) $(m-1) \rightarrow 0$

(28)
$$x = \frac{2\pi r}{\lambda} < 0.3.$$

In this approximation, the particle is treated as a point dipole with a dipole strength proportional to particle volume. From Van de Hulst [V4], the intensity I at angle θ is given by

(29)
$$I_{\theta} = |\alpha|^2 \frac{2\pi}{\lambda_m} \frac{4}{2Z^4} \frac{(1+\cos^2\theta)}{2Z^4}$$

where α is the volume polarizability, z is the distance from particle to detector, and λ_m is the wavelength in the medium. For homogenous spheres:

(30)
$$\alpha = \frac{3(m^2 - 1)}{(m^2 + 2)} \frac{v}{4}$$

which for the condition $(m - 1) \rightarrow 0$ reduces to

(31)
$$\alpha = 2(m-1) \frac{V}{A}$$

Since $v \sim r^3$ and $I \sim \alpha^2$,

(32) $I_{\circ} \sim r^{6}(1+\cos^{2}\theta)$

where the angle-dependent and angle-independent terms correspond to two polarizations. In Rayleigh scattering, the intensity distribution is symmetric about 90°.

Rayleigh-Gans (or Rayleigh-Debye or Rayleigh-Gans-Debye) scattering applies to particles somewhat larger than air molecules, such as macromolecules. In this approximation, the dipole scattering of the Rayleigh approximation is modified to take into account phase-shifts of the differential volume elements over the finite volume of the sphere. Here the constraints are relaxed somewhat and the approximation applies to either:

(33) small spheres where D << λ

or a particle with an index close to that of the medium:

(34) $(m - 1) \rightarrow 0,$

while the overall constraint is maintained:

(35) $\frac{2\pi a}{\lambda}$ (m-1) << 1.

According to Van de Hulst [A3, V4], the intensity varies in the form:

(36)
$$I_{\theta} = I_{\theta} \left[\frac{k^4 v^2 (m-1)^2}{8\pi Z^2} \right] \left[\frac{3}{\mu} (\sin \mu - \mu \cos \mu) \right]^2 (1 + \cos^2 \theta)$$

where

(37)
$$\mu = \frac{2 \pi D}{\lambda m} \sin \frac{\theta}{2} \text{ and } \mathbf{k} = \frac{2 \pi}{\lambda m}$$
.

Here the scattering intensity is asymmetric about 90° and shows maxima and minima. At the other end of the size spectrum are large particles, where D >> λ is the basic diffraction scattering and its phase-shift modification.

Fraunhofer diffraction applies to particles large in comparison to the wavelength, $D >> \lambda$, and treats the particle in the limit as a circular disc. The intensity pattern is described by the familiar Bessel function equation of the Airy pattern:

(38)
$$I_{o} \sim \frac{J_{1}(x\sin\theta)^{2}}{x\sin\theta}$$

where again x = $2\pi a/\lambda_m$. The intensity shows maxima and minima, with the first zero of the function at sin = 1.22 /2a.

Anomalous diffraction applies to particles large in comparison to the wavelength $D>\lambda$, but not at the limit of geometric diffraction. In this approximation:

(39) x >> 1

while

(40)
$$(m - 1) \rightarrow 0$$
.

Phenomenologically, the model treats a transparent sphere as having an incident ray which passes through the sphere without reflection or refraction but has a significant phase shift because of the long path length through the sphere. The total scattered field results from the interference of the Fraunhofer-contribution and the forward-scattered phase-delayed contribution.

Resonant scattering occurs when the incident electromagnetic wave physically interacts with the material of the scatterer in such a way so as to produce in the scattering properties maxima and minima which cannot be accounted for by diffraction and interference phenomena alone. The current theory best suited to handle this situation is one variously described as Mie [V4], Lorentz-Mie [R10], or Debye [K7].

<u>Mie theory</u> treats plane electromagnetic waves incident on and scattered from homogeneous dielectric spheres described by a size parameter $x = 2\pi a/\lambda$ and a complex index of refraction m. Scattered fields are determined from solutions of Maxwell's equations with boundary conditions consisting of continuity of field vector components at mathematical discontinuous boundaries [K7]. The resulting expressions for the angular intensity distributions for the two polarizations are:

(41) $i_1(x, m, \theta) = i_2(x, m, \theta)$

These are infinite series whose terms are functions of spherical Bessel and Le Gendre polynomials. The response R of a light-scattering instrument in terms of i_1 , i_2 , $f_S(\lambda)$ (the source spectral emission function), $f_d(\lambda)$ (the detector spectral sensitivity function), $f_g(\theta, \phi)$ (the source-particle-detector geometry function), and k (a scale factor) is:

(42) R(m, x,
$$\theta$$
, ϕ , λ ,) = kf_s(λ)f_d(λ)f_g(θ , ϕ)

 $x (i, (m, \theta, x) + i_2(m, \theta, x)).$

While classic texts such as those by Born and Wolf [B11], Kerker [K7], and Van de Hulst [V4] show the behavior of scattering functions from Mie theory calculations for many values of the parameters m, θ , λ , and x, particle size measurements based on such calculations have serious practical limitations. First, they apply only to spheres; second, they apply solely to collections of identical spheres; third, they predict angular intensity from known index and size parameters, not vice versa; and finally, they require extensive computer calculations to numerically evaluate the series.

As a result of this latter condition, particle-size determination via Mie theory has been done in a number of ways: the most common being manual-visual matching, with interpolation, of experimentally-measured intensity curves against theoretical curves such as those in textbooks [V4] or instrument-manufacturers catalogue of curves [W5]: similar matching against individually calculated curves with best-guess input values of m and x: and computer best-fit determinations [R10].

In the evaluation of the results of the particle size determination via the Mie calculations, a number of factors have been pointed out and examined as sources of systematic error. An important source is the effect of particle non-sphericity and this subject has been extensively treated theoretically and experimentally for the cases of ellipsoids, oblate and prolate spheroids [A6, L3, L5, L7, C14, C16, W16]. The effect of a finite width of size distribution [W5] and the assumed shape of the distribution [W3, C11] has been examined, while an effect of finite detector acceptance angle has been calculated and compared using experimental results [R10].

3.B.3. Automatic Counting (and Sizing) of Particles.

a. Particle counters

The capabilities of automatic liquid-borne particle counters for providing fast, explicit histogram measurements of particle sizes over ranges of about 5 μ m up to 100 μ m makes them attractive as candidates for comparison calibrations of standard particles such as latex spheres and glass microbeads. Both types, optical and electrical-resistance, have comparable basic capabilities although they differ significantly in specifics. Commercially available instruments are described by Allen [A3], Davies [D8] and Willeke [W10].

Electrical-sensing-zone (or electrical resistance) particle size instruments, based on the original device by Coulter [C25], measure an effective particle volume in terms of a change in resistivity of an electrolyte from which some fraction is displaced by the particle. In a first-order model [A3], the change in resistance due to the presence of a particle in the orifice of the device can be expressed in terms of the resistivities of the electrolyte fluid $_{\rm e}$ and the particle $_{\rm p}$, the cross-sectional areas of the aperture A_a and the particle A_p, and the effective fraction of the particle dimension $_{\rm e}$ subtended by the aperture. This change in resistance is given by [A3]:

(43)
$$\Delta R = \frac{\rho e^{A_p}}{A} \left(1 - \frac{\rho e}{\rho_p}\right) \frac{1}{\{1 - (1 - \rho_e/\rho_p)A_p/A_s\}}.$$

According to Allen, terms ρ_e / ρ_p can be neglected since, in practice, the response is independent of the resistivity of the particle. The equation above then reduces to

(44)
$$\Delta_{R} \cong \left(\frac{\rho}{A_{a}^{2}}\right) \times (A_{p} \delta 1) \times 1 - \frac{A_{p}}{A_{a}}$$

or

(45) R ~ (particle volume) x l
$$-\left(\frac{A_p}{A_a}\right)^{T}$$

The magnitude of the deviation from a straight volume proportionality is shape- and size-dependent, causing a 6% effect for rod-shaped particles as well as a 5.5% error for large spherical particles ($D_p \ge 0.4$ D aperture) [A3].

Characteristic precisions, attributed to such instruments by their manufacturers and evidenced by round-robin intercomparison [ASTM Circular C690], include repeatabilities of $\pm 1\%$ (at 95% confidence, for all size levels) and reproducibilities of $\pm 3\%$. As mentioned earlier, the literature on the technique, its systematic effects, and error sources is extensive, with Allen's treatment [A3], the manufacturer's technical literature including the Coulter, Inc. bibliography, and other sources [S10, D8-13], providing input.

Optical particle counters vary in the way they measure particle dimensions, although many are characterized as measuring some projected area [Gl, D8]. Using more than fifty literature citations, Willeke and Liu [W12] identify laboratory prototype and commercial devices, discuss them in terms of the effects of angular geometries, theoretical response calculations, calibration techniques, sampling efficiency, particle shape and refractive index, counting accuracy, coincidences, pulse processing, and size resolution.

In general the response R of most optical counters can be described formally as an integral over the instrument geometry, its spectral response f_s and the Mie scattering functions and their variables as described in Section 3.B.2.b. such that:

(46)
$$R(\mathbf{m}, \mathbf{x}) = \iiint [kf_{S}(\lambda)f_{g}(\theta, \phi) \\ \times (i, (\mathbf{m}, \theta, \mathbf{x}) + i_{2}(\mathbf{m}, j, \mathbf{x}))]d\theta d\phi d\lambda.$$

Resulting theoretical response functions for specific optical counters are given in graphs, discussed, or cited in the literature by Willeke [W12]. Two instruments described by Gebhart [G1] are relatively representative of the basic capabilities. One instrument, designed for particles small compared to the wavelength of light, uses a laser source and near-forward collection described as giving a volume-equivalent size independent of shape but dependent of the index of refraction in a scaling-factor type behavior; the second instrument, for particles large in comparison to wavelength, uses a white light source and low-angle collection described as giving a projected area size independent of both shape and index of refraction. A major reason for using white light is to average out the theory-based oscillations in instrument response to monochromatic light which can give apparently multivalued particle size [G1, B12]. The laser instrument is described as being able to measure particles over the size range 0.05 μ m to 0.7 μ m with an uncertainty of 2%; the white light instrument's range is given as 0.7 to 6 m [G1]. A new addition to the field is a commercial optical aerosol size instrument which masks and measures segments of the Fraunhofer diffraction pattern to obtain second, third and fourth power of radius dependence [W18].

Some of the more apparent potential sources of systematic error in flow-through particle counters as reported in the literature are common to both optical and electrical-sensing types. Among these are errors in accurately counting and characterizing the whole particle

population distribution due to, for example, more than one particle in the sensing zone (coincidence), electronic noise, preferential sampling of sizes, non-discrimination of debris or agglomeration, finite-width size-interval channels, and a fine size lower detection limit.

Other potential sources of systematic error in flow-through counters are specific to the type. Among those for electrical sensing instruments, for example, are finite size of particle relative to aperture dimensions and pulse-shape dependence on wall-proximity effects. Potential error sources specific to optical counters are possible non-unique response as a function of particle size and unaccounted for dependence on particle shape or index of refraction. In comparisons of measurements by the two devices, there is the difference in volume-versus-area (or other power of radius) dependence. Some of the more apparent sources of systematic error are reported in the literature.

b. Image analyzers

Image analyzers, as adjuncts to optical or electron microscopes, can provide some degree of automatic counting and sizing of the magnified images from the microscopes. Like flow-through particle counters, they allow explicit histograms of particle size distributions to be derived from counts of individual particles of measured sizes. There are two major types of image analyzers, and they are distinguished by their basic method of measuring image size and the degree of automation in the process; in the first type of image analyzer, operator judgment is the basis of size measurement, while in the other type, the decision is machine-made.

Projected-spot image analyzers are machine-assist devices which project a variablesize light spot onto a photographic print or negative and record the aperture size corresponding to the one which the operator decides gives the best fit between the size of the projected spot and the photographic image of the particle. The device is a conventional means of semi-automatically sizing and counting images of particles on TEM plates or optical microscope photos and has been applied to the sizing of latex spheres [A5, B3, C3, D3].

The second type of image analyzer is a machine-decision device and includes both digital computer-based and analog circuitry-based image processing. For either one, there are two types according to whether the image produced by the microscope is measured directly or whether the image is photographed and the photographic image is measured. Image analyzers of each type are available commercially, and their application to particle size measurement has been discussed in the literature [A3, D11-14, S10].

The relationship of image analyzers of various types to each other and to other ways of measuring the size of microscope images of particles is shown in Figure 2. Starting with particle, (A), as an object, the figure shows that the image, (B), produced by the electron or optical microscope can be processed one of three ways. In an optical microscope, the image can be viewed (C) by eye directly and the size of the light image measured with a visual eyepiece such as a reticle, a movable cross-hair filar, or an image-splitting (shearing) device. It is also possible to photograph the light image (D) and scan it by a photodetector (E). In an electron microscope, the electron beam image can be recorded directly onto a photographic plate, as in a TEM, collected to produce an image on a CRT which is in turn photographed (D), or collected for electronic processing (E).

Whether the images are recordings of the light in an optical microscope, the electrons in a TEM, or the light from the CRT screen of an SEM, photomicrographs (D) can be analyzed in one of two ways. They can be viewed (F) under low-power optical magnification and measured as in (C), a project-spot can be matched to the image size as discussed previously, or the photographs can be reimaged and scanned with a photodetector (G). A vidicon as a detector can be used to produce a TV image which has a movable electronic-crosshair for visual settings (H), or a vidicon, together with an apertured photomultiplier, a diode array, or other photodetector can be used to generate digitized or analog waveforms for a machine-based judgment of image size (I). This process, which eliminates the operator's subjective judgment of image size, can be applied directly to the original microscope image (as opposed to the photographed image), as in E to I.



Figure 2. Alternative Ways of Mesuring the Size of an Image

Systematic errors related to different edge-location criteria and related effects were discussed earlier, and image-analyzers are also susceptible. Since the effects depend on the relation of the edge-region to the image as a whole, they can be relatively independent of the microscope magnification and are observed over a range of particle sizes. For 3 μ m latexes, the manufacturer reports that TEM measurements using a projected-spot analyzer differ by about 0.5 μ m or about 20% from those obtained using a reticle directly on the TEM plates [B3]. For 0.25 μ m latexes, another manufacturer's laboratory reports difference up to 0.05 μ m or about 20% for the same two techniques [D3], depending on the size and polarity (clear spot on opaque background or vice versa) of the images processed by the analyzer. Similar systematic differences among filar, image-shearing, and TV-microscope systems, as well as a discussion of polarity-dependence, have been reported for the related case of planar objects, where differences on the order of 0.25 μ m for measurements directly on the light images of 1, 3, and 10 μ m objects were observed [S11, S12].

Two methods of overcoming the arbitrariness of such systematic differences have been reported. For TEM measurements on the 0.25 μ m latexes, the reticle measurements were reported as producing the best agreement between the TEM results and those from other unspecified methods [D3]. For optical microscope measurements on clear and opaque planar objects, no one optical method other than photometric scanning using, for example, a theoretically-predicted threshold on the image for object-size determination, was found acceptable and free from large systematic error [N5, S11].

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This brief examination of automatic particle counting techniques, especially those of flow-through counters, follows a similar examination of light-scattering and electron microscopy techniques. Each has strengths and weaknesses which complement the other two. Taken together, the three provide an attractive scheme for primary and secondary calibration of microscopic particle size reference materials, especially standard spherical particles such as polymer and glass microspheres.

Electron microscopy with its unambiguous, high-resolution, high depth of focus imaging, can yield precise and potentially accurate dimensional measurements on individual particles, in vacuo, and explicitly differentiates among particles of different shapes and morphological composition. Light-scattering can determine mean size of narrow-distribution spherical particles in their original liquid environment, averaging over many particles more or less instantaneously. Flow-through counters can provide histograms of distributions as verification of the validity of the assumptions made in light-scattering as well as rapid comparison calibrations of particles of unknown size against particles of known size as determined by electron microscopy and light-scattering taken together.

With this potential complementary relationship of electron microscopy, lightscattering, and flow-through counting as a back-drop, Part 4 of this report presents reported intercomparison measurements by these techniques on polymer spheres. As was noted in the introduction to this report, in order to best understand the behavior of a measurement technique itself, the object-to-be-measured should be as simple and lacking ambiguity as possible. Polymer spheres are in general highly spherical and therefore susceptible to dimensional characterization by a single number, the diameter; further, the distribution of sizes in a population can be very narrow (1%); and the spheres are assumedly dimensionally stable under a variety of handling conditions and over time. Further, the latex spheres marketed by Dow [B2, B3] over a period of two and nearly three decades have been measured using the same basic technique and even the same people [B16, R10]. This history has provided a metrological baseline for detailed comparisons of measurements over a range of particle sizes from <0.1 μ m, most often to 1 μ m, but ranging up to as much as 100 μ m. This next section looks at the results of measurements on these materials, specifically the mean particle size of a number of Dow latexes as determined by different techniques. From these data, conclusions are drawn about the techniques and the materials themselves, and these conclusions are summarized in the fifth and final section of the body of this report.

4. INTERCOMPARISON OF MEASUREMENTS

This section of the report summarizes and discusses results of particle-size measurements by a number of techniques on polymer spheres, primarily Dow latex spheres, over a range of sizes from 0.08 μ m to 3 μ m or more. In most cases, the results are given in tables of mean diameter measured by one technique versus mean diameter measured by a second technique. The second technique is usually that of electron microscopy and is performed by the manufacturer of the polymers. Also given in most tables are the incremental- and percent fractional-differences between the apparent diameters measured by the different techniques. In order of presentation, the tabular data deal first with an overviewcomparison of results for six latexes which span the range of sizes, then with flow-through counter results, followed by light-scattering results, and finally with electron microscopy measurements.

A. Comparisons of Latex Particle Measurements.

4.A.1 Specific Results Compared

Polymer spheres, especially Dow latexes, have been measured independently by various techniques and workers. They have especially desirable properties, which include a high order of sphericity, narrow size distribution, and, in many cases, a nominal size measured by the manufacturer, quoted, and assumedly accurate to hundredths or even thousandths of a micrometer (the implied accuracies are in range 0.01 to 0.001 μ m) [B16].

In order to provide some estimate of the scatter among results by different techniques, Tables 6 through 11 show redrafted published compilations of mean diameters of six Dow latexes as measured by various techniques. The measurement methods include those of electron microscopy, light scattering of a number of types, and other specific techniques as indicated. Inspection of the individual tables indicates a relatively wide variation among reported values. As a basis for comparison without selecting or excluding values, the following table gives (in rounded-off numbers) the average of the values in each table, the number which constitutes the average, the RMS (root-mean-square) average deviation in μ m and percent, and the range of values in μ m and percent.

Mean	Number in	Avera	ge	Rang	e of
Value	Average	Devia	tion	Val	ues
(µm)		(µm)	(%)	(µm)	(%)
3.02	12	0.048	1.6	0.08	2.6
2.70	5	0.013	0.5	0.03	1.1
1.18	16	0.058	4.9	0.26	22
0.80	9	0.033	4.1	0.09	11
0.025	16	0.008	3.2	0.026	10
0.078	6	0.005	6.4	0.014	18

Some general observations about the data in Tables 6-11 can be made based on the summary table, above. First, for the four latexes with mean diameters of less than 1.2 μ m, the average deviation (which describes the spread of the results from the various techniques) is on the order of 5% and the range is on the order of 15%; as for random variations, the range of ten measurements here is about three times the average deviation [Appendix F]. Second, while there are large variations from the behavior for the smallest and largest latexes, the average deviation is very comparable to the standard deviation of the particle distributions for the latexes (as determined by electron microscopy measurements of the manufacturer, see p. 7 of the report). Third, a cursory inspection shows no readily apparent systematic relationships as, for example, between the electron microscopy and light scattering values. Finally, the data alone does not suggest which if any method is more definitive.

Table 12 shows a compilation of some other latexes for which one or more measurements besides the manufacturer's have been reported. Again, no readily apparent systematic behavior is present. Later, it will be seen that where published data has

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Diameter of Dow Latex LS-1358-38 Spheres Measured by Various Workers [Ref. K10]

Measurement Method	Mean Diameter (µm)
Microscopy Electron Optical	2.958a 3.075b 3.036¢ (See Array)
Angular Light Scatter Indiv. particles Collections	3.011 ^e (Dry)
Light Scatter Other	2.96f 2.975f 3.02d
Flow-Through Resistance Light Blockage Light Scatter	3.128 ^c
Array Length-Count Diffraction	3.00b 3.02f (Dry) 3.03b 3.04f (Dry)
Centrifuge Spiral Ultra	
Sedimentation	
Turbidity/Extinction	
a. Dow quoted Ref. K10 b. Krieger, O'Neill 1968 [Ref.K10] c. Davidson, et al. 1967 [Ref. D6]	d. Wallace, Kratohvil [in Ref. W6] e. Marshall, et al. 1976 [Ref.M1] f. Robillard,Patitsas 1973 [Ref. R5]

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Diameter	of	Dow	Latex	(LS-642-6)) Sphei	res
Measu	ire	1 by	Variou	is Workers	[Ref.	R4]

Measurement Method	Mean Diameter (µm)
Microscopy Electron Optical	2.682* (See Array Count)
Angular Light-Scatter Indiv. particles Collections Light Scatter Other	2.714 2.696
Flow-Through Resistance Light Blockage Light Scatter	
Array Length-Count Diffraction	2.708 (Dry) 2.688 (Dry)
Centrifuge Spiral Ultra	
Sedimentation	
Turbidity/Extinction	
* Attributed to Dow	

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	u D		

Diameter of Dow Latex LS-1028-E Spheres Measured by Various Workers [Ref. R10]						
Measurement Method Mean Diameter (µm)						
Microscopy Electron Optical	1.10 ^a].]9a	1.18 ^b	1.17 ^c	1.16 ^d	1.26 ^e
Angular Light-Scatter Indiv. particles Collections	1.20f 1.20i	1.209 1.21j	1.19h			
Light Scatter Other	1.20j					
Flow-Through Resistance Light Blockage Light Scatter	1.21 ^b					
Array Length-Count Diffraction	1.20k					
Centrifuge Spiral Ultra	1.22 ^e 1.00 ¹					
Sedimentation						
Turbidity/Extinction						
X-Ray Scatter						
 a. Bradford 1979 [Ref.R10] b. Davidson, et al. 1967 [Re c. Porstendorfer 1971 [Ref.] d. Heard, et al. 1970 [Ref. e. Stober, Flaschart 1971 [f. Phillips, et al. 1970 [R 	g. f. D6] h. R10] i. H4] j. Ref.R10] k. ef.R10] l.	Gucker, Marshal Wims, M Rowell, Bierhui Van der [Ref.R]	et al. l, et a Meyer 19 et al. izen, Fe n Hul., 10]	1973 [al. [in 972 [Ref [Ref.F erron 19 Vanderh	Ref.R10 Ref.M1 .R10] 10] 975 [Ref noff 197)]] f.R10] 71

Tab	le	9
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Diameter of Dow Latex 449E Spheres Measured by Various Workers [Ref. C23]

Measurement Method Microscopy Electron Optical Angular Light Scatter Indiv. particles	Mean Diameter (µm)				
Microscopy Electron Optical	0.796ª	0.777b	0.765c	0.850d	
Angular Light Scatter Indiv. particles Collections	0.784e 0.797e	0.764 ^e 0.773 ^f			
Light Scatter Other					
Flow-Through Resistance Light Blockage Light Scatter	0.849C				
Array Length-Count Diffraction					
Centrifuge Spiral Ultra					
Sedimentation					
Turbidity/Extinction					
X-Ray Scatter					
a. Attributed to Dow b. Robbins, Jizmagian 1966 c. Davidson, et al. 1967 d. Cooper, Parfitt 1968	e. Cook f. Krat	e, Kerker ohvil, Wa	1973 11ace 1973	3	

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Diameter of Dow Latex LS-057-A Spheres Measured by Various Workers [Ref. K10]

Measurement Method	Mean Diameter (µm)			
Microscopy Electron Optical	0.264a	0.262 ^b	0.262 ^c	0.245d
Angular Light Scatter Indiv. particles Collections	0.242e	0.245f	0.2459	0.25h
Light Scatter Other				
Flow-Through Resistance Light Blockage Light Scatter	0.238i	0.244i		
Array Length-Count Diffraction				
Random Diffraction				
Centrifuge Spiral Ultra				
Sedimentation	0.248j			
Turbidity/Extinction	0.245 -	0.259k	0.2491	
X-Ray Scatter	0.254m	0.248n		
 a. Bradford 1955 [Ref.B16] b. Dobbins 1966 [Ref.D20] c. Davidson, et al. 1967 [Ref. D6] d. Davidson, Haller 1974 [Ref. D3] e. Kratohvil, Wallace 1970 [Ref.K12] f. Querfeld, et al. 1972 [Ref.K10] g. Dezelic, Kratohvil 1961 [Ref. D19] 	h. Jenni i. David j. McCon k. Bater 1. Deze m. Bonse n. Brady	ings, Plun dson, et a rmick 1964 nan, et a lic, et a e, Hart 1 7, Gravat	nmer 1968 al. 1971 4 [Ref.K10 1. 1963 [1 1. 1963 [1 966 [Ref.H t 1971 [Ref.H	[Ref.K10] [Ref.D5] D] Ref.K10] Ref.D18] K10] ef. K10]

Table 11

Diameter of Dow Latex LS-040-A Spheres Measured by Various Workers [Ref. D3]			
Measurement Method	Mean Diameter (µm)		
Microscopy Electron Optical	0.088a 0.078b		
Angular Light Scatter Indiv. particles Collection	0.076 ^c		
Light Scatter Other			
Flow-Through Resistance Light Blockage Light Scatter	0.074 ^d		
Array Length-Count Diffraction			
Centrifuge Spiral Ultra			
Sedimentation	0.074 ^e		
Turbidity/Extinction			
X-Ray Scatter	0.078f		
a. Bradford 1955 [Ref.B16] b. Davidson, Haller 1974 [Ref. D3] c. Kratohvil, et al. [in Ref. D3]	d. Davidson, Collins 1972 [in Ref. D4] e. McCormick 1964 [in Ref. D3] f. Bonse, Hart 1966 [in Ref. D3]		

allowed comparisons of the same individual techniques over a series of latexes of different sizes, systematic differences are manifest. In the next three sections, illustrative comparisons are made for resistive-counters, light-scattering, and electron microscopy.

a. Resistive Counter Measurements

Most flow-through particle counters are comparators which can provide precise measurement of particles of unknown size relative to particles of known size against which the instruments are calibrated. Tables 13-18 show reported results for measurements made on polymer spheres with flow-through counters or calibrated against other such spheres. These tables are included here as a sampling of the levels of agreement that have been observed and reported for such measurements.

Tables 13-16 are extracted from one study involving polymer spheres from three suppliers, two different resistive-type counters, and a special electron microscopy technique [A5]. (As noted earlier, the special technique involves measurement of the shadow, through an opening in a metal film, cast by a particle as a result of metal vapor deposition [C9, C20, D5]). Over the range 0.8μ m to 11.5 μ m of the six latexes in Table 13, the resistive counter measurements agree with the special electron-microscopy measurements to within $\pm 5\%$ or so, with an arithmetic average deviation of $\pm 0.25\%$ and an RMS average deviation of 4.3%. Some hint of systematic effects appear in the correlation of the error sign with latex source for two of the three cases; these apparent incremental differences also appear in Table 14 for two other latexes. Over the same range, $0.8 \ \mu$ m to 11.5 μ m of latexes, in Table 15, a second resistive counter's measurements agree with the special electron micro-scopy measurements within 5\% or so, with an arithmetic average difference of -1.2% and an RMS average deviation of 3%.

Direct comparison of the two counters for four latexes over the 0.8 μ m to 11.5 μ m range in Table 16, shows agreement within 5% or so, with an arithmetic average deviation of 0.25% and an RMS deviation of 3.2%. Differences this large exceed the precision reported to be characteristic of the devices themselves. For comparisons of the same types of counters, repeatabilities of 1% (95% confidence) and reproducibilities of 3% (95% confidence) are reported (ASTM circular C90), such agreement being consistent with results in Table 17 for one company's comparison of instruments at sites in three countries. For the 6.6 μ m latex shown, the three instruments produced results which agree with an RMS deviation of 0.9% on median size. (They also agree with an RMS deviation of 2% on the size distribution index D84/D50, which is the ratio of the size greater than that of 84% of the population to the size greater than 50%).

b. Optical Microscope Measurements

In tables 18-23, measurements on polymer spheres made by three different optical microscope techniques are compared with other methods. In Table 18, the comparison is for some large (10 μ m to 20 μ m) DVB latexes and is between flow-through counter measurements and optical microscope/projected-spot analyzer measurements [A5]. Here the difference is clearly systematic, with the optical microscope measurements always exceeding the counter measurements by 2 to 11%, corresponding to 0.3 μ m to 2.5 μ m.

Table 19 shows results for nominally 5, 10, and 20 μm DVB latexes using visual imagesplitting optical microscopy, visual array-counting optical microscopy, and scaled-photography scanning electron microscopy [S5]. With observed variations on the order of 0.2 μm for both the visual eyepiece and SEM measurements and 0.5 μm for the array count, the 0% to 6.5% differences between entries is on the order of the combined uncertainties and is apparently non-systematic.

While the optical microscope-vs-electron microscope comparison for large spheres in Table 19 shows some level of agreement, a more detailed and precise comparison for small spheres [C8, C9] given in Table 20 shows large systematic disagreement. Table 19, which applies to wide-distribution DVB latexes from 5 to 20 m in size, shows optical microscope measurements (with an image-splitting eyepiece) within +0.3 μ m of some (scaled photograph) SEM measurements. Table 20, which applies to narrow-distribution PS latexes from 0.5 to 3.5 μ m in size, shows (using a filar eyepiece) optical microscope measurements differing

	Mean Particle Size of Ten Dow Latexes by Various Methods						
Des	Latex signation	Value Attributed to Dow EM		Value By Re	Various lated Tec	Scatterin hniques	g
LS-	-1132-B	0.091		0.085a	(0.094R)*	b	
LS-	-055-A	0.188		0.171FC	0.175Ld		
LS-	-1047-A	0.234		0.210Xe			
LS	-1010-E	0.357		0.343R ^a			
LS-	-06-A	0.365		0.339Lf	0.342H9		
LS	-15N-8	0.511		0.503Lh	0.515H9		
LS-	-06-A	0.557		0.537Lh	0.594FC	0.561H9	
LS-		0.822		0.82Ai	0.80Zi		
LS-	-113-В	1.011		1.04A ⁱ	1.02Z ⁱ		
LS-	-067-A	1.171		1.120L ^h	1.136Lj	1.146L ^k	1.160L9
LS-	-464-E	1.305		1.276Lh	1.242FC		
R: F: L: X:	R: Rayleigh linewidth F: Flow microscopy L: Angular light scatter X: X-Ray scatter		H: Z: A: *:	Higher-o Various Array Ambiguou	order-Tynd settling s value	all	
a. b. c. d. e.	a. Lee, et al. 1972 [Ref.L13]. b. Gulari, et al. 1979 [Ref.G10]. c. Davidson, et al. 1967 [Ref. D6]. d. Dezelic, et al. 1963 [Ref.D18]. e. Hachisu, S. 1976 [Ref. H2].		f. g. h. j.	Davidson Pierce, Wallace, Ferron l Rowell,	, Haller Maron 196 Kratohvi 975 [Ref. et al. 19	1974 [Ref 4 [Ref. P 1 1972 [R F3]. 67 [Ref.R	. D3]. 4]. ef. W3]. 10].

Table 12

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Latex Source	Shadowed TEM Value	Coulter Counter Value	Difference µm %	
Coulter	0.84	0.80	-0.04	-5.0
Coulter	1.31	1.35	+0.04	+3.0
Dow	1.81	1.90	+0.09	+5.0
Dow	3.36	3.54	+0.18	+5.4
Duke	5.10	4.89	-0.21	-4.3
Duke	11.55	11.26	-0.29	-2.5

Mean	Particle	Size	of	Some	Star	ndard	Polymer	Spheres	
by	/ Shadowed	d TEM	and	d Cou	lter	Count	er [Ref.	A5]	

Table 13

Mean Particle Size of Two PVC Latexes by Shadowed TEM and Coulter Counter [Ref. A5]						
Latex	Shadowed TEM Value	Coulter Counter Value	Diff µm	erence %		
PVC	0.87	0.99	+0.08	10.7		
	0.98	1.09	+0.10	15.9		

Table 1	4
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Tabl	e	15
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by EM and Celloscope [Ref. A5]						
Latex Source	Shadowed TEM Value	Celloscope Value	Diff µm	erence %		
Coulter	0.84	0.82	0.02	2.5		
Coulter	1.31	1.28	0.03	2.3		
Coulter	3.59	3.45	-0.14	-3.9		
Duke	3.63	3.45	-0.18	-5.0		
Duke	5.10	5.00	-0.10	-2.0		
Duke	11.55	11.45	-0.10	-0.9		

Mean Particle Size of Some Standard Polymer Spheres by EM and Celloscope [Ref. A5]

Table	16

Mean Particle Size of Some Standard Polymer Spheres by Coulter Counter and Celloscope [Ref. A5]					
Latex Source	Coulter Counter	Cello- Scope	Diff µm	erence %	
Coulter	0.80	0.82	+0.02	2.5	
Coulter	1.35	1.28	-0.07	-5.2	
Duke	4.89	5.00	+0.11	2.2	
Duke	11.26	11.45	+0.17	1.5	

Table 17

Intercomparison of Coulter Counters in Round-Robin [Ref. A5] (µm)					
Location	D ₅₀	D ₈₄ /D ₅₀	D ₈₄	σ	
USA	6.6	1.35	8.90	2.31	
GB	6.7	1.34	8.98	2.28	
GDR	6.6	1.30	8.58	1.98	

Table 18

Sizes of Some DVB Latexes by Various Techniques [Ref. A5]				
Image-Analyzer Optical Microscope	Coulter Counter	Diffe µm	rence %	
10.2 µm	9.9 µm	+0.3	2.9	
13.4	13.1	+0.3	2.2	
22.9	21.9	+1.0	4.4	
22.2	19.7	+2.5	11.3	

Table 19

Sizes of Some DVB Latexes ^b y Various Techniques [Ref. S5]			
Visual-Eyepiece Optical Microscopy	Array Count	Scanning Electron Microscope	
5.1 <u>+</u> 0.2 µm	5.1 <u>+</u> 0.5 μm	5.2 <u>+</u> 0.2 μm	
10.2 <u>+</u> 0.1	10.4 + 0.1	10.5 <u>+</u> 0.1	
19.7 <u>+</u> 0.1	20.8 <u>+</u> 0.5	19.5 <u>+</u> 0.2	

Latex Designation	Electron Microscope*	Optical Microscope (Filar)	Difference (µm)
LS-057-A	0.264	0.466	0.202
LS-061-A	0.365	0.576	0.211
LS-15N-8	0.511	0.824	0.313
LS-063-A	0.556	0.818	0.362
LS-066-A	0.814	1.181	0.367
LS-067-A	1.171	1.553	0.382
LS-886-43	1.83	2.7	0.340
LS-?	2.79	3.49	0.70

Mean Particle Size of Seven Dow Latexes ^by Filar-Eyepiece Optical Microscope and Electron Microscope [Ref. C9]

Table 20

*Note: Presumedly Dow latexes of these designations; author identifies them only as polystyrene spheres and gives the values here associated with Dow EM.

lable Li	Ta	b	le	21
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	TEM and Optical Array Values of Some PVC Latex Sizes [Ref. D7]		
TEM-Image of Shadow	Optical Array	Differ µm	rence %
0.484	0.491	-0.007	- 1.5
0.503	0.510	-0.007	- 1.3
0.662	0.694	-0.032	- 4.8
0.868	0.991	-0.123	-14.1
0.938	0.996	-0.058	- 6.2
0.976	1.03	-0.058	- 5.5

Т	ah	10	22
	aυ	1e	<u> </u>

TEM-Measured Metal-Vapor Shadowed PVC Latex Particles [Ref. D7]			
Size of Images of Shadows	Size of Images of Particles	Differ µm	ence %
0.198	0.166	-0.032	16.2
0.200	0.161	-0.039	19.5
0.662	0.560	-0.102	15.4
0.938	0.773	-0.165	17.6
0.976	0.816	-0.160	16.4
Table 23

Sizes of Some DVB Latexes by Various Techniques [Ref. T1]					
TEM Images of Shadows	TEM Images of Particles	Differe µm	nce %		
0.43	0.35	0.08	18.6		
0.54	0.37	0.17	31.5		
0.70	0.52	0.18	25.7		
1.20	0.91	0.29	24.2		

systematically from ± 0.2 to $\pm 0.7 \ \mu m$ from (replica-grating) TEM measurements. In this latter case, the largest portion of the sytematic difference is attributable to error in the optical measurements which are due to, first, edge-location effects and, second, limiting resolution [C8, N5, S11-12]. An application of the array-counting technique to overcome these limitations is illustrated in Table 21 [D7]. Here special TEM measurements and optical array measurements on 0.5 to 1 μm latexes agree within 0.01 to 0.1 μm or so.

The special TEM technique of Table 21 is the vapor-shadowing one briefly described earlier. In this technique, an anticipated change in particular diameter due to shrinkage upon exposure to the electron beam is avoided by measurement of the diameter of the shadow of the particle produced by metal vapor deposition prior to electron irradiation. Table 22 shows the apparent diameters of the particles and their shadows for five PVC latexes [D7]; the shadow diameters are larger by a fairly consistent 17%. Table 23 shows similar data for four DVB latexes [T1]; again the shadow diameters are larger, this time by an average 25%. In the tables which follow, those electron microscopy (EM) measurements which use the vapor-shadow technique are indicated, and the shrinkage and compensation effects should be kept in mind when comparisons are made.

c. Various Optical Techniques versus Electron Microscopy

In the next eleven tables (24-34), the results of measurements on polymer spheres by various light-scattering-based techniques are given and, in most cases, compared with results from electron microscopy. For the majority of cases, the differences among results are sizable and, while often random-appearing, they occasionally hint at systematic behavior.

In Table 24 are results for four styrene latexes measured by EM and dark-field microscopy, a light-scattering technique using annular illumination or collection in an optical microscope-differences range from -24% to +12% with no apparent systematic behavior. In table 25, differences between disc centifuge and TEM shadow measurements range between -10% and +10%. In Table 26, results for fractional creaming [D2] are similar.

However, in Table 24, for eight of nine Dow latexes, results from the flow ultramicroscope, another type of angular scattering device, are consistently an average 8% above the TEM shadow values. A similar systematic difference which averages 9% is manifest for the light-scattering values from the higher-order Tyndall spectra (HOTS) for six PVC latexes in Table 28. (In Table 29, a few HOTS measurements on six DOW latexes do not exhibit such systematic behavior.)

Table 30 summarizes an early, pre-laser-era comparison of results from five lightscattering techniques on eleven latexes, including eight Dow latexes, and it first demonstrated probable systematic differences between results from light-scattering measurements and electron-microscopy measurements made by the latex manufacturer. The light-scattering (LS) techniques included transmittance, 90° scattering, dissymmetry ratio, polarization ratio, and location of extrema in the angular scattering patterns. Averages for the various LS techniques appear in column 8; for the eight Dow latexes, the mean LS values systematically differ from the EM values in column 2, with the EM values being greater by an average $0.016 \mu m$.

The comprehensiveness of measurements such as those summarized in Table 30 allows comparisons and conclusions which more limited data collection do not. For example, in Table 31, the few results available for Rayleigh linewidth light-scattering measurements, based on Stokes' size-dependent velocity equations rather than Mie-type scattering equations, do not show consistent behavior. Enough internal consistency among various light-scattering results does exist, however, to make averages over various LS techniques legitimate. The degree of consistency is shown in Tables 32-34 for individual latexes.

Table 32 shows the mean values at 95% confidence limits of the particle size of a nominally 0.25 μ m Dow latex using various light scattering techniques. The mean of the twelve entries for various techniques (Table 10) is 0.247 ± 0.005 μ m, a value which overlaps all but the flow ultramicroscopy values. Table 33 shows similar results for a nominal 1.2 μ m latex, with the average of seven mean LS values being 1.196 ± 0.009 μ m. Table 34 for nominal 3 μ m spheres, which have size distributions about 10% of nominal (Figure 1),

Τa	b1	e	24

Electron and Dark-Field Optical Microscopy [Ref. D2]						
Styrene Latex	Electron Microscopy	Dark Field Optical M.	Diffe µm	erence %		
\$39	0.213	0.265	-0.052	~24.4		
S39	0.126	0.140	-0.014	-11.1		
S37	0.091	0.078	+0.013	+14.2		
S36	0.074	0.065	+0.009	+12.2		

Mean Farticle Size of Some Styrene Latexes by Electron and Dark-Field Optical Microscopy [Ref. D2]

Table	25
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Some PVC Latex Sizes [D7]				
TEM Image of Shadow	Disc Centrifuge	Diffe µm	rence %	
0.0525	0.0471	0.0054	10.3	
0.0822	0.0780	0.0042	5.1	
0.200	0.215	-0.015	- 7.5	
0.285	0.289	-0.004	- 1.4	
0.484	0.543	-0.059	-12.2	
0.503	0.552	-0.049	- 9.7	

TEM and Disc Centrifuge Value of Some PVC Latex Sizes [D7]

	Τa	ЬÌ	е	26
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	TEM and Fractional Creamir of Some PVC Latex Sizes [R	g Values ef. D7]	
TEM Shadow of Image	Fractional Creaming	Differ µm	ence %
0.0525	0.0490	0.0035	6.7
0.0822	0.0840	-0.0018	- 2.2
0.200	0.195	0.005	2.5
0.662	0.770	-0.108	-16.3

Mean Particle Size of Some Dow Latexes by TEM and Light-Scatter Technique [Ref. D5,D6]					
Latex Designation	TEM-Image of Shadow	Flow-Ultra- Microscope	Diffe µm	erence %	
LS-055-A	0.177	0.171	0.006	3.4	
LS-057-A	0.262	0.280	-0.018	- 6.9	
LS-061-A	0.350	0.365	-0.015	- 4.3	
LS-063-A	0.510	0.594	-0.084	-16.5	
LS-449-E	0.765	0.849	-0.084	-11.0	
LS-464-E	1.087	1.242	-0.155	-14.3	
LS-1028-E	1.183	1.213	-0.030	- 2.5	
L6064-36	2.024	2.211	-0.187	- 9.2	
EP-1358-36	3.036	3.128	-0.092	- 3.0	

Table 27

I aD TE ZO	Τa	bl	е	28
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	TEM and Higher-Order Tyndall Spectra Values of Some PVC Latex Sizes [Ref. D7]		
TEM-Image of Shadow	Higher Order T-Spectra	Diffen µm	rence %
0.285	0.326	-0.041	-14.4
0.484	0.512	-0.028	- 5.8
0.503	0.548	-0.045	- 8.9
0.662	0.720	-0.058	- 8.8
0.868	0.953	-0.085	- 8.9
0.976	1.04	-0.064	- 6.6

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Mean Particle Diameter of Six Dow Latexes by Higher-Order-Tyndall Spectra [Ref. P4]						
Latex Designation	Value Attributed to Dow EM	HOTS* Value	Diffen µm	rence %		
LS15N-7	0.340	0.329	-0.011	-3.2		
LS-061-A	0.365	0.342	-0.023	-6.3		
LS-15N-8	0.511	0.515	+0.004	7.8		
LS-063-A	0.557	0.561	+0.004	7.2		
LS-066-A	0.814	0.799	-0.015	-1.8		
LS-067-A	1.171	1.160	-0.011	0.9		

Table 29

*Entries are single value or average of two which differ from 0.2 to 2%.

Ta	h1	P	30
īα	υı	C	20

Latex Numbers	EM Value	Light Trans	90 Scttr	Dissym Ratio	Polar Ratio	Extrm Locat	Mean LS
BASF-1**	0.037**	0.030	0.029				0.029
BASF-2**	0.047**	0.042	0.042	0.050			0.045
BASF-3**	0.072**	0.069	0.058				0.064
LS-040-A	0.088	0.076	0.073 0.074	0.078 0.080		0.076	0.076
LS-15N-23	0.138	0.120	0.118 0.120	0.124 0.120		0.118	0.120
LS-055-A	0.188	0.167	0.182 0.176	0.175			0.175
LS-057-A	0.264	0.240	0.249 0.240	0.241 0.242	0.254	0.248	0.245
LS-061-A	0.365	0.329	0.333 0.338	0.346 0.334	0.331	0.360	0.339
LS-063-A	0.557	0.522	0.526 0.537	0.552	0.534	0.531	0.534
LS-066-A	0.814	0.784	0.808 0.807	0.802 0.805	0.803	0.805 0.808	0.803
LS-067-A	1.171	1.185	1.156 1.180	1.164 1.190	1.146	1.158 1.155	1.167

Comparison of Mean Particle Diameter of Eleven Dow and non-Dow Latexes by Various Light-Scattering Techniques by Same Workers* [Ref. 19]

* Dezelic and Kratohvil 1961 [Ref. 19]

** Non-Dow latexes; all others Dow latexes with electron microscopy by Dow. Note: Second values at different wavelengths of mercury arc source (col. 4,5) or different angular widths of the detector acceptance aperture (col.7)

Ta	b1	le	31

Mean P Line	article Size of Som width Light Scatter	e Dow Latexes by Ray and Electron Micros	leigh- copy	
Latex Designation	EM	Rayleigh Linewidth	Diffe: µm	rence %
LS-1028-E	1.192 ^a	1.20 ^b	-0.01	+0.7
LS-1010-E	0.357c	0.343c	+0.018	-3.9
LS-1047-E	0.234	[moments only]d		
LS-1132-B	0.091	0.0847 ^c	+0.063	-6.9
LS-"910"d	?0.0884d	0.0942d	+0.006	+6.6
a. Bradford 197 b. Rowell, et a c. Lee, et al.	9 in Ref. R10 1. 1979 [Ref. R10 1972 [Ref. L13]	d. Gulari, et al. e. Chu, et al. 197	1978 [Ref. (9 [Ref. C11]	G10]]

Averaged Value from	es of Mean Partic n Various Optical	le Size of Dow Latex Techniques [Table](LS-057-A D]
Method of Measurement	Number in Average	Average of Means	Tolerance of Average*
Angular Scatter	4	0.245 µm	+0.004µm
	6	0.247	+0.007
Flow Microscopy	2	0.241	+0.008
Other-Light-Type**	2	0.249	+0.001
	4	0.250	+0.006
X-Ray Scatter	2	0.251	+0.008

0.247

+0.005

Table 32

*See Appendix G for method of calculating tolerances.

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**Sedimentation and turbidity entries of Table 10.

All But X-Ray

Averaged Values of Mean Particle Size of Dow Latex LS-1028-E from Various Optical Techniques [Table 8]

Method of Measurement	Number in Average	Average of Means	Tolerance of Average*
Angular Scatter	7	1.196 µm	<u>+</u> 0.009 μm
Array Diffraction	1	1.20	
Flow Microscopy	١	1.213	
Other-Light-Type	1	1.220	

*See Appendix G for method of calculating tolerances.

Averaged Values from V	of Mean Particle : arious Optical Te	Size of Dow Latex L chniques [Table 6]	S-1358-38
Method of Measurement	Number in Average	Average of Means	Tolerance of Average*
Angular Scatter	4	2.992 µm	+0.027 µm
Array Count	2	3.010	+0.025
Array Diffraction	2	3.035	+0.013
Flow Microscopy	1	3.128	

Table 34

*See Appendix G for method of calculating tolerances.

also shows light-scattering values agreeing within about 1% at the 95% confidence level. It is the consistency of data such as these which permits combining mean values from various light-scattering techniques to obtain an aggregate "light-scattering value" of particle diameter which may be compared, as it later will be, with an electron microscopy value. In the next eight tables (35-42), the internal consistency of electron microscopy results are examined.

d. Intercomparison of Electron Microscopy Results

Table 35 shows electron-microscope values of mean particle size for twenty-one Dow latexes as measured by Dow and various others with thirteen different workers. For latexes nominally 0.09 μ m to 3.5 μ m in size, the results differ from -7% to +16% and -0.08 μ m to +0.22 μ m. Of the thirty-six entries in Table 35, the differences between the size attributed to Dow EM and those of others is negative in only six of the thirty-six. Thus, there is a suggestion that the mean diameters as measured by Dow are systematically higher than those by other EM workers. In the next five tables, comparisons are made between results of Dow and those of four other workers for a series of latexes over a range of sizes.

Table 3 shows EM results for nine Dow latexes from Dow EM measurements and as measured by Davidson, et al. [D5, D6]. Except for three latexes where results are suspect because widely different distributions in sizes were observed (see Table 37), the six latexes have Dow EM values which are an average 0.021 μ m greater. Table 38 shows EM results for another group of nine Dow latexes in a comparison of Dow results and those of Heard, et al. [H4]. Except for one of the nine latexes, the mean particle diameters attributed to measurements by Dow are greater by an average of 0.02 μ m. While the measurements on six latexes by Dobbin in Table 29 show three values which are greater than Dow and three which are less, the results on four latexes by Davidson and Haller in Table 40 are less than the Dow values by an average of 0.02 μ m.

The likely cause of systematic differences in the measurements of mean particle size by various electron microscopy groups lies in the edge-location aspect of dimensional measurements by imaging techniques as discussed earlier. The effect of choosing, explicitly or implicitly, a different relative intensity level on an image intensity profile is shown in Tables 41 and 42. Table 41 shows that the apparent size of a nominal 0.25 μ m particle imaged with a TEM varies by up to 20% depending on the method used to measure the size of the image on the plate: with a filar eyepiece or an image analyzer, and whether directly on the plate, a contact print, or an enlargement photo. Analogously, Table 42 shows that the apparent size of a nominal 3 μ m particle imaged with a TEM varies by up to 30% depending on whether a reticle eyepiece or projected-spot analyzer is used to measure the size of the image. With these potential effects as background, the final five tables (43-47) show comparisons between various light-scattering and electron microscopy results for a number of Dow latexes.

4.A.2. Generalizations from Comparisons

Table 43 is a compilation of electron microscopy and light-scattering results for twenty-five Dow latexes covering a range of sizes from nominally 0.09 μ m to 3.5 μ m. In columns 2 through 4 are given mean particle diameters for the latexes as attributed to Dow's electron microscopy measurements as an average electron microscopy measurements by other groups, and as an average of various light-scattering techniques. Where averages are given, the number of means averaged, the average mean, the 95% confidence limits, and the source tables are indicated. Of the twenty-five latexes, twenty-one have two or more independent electron microscopy measurements, fifteen have light-scattering measurements, and ten have two independent electron microscopy measurements as well as light scattering measurements. In Table 43, comparison of the Dow EM and other EM entries indicates that in sixteen of the twenty-one cases, the Dow value is greater than the other.

In the next two tables, comparisons are made between the average light scattering results and the Dow and non-Dow EM results. Table 44 shows a comparison of Dow electron microscopy values and average angular light-scatter values for the mean particle diameter of twelve Dow latexes over a range of sizes from nominally 0.09 μ m to 1.2 μ m. In eleven of the twelve cases, the Dow EM values are greater than the light-scatter value, the average difference being 0.014 μ m. Table 45 shows a comparison of non-Dow electron microscopy

Table 35

Electron-Microscope Values of Mean Particle Size of Some Dow Latexes by Various Workers

Latex	Size Attributed	Size By	Differ	rence
Designation	to Dow EM	Others EM	μm	%
LS-040-Aa	0.088	0.078b	0.01	11.3
LS-1132-B	0.091	0.085k	0.01	6.9
LS-1044-E	0.109	0.100e	0.01	8.3
LS-052-A	0.126	0.119 ^c	0.01	5.6
LS-1045-E	0.176	0.16 ^e	0.02	9.1
LS-055-A	0.188	0.177d	0.01	5.9
LS-1047-E	0.234	0.22e	0.01	6.0
LS-057-Aa	0.264	0.262d	0.00	0.8
	0.264	0.262 ^C	0.00	0.8
	0.264	0.245 ^b	0.02	7.2
LS-1010-E	0.357	0.343	0.01	3.9
	0.357	0.33e	0.03	7.9
LS-061-A	0.365	0.33e	0.04	9.6
	0.365	0.350a	0.02	4.1
	0.365	0.331	0.04	9.6
	0.365	0.336 ^D	0.03	8.0
	0.365	0.368C	0.00	0.8
LS-1029-E	0.500	0.50e	0.00	0.0
LS-063-A ^a	0.557	0.510a	0.05	8.4
	0.557	0.5870	-0.03	-5.4
LS-1012-E	0.714	0.74e	-0.03	-3.6
LS-449-E	0.796	0.7770	0.02	2.5
	0.796	0.7650	0.03	3.9
	0.796	0.850J	-0.05	-6.8
	0.790	0.7600	0.03	3.8
LS-1114-B	0.813	0.764	0.05	6.5
LS-1028-E	1.1921	1.183 ^u	0.01	0.8
	1.192	1.1/"	0.02	1.8
	1.192	1.105	0.03	2.1
	1.192	1.20"	-0.07	-5./
LS-464-E	1.305	1.08/0	0.22	10.8
10.005.40	1.305	1.343~	-0.04	-2.9
LS-886-43		1.012	0.00	1 2
LS-6064-36	2.050	2.024ª 2.026d	-0.03	- 2 6
LS-1358-38	2.900	3.0304	~0.08	-2.0
EP-1358-35	3.49	2.302	0.13	3./
a. Bradford, V	anderhoff 1955 [Ref.Bl6	5] h. Kerker 1	1973 [Ref.C2]	3]
b. Davidson, H	laller 19/4 [Ref. D3]	1. Bradford	1 19/9 Lin R	et.K[0]
c. Dobbins 196	6 [Ref.D20]	j. Aliet 19	1/6 LRef. A4	
d. Davidson, e	et al. 1967 [Ref. D6]	k. Chu, et	al. 1979 [R	et.UII]
e. Heard, et a	1. 1970 [Ref. H4]	I. Lee, et	al. 19/2 [R	et.L[3]
f. Claver, Farr	ham 1972 [Ref.C20]	m. Porstend	lorter 1972	
g. Cooper 1968	3 Lin hj	n. Stober,	et al. 19/1	เาก ก)

Electron-Mic	roscope Values of Me by Tw	ean Particle Size of Son vo Workers	me Dow late:	kes
Latex Designation	Dow-Bradford EM [Ref. B16]	Davidson, et al. EM [Ref.D5,D6]	Differo µm	ence %
LS-055-A	0.1881	0.1770	0.011	5.8
LS-057-A	0.2638	0.2617	0.002	0.8
LS-061-A	0.3646	0.3499	0.015	4.0
LS-063-A	0.5567	0.5101	0.047	8.4
LS-449-E	0.7962	0.7646	0.032	4.0
LS-464-E	1.3046	1.0867	0.218	16.7
LS-1028-E	(1.0992)	(1.1827)	(-0.084)	(-7.6)
	1.199*	1.1827	0.016	1.4
L6064-36	2.049	2.0240	0.025	1.2
EP-1358-36	2.9583	3.0356	-0.077	-2.6

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*Redetermination [Ref. R10]

lable s/	T	ab	le	- 37
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Latex Designation	Normal Size (µm)	Distribu Dow-Bradford 	ıtion (μm) Davidson, et al.	Ratio
LS-055-A	0.19	0.0076	0.0106	1.4
LS-057-A	0.26	0.006	0.0144	2.4
LS-061-A	0.37	0.0079	0.0198	2.5
LS-063-A	0.56	0.0108	0.0267	3.4
LS-449-E	0.80	0.0083	0.0624	7.5
LS-464-E	1.30	0.0158	0.2348	14.9
LS-1028-E	1.20	0.0159	0.636	40.0
L-6064-36	2.05	0.0180	0.1088	6.0
EP-1358-38	2.96	0.0150	0.1904	12.7

Comparison of Size Distribution Standard Deviations of Some Dow Latexes by Two Workers [Ref. D5,D6]

Tab le	38
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	Electron-Microscope Val of Some Dow Latexes b	ues of Mean Particl y Two Workers [Ref.	e Size H4]	
Latex Designation	Bradford-Dow EM	Heard, et al. EM	Diffe µM	rence %
LS-1044-E	0.109	(0.103)*	(0.006)	5.5
		0.100*	0.009	8.3
LS-1045-E	0.176	0.16*	0.016	9.1
LS-1047-E	0.234	0.22*	0.014	6.0
LS-1010-E	0.357	0.33	0.027	7.6
(LS-061-A)	0.365	(0.33)*	(0.035)	(9.6)
LS-1029-E	0.500	0.50	0.00	0.0
LS-1012-E	0.714	0.74	-0.026	-3.6
LS-1114-E	0.813	0.76	0.053	6.5
LS-1028-E	(1.099)	(1.16)	(-0.061)	(-5.6)
	1.192**	1.16	0.032	2.7

*Dimensionally measured by ratio of image size with other particles; other unstarred entries were scaled with grating replica.

**Redetermination by Dow [Ref. R10]

Tab le	: 39
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Latex Designation	Value Dow EM	Dobbins, et al. EM	Diffe≀ µm	rence %
LS-052-A	0.126	0.119	-0.007	-5.6
LS-057-A	0.264	0.262	-0.002	-0.8
LS-061-A	0.365	0.368	+0.003	+0.8
LS-063-A	0.557	0.587	+0.030	+5.4
LS-449-E	0.796	0.777	-0.019	-2.4
LS-404-E	1.305	1.343	+0.038	+2.9

Electron-Microscope Values of Mean Particle Size of Some Dow Latexes by Two Workers [Ref. D20]

T	ab	le	40

Electron-Microscope Values of Mean Particle Size of Some Dow Latexes by Two Workers [Ref. D2, D3]

Latex	Dow-Bradford	Davidson Haller	Differ	ence
Designation	EM	EM	μM	%
LS-040-A	0.088	0.078	+0.01	11.4
LS-057-A	0.264	0.245	+0.02	7.2
LS-061-A	0.365	0.336	+0.03	8.0
LS-449-E	0.796	0.760	+0.04	3.8

10010 11	Τ	ab	le	41
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Meth	Method of Sizing Image on TEM Plate [Ref. D3]						
Method of Sizing Image	Image Sharpness Index	Apparent Size	Relative Differe	e Size ence			
			Ratio	%			
Filar Eyepiece							
Orig. negative with	1.0	0.254	1.03	+3			
clear spot	0.9	0.249	1.01	+1			
3mm diameter	0.6	0.247	1.00				
Orig. negative	1.0						
opaque spot	0.9	0.218	0.88	-12			
3mm diameter	0.6	0.215	0.87	-13			
Contact print	1.0	0.219,0.202	0.89,0.82	-11,-18			
clear spot	0.9	0.222,0.212	0.90,0.86	-10,-14			
3mm diameter	0.6	0.199,0.196	0.80,0.79	-20, -21			
Image Analyzer							
Enlargement* with	1.0*	0.247	1.00*	0%			
clear spot	0.9	0.242	0.98	-2%			
6-8 mm diameter	0.6	0.220	0.89	-11%			

Dependence of Apparent Particle Size on

* Method recommended by authors quoted

Reticl	le Eyepiece	Projec	ted-Spot	RE/PS	Diffe	rence
D _n	σn	D _n	σn		μm	%
2.82	0.25	3.72	0.27	1.1	-0.9	+32
3.00	0.12	3.20	0.19	1.6	-0.2	+ 7
3.08	0.21	3.55	0.23	1.1	-0.5	+15
3.14	0.28	3.61	0.24	0.9	-0.5	+15
6.4	2.0	6.8	1.9	0.9	-0.4	+ 6

Dependence	of Apparent P	article S	ize of	Four Dow Latexes on
Method of	Sizing Images	on TEM P	late:	Reticle Eyepiece-
Vei	rsus-Automatic	Projecte	ed Spot	Analyzer [B3]

Table 42

Latex Designation	Value Dow EM	Oth Number	er EMa Average	Ligl Number	nt-Scatter Average
	0.088	1	0 078	6	0 076 + 0 002b
LS-1132-B	0.091	i	0.085	1	0.085
LS-1044-F	0.109	i	0.100	-	0.000
LS-15N-23	0.138		0.100	6	0.120 ± 0.002^{b}
LS-052-A	0.126	1	0.119	U	
LS-1045-E	0,176	i	0,160		
LS-057-A	0,188	i	0.177	5	$0.175 + 0.007^{b}$
LS-1047-E	0,234	i	0.220	-	_
LS-057-A	0.264	3	0.256 + 0.013	10	0.245 + 0.004c
LS-1010-E	0.357	2	0.337 + 0.016	1	0.343
LS-061-A	0.365	5	0.335 + 0.008	7	0.339 + 0.008b
LS-1029-E	0.500	1	0.50 -		-
LS-15N-8	0.511			1	0.503
LS-063-A	0.557	2	0.549 + 0.096	6	$0.534 \pm 0.007b$
LS-1012-E	0.714	1	0.74		
LS-449-E	0.796	3	0.788 + 0.046	4	0.780 ± 0.014^{d}
LS-1114-E	0.813	1	0.76		-
LS-066-A	0.814			8	$0.803 \pm 0.006^{\text{b}}$
LS-067-A	1.171			8	$1.167 \pm 0.011^{\text{D}}$
LS-1028-E	1.192	4	1.193 ± 0.050	6	$1.195 \pm 0.009^{\circ}$
LS-464-E	1.305	1	1.215	1	1.276
LS-886-43	1.81	1	1.81		
LS-6064-36	2.050	1	2.024		
LS-1358-38	2.958	1	3.036	4	$2.992 \pm 0.027^{\dagger}$
EP-1358-35	3.49	1	3.36		
a. Table 35			d. Table 9		
b. Table 19			e. Table 33		
c. Tables 32			f.Table 34		

Comparisor	of D	ow Elec	tron	Microscopy	Values
with	0ther	EM and	d Ligl	nt-Scatteri	ng

Table 43

Latex Designation	Value Attributed to Dow EM	Average Value Light Scatter	Difference µm	
LS-040-A	0.088	0.076	0.012	
LS-1132-B	0.091	0.085	0.006	
LS-15N-23	0.138	0.120	0.018	
LS-055-A	0.188	0.175	0.013	
LS-057-A	0.264	0.245	0.019	
LS-1010-E	0.357	0.343	0.014	
LS-061-A	0.365	0.339	0.026	
LS-15N-8	0.511	0.503	0.008	
LS-063-A	0.557	0.534	0.023	
LS-449-E	0.796	0.780	0.016	
LS-067-A	1.171	1.167	0.004	
LS-1028-E	1.192	1.196	-0.004	

Comparison of Dow Electron Microscopy and Average Angular Light Scatter Values of Mean Particle Size for Twelve Dow Latexes [Table 43]

Table 44

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Table 4	5
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Latex Designation	Average of Non-Dow EM	Average Light Scatter
LS-040-A	0.078 µm	0.076 <u>+</u> 0.002 µ
LS-1132-B	0.085	0.085
LS-055-A	0.177	0.175 <u>+</u> 0.007
LS-057-A	0.256 <u>+</u> 0.013	0.245 ± 0.004
LS-1010-A	0.337 + 0.016	0.343
LS-061-A	0.335 ± 0.008	0.339 ± 0.008
LS-063-A	0.544 <u>+</u> 0.096	0.534
LS-1012-E	0.788 + 0.046	0.780 <u>+</u> 0.014
LS-1028-E	1.193 + 0.050	1.196 <u>+</u> 0.009

Comparison of Non-Dow Electron Microscopy and Average Light Scatter Values of Mean Particle Size for Eight Dow Latexes [Table 43] values and average angular light-scatter values for nine Dow latexes over the same range of sizes as in Table 44. For these nine latexes, there is no significant difference between the light-scattering and non-Dow EM values, and in most cases, the respective values agree within the uncertainty of either value. It can be seen from Tables 44 and 45 that other non-Dow EM values are in essential agreement with LS values. As a result, a comparison was made between Dow EM values and a combined average of other EM and LS values.

Table 46 shows the comparison for twenty-four Dow latexes between the mean particle diameter as attributed to Dow electron microscopy and the average value of light-scattering and other electron microscopy values as compiled in this report. For twenty-one of the twenty-four latexes, the Dow EM value is greater than the average other-EM and LS value, and for the twenty-four latexes shown, the average difference, computed as a number (n)-weighted average, is +0.0130 μ m. For the seventeen narrow-distribution particles, that is those with mean diameters of less than $l \mu m$, the number (n)-weighted average difference is 0.0158 μ m. Based on this table, the conclusion drawn is that the mean particle diameters measured by the manufacturer of the latexes is systematically different from other EM and LS values by about 0.015 μ m and that this difference may be a result of systematic effects in the EM values. This conclusion is in accord with the observations made by Kratohvil (as in Table 7 here) except that it is a more restricted one; for as Tables 44 and 45 indicate, EM values can be in accord with LS values, although Dow's EM values in these cases may not be.

As a note on the efficacy of vapor-shadow techniques, Table 47 shows results for six Dow latexes by TEM shadow and the average of LS and other EM. While the arithmetic average difference is $\pm 0.0015 \ \mu\text{m}$, the large RMS average difference of $0.015 \ \mu\text{m}$ makes it impossible to conclude whether the vapor-shadow method yields results more in agreement with other techniques than the direct EM measurements on particles themselves.

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Average of Light Scatter and Other EM Values				
Latex Designation	TEM Shadow Image*	Av. LS + Other EM	Difference (µm)	
LS-055-A	0.177	0.175	+0.002	
LS-057-A	0.262	0.248	+0.014	
LS-061-A	0.350	0.337	+0.013	
LS-063-A	0.510	0.538	-0.028	
LS-449-E	0.765	0.783	+0.018	
LS-1028E	1.183	1.193	-0.010	

Comparison of Vapor-Shadow Diameter and Average of Light Scatter and Other EM Values

Latex Designation	Value Attributed to Dow EM	Av. L n	S & Other EM Value	Difference* µm
LS- 040-A	0.088	7	0.076	0.012
LS-1132-B	0.091	2	0.085	0.006
LS-1044-E	0.109	1	0.100	0.009
LS- 052-A	0.126	1	0.119	0.007
LS- 15N-7	0.138	6	0.120	0.018
LS-1045-E	0.176	1	0.160	0.016
LS- 055-A	0.188	6	0.175	0.013
LS-1047-E	0.234	1	0.220	0.014
LS- 057-A	0.264	13	0.248	0.016
LS-1010-E	0.357	3	0.339	0.018
LS- 061-A	0.365	12	0.337	0.028
LS-1029-E	0.500	1	0.500	0.000
LS- 15N-8	0.511	1	0.503	0.008
LS- 063-A	0.557	8	0.538	0.019
LS-1012-E	0.714	1	0.74	-0.026
LS- 449-E	0.796	7	0.783	0.013
LS-1114-B	0.813	1	0.76	0.053
LS- 067-A	1.171	4	1.167	0.004
LS-1028-E	1.192	10	1.195	-0.003
LS- 464-E	1.305	2	1.246	0.059
LS-886-43	1.81	1	1.81	0.000
LS6064-36	2.050	1	2.024	0.026
LS1358-38	2.958	5	3.001	-0.043
EP1358-35	3.49	1	3.36	0.13

Comparison of Mean Particle Size Attributed to Dow EM and Average Value from Light-Scattering and Others' Electron Microscopy [Tables 44 and 45]

Table 47

*Average deviation, computed from the number-n weighted differences for the 17 latexes of D<l μm is + 0.0158 μm; for the 24 latexes shown, the average is + 0.0130 μm.

5. REPORT CONCLUSIONS

The purpose of this report has been to look at those particle measurement techniques which potentially can be used as:

- (1) reference methods for definitive primary dimensional-calibration of microscopic spherical particle reference materials; and
- (2) comparison methods for convenient transfer calibrations from the reference method to bulk calibrations.

The impressive consistency of measurements of mean particle diameters of Dow polystyrene latex sphere by transmission electron microscopy in the laboratories of the latexes' manufacturer has provided a substantial basis for conclusions regarding both reference and comparison techniques.

From comparisons among EM measurements by the manufacturer, EM measurements by independent workers, and LS measurements by various groups, the following conclusions were drawn:

- Electron microscopy and light-scattering can yield mean particle diameters for narrowdistribution populations of polystyrene spheres which agree within the combined uncertainties and sometimes at the level of a few thousandths of a micrometer, i.e. nanometers.

- The electron microscopy values attributed to Dow differ systematically by an average value of approximately 0.015 µm from the average of other electron microscopy and light-scatter values.

- Electron microscopy and light-scattering measurements provide good cross-checks of each other and the two in combination can provide a definitive reference method for particle diameter calibrations.

- Flow-through particle counters can provide effective comparison transfer calibrations. The three methods complement each other, each yielding unique information. Electron microscopy can give definitive measurements of a limited number of particles; lightscattering can give an average diameter for a narrow distribution of particles in their normal liquid environment; flow-through counters can give an explicit histogram of the size distribution of the population, whenever the instrumental uncertainty is significantly less than the population distribution.

Finally, comparison of results by various techniques indicates that by means of the complementary electron microscopy - light scatter - flow-through counter approach, narrow distribution spherical polymer particles with mean diameters in the range 0.1 μ m to 0.5 μ m can be calibrated with total uncertainties on the order of ±0.005 μ m, 1 μ m particles with an uncertainty of 0.01 μ m, and larger particles with total uncertainties on the order of the width of the total population distribution.

In conclusion, the evidence compiled in this report concerning some of the advantages, disadvantages, and relative performance characteristics of light-scattering, flow-through counting, and electron microscopy has lead to developmental work at NBS on these techniques for calibration of particle size standard reference materials.

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Appendix A

Identified Domestic Suppliers of Standard Spherical Particles or Test Dusts

- AC Spark Plug Division General Motors Corporation AC Spark Plug Bldg. Flint, MI 48556
- Coulter Electronics 590 West 20th Street Hialeah, FL 33010
- Dow-Diagnostics Division Dow Chemical Company Box 68511 Indianapolis, IN 46268
- Duke Scientific Corporation 445 Sherman Avenue Palo Alto, CA 94306
- Fluid Power Research Center Oklahoma State University Stillwater, OK 74074
- HIAC Division Pacific Scientific Company 4719 West Brook Street Montclair, CA 91763
- Microspheres Incorporated 14930 East Romona Blvd. Baldwin Park, CA 91706
- Particle Information Service Incorporated 2957 Woodland Park Road Grants Pass, OR 97526
- Poly Sciences Paul Valley Industrial Park Warrington, PA 18976
- Royco Instrument Company 141 Jefferson Drive Menlo Park, CA 94025

Size-Related Equipment [Ref. A3] Part I. Manufacturers and Addresses Adams, L. Ltd, Minerva Road, London, NW10. Addy Products Ltd, Solent Industrial Estate, Botley, Hampshire SO3 2FQ. Aerograph Co., Lower Sydenham, London SW26. Agar, Alan, W., 127 Rye Street, Bishop's Stortford, Hertfordshire. Airflow Development, 31 Lancaster Road, High Wycombe, Buckinghamshire. Airsupply International Gateway House, 302-8 High Street, Slough, Berkshire. Alpine, Augsberg, W. Germany. Ameresco Inc., 101 Park Street, Montclair, New Jersey 07042, U.S.A. American Instruments Co., 8030 Georgia Avenue, Silver Springs, Maryland, U.S.A. Anderson 2000 Inc., P.O. Box 20769, Atlanta, Georgia 30320, U.S.A. Applied Research Laboratories, Wingate Road, Luton, Bedfordshire. A.T.M. Corporation, Sonic Sifter Division, P.O. Box 2405, Milwaukee, Wisconsin 53214, U.S.A. Bailey Meters and Controls, 218 Purley Way, Croydon, Surrey. Bausch & Lomb Inc., 820 Linden Avenue, 30320 Rochester, New York 14625, U.S.A. Bendix Vacuum Ltd, Scientific Instruments and Equipment Division, Easthead Avenue, Wokingham, Berkshire RG11 2PW. Berg, R., Particle Data Inc., P.O. Box 265, Elmhurst, Illinois 60126, U.S.A. Brezina, J., Hauptstrasse 68, D-6901 Waldhilsbach, W. Germany. British Rema, P.O. Box 31, Imperial Steel Works, Sheffield S9 1RA. Buckbee Mears Co., 245 East 6th Street, St. Paul 1, Minnesota, U.S.A. Bush, G. F. & Associates, Princeton, New Jersey, U.S.A. Carl Zeiss, 7082 Oberkochen, W. Germany. Carl Zeiss Jena Ltd, VEB Carl Zeiss, Jena, W. Germany; also England House, 93-7 New Cavendish Street, London W1. Carlo Erba, via Carlo Imbonati 24, 20159, Milan, Italy. Casella, C. F. & Co., Regent House, Britannia Walk, London Nl. Charles Austin Pumps, Petersham Works, 100 Royston Road, Byfleet, Surrey. Chemishes Laboratorium fur Tonindustrie, Goslar, Harz, W. Germany. Cristison, Albany Road, East Gateshead Industrial Estate, Gateshead, Co. Durham NE8 3AT. Coleman Instruments Inc., 42 Madison Street, Maywood, Illinois, U.S.A. Coulter Electronics, High Street, Dunstable, Bedfordshire. Coulter Electronics, 590 West 20th Street, Hialeah, Florida, U.S.A. Degenhardt & Co. Ltd, 6 Cavendish Square, London W1. Delviljem (London) Ltd, Delviljim House, Shakespeare Road, Finchley, Middlesex. Dietert, H. & Co., 9330 Roselawn Avenue, Detroit, Michigan, U.S.A. Donaldson Co. Inc., 1400 West 94th Street, Minneapolis, Minnesota 55431, U.S.A. Draeger Normalair Ltd, Kitty Brewster, Blythe, Northumberland. Dragerwerk Lubeck, D-24 Lubeck 1, P.O. Box 1339, Moislinger Allee 53-55, W. Germany. Endecottes Ltd, Lombard Road, London SW19. Erwin Sick Optik-Elektronik, D-7808 Waldkirch, W. Germany, An der Allee 7-9, Postfach 310. Evans Electroselenium Ltd, Halstead, Essex. Ficklen, Joseph, B., 1848 East Mountain Street, Pasadena 7, California, U.S.A. Fisher Scientific Co., Pittsburgh 19, Pennsylvania, U.S.A. Fleming Instruments Ltd, Lever Street, Bolton, Lancashire BL3 6BJ. Foster Instruments, Sydney Road, Muswell Hill, London N10. Franklin Electronics Inc., Bridgeport, Pennsylvania, U.S.A. Freeman Labs Inc., 9290 Evenhouse Avenue, Rosemount, Illinois 60018, U.S.A. Fritsch, Albert & Co., D6580 Idar-Oberstein 1, W. Germany. Gallenkamp Ltd, Portrack Lane, Stockton-on-Tees, Co. Durham. Gardner Laboratory, Bethesda, Maryland, U.S.A.

Some International Suppliers of Particle-

Appendix B.

Gelman Hawksley, 12 Peter Road, Lancing, Sussex. Gelman Instruments Co., 600 South Wagner Road, Ann Arbor, Michigan 48106, U.S.A. General Electric Co., Schenectady, New York, U.S.A. Glass Developments Ltd, Sudbourne Road, Brixton Hill, London SW2. Glen Creston, The Red House, Broadway, Stanmore, Middlesex. Goring Kerr Ltd, Hanover Way, Windsor, Berkshire. Greenings, Britannia Works, Printing House Lane, Hayes, Middlesex. Griffin & George Ltd, Wembley, Middlesex.

Hawksley & Sons Ltd, 12 Peter Road, Lancing, Sussex. High Accuracy Products, Corp., 141 Spring Street, Claremont, California 91711, U.S.A. Hird-Brown Ltd, Lever Street, Bolton, Lancashire BL3 6BJ. Howe, V. A. & Co. Ltd, 88 Peterborough Road, London SW6.

Image Analysing Computers Ltd, Melbourne, Royston SG6 6ET, Hertfordshire; also 40 Robert
Pitt Drive, Monsey, New York 10952, U.S.A.
Imperial Chemical Industries Ltd, Nobel Division, Stevenston, Ayshire, Scotland.
Infrasizers Ltd, Toronto, Ontario, Canada.

Japan Electron Optics Ltd, Jealco House, Grove Park, Edgware Road, Collindale, London NW9; also 477 Riverside Avenue, Medford, Massachusetts 02155, U.S.A. Joyce Loebl Ltd, Princesway, Team Valley, Gateshead 11, Co. Durham.

Kek Ltd, Hully Road, Hurdsfield Industrial Estate, Macclesfield, Cheshire SK10 2ND.

La Pine Scientific Co., Chicago 29, Illinois, U.S.A. Lars, A. B. Ljungberg & Co., Stockholm, Sweden. Laser Associates Ltd, Paynes Lane, Rugby, Warwickshire. Lavino, Garrard House, 31-45 Gresham Street, London EC2.

Manufacturing Engineering and Equipment Corporation, Warrington, Pennsylvania, U.S.A. Mason & Morton Ltd, 32-40 Headstone Drive, Wealdstone, Harrow, Middlesex. Metals Research Ltd, 91 King Street, Cambridge. Micromeretics Instrum Corporation, 800 Goshen Springs Road, Norcroft, Georgia 30071, U.S.A. Microscal Ltd, 20 Mattock Lane, Ealing, London. Millipore Corp., Ashby Road, Bedford, Massachusetts 01730, U.S.A. Mines Safety Appliances Co. Ltd, Greenford, Middlesex. Mines Safety Appliances Co. Ltd, 201 Braddock Avenue, Pittsburgh 8, Pennsylvania, U.S.A. Mullard Equipment Ltd, Manor Royal, Crawley, Sussex.

Nautamix, N. V., P.O. Box 773, Haarlem, Holland.
Nethreler & Hinz. GmbH, Hamburg, W. Germany.
NEU Engineering Ltd, 32-4 Baker Street, Weybridge, Surrey.
NEU, Etablissement, P.O. Box 28, Lille, France.
Northgate Traders Ltd, London EC2.
Nuclepore Corp., 7035 Commerce Circle, Pleasanton, California 64566, U.S.A.
Numek Instruments and Controls Corporation, Appolo, Pennsylvania, U.S.A.
Numinco, 300 Seco Road, Monroeville, Pennsylvania 15146, U.S.A.

Pascall Ltd, Gatwick Road, Crawley, Sussex.
Pearson Panke Ltd, 1-3 Halegrove Gardens, London NW7.
Pennwalt Ltd, Doman Road, Camberley, Surrey.
Perkin Elmer Ltd, Beaconsfield, Buckinghamshire.
Phoenix Precision Instrument Co., 3803 Fifth Street, Philadelphia, Pennsylvania 19140, U.S.A.
Photoelectronics Ltd, Arcail House, Restmor Way, Hockbridge, Wallington, Surrey.
Pola Laboratory Supplies Inc., New York 7, U.S.A.
Polaron, 4 Shakespeare Road, Finchley, London N3.
Polymer Consultants Ltd, London.
Procedyne Corporation, 221 Somerset Street, New Brunswick, New Jersey, U.S.A.
Production Sales and Services Ltd, New Malden, Surrey.
Prosser Scientific Instruments Ltd, Lady Lane Industrial Estate, Hadleigh, Ipswich, Suffolk

Ouantachrome Corp., 337 Glen Cove Road, Greenvale, New York 11548, U.S.A. Rao Instrument Co. Ltd, Brooklyn, New York, U.S.A. Research Appliance Co., Route 8, Gibsonia, Pennsylvania 15044, U.S.A. Ronald Trist Controls Ltd, Bath Road, Slough Berkshire. Rotheroe & Mitchell Ltd, Aintree Road, Greenford, Middlesex. Royco Instruments, 141 Jefferson Drive, Menlo Park, California 94025, U.S.A. Sartorious Werke, GmbH, D-34 Gottingen, W. Germany. Schaar & Co., Chicago, Illinois, U.S.A. Science Spectrum, 1216 State Street, P.O. Box 3003, Santa Barbara, California, U.S.A. Sharples Centrifuges, Ltd, Camberley, Surrey. Shimadzu Seisakusho Ltd, Kanda, Mitoshirocho, Chiyodra-Ku, Tokyo, Japan. Simon Carves Ltd, Stockport, Lancashire. Societe Fransaise d'Instruments de Controle et d'Analuses, Le Mesmil, Saint Denise, France. Sondes Place Research Institute, Dorking, Surrey. Strohline, Dusseldorf, W. Germany. Systems and Components Ltd, Broadway, Market Lavington, Devizes, Wiltshire. Techmation Ltd, 58 Edgware Way, Edgware, Middlesex. Telefunken, A. E. G., 79 Ulm, Elisabethstrasse 3, W. Germany. Thermal Control Co. Ltd, 138 Old Shoreham Road, Hove, Sussex. Thermo-Systems Inc. 2500 Cleveland Avenue, North St. Pauls, Minnesota 55113, U.S.A. TOA Electric Co., Kobe, Japan. Ultrasonics Ltd, Otley Road, Bradford, Yorkshire. V.E.B. Transformratoren und Rontegemwerk, 48 Overbeckstrasse 8030, Dresden, West Germany. Veco N. V. Zeefplatenfabrick, Eerbeck (Veluive), The Netherlands. Vickers Instruments Ltd, Haxby Road, York. Walther & Co., Aktiengesellschaft, 5 Koln-Dellbruck, W. Germany. Warmain International Pty Ltd, Artarman, N. S. W., Australia. Watson, W. & Sons Ltd, Barnet, Hertfordshire. Zimney Corporation, Monrovia, California, U.S.A. Part II. Partizle-Size-Related Equipment Noted in Ref. A3. SAMPLING DEVICES Microscal Spinning Riffler Sample Divider Pascal Freeman Laboratories Rotary Riffler Rotary Sample Divider Glen Creston Sample Splitter Fritsch (Christison) FLUE SAMPLERS Smoke Dust Monitor Airflow Development BCURA Gas Flow Monitor Smoke Density meter(chimneys/ducts) Bailey Meters and Controls Stack Monitors Research Appliance Company In Stack Samplers Anderson Dust Samplers Anderson Smoke Density Measuring Instruments Erwin Sick, Pearson Panke C.E.R.L. Flue Dust Monitor Foster Instruments Photoelectronics High Sensitivity Air Monitor AEROSOL SAMPLERS Thermal Precipitators(Standard Casella and Long Term) Gravimetric Dust Sampler (U.S. Agents M.S.A.) Cascade Impactor, Hexhlet (U.S. Agents M.S.A.)

Wrights T. P. Hamiltons T. P. Konisampler T. P. British Standard Deposit Gauge Continuous Oscillating and Gravimetric T. P. Thermopositor Drager Dust Sampler Thermal Precipitors, Konimeter, Dust Collectors, Gravicon, Porticon Dust Sampler (filters) Electrostatic Air Sampler Kit Olin Particle Mass Monitor Electrostatic Air Sampler Smoke Pollution Sampler Cascade Centripeter Membrane Filters Membrane Filters Settlement Dust Counter Hexhlet Gravimetric Personal Sampler Settlement Dust Sampler Cascade Impactor Portable Dust Sampler Periodic Air Sampler Personal Sampler Cascade Sampler Aerosol Gravimetric Spectrometer Air Pollution Monitors Particle Sampling Unit Dust Sampling Unit Millipore Sampling Set Konimeter AERA Portable Air Sampler Light Scattering Counters

Light Reflectance Monitor Aerosol Spectrometers Sigrist Dust Measuring Equip. Electricon Smoke Monitor Coulter Contamination Counter LIDAR, Smoke Plume Tracking Laser Light Scattering Particle Counter

SIEVING EQUIPMENT Woven Wire Sieves Inclyno Sieve Shaker, Turbine Sifter Electroformed Sieves

Electroformed Sieves Electroformed Sieves Fisher Wheeler Sieve Shaker Sieve Shakers Allen-Bradley Sonic Sifter Small Portable Sieve Shaker Tyler Ro Tap Alpine Air Jet Wet and Dry Sieve Shakers

Adams Adams Ficklen Glass Developments American Instruments American Instruments Dragerwerk Sartorious (Howe) Bendix Thermo-Systems, Proner Thermo-Systems, Proner Charles Austin Bird and Tole Nuclepore Gelman, Millipore Casella, M.S.A. Casella, M.S.A. Research Appliances Research Appliances Rotheroe and Mitchell Rotheroe and Mitchell Anderson Anderson Fleming Fleming Fleming Fleming Thermal Control Carl Zeiss Jena Addy Products High Accuracy Products (Air Supply) Royco (Hawksley) Bausch and Lomb (Applied Research Laboratories) Research Appliance Sartorious (Howe) Ronald Trist Coulter Laser Associates

Endecattes, Pascall, Greenings Pascall Buckbee Mears (Production Sales and Services) Veco Endecottes Fisher American Instruments, Pascall Endecottes ATM Corporation (Kek) La Pine La Pine Alpine, Lavino Fritsch (Howe) MICROSCOPES Watson Image Splitting Push Button Counter Vicker Image Shearing Eyepiece Zeiss Endter P.S.A. Metals Research P.S.A. Quantimet MC Spri Analyser Superscope Electron Microscope (also SEMs) Magnifiers E.M. Grids Aides for E.M. The Timbrell Analyser The Q.M.S. System

MISCELLANEOUS DISPERSING EQUIPMENT Ultrasonic Dispersers Pyknometers Ultrasonic Cleaner Helium Air Pyknometer Anti-Static Agent M441 Spraygun for Electron Microscopy

SEDIMENTATION EQUIPMENT Pipettes and Hydrometers Granulometer WASP Photosedimentometer Wagner Turbidimeter EEL Photosedimentometer Bound Brook Photosedimentometer Micromerograph Shimadzu Sedimentograph

Satorious Sedimentation Balance Micron Particle Distributometer Palo-Travis Particle Size Apparatus Fisher Dotts Apparatus Travis Method of Two Layer Analysis LADAL X-Ray Sedimentometer Sedigraph X-Ray Sedimentometer

CLASSIFIERS Walther Cascade Elutriator Microsplit Separator Major Classifier Centrifugal Classifier Andrews Kinetic Water Gonell Haultain Infrasizer Roller Bahco Hexhlet Collector(Walton's Horizontal) Casella Microplex Classifier Nauta Hosokawa Classifier Alanysette 8 Donaldson Classifier

CENTRIFUGES Simcar Joyce Loebl Disc Watson Casella Vickers Carl Zeiss (Degenhardt) Metals Research Image Analysing Computors Millipore Sondes Place Research

Polaron Maron and Morton Alan Agar Coulter U.S.A. Bausch and Lomb

Mullard, Ultrasonics Numinco Fritsch (Christison) Micrometetics (Coulter UK) I.C.I. Aerography

Gallenkamp Brezina Microscal La Pine Evans Goring Kerr Franklin Shimadzu Northgate Traders Sartorious Bush GF Pola Fisher Schaar Microscal Micromeretics (Coulter UK)

Walther American Instrument British Rema Donaldson Micromeretics Griffin and George Chemisches Laboratorium Infrasizers American Instrument Dietert (Neu) Casella Lavino Nautamix Fritsch (Howe) Donaldsons

Simon Carves Joyce Loebl Kaye Disc Martin Sweeny Sharples Centrifuge Pennwalt Appliances (U.S.A.) Whitby Apparatus Mines Safety LADAL X-Ray Microscal Modified Pipette Allen STREAMING PRINCIPLE Coulter Counter Coulter Celloscope Lars P.D. Analyser Berg Particle Volume Detector Telefunken TOA Microcellcounter Toa Granulometer V.E.B. LIGHT SCATTERING (see also Aerosol Samplers) Shimadzu Light Scattering Photometer Shimadzu Sinclair Phoenix Forward Phoenix Scattering Light Photometer Phoenix Brice-Phoenix L.S.P. Phoenix American Instruments Absolute L.S.P. Photo-Nephelometers Coleman Recording Turbidimeter General Electric Company Manufacturing Engineering Company Scattermaster Photometers Shimadzu, Societe Francaise, Nethreler, Polymer Consultants Differential Light Scattering Science Spectrum Photometers Atlas of Light Scattering Curve Science Spectrum PERMEAMETRY Fisher Sub-Sieve Sizer Kek **Rigden** Apparatus Gallenkamp Knudsen Flow Permeameter Micromeretics The Griffin Surface Area of Powders Griffin and George Apparatus GAS ADSORPTION (Surface Area and Porosimetry) Perkin-Elmer Shell Sorptometer Perkin-Elmer Strohline Areameter Strohlin Quantasorb and Monosorb Ameresco, Quantachrome Corporation Gravimat Sartorious A Range of Instruments Micromeretics (Coulters UK) Carlo Erba (Systems and Components) Sorptomatic Areatron Leybold Air Displacement Porometer Numi nco Numinco Surface Area and Gas Adsorption Equipment Flow Microcalorimeter Microscal American Instrument, Carlo Erba Mercury Porosimeters (Systems and Components), Micromeretics (Coulters UK), Carlo Erba

Appendix C

Documentary Standards Related to Microscopic Particle-Size Measurement

A. American National Standards Institute

ANSI B93.28 1973

"Method for Calibration of Liquid Automatic Particle Counters Using AC Fine Test Dust"

ANSI B93.30 1973

"Method of Reporting Contamination Analysis Data of Hydraulic Fluid Power Systems"

ANSI B93.31 1973

"Multi-Pass Method for Evaluating the Filtration Performance of a Fine Hydraulic Fluid Power Filter Element"

ANSI Z168.1

"Analysis by Microscopical Methods for Particle-Size Distribution of Particulate Substances of Sub-Sieve Sizes"

ANSI Z173.31

"Method of Test for Continuous Sizing and Counting of Airborne Particles in Dust-Controlled Areas Based on Light-Scattering Principles"

ANSI Z146.1

"Method for Measuring and Counting Particulate Contamination on Surfaces"

ANSI Z173.5 (1973)

"Method for Sizing and Counting of Airborne Particulate Contamination in Clean Rooms and Other Dust-Controlled Areas Designed for Electronic and Similar Applications"

ANSI 173.16 (1973)

"Method for Sizing and Counting Particulate Contaminants in and on Clean Room Garments"

ANSI B93.19

"Method for Extracting Fluid Samples from the Lines of an Operating Hydraulic Fluid Power System (For Particulate Contamination Analysis)"

ANSI Z173.9

"Method for Identification of Minute Crystalline Particle Contaminants by X-Ray Diffraction"

ANSI PTC28-1973

"Determining the Properties of Fine Particle Matter"

ANSI Z257.3

"Sampling Stalks for Particulate Matter"

B. American Society of Testing and Materials

ASTM E20-68 (1974)

"Analysis by Microscopical Methods for Particle-Size Distribution of Particulate Substances of Sub-Sieve Sizes"

ASTM F321-70T

"Automatic Particle Counter Size Setting"

ASTM F323

"Precision Classificaiton of Particles"

ASTM F490

"Microscopical Sizing and Counting of Particles on Membrane Filters Using Image Shear"

ASTM F312 - 1969

"Microscopic Counting and Sizing of Particles from Aerospace Fluids on Membrane Filters"

ASTM F21.13 Draft in Committee

"Recommended Practice for Particle Count and Size Distribution Measurement in Batch Samples for Filter Evaluation Using an Optical Particle Counter"

ASTM F21.13 Draft in Committee

"Standard Practice for Comparing the Particle-Size Distribution of Solids in a Powder or Suspended in Liquid by Means of Automatic Particle Counters"

ASTM F21.13 Draft in Committee

"Method for the Measurement of Particle Count and Size Distribution in Batch Samples for Filter Evaluation Using an Electrical-Resistance Particle Counter"

ASTM Draft in Committee (F.07.01.05-10)

"Median Method for Particle Counter Single Point Size Calibration"

ASTM Draft in Committee (F.07.01.05-12)

"Practice for Defining Counting and Size Accuracy of a Liquid Borne Particle Counter Using Near-Monodisperse Spherical Particulate Materials"

ASTM Draft in Committee (F.07.01.05-13)

"Recommended Practice for On-Site Calibration of Liquid Borne Automatic Particle Counters with Adjustable Individual Size Thresholds"

ASTM Draft in Committee (F.07.01.05-14)

"Method for Determining the Quality of Calibration Particles for Automatic Particle Counters"

C. National Fluid Power Association

NFPA T2.9.6 1972

"Method for Calibation of Liquid Automatic Particle Counters Using AC Fine Test Dust"

NFPA T3.10.8.8 1973

"Multi-Pass Method for Evaluating the Filtration Performance of a Fine Hydraulic Fluid Power Filter Element"

NFPA T2.9.3 1973

"Method for Reporting the Contamination Analysis Data of Hydraulic Fluid Power Systems"

D. Society of Automotive Engineers

SAE ARP 1192

"Method for Calibration and Verification of Automatic Liquid Borne Counter (Light Method)" ISO TC 131/SC (USA) N-12

"Method for Calibration of Liquid Automatic Particle Counters Using AC Fine Test Dust"

E. Other ASTM Standards Related to Particle-Size Measurements

1. Material Characterization		2. System Characterization		
Refractory Metals		Airborne Collected in Liquid	D3365	
Fishersizer	B330	Airborne Collected in Thimble	D3563	
Turbidimetry	B430			
Atmospheric Particles		Glass-Blow Down Systems		
Optical Sizing	D2009	Automatic Counter	F327	
Electronic Counter	D3365	Manual Measure	F308	
Alundum Thimble	D3563	Aerospace Fluids		
Pigment-Vehicles	D1210	Metal/Fiber Ident	F314	
Print Inks	D1316	Microelectronic Components		
Polymers/Chloride	D1705	Ring Oven Technique	F59	
Soils	D422	Non-Cryogenic Fluid Sampling	F301	
Whiteware Clays	C775	Particles/Matter in Water	D1883	
Alumina, Quartz		Aviation Turbine Fuels	D2276	
Air Permeability	C721	Surfaces	F24	
Electronic Counter	C690	Aerospace Fluids/Convolutes	F304	
Centr. Sedimentation	C678	Man-Accessible Aerospace Tanks	F306	
Activated Carbon	D2862	Reservoir-Type Pressure Sensors	F305	
White Extender Pigment	B3360	Aerospace Fluids/Membranes	F311	
Multicolor Lacquers	D2338	Sampling Stacks	D2928	

1. Material Characte	erization (con't)
Soap/Detergents	D502
Metal Ores	E383
Plastics	D1921
Resins	D2451
Asbestos By Screens	D2947
Metal Powders	B293
TFE-Fluorocarbon Mat	tl's. D1457

During the preparation of this report, a number of bibliographic sources have been used. These include science and engineering indices, books and articles with extensive references, instrument company application notes, and individual journals.

Computer Literature Search

The science abstracts and the engineering index entries for the period 1969 to September 1979 were searched on the key words related to the dimensional measurement of particles, and including instruments, techniques, and calibration methods. Approximately 150 titles and abstracts of papers having varying degrees of relevance were compiled.

Published Sources With Extensive References

Stockham and Fochtman's monograph, <u>Particle Size Analysis</u> (Ann Arbor Science, 1977) contains 58 cited and 42 uncited references on the general subject of its title.

Among the numerous references in the 1976 volume <u>Fine Particles</u>, Willeke and Liu give 50 references related to single particle optical counters and Gebhart and his co-authors give 50 related to optical aerosol size spectrometry above and below the wavelength of light.

Kratohvil's review of the literature on "Light Scattering", which appeared in Analytical Chemistry in 1966, provides 338 references on that subject with explicit consideration given to work on scattering by spherical and nonspherical particles including latexes.

Allen's scholarly chemical-engineering textbook, <u>Particle Size Measurement</u> (Wiley, 1975), contains over 950 references closely related to various aspects of the title subject and also contains names and addresses of international manufacturers and suppliers of particle sampling and size measurement equipment.

Davies' four articles on "Rapid Response Instrumentation" (American Laboratory, Dec. 1973 - Feb. 1974 and April 1978) include over 150 references primarily on equipment commercially available at those times.

McCrone and Delly's encyclopedia of techniques for small particle identification, The Particle Atlas (Edition III, Volume 4, 1973), lists over 2000 references up to 1972 on subjects related to the general subject of particle characterization.

Instrument Company Bibliographies

Coulter Electronics Company provides a listing of over 560 references up to 1975 on the applications of their electrical-resistance type liquid-borne counter such subjects as air contamination and water and sewage.

Pacific Scientific Company provides a listing of nearly 200 references up to 1975 on the application of their HIAC light-obscuration type liquid borne counter on subjects ranging from basic technology to military specifications.

Science Spectrum Company provides a listing of over 70 references up to 1978 on the application of their various light-scattering type instruments on subjects such as microbiology and molecular weights.

Thermo Systems Incorporated provides a listing of 77 references into 1974 on the theory, practice, and applications of instruments such as theirs used for laser doppler velocitimetry.

Journals

Articles on the most fundamental aspects of particle size measurement have appeared most frequently in Powder Technology, The Journal of Colloid and Interface Science, Applied

Optics, The Journal of the Optical Society of America, Review of Scientific Instruments, and The Journal of Microscopy and Microscope.

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Appendix E

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Certificate of Calibration

Standard Reference Material 1003

Calibrated Glass Spheres

(5 to 30 Microns)

This standard sample of microscopically measured beads is issued for use in calibrating equipment and in evaluating methods for measuring particle size in the 5 to 30 micron range.

The values given are based on measurements of 10,000 particles, of which 96 percent by volume are spheres. Four particle-size distributions are given with this sample in the form of graphs. These graphs represent a distribution according to volume (figure 1), a distribution according to weight (figure 2), and two Stokes' law distributions (figures 3 and 4). The volume distribution permits comparison with electronic particle counters which respond according to the volume of the particle. The weight distribution permits comparison with ultrafine sieves, and the Stokes' law distributions permit comparison with certain types of sedimentation and elutriation methods.

Four distributions instead of one arise from the fact that some of the beads contain spherical gas voids which are large enough to affect the weight and sedimentation rate of the bead. Void diameters have been measured and corrections applied. The diameters given in the weight and volume distribution (figures 1 and 2) are actual physical diameters. Those given in the Stokes' law distributions (figures 3 and 4) are diameters corresponding to an equivalent distribution of solid spheres, which, on a weight basis, would settle at the same rate as the actual sample. Comparison of figures 3 and 4 shows the effect of a comparatively large change in the density of the sedimentation medium on the calculated Stokes' law distribution of the sample.

The vertical lines in the graph are an estimate of reproducibility based on three times the standard error of the mean for ten samples of 1,000 beads, each of which represents ten subsamples of 100 beads. This corresponds to less than ± 4 percent of the particle diameter for particles smaller than 20 microns with somewhat greater uncertainty for particles larger than this size.

The average specific gravity of the beads for purposes of weight-to-volume conversions is 2.39 \pm 0.01. The specific gravity of the solid glass for Stokes' law calculations is 2.54 based on measurements of a single prism of the same glass. The specific surface computed from microscopic measurements is 1730 \pm 50 cm²/g, which corresponds with a specific-surface mean diameter of 14.5 \pm 0.4 microns. The sample contains between 500,000 and 600,000 particles per milligram.

Two bottles of beads are provided. It is recommended that each bottle be shaken vigorously for a minute before sampling, and beads be taken from a number of places in each. When the results of the two bottles are analyzed separately, there should be no systematic difference between the two sets of results in excess of the reported reproducibility limits of the sample.

The surface of the glass in these beads can react with atmospheric moisture, which, with time, tends to make them more difficult to disperse. Direct exposure to relative humidities above 90 percent will produce a noticeable effect on dispersibility within three days, whereas the effect is exceedingly slow at relative humidities less than 50 percent, and can be minimized, if not eliminated entirely by storing the beads in a desiccated atmosphere.

Washington, D. C. 20234 July 1, 1965. W. Wayne Meinke, Chief, Office of Standard Reference Materials







FIG. 2. WEIGHT DISTRIBUTION



FIG. 3. STOKES' LAW DISTRIBUTION (CALCULATED FOR WATER)



U. S. Department of Commerce Peter G. Peterson Secretary

National Bureau of Standards Certificate of Calibration Standard Reference Material 1004 Calibrated Glass Beads

R. K. Kirby

This Standard Reference Material is intended for use in the evaluation of the effective opening of wire-eloth sieves in the range $34 \,\mu\text{m}$ through $120 \,\mu\text{m}$ (Test Sieve Nos. 400, 325, 270, 230, 200, 170, and 140). The weight of glass beads in each bottle is about 63 g. While most of the beads are spherical about 6 percent by number range from nearly spherical beads to ellipsoidal beads and fused beads.

The distribution of sizes in this SRM as determined by microseopic measurement is given in Table 1 as the weight percent of glass beads that are smaller than those that have the indicated diameter.

Over 13,000 beads were measured in the eourse of this ealibration. These beads were sampled from 6 bottles that were selected at intervals throughout the bottling process. Repeat measurements were made on 2 of the bottles. The beads in these bottles were also earefully compared by sieving with the beads from 21 other bottles, also selected at random. These intereomparisons show no significant difference between beads from all 27 bottles. Considering the values of percent finer to be exact, the mean of the standard deviations associated with each diameter is $0.9 \pm 0.4 \,\mu\text{m}$. This error includes those errors due to the bottling and measuring processes and is to be expected when a given sieve is ealibrated with different bottles of this SRM. In addition to this error, the user may impose a sieving error of about $\pm 2 \,\mu\text{m}$, the result of differing ambient conditions. The reproducibility is, of course, dependent upon the sieving method and the eare excreised by the operator.

The method that was used in the preparation of these ealibrated glass beads (U.S. Patent No. 2,693,706, November 9, 1954) is described in a paper by F. G. Carpenter and V. R. Deitz, Glass Spheres for the Measurement of the Effective Opening of Testing Sieves, J. Research NBS 47, 139 (1951).

The overall eoordination and evaluation of data leading to eertification of this SRM was performed by R. K. Kirby.

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 W. P. Reed.

Washington, D. C. 20234 April 3, 1972 J. Paul Cali, Chief Office of Standard Reference Materials

(over)

Table 1

Weight percent finer	Diameter (Effective sieve opening)	Weight percent finer	Diameter (Effective sieve opening)	Weight percent finer	Diameter (Effective sieve openiing)
%	$\mu \mathrm{m}$	%	μm	%	μm
2	28	34	61	68	89
4	31	36	62	70	90
6	34	38	63		
8	36	40	65	72	92
10	38			74	94
		42	67	76	96
12	40	44	69	78	100
14	42	46	71	80	105
16	45	48	74		
18	47	50	76	82	109
20	49			84	111
		52	78	86	113
22	51	54	80	88	115
24	53	56	82	90	117
26	55	58	83		
28	56	60	84	92	119
30	58			94	121
		62	86	96	123
32	59	64	87	98	126
	-	66	88	, .	

Directions for Using Calibrated Glass Beads for the Evaluation of the Effective Opening of Sieves

The Calibration Process

The aperture size of a sieve can be determined as the average size of the openings in the sieve. However, the purpose of a sieve is to measure the size of particles, and therefore, it is the effective opening that must be determined. This is done by using particles of known size. Thus the effective opening is determined by the size of calibrated glass beads that will just pass through the sieve. This in turn permits the measurement of the particle size of an unknown material that will also just pass through the sieve.

The openings of a sieve are not all the same size, and particles that are coarser than the average opening can pass through the larger holes. Thus, the effective opening is generally larger than the average opening. In addition, the separation achieved by a sieve is not sharp. A few particles capable of passing the sieve are always retained. The number of particles retained or passed depends upon the manner and time of shaking, and any measurement of the effective opening must take these variables into account. To a large extent, the glass bead method of calibration automatically includes these effects because the sieves are shaken in the same manner when calibrated as when measuring an unknown material.

The sieve openings are essentially square in shape and particles of irregular shape can pass through even though one of the dimensions of the particle is considerably larger than the diameter of the opening. This is especially true for needlelike shapes. The average diameter of such irregular particles that pass a sieve eannot be considered equal to the effective opening of the sieve as measured by the diameter of spheres that just pass.

For the application of the calibrated glass beads to sieve analysis, see Carpenter, F. G., and Deitz, V. R., Methods of Sieve Analysis with Particular Reference to Bone Char, J. Research NBS 45, 328 (1950).

Calibration Procedure

To evaluate the effective opening of testing sieves with glass beads, the entire standard is placed on the top sieve. The sieves are then shaken in a shaking device, or by hand, in exactly the same manner as that to be followed in routine analysis.

After the shaking has been completed, the stack of sieves is disassembled, and the beads are removed from each sieve and placed into a suitable weighing bottle. Experience has shown that loss of beads is very likely to occur during this operation. Therefore, the whole operation should be carried out over a large piece of glazed paper to permit recovery of any beads that may accidently be spilled. Such loss can also be minimized by the use of a funnel large enough to completely contain the sieve. The stem of the funnel should be fitted snugly into the mouth of the weighing bottle so that none of the beads can escape. The sieve is inverted into the top of the funnel and all of the glass beads are removed with a soft brush. Any beads that stick to the funnel should be swept into the weighing bottle with the brush.

Each of the sieve fractions is weighed to the nearest 0.01 g. After weighing, all beads are returned to the original container and kept for reuse. The weight percent retained on each sieve is calculated from the weights of the sieve fractions. The percent passing through each sieve is determined by subtracting the percentage on the coarsest sieve from 100 percent, the percentage on the next sieve from that result, and so on. The effective size of the sieve opening is determined by interpolation between the nearest values given in the ealibration table.

Example of Calculation Procedure

An example of data and calculations are shown below. Seven sieves were calibrated at the same time. The original weight of the glass beads was 63.30 g. It may be noted that the sum of the weights shows a loss of 0.09 g. This loss is assumed to be evenly distributed and the sum of the weights is used to evaluate the percentages.

U.S. sieve No.	Weight on sieve	Weight percent		Opening of sieve	
		On sieve	Finer than sieve	Effective ^a	Nominal
140 170 200 230 270 325 400 Pan	$\begin{array}{r} 9.99 \text{ g} \\ 5.88 \\ 14.86 \\ 8.12 \\ 6.44 \\ 7.73 \\ 3.29 \\ \underline{6.90} \\ \overline{63.21} \end{array}$	$15.81 \\ 9.30 \\ 23.50 \\ 12.84 \\ 10.19 \\ 12.23 \\ 5.21 \\ 10.92$	84.2 74.9 51.4 38.6 28.4 16.1 10.9	111 μm 95 77 64 56 45 39	106 μm 90 75 63 53 45 38

Example of calculation for effective opening

^aDetermined by interpolation between values given in the calibration table.

Foreign Material and Dirt

If the sieves are not cleaned sufficiently before the calibration, some foreign material will be found among the glass beads. If possible, this foreign material must be removed by hand. A dirty appearance of the glass beads indicates that they have picked up a small amount of dust. The weight of the dust is usually so small that only a negligible error is introduced.

If the sieves to be calibrated have been used they may be cleaned thoroughly with a soft brush, soap and water or solvents. Under no circumstance should a sharp object be used to dislodge particles that are stuck in the meshes.

Loss of Weight with Use

Experience has shown that there is a loss in weight of the beads with use. How great a loss can be tolerated without introducing large errors in the calibration is difficult to state. However, a quick check of the accuracy of the beads can be made by "cross-calibrating" a single sieve with the questionable beads and new or relatively little used beads. A variation significantly greater than $\pm 3 \,\mu$ m would indicate that the accuracy of the questionable beads has suffered from a loss of weight. If an SRM is ruined by either repeated use or accident, the only recourse is to purchase a new SRM from the National Bureau of Standards.

National Bureau of Standards Certificate of Calibration Standard Reference Material 1017a Calibrated Glass Beads

R. K. Kirby

This Standard Reference Material is intended for use in the evaluation of the effective opening of wire-cloth sieves in the range 100 μ m through 310 μ m (Test Sieves Nos. 140, 120, 100, 80, 70, 60, and 50). The weight of glass beads in each bottle is about 84 g. While most of the beads are spherical about 8 percent by number range from nearly spherical beads to ellipsoidal beads and a few conglomerates.

The distribution of sizes in this SRM as determined by microscopic measurement is given in Table 1 as the weight percent of glass beads that are smaller than those that have the indicated diameter.

Over 60,000 beads were measured in the course of this calibration. These beads were sampled from 24 bottles that were selected at intervals throughout the bottling process. Repeat measurements were made on 7 of the bottles. Considering the values of percent finer to be exact, the mean of the standard deviations associated with each diameter is $4.6 \pm 2.0 \,\mu\text{m}$. This error includes those errors due to the bottling and measuring processes and is to be expected when a given sieve is calibrated with different bottles of this SRM. In addition to this error, the user may impose a sieving error of about $\pm 3.5 \,\mu\text{m}$, the result of differing ambient conditions. The reproducibility is, of course, dependent upon the sieving method and the care exercised by the operator.

The method that was used in the preparation of these calibrated glass beads (U.S. Patent No. 2,693.706, November 9, 1954) is described in a paper by F.G. Carpenter and V. R. Deitz, Glass Spheres for the Measurement of the Effective Opening of Testing Sieves, J. Research NBS 47, 139 (1951).

The overall coordination and evaluation of data leading to certification of this SRM was per formed by R. K. Kirby.

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 W. P. Reed.

Washington, D. C. 20234 September 24, 1971 J. Paul Cali, Chief Office of Standard Reference Materials

(over)

Table 1

Cumulative Size Distribution by Weight

Weight percent finer	Diameter (Effective sieve	Weight percent finer	Diameter (Effective sieve	Weight percent finer	Diameter (Effective sieve
	opening)		opening)		opening)
%	$\mu { m m}$	%	$\mu { m m}$	%	$\mu \mathrm{m}$
1	82	34	163	67	219
-2	88	35	165	68	222
3	92			69	226
4	94	36	167	70	229
5	97	37	169	10	
9		38	170	71	232
6	100	30	179	79	235
7	104	40	173	73	238
ģ	107	40	140	74	240
0	107	41	175	75	240
10	110	49	175	10	240
10	112	42	170	76	945
	114	40	170	(0 77	240
11	114	44	179	((70	247
12	110	45	180	78 70	250
13	118	16	101	79	252
14	119	46	181	80	256
15	120	47	182		
16	100	48	184	81	259
10	122	49	185	82	263
17	123	50	180	83	269
18	124		10-	84	274
19	125	51	187	85	279
20	127	52	189		
		53	190	86	283
21	128	54	191	87	287
22	130	55	193	88	291
23	131			89	295
24	133	56	194	90	299
25	135	57	196		
		58	197	91	303
26	137	59	199	92	308
27	140	60	201	93	312
28	143			94	316
20	146	61	203	95	320
30	150	62	205		
00	100	63	207	96	324
31	153	64	210	97	328
39	157	65	213	98	333
33	160	00	<i></i>	<u>00</u>	341
υŪ	100	66	916	,,	0.11

Directions for Using Calibrated Glass Beads for the Evaluation of the Effective Opening of Sieves

The Calibration Process

The aperture size of a sieve can be determined as the average size of the openings in the sieve. However, the purpose of a sieve is to measure the size of particles, and therefore, it is the effective opening that must be determined. This is done by using particles of known size. Thus the effective opening is determined by the size of calibrated glass beads that will just pass through the sieve. This in turn permits the measurement of the particle size of an unknown material that will also just pass through the sieve.

The openings of a sieve are not all the same size, and particles that are coarser than the average opening can pass through the larger holes. Thus, the effective opening is generally larger than the average opening. In addition, the separation achieved by a sieve is not sharp. A few particles capable of passing the sieve are always retained. The number of particles retained or passed depends upon the manner and time of shaking, and any measurement of the effective opening must take these variables into account. To a large extent, the glass bead method of calibration automatically includes these effects because the sieves are shaken in the same manner when calibrated as when measuring an unknown material.

The sieve openings are essentially square in shape and particles of irregular shape can pass through even though one of the dimensions of the particle is considerably larger than the diameter of the opening. This is especially true for needlelike shapes. The average diameter of such irregular particles that pass a sieve cannot be considered equal to the effective opening of the sieve as measured by the diameter of spheres that just pass.

For the application of the calibrated glass beads to sieve analysis, see Carpenter, F. G., and Deitz, V. R., Methods of Sieve Analysis with Particular Reference to Bone Char, J. Research NBS 45, 328 (1950).

Calibration Procedure

To evaluate the effective opening of testing sieves with glass beads, the entire standard is placed on the top sieve. The sieves are then shaken in a shaking device, or by hand, in exactly the same manner as that to be followed in routine analysis.

After the shaking has been completed the stack of sieves is disassembled, and the beads are removed from each sieve and placed into a suitable weighing bottle. Experience has shown that loss of beads is very likely to occur during this operation. Therefore, the whole operation should be carried out over a large piece of paper to permit recovery of any beads that may accidently be spilled. Such loss can also be minimized by the use of a funnel large enough to completely contain the sieve. The stem of the funnel should be fitted snugly into the mouth of the weighing bottle so that no beads can bounce out. The sieve is inverted into the top of the funnel and all of the glass beads are removed with a stiff brush.

Each of the sieve fractions is weighed to the nearest 0.01 g. After weighing, all beads are returned to the original container and kept for reuse. The weight percent retained on each sieve is calculated from the weights of the sieve fractions. The percent passing through each sieve is determined by subtracting the percentage on the coarsest sieve from 100 percent, the percentage on the next sieve from that result, and so on. The effective size of the sieve opening is determined by interpolation between the nearest values given in the calibration table.

Example of Calculation Procedure

An example of data and calculations are shown below. Seven sieves were calibrated at the same time. The original weight of the glass beads was 87.46 g. It may be noted that the sum of the weights shows a loss of 0.11 g. This loss is assumed to be evenly distributed and the sum of the weights is used to evaluate the percentages.

Example of calculation for effective opening

U.S. sieve No.	Weight on sieve	Weight percent		Opening of sieve	
		On sieve	Finer than sieve	Effective ^a	Nominal
50 60 70 80 100 120 140 Pan	7.81 g 11.24 9.79 19.29 12.86 8.54 11.32 -6.50 -87.35	$\begin{array}{c} 8.94 \\ 12.87 \\ 11.21 \\ 22.09 \\ 14.72 \\ 9.77 \\ 12.96 \\ 7.44 \end{array}$	$91.1 \\78.2 \\67.0 \\44.9 \\30.2 \\20.4 \\7.4$	304 μm 250 219 180 150 127 105	300 μm 250 212 180 150 125 106

^a Determined by interpolation between values given in the calibration table.

Foreign Material and Dirt

If the sieves are not cleaned sufficiently before the calibration, some foreign material will be found among the glass beads. If possible, this foreign material must be removed by hand. A dirty appearance of the glass beads indicates that they have picked up a small amount of dust. The weight of the dust is usually so small that only a negligible error is introduced.

If the sieves to be calibrated have been used they may be cleaned thoroughly with a sturdy brush, not too stiff, soap and water or solvents. Under no circumstance should a sharp object be used to dislodge particles that are stuck in the meshes.

Loss of Weight with Use

Experience has shown that there is a loss in weight of the beads with use. How great a loss can be tolerated without introducing large errors in the calibration is difficult to state. However, a quick check of the accuracy of the beads can be made by "cross-calibrating" a single sieve with the questionable beads and new or relatively little used beads. A variation significantly greater than ± 5 μ m would indicate that the accuracy of the questionable beads has suffered from a loss of weight. If an SRM is ruined by either repeated use or accident, the only recourse is to purchase a new SRM from the National Burcau of Standards.

U. S. Department of Commerce Frederick B. Dent Secretary

National Bureau of Standards Richard W. Roberts, Director

National Bureau of Standards Certificate of Calibration Standard Reference Material 1018a Calibrated Glass Beads

R. K. Kirby

This Standard Reference Material is intended for use in the evaluation of the effective opening of wire-cloth sieves in the range $225 \ \mu$ m through 780 μ m (Test Sieve Nos. 60, 50, 45, 40, 35, 30, and 25). The weight of glass beads in each bottle is about 74 g. While most of the beads are spherical about 6 percent by number range from nearly spherical beads to elliposidal beads and fused bcads.

The distribution of sizes in this SRM as determined by microscopic measurement is given in Table 1 as the weight percent of glass beads that are smaller than those that have the indicated diameter.

Over 18,000 beads were measured in the course of this calibration. These beads were sampled from 10 bottles that were selected at intervals throughout the bottling process. The bcads in these bottles were also carefully compared by sieving with the beads from 20 other bottles, also selected at random. These intercomparisons show no significant difference between beads from all 30 bottles. Considering the values of percent finer to be exact, the standard deviation associated with each test sieve is: No. 60, 2.1 μ m; No. 50, 2.5 μ m; No. 45, 2.9 μ m; No. 40, 2.7 μ m; No. 35, 3.8 μ m; No. 30, 3.3 μ m; and No. 25, 4.5 μ m. It was assumed that the effective opening would be within the permissible variation of average opening as specified in the ASTM Standard Specification for Wire-Cloth Sieves, E11-70. This error includes those errors due to the bottling and measuring processes and is to be expected when a given sieve is calibrated with different bottles of this SRM. In addition to this error, the user may impose a sieving error of about $\pm 2 \mu$ m, the result of differing ambient conditions. The reproducibility is, of course, dependent upon the sieving method and the care exercised by the operator.

The method that was used in the preparation of these calibrated glass beads (U. S. Patent No. 2,693,706, November 9, 1954) is described in a paper by F. G. Carpenter and V. R. Deitz, Glass Spheres for the Measurement of the Effective Opening of Testing Sieves, J. Res. NBS 47, 139 (1951).

The overall coordination and evaluation of data leading to certification of this SRM was performed by R. K. Kirby.

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 W. P. Reed.

Washington, D. C. 20234 May 16, 1973 J. Paul Cali, Chief Office of Standard Reference Materials

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Directions for Using Calibrated Glass Beads for the Evaluation of the Effective Opening of Sieves The Calibration Process

The aperture size of a sieve can be determined as the average size of the openings in the sieve. However, the purpose of a sieve is to measure the size of particles, and therefore, it is the effective opening that must be determined. This is done by using particles of known size. Thus the effective opening is determined by the size of calibrated glass beads that will just pass through the sieve. This in turn permits the measurement of the particle size of an unknown material that will also just pass through the sieve.

The openings of a sieve are not all the same size, and particles that are coarser than the average opening can pass through the larger holes. Thus, the effective opening is generally larger than the average opening. In addition, the separation achieved by a sieve is not sharp. A few particles capable of passing the sieve are always retained. The number of particles retained or passed depends upon the manner and time of shaking, and any measurement of the effective opening must take these variables into account. To a large extent, the glass bead method of calibration automatically includes these effects because the sieves are shaken in the same manner when calibrated as when measuring an unknown material.

The sieve openings are essentially square in shape and particles of irregualr shape can pass through even though one of the dimensions of the particle is considerably larger than the diameter of the opening. This is especially true for needlelike shapes. The average diameter of such irregular particles that pass a sieve cannot be considered equal to the effective opening of the sieve as measured by the diameter of spheres that just pass.

For the application of the calibrated glass beads to sieve analysis, see Carpenter, F. G. and Deitz, V. R. Methods of Sieve Analysis with Particular Reference to Bone Char, J. Res. NBS 45, 328 (1950).

Calibration Procedure

To evaluate the effective opening of testing sieves with this SRM all of the glass beads are placed on the top sieve. The sieves are then shaken in a shaking device, or by hand, in exactly the same manner as that to be followed in routine analysis.

After the shaking has been completed the stack of sieves is disassembled, and the beads are removed from each sieve and placed into a suitable weighing bottle. Experience has shown that loss of beads is very likely to occur during this operation. Therefore, the whole operation should be carried out over a large piece of paper to permit recovery of any beads that may accidently be spilled. Such loss can also be minimized by the use of a funnel large enough to completely contain the sieve. The stem of the funnel should be fitted snugly into the mouth of the weighing bottle so that no beads can bounce out. The sieve is inverted into the top of the funnel and all of the glass beads are removed with a stiff brush.

Each of the sieve fractions is weighed to the nearest 0.01 g. After weighing, all beads are returned to the original container and kept for reuse. The weight percent retained on each sieve is calculated from the weights of the sieve fractions. The percent passing through each sieve is determined by subtracting the percentage on the coarsest sieve from 100 percent, the percentage on the next sieve from that result, and so on. The effective size of the sieve opening is determined by interpolation between the nearest values given in the calibration table.
Table 1

Cumulative Size Distribution by Weight

Weight percent finer	Diameter (Effective sieve opening)	Weight percent finer	Diameter (Effective sieve opening)	Weight percent finer	Diameter (effective sieve opening)
%	μm	%	μm	%	μ m
1	200	34	349	67	581
2	207	35	354	68	583
3	212			69	585
4	217	36	360	70	588
5	221	37	367		
		38	375	71	590
6	225	39	385	72	592
7	229	40	396	73	595
8	233			74	598
9	236	41	408	75	602
10	239	42	420	10	001
		43	432	76	606
11	94.9	10	444	77	611
19	242	15	454	78	617
12	240	40	TOT	70	697
13	249	16	469	80	646
14	200	40	402	00	040
15	207	40	409	01	690
16	969	40	473	01	602
10	202	49	400	02	700
17	207	30	400	00	700
10	274	C 1	402	04	700
19	201	51	493	00	(12
20	289	52	500	04	717
01	204	03 54	507	80	(1)
21	290	54 55	515	87	(23
22	302	55	523	88	729
23	307	FC	501	89	730
24	312	50	531	90	743
25	316	57	539	01	750
24	0.00	58	540	91	750
26	320	59	552	92	759
27	323	60	557	93	769
28	326	()		94	779
29	329	61	561	95	791
30	332	62	565	0.6	0.02
0.1	0.07	63	569	96	803
31	336	64	572	97	817
32	340	05	575	98	832
33	344		F7 0	99	849
		00	578		

Example of Calculation Procedure

An example of data and calculations are shown below. Seven sieves were calibrated at the same time. The original weight of the glass beads was 73.91 g. It may be noted that the sum of the weights shows a loss of 0.02 g. This loss is assumed to be evenly distributed and the sum of the weights is used to evaluate the percentages.

Example of calculation for effective opening

U. S. sieve No.	Weight	Weight percent		Opening of sieve	
	on sieve	On sieve	Finer than sieve	Effective	Nominal
25	8.43 g	11.41	88.6	$733\mu\mathrm{m}$	710 µm
30	7.76	10.50	78.1	618	600
35	18.63	25.21	52.9	506	500
40	7.86	10.64	42.2	422	425
45	4.63	6.27	36.0	360	355
50	10.48	14.18	21.8	301	300
60	5.99	8.11	13.7	252	250
Pan	10.11	13.68			
	(3.89				

^aDetermined by interpolation between values given in the calibration table.

Foreign Material and Dirt

If the sieves are not cleaned sufficiently before the calibration, some foreign material will be found among the glass beads. If possible, this foreign material must be removed by hand. A dirty appearance of the glass beads indicates that they have picked up a small amount of dust. The weight of the dust is usually so small that only a negligible error is introduced.

If the sieves to be calibrated have been used they may be cleaned thoroughly with a sturdy brush, not too stiff, soap and water or solvents. Under no circumstance should a sharp object be used to dislodge particles that are stuck in the meshes.

Loss of Weight with Use

Experience has shown that there is a loss of weight of the beads with use. How great a loss can be tolerated without introducing large errors in the calibration is difficult to state. However, the variation of the accuracy of the "working sample" can be monitored by periodically calibrating a set of sieves with it and one or two others that are kept in reserve. A variation significantly greater than $\pm 5 \,\mu$ m would indicate that the accuracy of the questionable beads has suffered from a loss of weight. If an SRM is ruined by either repeated use or accident, the only recourse is to purchase a new SRM from the National Bureau of Standards.

U. S. Department of Commerce Philip M. Klutznick Secretary National Bureau of Standards Ernest Ambler, Director

National Bureau of Standards

Certificate

Standard Reference Material 484b Scanning Electron Microscope Magnification Standard (A Stage Micrometer Scale)

David B. Ballard and Fielding Ogburn

This Standard Reference Material is intended for use in calibrating the scanning electron microscope (SEM) magnification scale to an accuracy of 5% or better within the range of 1,000 to 20,000X. Each SRM bears an identification number and has been individually measured.

The certified distances between the centers of specific lines opposite the Knoop indentation (see the sketch on page 2) are provided with each SRM together with a photomicrograph that shows the area used in the measurement. The certification is valid within an area 24 μ m wide centered about a line extending from the Knoop indentation.

The distances between the lines were determined from measurements made on photographs taken with an SEM in which each SRM was compared by substitution with a Master Standard; thus each reported interval has been corrected for SEM magnification drift. The operating conditions of the SEM were monitored and a resolution of 0.050 μ m was maintained using an SEM resolution test specimen.

The Master Standard was calibrated by an interferometry technique using a helium-neon iodine-stabilized laser as the length standard in the NBS Mechanical Processes Division. The uncertainty of this calibration, based on 160 independent measurements on each spacing, is 0.006 μ m for distances from 1 to 50 μ m.

The total uncertainty for the distances between line pairs $0 \rightarrow 1$ and $0 \rightarrow 2$ (nominal distances of 1 and 2 μ m) is 0.032 μ m, between line pairs $2 \rightarrow 3$ and $3 \rightarrow 4$ (nominal distances of 3 and 5 μ m) is 0.056 μ m, and for the distance between line pair $0 \rightarrow 6$ (nominal distance of 50 μ m) is 0.580 μ m. These total uncertainties are the linear sums of errors associated with the Master Standard calibration and the comparison of each SRM with the Master Standard.

The technical and support aspects involved in the certification and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R.K. Kirby.

Washington, D.C. 20234 November 26, 1980 George A. Uriano, Chief Office of Standard Reference Materials

(over)



The polished surface of each SRM has been carefully ground and polished using metallographic techniques. The carbonaceous contamination (a product of SEM electron beam bombardment) can be removed by light hand polishing on a stationary surface covered with micro cloth using metallographic 0.05- μ m γ -alumina powder. This cleaning process does not alter the certified spacing of the lines by more than 0.010 μ m. Other cleaning techniques that remove surface material sufficient to obliterate the Knoop indentation will void the calibrated distance values.

A recommended procedure for calibrating the magnification of the SEM using SRM 484b is given on the following page and by ASTM E766-80 Practice for Calibrating the Magnification of SEM Using SRM 484. It is suggested that the user extend the calibration to adjacent areas outside of the certified area on the SRM for routine use as a "Working Standard." A list of parameters that may affect the resultant magnification of an SEM is given on page 4.

The significant contributions of the following NBS staff members are hereby acknowledged: J.P. Young for techniques of electroplating; D.R. Black for metallographic services; J.S. Beers for calibration of the Master Standard; and M.C. Croarkin for statistical analysis.

SRM 484b Page 2 The operational steps indicated by the manufacturers of scanning electron microscopes to calibrate the magnification scale are different and often do not consider all the instrument parameters that may change the resultant magnification (see next page). The following procedure details the use of NBS SRM 484b to calibrate one particular SEM, but may be used as a guide for calibration of other SEMs.

Outline of Procedure for Calibrating SEM Magnification Scale

- 1. After the surface of the SRM 484b has been inspected for cleanliness rigidly mount it on an SEM stub with electrically conductive cement or clamp it onto the SEM stage.
- 2. The surface of SRM 484b should be normal to the electron beam or the tilt axis of the stage should be perpendicular to the gold lines of the SRM.
- 3. A clean vacuum of 10^{-2} Pa (10^{-4} Torr) or better is necessary to keep the contamination rate as low as possible.
- 4. Allow a 30-minute or more warm-up of electronic circuits to achieve operational stability.
- 5. Adjust electron gun voltage (between 5 to 30 kV), saturate filament, and check filament alignment.
- 6. Adjust all lens currents at a resettable value. Cycle lens circuit OFF-ON 3 times to minimize hysteresis effects.
- 7. Adjust lens apertures and stigmator for optimum resolution (minimum astigmatism).
- 8. SEM resolution should be a minimum of 0.05 μ m (500 Å), or better.
- 9. Position the SRM, at a nominal magnification of 1 KX, so that the image of the Knoop indentation is centered at one edge of the viewing cathode ray tube (CRT). The width of the gold line calibrated area extends $12 \mu m$ above and below this indentation.
- 10. The same working distance or magnification scale of the SEM can be reproducibly obtained by focusing on the image of the gold lines with Z axis control at highest possible magnification to minimize depth of focus. An alternate focus method is to use single line wave form ("y" mode) and adjust Z axis for maximum signal height.
- 11. To minimize the effect of linear distortions produced by the recording system, the procedure is as follows: The SRM is substituted for the unknown sample and photographed. The lines on the SRM to be used in the calibration should be chosen so that the distance between them matches the length of the object to be measured with both images positioned in the same area on the CRT. A millimeter scale taped onto the edges of the CRT in the x and y directions will assist in the relocation of the respective images.
- 12. Add contrast, if necessary, S/N ratio should be 2:1 minimum.
- 13. After photo recording, if using Polaroid, allow prints to dry 15 to 20 minutes or more to minimize effects due to emulsion and coating shrinkage.
- 14. Measure the perpendicular distance between the lines using the *CENTER* of each line image on the photograph with a TEM Diffraction Plate Reader or use an equivalent instrument, the precision of which (about 0.2 mm) is suitable for this purpose.
- 15. Repeat measurements 3 times on each photograph to determine the average spacing.
- 16. Magnification = Distance measured between image lines on photograph Certified distance between same lines
- 17. To determine the SEM stability and reproducibility, repeat all steps at hourly or daily intervals or after adjustments and repairs.

SRM 484b Page 3

PARAMETERS THAT INFLUENCE THE RESULTANT MAGNIFICATION OF AN SEM

The parameters listed below may interact with each other. They are considered in order of their location in the instrument from electron source to the recorded photograph.

- 1. Electron gun high-voltage instability can change the wavelength of the electrons and thus the final focus.
- 2. Different condenser-lens strength combinations change the focal point of the final lens.
- 3. Uncorrected final lens astigmatism can give a false indication of exact focus.
- 4. Residual magnetic hysteresis, particularly in the final lens, can change the focal conditions.
- 5. Long depth of focus, particularly at low magnification and small beam divergence controlled by lens and aperture selection, can lead to incorrect focus.
- 6. Nonorthogonal deflection (x-y axis) can be produced by scan coils.
- 7. Scan generator circuits may be nonlinear and/or change with aging of circuit components.
- 8. Zoom control of magnification can be nonlinear.
- 9. Nonlinearity of scan rotation accessory can distort magnification at different degrees of rotation.
- 10. Distortion of the electron beam sweep may occur from extraneous magnetic and electrostatic fields.
- 11. The percent error in magnification may be different for each magnification range.
- 12. A tilted sample surface (not perpendicular to the beam axis) will introduce foreshortening and magnification variation.
- The tilt correction applied may not be relative to the tilt axis of the sample or of a particular area on the sample surface.
- 14. Signal processing, particularly differentiation or homomorphic processing, can give a false impression of focus. DC suppression (sometimes called differential amplification, black level/gain, dark level or contrast expansion) may be used because of the isotropic affect on the image.
- 15. The objective lens on some instruments may be electrically coupled to the magnification meter, thus focus and magnification are operator dependent.
- 16. For the same apparent magnification, two different combinations of working distance and beam scan-raster will produce different linear magnification.
- 17. Thermal and electronic drift of circuit components related to the above parameters can affect magnification with time in a random manner.
- 18. Distortion of faceplate and nonorthogonal beam deflection of the CRT can produce nonlinear magnification.
- 19. Camera lens distortion and change of photo image-to-CRT atio can lead to magnification errors.
- 20. Expansion or contraction of photographic material, photographic enlarging, and control of contrast, can all have a significant affect on final apparent image magnification.

SRM 484b Page 4 Appendix G

Tolerances Attached to the Average Quoted in Certain Tables

The uncertainties attached to the averages are the "2 σ_M " uncertainties in the mean. The average of N values, assumed to be independent, is given by:

 $\overline{x} = \frac{1}{N} \sum x_1$

The sample standard deviation σ_s is given by

$$\sigma_{s} = \left[\frac{1}{N-1} \sum_{n=1}^{\infty} (x_{1} - \overline{x})^{2}\right]^{1/2}$$

where N is very large.

The " $2\sigma_M$ " uncertainty is given by:

$$2\sigma_{\rm M} = k_{\rm I}\sigma_{\rm S}$$

where σ_s is the sample deviation, σ_M is the standard deviation or the mean of the population, and k_1 is the factor which relates the sample average deviation and the population standard deviation.

For N small (i.e., less than about 30), the " 2σ limit" differs significantly from the "95% confidence limit". The factor k₂ relates the sample average deviation and the 95% confidence interval:

(95% confidence interval) = $k_2\sigma_s$.

Only as N \geq 30, does K = k₁/k₂ have a value within about 1% of unity.

Number of Determinations	Unbiased Estimator	2σ _m Estimator	Sample 95% Confidence	Mean 95% Confidence	
n	k _l [1]	k ₁	k ₂ [2]	k ₂	$\frac{k_1}{k_2}$
2	0.797	1.77	12.71	8.99	0.20
3	0.886	1.30	4.30	2.48	0.52
4	0.921	1.09	3.18	1.59	0.69
5	0.940	0.95	2.78	1.24	0.77
6	0.952	0.86	2.57	1.05	0.82
7	0.959	0.79	2.45	0.93	0.85
8	0.965	0.73	2.37	0.84	0.87
20	0.987	0.45	2.09	0.47	0.94
30	0.991	0.37	2.04	0.37	1.00
60	0.996	0.26	2.00	0.26	1.00

The Factors $k_1,\ K_1,\ k_2,\ and\ K_2$ are Given in the Following Table for Various Values of n from 2 to 60

- Natrella, M. G. and C. Eisenhart, "Basic Statistical Concepts and Preliminary Considerations," <u>NBS Handbook 91</u> (1966).*
- Ku, H., "Statistical Concepts in Metrology," <u>Handbook of Industrial</u> <u>Metrology</u>, ASTME, Prentice Hall (1967).*
- * Reprinted in <u>Precision Measurement and Calibration: Statistical</u> <u>Concepts and Procedures</u>, NBS SP-300, Vol. I (Feb. 1969).

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NOTE: The principal publication outlet for the foregoing data is the Journal of Physical and Chemical Reference Data (JPCRD) published quarterly for NBS by the American Chemical Society (ACS) and the American Institute of Physics (A1P). Subscriptions, reprints, and supplements available from ACS, 1155 Sixteenth St., NW, Washington, DC 20056. **Building Science Series**—Disseminates technical information developed at the Bureau on building materials, components, systems, and whole structures. The series presents research results, test methods, and performance criteria related to the structural and environmental functions and the durability and safety characteristics of building elements and systems.

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