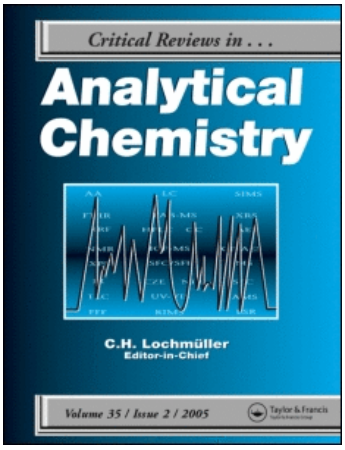

Critical Reviews in Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

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To cite this Article Miller, Brian V. and Lines, Roy W.(1988) 'Recent Advances in Particle Size Measurements: A Critical Review', Critical Reviews in Analytical Chemistry, 20: 2, 75 — 116
To link to this Article: DOI: 10.1080/00078988808048808
URL: http://dx.doi.org/10.1080/00078988808048808

RECENT ADVANCES IN PARTICLE SIZE MEASUREMENTS: A CRITICAL REVIEW

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I. INTRODUCTION

The effect of particles on the final properties of materials has been known for a long time and methods for measurement have developed accordingly. There is evidence that the ancient Egyptians used sieves to "size" and separate precious metal ores around 4000 B.C.

A great many modern industrial processes involve small particles. These particles may be solid, such as milled silica sand, or liquid, such as oil droplets, and may be suspended in air or in liquids. Alternatively, the particles may make up a powder and reside in a hopper or a plastic bag. The range of sizes of such particles is usually large, at least 10 to 1 and often in excess of 100 to 1 by diameter. They may vary from several hundred micrometers in diameter to well below 1 μm.

Chemically, the range of composition of particles is very extensive, as are the uses to which they are put. Powdered plastics may be used to coat metals, to replace paints having expensive solvents, or to make false teeth. Power stations should give essentially dust-free "smoke" emissions. Particles in smooth foodstuffs, such as chocolate, should be small so that they do not taste gritty (e.g., sugar particles below 40 μm), but not too small to affect the viscosity and flow conditions. The tomato "cells" in ketchup should be of an appropriate size to give a good natural color to the product (about 20 to 25 μm). Drugs should be reduced to a size that will give the correct rate of absorption into the body (usually below 35 μm). Intravenous saline "drips" should be free of foreign particles down to 2 μm, as far as possible. Dust in mines and quarries should not be inhaled in the hazardous 2- to 5-μm size range, to reduce the possibility of silicosis or other occupational diseases. Insecticidal sprays should give the maximum coverage area, with small droplet sizes, but not be too small to drift or to be blown off the area being sprayed. Particles in grinding pastes and polishes should all be of a similar size to avoid scratching. Alloys are made stronger and more economically by blending milled metal powders before fusing, rather than by mixing molten metals. Many metal components are made by sintering powdered metals, leaving a porous but solid structure which allows lubricant to pass freely through to the moving surface. The size distribution of the particles in rocket propellants and explosives controls their efficiency.

This wide range of sizes and compositions has resulted in the development of a number of techniques for measuring the sizes of the many different "particles".

Methods of particle size analysis can be divided into essentially two types: those which measure individual particles one by one (i.e., stream scanning methods), such as the electrical sensing zone (ESZ) or Coulter principle, and those which measure the properties of a number or "ensemble" of particles, such as sedimentation and diffraction.

The major techniques currently in use for fine-particle distribution measurement are based

upon sedimentation, image analysis, electrical and optical sensing zones, light diffraction, and, to a lesser extent, photon correlation spectroscopy and chromatography. Sieving is, of course, widely used for characterizing and classifying the coarser particulate systems (e.g., those of 200 to 300 μm or larger), but it is not our intention in this article to review sieving as a major method of particle size measurement since little original work has occurred in this area in the last 2 or 3 years.

Recently, there have been few major innovations in the field of particle size measurement as far as analysis techniques are concerned. However, some significant improvements in existing techniques have been made possible by advances in electronics. The calculating power needed to generate the best-fit size distribution from a Fraunhofer light-diffraction pattern would have required a computer which was large, expensive, and slow a few years ago, but the current desktop machines allow such data to be available within seconds. However, one must remember that, whatever the improvements in speed and ease of operation of any instrumentation offered by such advances, the value of the data is solely dependent upon the principle of measurement of the particles and the integrity of the device's engineering. This point cannot be emphasized too strongly.

Worldwide interest in the methods of particle size measurement and their applications continues to grow, which is evident from the origins of much of the recently published work. Reviews of some 1400 papers on particle size analysis, which were listed in *Chemical Abstracts* from 1982 to 1984 and from 1984 to 1986, were made by Barth and co-workers.[1,2] The number of standardized and certified particle reference materials continues to increase. The subject of particle size analysis is now included in many undergraduate course curricula. The year 1987 saw the 25th anniversary of the Royal Society of Chemistry's Particle Characterisation Group in Britain and the 18th annual meeting of the Fine Particle Society in the U.S. The first World Congress of Particle Technology took place in West Germany in 1986. A number of national societies have been inaugurated in the last few years, specialist groups being formed in Belgium, Holland, and Finland, as well as the Chinese Society of Particuology (from Latin *particula*, particles + Greek *logia*, a subject of study). The second World Congress of Particle Technology will be held in Japan in 1990.

It is at conferences and exhibitions that much useful interchange of ideas takes place and many innovative ideas are first aired. Other sources of "state-of-the-art" published work are varied. Three specific publications, *Particle Characterization*, *Powder Technology*, and *Particulate Science and Technology* are widely read throughout the world and regularly carry significant articles in the field of particle size analysis. In general, such articles tend toward the purer research area and so they are where one would expect to find the in-depth theoretical and practical studies of the techniques.

Detailed information on new and novel applications of particle size analysis is more often found in the industry-specific journals, such as the *Journal of Colloid and Interface Science*, the *Journal of Pharmaceutical Science*, the *Journal of Aerosol Science, Limnology and Oceanography, Ceramics Bulletin*, the *Journal of Polymer Science*, and the *Journal of Food Science*, to name but a few. A remarkably efficient title review is *Current Awareness in Particle Technology*, generated at the University of Loughborough in England and published monthly by their Particle Science and Technology Information Service. They also publish the monthly *Contamination Control Abstracts*.

This review covers some of the more significant and interesting literature which has described the development and application of the various measurement techniques over the last few years. We classify the work by the techniques used and draw attention to comparisons between the techniques, an understanding of which is becoming ever more important in view of the increasing need for standardization.

II. SEDIMENTATION

Now that sedimentation is a mature subject, there is not a great deal more being learned about its principle, but some development continues in modifications to the existing instrumental methods for particle-size distribution analysis, of which the Andreasen pipet and the Micromeritics Sedigraph X-ray sedimentometer are two major cornerstones. Centrifugal devices continue to be perhaps of greater current interest than gravitational types since they speed up the sedimentation and, hence, allow more convenient measurement, especially in the submicrometer size range.

An excellent review of the subject was provided by Allen,[3] who also discussed the effects due to concentration, the container's walls, and Brownian motion. A correction for wall effects was examined by Kasper.[4] Nowak and Sztaba studied the influences of particle shape on the settling velocity[5] in the intermediate region between laminar and turbulent flow, called the Allen range. Their work should eventually allow particle sizes to be evaluated in this region.

Bernhardt dealt with the practical problems of making efficient and stable sample dispersions,[6] including mechanical pretreatment methods. He listed the sedimentation liquids and dispersants which had been reported for 250 different particulate materials (the relevant British Standards also cover 150)[7,8] and also provided density and viscosity values for the liquids and details of the dispersants. Hoffmann and Bernhardt drew attention to the need for a complete dispersion of the particles, particularly hydrophobic ones which must be dispersed in organic liquids,[9] and to the need to use the correct density values in the case of porous particles.

Brownian motion was dealt with in some detail by a mathematical simulation of Chung and Hogg,[10] who showed that the effects could be correlated with an effective mean Péclet number (the ratio of settling velocity to diffusive velocity for the particle). For small Péclet numbers, of course, diffusion dominates and sedimentation methods should not be used. For larger numbers, the errors due to Brownian motion are clearly less, but are still important when analyzing either very narrow or very broad particle size distributions. The authors said that it was known that the Andreasen pipet usually overestimates the amount of fines below 1 μm, an effect often attributed to Brownian motion. However, analysis of the Péclet number shows that Brownian motion is insignificant, so the limitations must be brought about by other effects, such as thermal gradients, and sampling errors. Practical fixed-height sedimentation devices are rarely limited by Brownian motion effects, but for scanning devices the effects can be reduced by increasing the distance of sedimentation to the highest sensing level. However, this, in turn, leads to longer settling times and a greater chance of errors due to convection.

A simple modification of the conventional Andreasen pipet, which samples from below the pipet tip, was described by Chen and Doo.[11] They closed off the tip and continued the stem to the base of the container, sampling through a horizontal slot in the pipet wall. This is an extension of Leschonski's modification, which used four radial apertures for sampling.[12] The authors claimed that log-normal particle size distributions were more reproducibly measured after their modification had been made.

Gravitational sedimentation was speeded up by the approach of Staudinger et al., which used three light-intensity detection zones at different depths to allow three sets of photosedimentation analyses to be simultaneously accumulated for later combination into one particle size distribution.[13] Results on a 5- to 15-μm grade of carborundum agreed with the Sedigraph. A conventional gravitational photosedimentometer, developed in the U.S.S.R., was described by Mirskii et al. and was used for subsieve microbead cracking catalysts and zeolites.[14]

A scanning X-ray sedimentometer, using a moving curium^{244} source and detector, was

developed by Wasan et al.[15] Quinternet et al. characterized flocs in a sedimentation column by filming their sedimentation velocity.[16]

An on-stream particle size analyzer for slurries, which measures the density difference between a column of suspension and a connected column of plain liquid, was described by Rosenblum et al.[17]

Centrifugal sedimentation continues to be of importance. Dumm and Hogg corrected the published procedure for the calculation of results from a pipet-withdrawal centrifuge[18] and also provided an alternative mathematical approach. The generation and use of density gradients as sedimentation fluids in the Joyce Loebl instrument were studied.[19,20] Once the raw photosedimentation curve is obtained, it can be converted on the time axis to particle diameter and the optical density can be corrected using Mie theory, which relates particle size to the extinction coefficient, for spheres. The authors used it to study time-dependent phenomena involving isometric (cubical, octahedral) particles of silver bromide. Coll et al. used a similar method to study adsorption layer thicknesses on such halides.[21]

Coll and Searles examined conditions which produced stable sedimentation in a disk centrifuge.[22] They found that temperature gradients caused by surface evaporation appeared to be the major cause of streaming, i.e., sedimentation of the bulk particle suspension rather than individual particles settling. They found better results when the surface of the spin fluid was covered with a nonvolatile oil and gave a modification to the Stokes equation for use with a density-gradient spin fluid and consecutive sample injections.

A new design of disk centrifugal photosedimentometer (DCP) was described by Koehler et al.[23,24] An AC motor operating at essentially constant speed powered a variable traction-drive transmission to a hollowed sample suspension disk made of a suitable plastic material. The rotational speed of the disk could be selected and monitored, to a maximum of 10,000 rpm. A fan reduced heat transfer to the sedimentation, or spin, fluid. Particle concentrations during sedimentation were detected by the change in optical density across the disk. It has been used especially to help characterize polymer lattices.[25,26]

Holsworth et al. also described the use of a DCP to provide information on lattices and pigments.[27,28] In their technique, the authors produced the spin-fluid density gradient outside the disk, which had an advantage over the conventional Joyce Loebl buffered line start technique in that it improved disk stability at high speeds (8000 to 10,000 rpm). Successive samples could be injected without changing the spin fluid and the disk speed could be changed without destroying the density gradient. The authors could clearly resolve individual latex populations from created mixtures of those populations.

The Horiba CAP 500 sedimentometer, which incorporates both gravitational and centrifugal modes of operation, was described by Gafford.[29] To simplify calculations, the extinction coefficient is assumed to be constant over the particle size range measured, which, of course, is not the case, but the instrument is said to be designed to minimize the effects of Mie scattering. Although the mean size produced for a 0.565-μm polymer latex sample was approximately correct, the size distribution was unnaturally broad, ranging from 0.2 to 4 μm.

Since the use of optical density is not ideal to characterize sample concentration, especially in the low- and submicrometer size range, attempts have been made to obtain better results using other techniques. Jimbo et al. have described a disk centrifuge whereby particle concentration is determined within the spinning tank by means of the differential pressure created at two different depths.[30] In another approach, Kaya et al. used the imbalance created in a suspension-filled particle rotor as the particles settle out.[31,32] The vibration generated is analyzed and used to determine the mass change against time. This technique produced results similar to the gravitational methods of the Andreasen pipet and X-ray extinction down to 0.5 and 0.1 μm, respectively, using a sample of talc. These results seem mildly surprising since gravitational sedimentation is generally accepted as becoming unreliable

below some 2-μm Stokes diameter,[7,8,33] although the method is often used below that size. The authors went on to show uncorroborated results on two other samples down to 0.03-μm Stokes diameter.

Finally, it is normally assumed during most sedimentation methods of particle size analysis that the particles fall singly and obey Stokes' law. Some workers, notably Dollimore and colleagues, have often worked deliberately in the hindered settling region, where the concentration range is so high that particle-particle interaction becomes a major effect. Brown and Dollimore have studied the phenomenon of electroviscosity in hindered settling conditions[34] (i.e., the relationship of the dielectric constant and the physical properties of both solid and liquid upon the settling rate). The phenomenon means that particles do not sediment as simple theory predicts; even single particles of the same size and composition will settle at different rates in deionized water than in water containing a low concentration of ions. They found that a definite relationship exists between the liquid's dielectric constant and the resulting measured particle size. Even the effect of surface tension, though small, would probably be enhanced in systems of small particle size. Sedimentation theory is not as simple as it might appear.

III. THE ELECTRICAL SENSING ZONE (ESZ) METHOD

This method, originally conceived and developed by Wallace H. Coulter,[35] has been in widespread use for particle-size distribution analysis and particle counting for over 25 years. Coulter Electronics Ltd. supplies reference lists of published works on the evaluations and use of their equipment; to date, over 5500 references have been recorded.[36] With this archive base, it might seem unlikely that anything of significant novelty could be forthcoming; however, both the method and the applications are still developing.

The basic idea of what is now commonly known as the Coulter principle, or ESZ method, is that the particles to be measured are suspended at low concentration in an electrolyte solution, which is drawn through a small aperture in an insulating wall, across which a current path also passes. As each particle enters the aperture, or sensing zone, the amount of electrolyte displaced by the presence of the particle is detected by a momentary change in the electrical impedance across the aperture. Thus, the particle's displaced volume can be registered by the amplitude of the electrical pulse produced as the particle passes through the sensing zone. By setting pulse-height discriminators (threshold levels or channels), the pulses can be accumulated to provide a particle size distribution. In the simplest form, a number vs. particle volume distribution can be obtained which can be converted, or directly measured in one model variant, to give particle mass (e.g., as cumulative weight percentage) against equivalent spherical particle diameter. The principle, then, produces a one-by-one, or stream-scanning, particle counter and sizer, with a typical counting rate of several thousand particles per second.

The primary size response is to displaced volume, but some errors are thought to exist with particles of extreme shapes, although the evidence is not wholly conclusive. In addition, in common with all stream-scanning devices, the presence of two particles in the sensing zone at the same time leads to a potential loss of count and a distortion of the size distribution toward coarser particle sizes, although a large and easily definable concentration range allows accurate results to be obtained. Such effects are well-covered in the literature and help to establish the ESZ technique as a potentially absolute reference method. Indeed, in the self-calibrating mode (where the instrument is calibrated with the sample material under test, a balance, graduated flasks, and pipets), it is already very close to being an absolute reference method. Hence, many recent publications are concerned with exploiting the method to the full.

Harfield and Cowan extended earlier practical work which had shown that, at least for

spheres, the volume response from an ESZ analyzer of the type COULTER COUNTER® model ZM was linear to about 80% of the aperture diameter.[37,38] It will be recalled that original response theories had predicted volumetric response linearity to only some 35 to 40% of the aperture diameter, a statement which is still occasionally repeated today.[39] It is, however, a practical limit on some earlier models. In this new work,[37] the authors used a two-dimensional model of an aperture made from conductive paper to record, with a specially constructed differentiator, the resulting potential gradients and the change in aperture impedance generated by "particles" (holes) of different sizes. This two-dimensional model was found to give a linear response to particle area up to some 77% of the aperture diameter, thereby implying confirmation of the earlier practical work on the volume response of spheres.

Elkington and Wilson used very narrow size range DYNOSPHERES® latexes produced by Sintef/Dyno to illustrate the errors in resulting size distributions which are recorded when some particles pass nonaxially through a conventional ESZ.[40] A skewing of the distribution, and distortion even leading to a falsely recorded second population, can be created when, by using a hydrodynamically focused particle flow into the sensing zone, the particles themselves could be shown to be of a single, narrow population. The nonaxial pulses produced in the normal aperture were shown to create a difference of some 6% between the so-called "half-count" median diameter and the diameter corresponding to the mode of the real population. These data illustrate well why standard instruments of this type are best calibrated to an assayed value of mean particle size rather than to the actual mean size of such closely monosized particles. For this reason, Coulter Electronics Ltd. provides an assay sheet for the calibration materials it supplies.[41] Of course, the use of wider size range calibration materials will greatly reduce this perceived 6% difference, while the proper use of the mass integration method of self-calibration of the equipment with particles of the material under test will eliminate it completely.[42,43]

Another approach is possible to reduce the effect of size distribution coarsening with narrow-range materials, that of electronically editing out the deformed pulses created within conventional apertures by nonaxial flow and coincident particle passage. Harfield et al. described a new multichannel size distribution accessory to a COULTER COUNTER® analyzer, the CHANNELYZER® 256.[44] They showed that its edit circuit markedly improved narrow-range size distribution results by rejecting much of both the baseline "noise" pulses inherent in all electronic devices and the misshapen particle-generated pulses. It was also shown that this 256 channel analyzer, of dynamic range about 3:1 by diameter, could be used with a logarithmic pulse-height converter to provide high resolution data over a wider dynamic range, of about 10:1 by diameter.

In a later publication,[45] Harfield went on to discuss obtaining definitive particle size distributions from the ESZ method. The performance of an editing circuit with a conventional aperture assembly was compared with a hydrodynamically focused particle flow which can generate near-perfect pulses. It was shown that for wide size-ranged materials, as are usually found in particle technology, hydrodynamic focusing gave no measurable advantage over the conventional analysis of particles produced in the normal sensing zone, but with very narrow size-ranged materials, such as "monosized" latexes, hydrodynamic focusing gives only marginally better results than does this edit design. Focusing was, however, superior when analyzing a mixture of two populations of latex which are well separated in terms of size. Harfield went on to introduce and describe a new wide-range instrument, the COULTER® MULTISIZER.

Developments in the products of Particle Data, Inc., were reviewed by Brown.[46] They included electronic monitoring of the aperture for possible blockage, an internal reference signal to allow compensation for changes of calibration due to changes of electrolyte solution conductivity or electronic component drift, and automatic coincidence correction — improvements which were present in their latest models, the ELZONE® 180 series.

Wilkinson et al. evaluated suspensions of the very narrow Sintef/Dyno latex particles for stability, both as particle-size and particle-count standards, over several years.[47,48] It was found that such suspensions would be good size calibrators for ESZ analyzers and perhaps also have some value as particle-count standards since the measured total count only tended to fall by some 3% per year. The work was performed under contract to the European Community Bureau of Reference (BCR), which now supplies well-characterized latexes as standard-size certified reference materials (CRMs).[49] The BCR latex CRM 165, 166, and 167, with certified mean diameters and 95% confidence limits of 2.223 (±0.013), 4.821 (±0.019), and 9.475 (±0.018) μm, respectively, were compared with the National Bureau of Standards (NBS) space shuttle reference latex particles SRM 1960 (9.89 ±[0.04 μm]) by Bradshaw and Harfield, who used the high resolution COULTER ZM/CHANNELYZER 256 combination with a novel nullpoint comparison technique to avoid possible systematic errors.[50] They showed that the stated sizes were all self-consistent to better than ±1% of the NBS-certified size and, thus, that these materials are equivalent. They are, therefore, all valuable reference standards which, when used in an appropriate manner, will improve the standardization of particle sizing internationally.

The sensitivity of the ESZ method has been put to use in several significant areas, such as determining the solubility and dissolution rates of materials for which no adequate technique of analyzing the dissolved fraction exists. Others had earlier performed such studies by monitoring the decrease in particle counts per unit volume at preset size levels against time, but Nyström et al. used a multichannel model to follow the change in both measured surface area and particle mass.[51-53]

De Jaeger and Gilleir found that the ability of the ESZ method to detect just a few large particles in the presence of a high concentration of much smaller ones allowed the presence of coagulum in latex preparations to be quantified.[54] This coagulum, an agglomeration of latex particles, creates a surface roughness or haziness when a photographic film is coated by the latex.

In an interesting investigation, the effect of coincident particle passage was apparently put to work to advantage. Sherwood had used the COULTER COUNTER® instrument to measure fat droplet size distribution down to its lower size limit, 0.31 μm in this case.[55] He then found that, if he worked at high concentrations, he could compare the average particle sizes of emulsions comprised of particles well below that size level. It appears that, by generating pulses from many coincident particles below the limit, he was causing the accumulated pulses to move up into the measurement range. The value of the results was confirmed by the use of photon correlation spectroscopy (PCS).

The sensitivity of the ESZ method to particle volume has also been exploited in order to monitor cell cultures. In one technique, cells are grown on the surface of microbeads, which act as carriers and are kept in suspension inside the bioreactor. Miller et al. showed that the increased volume of the microbeads, as the cells grew on the surface, was detectable with a model ZB instrument fitted with a pulse-height analyzer[56] and was directly related to cell concentration. The microbeads could be repeatedly cycled through the aperture, with the cells still attached, to allow the continual monitoring of cell growth. Later work,[57] with a more advanced commercial pulse-height analyzer to monitor the *in situ* growth kinetics, showed that the number of cells attached to the microbeads varied linearly with the average size of the covered microbeads and so cell numbers, or biomass, could be directly measured.

A simple application of the Coulter principle is to measure particulate contamination in electrolyte solutions, such as those used as parenteral fluids (e.g., intravenous saline solutions).[58] However, since particles are detected by their modulation of an electrical path, they do not have to be suspended in an electrolyte solution. A new and direct method of determining the size distribution of insoluble particles, or inclusions, in molten metals has been mentioned by Simensen,[59] who developed a device apparently similar to that patented and

described by Doutre and Guthrie.[60,61] In the latter system, a specially constructed 300- or 100-μm aperture assembly was placed directly into the molten metal. Electrodes, fabricated from mild steel, were used to provide some 60 A of current across the aperture and the pulses produced by the inclusions being passed through the aperture were analyzed by the conventional method. Particles were detected down to 20 μm when using the 300-μm aperture and the device was said to have been used successfully on molten aluminum, zinc, lead, gallium, iron, steel, and even mercury to provide both particle concentration and size distribution, with results being produced every 2 min.

Other applications which have been described recently include filter and cyclone performance testing,[62-65] for which the technique is an ASTM standard method,[66] pharmaceuticals,[67] crystallization kinetics,[68,69] metal powders,[70] seawater injection into oil wells for "secondary recovery",[71] cream liqueurs,[72,73] other oil in water and water/oil/water emulsions,[74-76] and oceanographic and limnographic research into suspended solids, microorganisms, and the feeding behavior of microorganisms.[77-79]

Since the volume of a particle detected by an ESZ analyzer might be expected to exclude any pores within the particle, unless the pores were filled with electrolyte solution, any practical investigation into the effects of porosity is of interest. De Jaeger and Janes showed that, for porous silicas, a reasonably linear relationship existed between the pore volume calculated from Coulter principle sizing of the samples, with and without the pores being filled with inert fluid, and the pore volume as measured from gas adsorption.[80] He concluded that the ESZ method could be used to determine the pore volume of porous silicas.

Ghadiri et al. derived a more reliable estimate for the Stokes diameter of airborne particles than can often be obtained directly from impaction or sedimentation.[81] To do this, the authors developed a relationship between Stokes diameter, the wet-dispersed ESZ equivalent volume diameter, and the equivalent area diameter from image analysis.

Since no one method of particle size analysis can be expected to be universally suitable for all applications, Heidenreich noted that the main difference between single particle counters was in the type of sensor involved and proposed the use of multiple sensors with common signal processing.[82] He showed an example of analysis results from ESZ and light extinction using a common electronics box. Later,[83] he reviewed the common features of both methods, such as sample dispersion, sample feeding, coincidence or concentration effects, and statistical confidence limits. At the same conference, Kachel described a new design of flow cytometer which, like other designs already commercially available, coupled the detection of cell volume by the ESZ method with simultaneous detection of two-color scattered light fluoresced from the treated cells to help identify the cells.[84]

Such multiple sensor devices point the way toward increasing the value of many forms of particle size analysis equipment.*

IV. OPTICAL SENSING ZONE (OSZ) METHODS

In this section, we are concerned with single particle, nonimaging light interaction methods. Methods depending upon light interaction with a cloud or "ensemble" or particles and upon image analysis are discussed in Sections V. and VI.

OSZ methods require the particles to be suspended in a transparent fluid (liquid or gas) of refractive index different from that of the particles. In the original designs, the particles are detected as they pass essentially one by one through an illuminated volume, usually of defined dimension. The amount of light produced in the detection system by the scattering or extinction (blockage) of the incident light by each particle is measured as an electrical

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pulse and is related to the size of the particle. Data on the number of particles and their sizes are accumulated and can be sorted, perhaps by pulse-height analyzer, to be presented as concentration- and particle-size distribution results. In more recent designs, other optical detection methods are used; for example, the particles can be counted and sized as they leave a nozzle under acceleration, by their time of flight, or by laser Doppler techniques.

Depending on the optical configuration used, the size response is often a function of cross-sectional area, modified to a greater or lesser degree by refractive index, surface texture, and shape effects, as well as by the wavelength of the light itself, especially when the particle size is of the same order. The subject has been well reviewed by Lieberman,[85,86] Liu et al.,[87] and Hirleman.[88] A remarkably comprehensive review of the air sampling and counting instruments which were available in the 1970s was published by the American Conference of Governmental Industrial Hygienists.[89] Single-particle optical counters and sizers are coming into fairly common use in cell biology, where they are known as flow cytometers and where not only can cells be counted and sized, but also can be identified by attached fluorescent markers.[90-93]

Accurate size measurement by OSZ devices is not simple. Liu et al. considered the differences between the apparent particle size, as indicated by the single-particle light-scattering methods, and the true geometric size of the particles in the so-called "Mie resonant" region.[87] This is where the amount of light scattered is not directly related to particle size; for instance, latex particles of 0.797, 0.822, and 1.01 μm all appeared to be about 0.9 μm diameter. The Mie resonant region of one laser-scattering device was shown to be some 0.8 to 3 μm when using polystyrene latex particles in air. Fully absorbing particles, such as carbon black, dispersed in air did not give a resonant response region and the calibration curve of scattered light intensity vs. particle size was different for different particle types. Several aerosol particle counters from various manufacturers were all found to give differing results for the same room aerosol. The authors considered that, while several different instruments could be used to measure the total particle count above 0.5 μm for the purposes of clean room monitoring, considerable care was needed to interpret the size distribution data which they presented. In general, a correct size distribution could only be measured after careful calibration of the instrument and interpretation of the results.

Particles smaller than the wavelength of the incident light scatter mainly as a function of their volume, according to Gebhart,[94] so the light-scattering distribution of such small particles, including nonspherical ones, is roughly the volume-equivalent diameter distribution. For particles greater than the wavelength of the incident light, the response is a function of the projected area of the particle in the light beam.

Zerull et al. showed that the amount of light scattered by a particle is closely related to its size, composition, structure, and shape — and, hence, to particle orientation.[95] There are strong differences in light-scattering response to spheres and nonspheres, as his plots of light-scattering intensity at angles from 0 to 180° showed. The deviations of response for particles of rough spheres, rounded quartz, a 4-μm agglomerate, and a 30-μm fly ash particle were so great that they should not be neglected when trying to interpret correctly the light-scattering results. A further evaluation of the light-scattering profile for spheres and non-spheres was made by Ravey.[96]

The performance of a narrow angle of collection within a light-scattering device was compared with a wide angle of collection by Szymanski and Liu for different particle sizes and refractive indices[97] and then compared with calculations from theory. The results indicated that, for a narrow angle, the scattered light intensity is an ambiguous function of particle size for transparent particles greater than about 0.7 μm and so this method is limited in its useful range to some 0.7 to 0.2 μm (its lower limit). For a wide angle, the output is monotonic for transparent particles, but the output is severely attenuated for light-absorbing particles above 0.3 μm, in which case it cannot be used for accurate measurements.

Seville et al. compared results from three commercial single-particle, light-scattering counters for test aerosols of fly ash and carbon char ("gasifier fines").[98] There were variations in results and calibration factors due to refractive index differences, particle shape, and light absorption. A comparison with other methods showed that the instruments which integrated scattered light in the forward direction generally oversized the fly ash by up to 150%, primarily due to particle shape, and generally undersized the highly absorbing gasifier fines by around 50%, primarily due to the particles' refractive index, for which the shape effect tended to partially compensate. They concluded that such instruments are best calibrated with the particulate material under test.

The effects of refractive index and particle size interval on the calculated Mie backscatter and extinction were evaluated by de Leeuw and Lamberts,[99] who also concluded that such particle counters calibrated with one type of material should be recalibrated for the different refractive index effects of another type or if the particle shape changed. Hinds and Kraske evaluated these effects on the PMS model LAS-X airborne optical particle counter.[100] Their calculations showed that nonabsorbing organic particles with unknown refractive index have size measurement errors which vary from −50 to +20%. Unknown particles, including absorbing particles, may give measurement errors from −60 to +250%. However, aerodynamic calibration using oleic acid droplets gave very close agreement with the manufacturer's calibration. It was found that inlet losses depended on sample flow rate and particle size. The overall sampling (or counting) efficiency was about 50% at 12 μm and 5 cm^3/s, increasing with smaller particle sizes. A comprehensive discussion of refractive index effects has been provided by Knollenberg.[101]

Counting efficiency was properly defined by Gebhart et al. as the ratio of the coincidence-corrected instrument count to the real count concentration, as determined by reference methods.[102] This ratio is, therefore, not a function of coincidence losses and is a specific property of the instrument. Efficiencies for ten white-light instruments were highly varied, ranging from 0.99 to 0.03 at 0.327 μm and from 1.78 to 0.71 at 2.02 μm. Especially for particle diameters above 2 μm, losses in the sampling system can lower the counting efficiency, particularly at low flow rates and with plastic sampling tubes and charged particles. However, all three laser-based instruments studied showed an efficiency of around unity in the whole submicrometer range (down to 0.163 μm).

The counting efficiencies of other commercial laser (airborne) particle counters were determined in the range of 0.1 to 4 μm by using latex spheres, as well as monodisperse organic and inorganic particles.[103] Again, particle losses due to the inlet pipework and particle flow rates were noted, as well as a decrease in performance at the smallest particle sizes due to the weak pulses being near the instrument's counting threshold, variations in light intensity across the sensing volume, and misalignment of the particle and light paths. Van der Meulen et al. showed that the tendency to judge the correct alignment of such devices from the symmetry of the observed pulse-height distribution resulted in definite alignment errors.[104] Even in the case of a complete misalignment, symmetrical distributions could be obtained that resulted in a 15% loss of particle counts, even under optimum operating conditions, and an order of magnitude error was possible as alignment deteriorated.

Zarrin and Dovichi noted that the light-scattering intensity observed in single-particle counters depends on the trajectory through the light beam.[105] Clearly, those particles which pass through a low-intensity light region will scatter less light than those which pass through a more intense region. To produce good size resolution, it is necessary to use a sheath-flow (hydrodynamically focused) particle stream and, with a Gaussian-profile light beam, the particle stream radius must be much smaller than the light beam spot size. The authors showed from a numerical model that a monosized particle suspension will generate a light-scattering size distribution with a coefficient of variation (cv) by diameter of 12.5% if the sample stream radius is half of the spot size. A 5% cv will be produced if the sample stream

radius is one fifth of the light beam spot size. They went on to show,[106] with a suitable instrument design, that monosized particles differing by 12% in diameter could easily be resolved into the individual components. In addition, both forward- and right-angle collection responses were evaluated. The former suffered from a high background signal, limiting its value to particles above 0.35 μm diameter, while the right-angle detection produced a lower background signal that allowed 0.176 μm to be reached, but at the expense of a more complex relationship between scattered light intensity and particle size.

In an evaluation of the PMS LAS-X laser aerosol spectrometer, Yamada et al. found a resolution of some 5% cv when using a series of latexes of 2% cv, as determined by electron microscopy.[107] However, they also found that some particles gave incorrect sizes, which suggested a problem with the calibration of the size-response curve.

Umhauer had earlier described a double-detector, 90°-scatter, particle counter and measuring system which allowed the signals from particles at the edge of the optical zone to be recognized and eliminated.[108] The apparatus also allowed an improved particle-size range to be detected, a higher concentration limit to be used, and unambiguous signals to be given from irregularly shaped particles. He noted that a 90° configuration was not a prerequisite for the design.

The two common methods of calibrating liquid-borne optical particle counters are by the use of A.C. Fine Test Dust (ACFTD) and latex spheres.[109] ACFTD is the method of ISO 4402 for calibrating to an angular material reasonably typical of filter contamination particulate matter[110] and involves calibrating the instrument's size thresholds so that the resulting count response equals that expected from a known concentration of a known size-distribution material. The latex method involves reasonably monosized spheres and is the method of ASTM F658 and SAE 1192B,[111-113] which relates instrument mean pulse-height response to the average size of these particles. The methods give different calibrations from each other and both have some advantages and disadvantages, but the latex approach is said by Lieberman to be beginning to gain favor over the original ACFTD method.[109] He has detailed the use of monosized latex particles to calibrate light blockage counters, especially for the measurement of the contamination levels of small-volume injectable solutions, as in the *U.S. Pharmacopoeia*[114,115] and pharmaceutical liquids in general.[116]

Day reported that many instruments of the light-blockage type had been surveyed within the CETOP Communal Research Programme interlaboratory sample exchange ("round robin") trials[117] and large variations in results had been obtained. It has been shown that interlaboratory reproducibility was improved by adopting a common method of calibration, that doubts surrounding the use of ACFTD as the calibrator led to a reappraisal within the U.S. and Europe, and that calibration by monosized latex particles has been adopted within Europe as the standard method for the field studies program. A similar calibration method using glass beads had been rejected because the beads tended to settle out.

The calibration of airborne particle counters is commonly performed using aerosols of dried monosized latex particles, but Büttner is one of many who believe that the calibration of particle size distribution in gas flows must be carried out using the particle types which are desired to be analyzed,[118] and preferably measured as an equivalent diameter based on settling rate. This calibration method can be performed by placing the optical particle counter before and after an impactor (for droplet systems) or a sampling cyclone (for solid particles). This technique allows the best use of the counter under relevant industrial conditions, which may have high particle concentrations, wide size distributions, nonideal particles, and an undefined state of dispersion. The author showed sample calibration curves for quartz, limestone, latex spheres, and glass spheres. The resulting airborne size distribution curves for quartz agreed well with those from a sedimentation technique, confirming the value of this calibration method.

Of course, with any of the requirements for calibration, it is not just the size response

which must be calibrated; the number response must also be verified since not all particles may be detected. The ACFTD method of calibrating liquid-borne optical particle counters may suffer in its intention because it interlinks both size and number calibration into one operation. Thus, an error in one response can be falsely compensated by an adjustment in the other response. Perhaps counting accuracy is marginally more important in airborne particle counters since they are used more for particle concentration determination than for size distribution. A precise count calibration technique was derived by Peacock et al. for a variety of liquid and aerosol light-scattering instruments, using polystyrene latex particles.[119] They derived so-called "counting efficiency" curves which, by using the ratio of instrument-indicated concentration to actual particle concentration at the sensor, only investigated coincidence loss and electronic saturation. The authors found that, at about 0.6 μm diameter, one instrument had 20% more coincidence loss than two others. They concluded that it was necessary to qualify each instrument individually in terms of its performance and recommended that instruments should be requalified each 6 months.

Since some airborne particle counters gave results differing by a factor of six or more from each other, Dahneke and Johnson believed that a calibration better than that provided by the manufacturers was required.[120] They derived a calibration method using a series of monosized latex aerosols to establish each instrument's response at the half-count (mean) latex size and showed that this allowed much more precise results to be achieved, of the order of some 10% variation.

Monodispersed cerium oxide particles were produced by a spinning top aerosol generator by Jenkins et al.[121] They had mean diameters in the range of 1.2 to 7.5 μm, with a cv by diameter of some 8 to 15%, and were found suitable to calibrate aerosol analyzers.

The effects of coincident particle passage were noted by Raasch and Umhauer to be twofold.[122] One is a reduction in the particle counts recorded and the other is a coarsening of the particle size distribution. The latter could be corrected for if the true size distribution were known, an unlikely event. The former is usually corrected by use of an experimental function, which is said by Janka and Kumala to be valid under ideal conditions.[123] However, they also considered the extra effect of the nonideality of the instruments' baseline restorer circuit and were able to make a better correction for real-life conditions.

The measurement of very small particles (i.e., less than 0.3- to below 0.1-μm diameter) was discussed by Knollenberg.[124] The advent of lasers has allowed light intensities to be generated which are many thousands of times greater than those from incandescent sources, thereby allowing very weakly scattering particles to be detected. In addition, the use of the resonant laser cavity itself has allowed particles to generate even greater signals without the need to go to higher powered, and higher priced, water-cooled lasers. The author described the optical behavior of very small particles and the lower size limits which are possible. The highest sensitivity is achieved from detecting particles in a vacuum since the sensitivity is limited by the Rayleigh scattering from the gas molecules in gases and by the strong scattering of the bulk medium in liquids. Liquid-borne particle counters were said to be able to reach down to 0.2 μm using low-power lasers. Beyer has described such a device,[125] which used the ratio of the light intensities scattered at two angles.

One application of liquid-borne OSZ particle counters is to measure contamination levels in the process fluids used in the semiconductor industry, where just one particle of 1 μm or less may be enough to bridge the tracks on a semiconductor chip and cause it to fail. Such process fluids include deionized water, as well as such hostile liquids as hydrofluoric acid, all of which must be ultraclean. Lieberman noted that there was no suitable classification level standards available to the industry[126] and called for the need to control inadvertent contamination from the sample handling and transport systems and to better understand the statistical effects of data validity at these relatively low count concentration levels. Sielaff and Harder also pointed out that other standards for bottled liquids (NAV AIR 10-1A-17

and NAS 1638 classification) did not go below 5 μm.[127-129] A proposed industry classification (denoted LSI), however, included a 1-μm level and was able to be logically extended to 0.5 μm and below; hence, it represented a flexible system for the future. Grant and Schmidt developed a counting methodology to measure particle concentrations accurately in semiconductor process fluids by reducing errors due to air bubbles, counter inefficiency, and refractive index and particle coincidence effects.[130]

Hutchinson described the use of 5 on-line HIAC counters and 24 sensors to provide number against size information for a water treatment process control system.[131,132] Particle counts were much more sensitive than the formerly used turbidity measurement as an indicator of potential filter breakdown, although the capital cost and maintenance was higher.

Light blockage or light scatter single-particle counters, calibrated with either ACFTD or latex particles, are suitable to evaluate filter performance by analyzing batch samples from both influent and effluent streams.[133]

The HIAC instrument has been used successfully to provide particle size distributions of ion-exchange resins.[134] It has an advantage over the ESZ method in that the particles can be suspended in any fluid (e.g., deionized water) and over Fraunhofer diffraction methods because the size resolution (in the range of 100 to 1500 μm) is very good. A noted potential problem with the HIAC instrument, however, is that if the incident light beam is not completely parallel, the area of the shadow cast by the particle is not the same as the area of the particle itself.

A modified HIAC instrument was constructed whereby metal powder particles were allowed to fall through air into the OSZ,[135] thereby avoiding having to suspend the dense material. It was used for 20- to 250-μm magnesium powder, but it always gave coarser results than expected, possibly due to a calibration error.

The scattering of light from clusters (flocculates) of particles was studied by Bowen et al.[136] since it differs fundamentally from the scattering by the subunits, or individual dispersed particles. For a single particle of size less than the wavelength of the incident light, the scattered light intensity at low angles was said to be proportional to the square of its volume, while if it is of a size of some 3 to 4 wavelengths or more, the response was said to become proportional to its volume. These statements are apparently in conflict with those of Gebhart.[94] For clusters, the scattered-light intensity at low angles was said to be proportional to the square of the number of subunits in the flocculate, even when the single particles were in the Mie region. The authors developed an optical particle analyzer to examine these effects and found that it could resolve up to eight or more separate peaks to the subunits, detect coincidence of particles, and provide cluster size distributions during salt-induced polystyrene latex flocculation.

Cooper and Clough used a PMS optical array spectrometer, of the light blockage principle, to obtain on-line particle size distributions in a fluidized bed process.[137] Corrections were applied to the raw data to account for the effective sample area changes which are brought about because of the depth of field associated with focusing the particle shadows onto the photodiode array detector and the larger particles having a larger depth of field, and because a larger particle has a smaller statistical chance of having its shadow focused within the boundary of the detector.

Blackford described two instruments suitable to measure the particle size distribution of industrial powders.[138] In one, a differential mobility classifier is used with a condensation nuclei counter (CNC) to measure in the range of 0.01 to 1 μm. An aerosol of the powder is produced by nebulizing and drying a liquid suspension of the particles, after which an electrostatic classifier removes a size fraction and passes it to the CNC concentration detector. In this way, a number against size distribution is accumulated. This system, denoted DMPSS, was later used to measure the size distribution of carbon black samples,[139] the results being compared with those from photon correlation spectroscopy (PCS). It appears, however, that

the mean volume diameter obtained from PCS compares more favorably with the DMPSS mean number diameter than with the mean volume diameter. The particle dispersion methods used were judged to be efficient and equivalent. In the second instrument, the Aerodynamic Particle Sizer (APS), an aerodynamic size distribution from 0.5 to 30 μm is measured. Particles are accelerated through a nozzle and the velocities of the individual particles are determined by their time of flight through two laser beams, deriving a number vs. transit time (particle size) plot. The use of the APS for samples of rice starch, coal dust, and photocopier toner was shown and it was suggested that the method could be used for on-line particle size distribution determination. Results for rice starch were compared with those from other methods, the APS results having the smallest average size.[140]

The APS was also evaluated by Griffiths et al.,[141] who found that liquid droplets could be distorted by their passage through the nozzle, thereby reducing their aerodynamic diameter. While the distortion was not detectable at 5 μm, it could be as much as a 20% reduction for 15-μm dioctyl sebacate droplets. By corollary, the authors concluded that, if solid particles are to be measured by the APS, the calibration particles should also be solid.

Flögel and Schulte,[142] among others, have described a modified laser-Doppler anemometer to measure simultaneously the velocity and size of droplets near the spray cone of an atomizer. In their design, the analyzer, with two photodetectors receiving information from different angles, could be up to 1.2 m removed from the measurement zone. For the same purpose, Grehan et al. used two beams produced by one laser, one for velocity by laser-Doppler effect and the other for particle size.[143] Bauckhage used the phase shifts of Doppler bursts, received as separate signals from photodetectors, to obtain his results.[144]

Not all analyzers can afford to be land based. Wyatt described a new instrument to record the light-scattering intensity profile at 16 separate angles of single marine particles *in situ*,[145] using a laser beam of 400-μm diameter and having a nearly uniform cross section.

The light scattering from blood cells continues to be studied. Latimer et al. evaluated the angular scattered light from nonnucleated red blood cells, modeled as oblate spheroids, from data generated by a photometer and the Lorenz-Mie equations.[146] Sloot and Figdor studied nucleated red blood cells,[147] made more complex by their irregular shapes, nonhomogeneous contents (hemoglobin, cytoplasm, and nucleus) and again having a cell membrane of indeterminate optical properties. Mie theory is also inadequate for this application and the authors proposed a simplified spherical shell model which, together with a modified Rayleigh-Debye-Gans approximation, gave predictions close to those from more complex theory. Such evaluations and models of light-scattering theories will undoubtedly continue in the future.

V. IMAGE ANALYSIS AND MICROSCOPY

In these methods, a detailed particle image, usually produced by optical microscopy, is presented to an image analyzer for automatic or semiautomatic characterization. A common use is to allow the particle's shape to be determined, but, in any case, the methods allow a lot of detailed information to be obtained about relatively few particles. In this way, they contrast with the single-particle, light-interaction methods.

Significant evaluations of the accuracy of optical microscopy itself have been made by Hartman of the NBS. For measuring more or less uniformly sized latex particles, a two-dimensional array method is often used. Hartman evaluated the errors in this method,[148] which are focusing, image distortion, reading of the photomicrographs, distortions in the photographic materials, anisotropy (possibly due to microcracks created within the array), other array defects, the particle size distribution, the coating of solutes on the particles, and contact deformation. The size distribution effect, also known as the Kubitschek effect, was later evaluated in more detail.[149] Hartman then introduced a new method, the center distance

finding technique, to obtain reference measurements of mean size and size distribution of latexes, using optical microscopy.[150] The idea was to let the latex spheres act as positive lenses, focusing the illuminating light to the centers of the spheres and allowing the center-to-center distances to be measured with high accuracy (e.g., an error of only ± 0.4 μm with 10-μm particles).

The most common image-analyzing systems are comprised of a microscope, a TV camera and display, and an image-analyzing computer. Several commercial designs are available, ranging from very simple to very sophisticated. The particles' images can also come from transmission or scanning electron microscopy or acoustic microscopy.[151-153] The latter, using sound waves, allows subsurface features to be studied. Developments in image analysis methods are mainly in the improvement of the data-handling software to extract the maximum information fastest and often at the highest definition and accuracy. However, an on-line apparatus has been developed to measure solid particle contamination in molten polymers by analysis of the images of their shadows, with a resolution of down to 5 μm at a flow rate of 25 kg/h.[154]

As with all methods of particle size measurement, good particle dispersion is important. Fath et al. pointed out that, not only must the particles be singly dispersed and not re-agglomerate, they also should be clearly separated from each other so that the image analyzer is not confused by touching (coincident) particles, as are obtained with a statistically normal sample.[155] The particles, whether wet or dry dispersed, must also be distributed homogeneously about the microscope slide so that all different fields are representative of the entire size distribution; otherwise, large errors can result. It was suggested that good dispersion could be determined by a high optical density, as recorded with a photometer.

The correct focusing of the image is clearly important. Groen et al.[156] evaluated 11 different mathematical functions for the automatic focusing of a microscope to determine which were best for use with real time-acquisition systems. A related problem is that of detecting the actual edge of the particle image, the so-called "gray-level" region. Because of diffraction and other effects, a sharp boundary does not exist at the particle's edge and the computer must decide where the edge really is. Kenny determined that the error, when using standard techniques, causes an oversizing of some 0.6 μm for 10-μm latex particles.[157] She outlined a simple boundary location method suitable for automatic image analyzers in which the light intensity distribution across the boundary was examined and the real boundary located by the application of image formation theory. She reduced the sizing error to about 0.11 μm at both 10 and 5 μm, again using latexes. In a postconference addendum,[158] she reported having used the method for liquid droplets, but with somewhat less success. When compared with the theoretical sizes expected from an aerosol generator, there appeared to be some error which, if real, may have been due to the inferior refractive index difference of the aerosol droplets.

Sufficient resolution of the detectors is also required. Harms and Aus called for a density of 15 to 30 pixels per micrometer for use with stained images of biological cells.[159]

To allow better standardization of image analyzers, Elkington and Wilson introduced a new National Physical Laboratory (NPL) certified stage graticule.[160] It can be used to test the linearity of the scanner over the whole field, the resolution obtained, and the effect of gray-level detection upon the measured size distribution. It has four separate fields: a major field subdivided into smaller but proportional fields, an array of equidistant monosized circles ("particles"), a root-two by diameter series of circles, and a log-normal number/diameter distribution of "particles" in an equicentered array. The value of the new graticule was illustrated by its use on Cambridge Instruments' Quantimet 900 image analysis system and it has since become commercially available.[161] It is, of course, only a two-dimensional representation of particles and, therefore, does not allow depth of field or focusing to be evaluated.

Image analysis is useful not only for particle size, but also for particle shape and surface texture, the three areas together being called particle morphology. Shape can be estimated by some aspect of the particle's behavior, as well as from image analysis, or course, but the approaches in the latter methods range from the simple measurement of aspect ratio[162] to the more sophisticated methods of Fourier, delta, and fractal analysis. Butters found that the simple sphericity factor of the Quantimet 720 (1000 times the projected area, divided by the perimeter squared) was adequate for his needs in characterizing polymer powders and that the more complex methods were not necessary.[163] Nevertheless, they have their uses.

In the Fourier method,[164] the radii of the particle edges are recorded from one central point at various angles. Fourier analysis of the generated data pairs allows shape characterization by recording the radius as a function of the swept angle. However, it cannot handle well any very rugged, jagged, or reentrant particle edges and is best used to measure subtle shape differences between more or less rounded particles.[165] Delta analysis is an extension of Piper's method, in which the angles formed between two neighboring line segments along the particle edge are measured and reported cumulatively. In Delta analysis, a third line segment separates the two line segments which subtend Piper's angle and, by varying its length, a measurement of roundness is obtained.[166] Fractal analysis provides a characterization of the roughness of a particle edge[167] and is discussed in some detail by Kaye et al.[168] Its basis is that the length of an irregular perimeter is not perceived to be constant when measured with different step lengths; the shorter the step length, the longer the perimeter. A proper appreciation of this fact is required in much of the evaluation of particle shape. Meloy and Clark have reviewed the image analysis methods for determining the shape of angular particles.[169]

Beddow, who described an instrument designed for the purpose of morphological analysis,[170] maintains that further evolution of theory is needed for the study of such topics as light-scattering effects, heat transfer, and fluid dynamics. Jones reviewed the requirements of the mineralogist interested in morphology[171] since particle shapes can often affect the properties of particles in a fluid.

Some key mathematical representations of particles in two and three dimensions were summarized by Luerkens.[172] These general expressions for particle and surface boundaries were derived from the morphological variation principle, which states that a mathematical representation of a surface may be derived by finding a function which causes the surface area integral to take on stationary values. The application of the principle led to boundary functions which, to a first approximation, were primarily composed of orthogonal polynomials. Their value for flakes and fibers was considered. He has also discussed the mathematics of particle and surface boundary functions.[173-175]

We believe that the major use for image analysis techniques will continue to be in the study of single particle morphology.

VI. DIFFRACTION

The technique which has resulted in the most rapid growth in instruments purchased over the past few years is that of Fraunhofer diffraction of laser light. Its ready acceptance has been largely due to its apparent ease of use — it is only necessary to spoon in some powder and press a button; dispersion and analysis are automated. Like PCS, it is a very appealing technique since it combines two recent developments, the laser and the microprocessor, into one instrument, thereby implying a new and better technology.

In fact, the principle is one of the oldest available. It was first described by Fraunhofer in 1817[176] and was proposed by Young in 1823 as a halometric method to determine the mean diameter of red blood cells,[177] a technique which was introduced in 1924.[178] However,

it was first described in its modern form by Talbot as a rapid and convenient means for making particle size analyses of dust from gold mines.[179] Later publications have described the development of commercial instruments, which have subsequently become available under the CILAS, MALVERN, LEEDS & NORTHRUP, and SYMPATEC badges.[180-183] Offering a particle size measurement from around two to several hundred micrometers, depending upon the manufacturer's claims, these Fraunhofer Diffraction Analyzers (FDAs) can be used for measurements in liquids or gases and in on-line situations. The method was well reviewed by Weiner.[184]

Fraunhofer diffraction, or far-field diffraction as it is also known, is a rapid, reproducible technique based upon the illumination of a cloud or "ensemble" of particles with a laser beam.

When the beam of light falls onto a particle, a diffraction pattern is formed when some of the light is deflected (diffracted) by an amount dependent upon, among other things, the size of the particle. If a suitable lens is placed in the light path behind the particle and a detector placed at the focal point of the lens, then the light not diffracted by the particle is brought to a point of focus along the axis of illumination and can be disregarded. Light diffracted by the particle will then be imaged concentrically at a distance from the axis, the distance being a function of the particle diameter (i.e., the smaller the particle, the larger the distance of diffraction). The position of individual particles and their state of motion are said to have little effect upon the generated diffraction pattern. If particles of different, but distinct, diameter are illuminated by the beam, then a series of concentric light rings will be generated at various radii, each being a function of a particular particle size. Since the concentric rings are obtained from parallel rays of light, it is a far-field pattern, with the lens operating as a "Fourier Transform" lens.

The wavelength of the incident light must be significantly smaller than the particle size to be measured; otherwise, Mie scattering occurs and the diffraction pattern is modified in a complex manner. Since helium-neon laser light has a wavelength of approximately 0.6 μm, the particles to be measured must be significantly larger than 1 μm.

If the diffracting particles are spherical, but not monodisperse (i.e., they have a range of sizes), the diffraction pattern becomes more difficult to analyze. Since each size of particle produces its own diffraction pattern whose radial position is determined by its particle size and whose intensity is determined by the number of particles present, each principal maximum will be overlapped by the secondary maxima of the other size particles.

Details of the procedures and the assumptions made in obtaining this back-calculation, or inverse matrix, are part of the manufacturers' "know-how" and are not available to the user. The calculations necessitate the use of a computer and the availability of high performance microcomputers was a prerequisite for the development of the method. It also accounts for the differences in the size distributions obtained from the same sample analyzed by the different algorithms since each manufacturer uses their own slightly different solution to the matrix.

A review of this technique 5 years ago would have been fairly brief since little was published, but over the past few years many publications have considered different aspects of the method. As usual with new instruments, after an initial description of their potential uses, researchers begin to probe the theory of operation and the value of the results obtained.

From an analyst's viewpoint, the need to calibrate an instrument can be seen as either necessary for confidence or unnecessarily time consuming. Early proponents of the diffraction technique were enthusiastic about its supposed absoluteness in terms of size, an instrument not needing calibration. This claim relied, at least in part, on the presumed linearity of the light detection system, which must measure intensities that vary by more than three orders of magnitude as a function of angle from the centerline. These detectors were assumed to have uniform response, while, in fact, the responsivity of different detector elements on a

single detector unit varies and the differences are not repeatable between different detector assemblies. Dodge showed the effect of correctly calibrating a Malvern instrument:[185]

	$\bar{x}$ (μm)
Malvern before calibration	38.5
Malvern after calibration	31.4

This requirement has since been recognized by the manufacturers and they now offer calibration reticles as optional accessories. The value of a two-dimensional system is open to discussion. Hirleman described the characteristics of calibration arrays and their potential use in the on-line measurement of sprays[186] and was able to show an acceptable agreement (to within 10%) between four FDAs. Dodge evaluated the performance of various drop-sizing instruments,[187] including FDAs, from 15 different laboratories using a defined protocol to produce a "standard" spray. The instruments tested included calibrated and uncalibrated Malvern FDAs and he found that the agreement between the calibrated Malverns was superior to that of the uncalibrated ones. This confirmed earlier work performed in conjunction with Hirleman,[188] and Hirleman himself has published information on differences between instruments from the same manufacturer of some 20% in terms of absolute size accuracy.[189]

The range of particle sizes covered in the diffraction technique varies, depending upon particle properties. Bayvel and Jones have shown that Fraunhofer diffraction should not be attempted below some 2 to 7 μm (depending upon whether the particles are opaque or transparent) since at those levels, sizing errors in excess of 20% by diameter will occur.[190] Chigier pointed out that the presence of density gradients, arising from temperature or concentration gradients within the fluid containing the particles to be measured, result in the deflection of the laser beam (beam steering).[191] Such deflections of the beam itself may cause it to be sensed by the inner detection diode, which normally detects light from the largest particles (~500 μm). Hence, it is necessary to ensure that no such gradients exist. This may be relatively easy for liquid-borne samples, but sprays may present more of a problem. Dodge and Cerwin proposed correction techniques for the beam steering problems associated with sampling sprays in hot gases[192] and were successful in measuring drop sizes in sprays evaporating in air at temperatures and pressures as high as 700 K and 685 kPa. Modifications were also developed to discriminate against background radiation, such as flame radiation, but in this instance the beam steering effect still precluded high quality results.

With most methods of particle size analysis, the quality of results may also be affected by having too much, or too little, sample in the measuring region. In the case of Fraunhofer diffraction, multiple scattering of light can occur with a resulting falloff in the quality of results produced as the measured width of the particle size distribution decreases rapidly with the increasing number density of particles. The problem becomes significant when more than 50% of the incident light is scattered by the particles. Gomi used a ray tracing method to simulate multiple scattering[193] and assumed that the angular distribution function of light scattered by a particle which is illuminated by a plane wave of light is applicable to the case in which a particle is illuminated by a light ray. This numerical simulation and his experimental data were consistent in mean sizes and width of particle size distribution and he was able to produce charts to correct the representative particle size and the narrowness index of the distribution.

Hamidi and Swithenbank went further and proposed a mathematical model which predicted the light energy distribution produced by a given size distribution at any level of incident light obscuration.[194] A three-dimensional matrix was derived which was used to establish a

systematic procedure to correct for the effect of multiple scattering on any type of size distribution. Of course, it is always necessary to assume that a given type of size distribution exists before you can make such a correction.

If the particle concentration is too low, with less than 5% of the incident light being scattered, errors arise due to optical noise. A further problem can occur if the particles are scattering the light at a point too far from the collection lens since vignetting occurs and the light scattered by small particles is lost due to the limited lens aperture. Wild and Swithenbank suggested the use of a beam stop to solve both problems.[195] The method was validated by comparison with computations and practical vignetting experiments, but it can only be applied where the particle field is homogeneous.

It should be expected that analysis within the two extremes of concentration effects should show reproducible analysis; however, Bürkholz and Polke showed that, within the limits of concentration set by the manufacturers, vast differences could be obtained.[196] They concluded that the finer the particles in the sample, the lower the concentration must be and that the effect of concentration within the instruments will vary from manufacturer to manufacturer.

Controversy still continues over the best method for inverting the light energy distribution. Since each of the manufacturers uses their own proprietary inversions, no two makes of FDA can be expected to agree. Even with one manufacturer, software changes can allow different models to give different results.

De Boer et al. reiterated that Fraunhofer diffraction theory can only be applied if the particles are large relative to the wavelength of light.[197] Their studies established that the optical response is, in fact, based on Mie scattering, particularly if the particles are small compared to the wavelength of light and the refractive indices (r.i.) of the particles and fluids are similar. The work showed that various latex samples in different suspending fluids gave differing results. The measured scattering energy pattern of a 4.5-μm latex sample (r.i., 1.58) in glycerin (r.i., 1.43) was less than half of that predicted by Fraunhofer diffraction and followed the Lorenz-Mie scattering much more closely. For a larger latex (18.3 μm), the Fraunhofer diffraction theory again gave much worse agreement than that calculated from Lorenz-Mie. The authors noted that as the particles got bigger, the effect of the r.i. on the scattering pattern became less. Naining and Hongjian came to the same conclusion,[198] recommending that Malvern change their software from Fraunhofer diffraction to Mie theory.

Tüzün and Farhadpour used a silicalite sample (1 to 10 μm) in dilute aqueous suspension to investigate the laser diffraction technique and three other techniques.[199] The rather surprising similarity of the results with particle sizes close to the wavelength of the incident light was explained by considering the relative refractive index and the light absorbancy of the crystals in the "anomalous diffraction" regime. Only when independently measured values of the optical properties are used is the calculation of a "unique size" distribution possible. This is shown quite clearly in the theoretical analysis. Commercial FDAs are said not to require such prior knowledge. Further work by the same authors showed that, if the measured values of the optical properties of the particles are used in the appropriate theories, laser diffraction is capable of producing quite accurate and reliable information.[200]

All of this has not been lost on the manufacturers, some of whom have recently introduced new instrumentation incorporating both Fraunhofer and Mie theories. Such instruments were outlined by Wedd[201] and Pugh.[202]

Other workers have taken different approaches. Nakadate and Saito suggested the use of a Hankel transform to the radial intensity spectrum, followed by a third derivative deconvolution to give a continuous size distribution as an alternative to the difficulties in calculating the inverse matrix,[203] but this approach does not seem to have been well received. Bayvel et al. showed that the use of Shifrin's inversion algorithm has a number of advantages over the Malvern "model independent" algorithm[204] and has the benefit of being a published technique. It also allows the possibility of calculating the particle size distribution function

for any desired increment and, hence, the user is not restricted to a predetermined set of size bands or obliged to interpolate between them. Another alternative is the approach of Heuer and Leschonski,[183] who believe that the solution methods first proposed by Phillips and Twomey offer a more viable alternative since there is no restriction on the number of possible solutions.

Tomographical transformation of measurements made on a Malvern FDA, which directly transformed the line-integral data point measurements for spray work, was described by Zhu and Chigier.[205] Such transformations were shown to agree well with experimental point methods and the technique was simple and effective.

Calculation of shape factors from FDAs has been investigated[206] and the application of a correction for known shapes of particles has been shown, but, for irregularly shaped particles, calibration was still preferred.

One major drawback to the more general use of the diffraction method is the fact that instruments from different manufacturers give different results; a well-known example of this was provided by Evers,[207] who sized starch particles by different instruments and obtained a difference in medians of 40 μm. Work done by Harfield et al. showed that, for a number of the BCR reference materials, some substantial discrepancies in FDA results occurred, particularly relating to the width of the apparent distribution and the reported presence of a second population of particles.[208]

Due to their rapid measurement time, FDAs may be used to study many different types of particulate systems, including kinetically changing ones, such as crystallization and precipitation. Creehan[209] and Zwicker[210] have investigated its use in controlling the production of Bayer plant material. Creehan approached the technique as an alternative to sieving, comparing the results from a Leeds and Northrup Microtrac model with those from ASTM E11-70 certified sieves. The probability of correlation on 68 slurry samples was found to be above 99.9% at three different mesh sizes and Creehan concluded that the Microtrac is a valuable tool to the process control engineer.

Zwicker also used sieves, but in conjuction with an ESZ instrument. He pointed out that the latter technique requires a user to be more analytically sophisticated than are most plant operatives and so FDAs appear more attractive. A narrow sieve cut of alumina was used to verify the agreement between sieve data and ESZ data and their data were classed as "correct". Various FDA analyses were carried out on a range of samples and compared to these "correct" values. As expected, differences were obtained. Such differences can be acceptable if the bias shown is constant; however, the assessment showed that the bias was far from constant and the technique's sensitivity was questioned. Zwicker also pointed out the problems of using the technique in processes where truncated distributions occur due to classification. As originally shown by Austin and Shah,[211] an artificial broadening of the size distribution occurs. Thus, in contrast to Creehan, Zwicker concluded that the diffraction technique could not be recommended for the control of Bayer plant. A Leeds and Northrup Microtrac FDA has been used on-line with a taconite concentrator.[212]

Soil and sediment analyses using FDAs have been investigated by a number of different groups. Wanogho et al. found that laser diffraction could help to identify correctly an unknown soil sample with a known one.[212] Cooper et al. found that, for a variety of soil samples, the results obtained with a Microtrac FDA agreed to acceptable levels with a pipet/sieve method, giving correlation values of 0.92 for two size ranges.[214] In complete contrast, McCave et al. concluded that the Malvern 3600 sizer determined the clay distribution and amount neither accurately nor precisely and produced different results with different lenses.[215]

Such conflicting results indicate the potential problems of trying to standardize instruments using the diffraction technique and the great need for doing so. Many laboratories may be prepared to sacrifice absolute accuracy in terms of size measurement, provided the technique is repeatable between instruments. This does not yet appear to be the case for Fraunhofer

diffraction devices. The requirement for easy to use, rapid, reproducible instruments is certainly met, but their sensitivity to small changes in size distribution, which can often prove to be both costly and wasteful in production control, has yet to be established. The increasing need for standardization between laboratories may be difficult to achieve.

VII. PHOTON CORRELATION SPECTROSCOPY (PCS)

One of the problems with this method is understanding that it has many different names: PCS, autocorrelation spectroscopy, quasi-elastic light scattering, intensity fluctuation spectroscopy, and dynamic light scattering, to name a few. PCS, as we will call it here, developed commercially at about the same time as Fraunhofer diffraction. The combination of a laser and a microprocessor enabled the familiar phenomenon of Brownian motion to be classified as a "new" method capable of measuring particles below some 3 μm. Brownian motion is, of course, well known, but what is perhaps less well known is that the frequency of motion is inversely proportional to particle size.

The technique uses a laser beam to illuminate a dilute suspension of particles in a liquid. The light scattered by the particles is detected, but it is not the intensity itself which is important; rather, changes in the intensity are detected as the particles move under Brownian motion. The intensity changes or fluctuations, though random in nature, occur on a time scale of microseconds to milliseconds. Large, relatively slow-moving particles change position slowly and cause slow intensity fluctuations at the detector; conversely small, fast-moving particles cause rapid intensity fluctuations. PCS measures particle size by characterizing the time scale of the random intensity fluctuations caused by the diffusing particles. The amount of scattered light detected will average about a mean, fluctuating apparently randomly as the particles move within the beam. The movement is a time-related effect due to the diffusion of the particles. By correlating sections of the signal with themselves at different periods of time (autocorrelation), this time dependency can be evaluated, resulting in an autocorrelation function from which particle size and size distribution can be determined. A comprehensive review of the method and its uses was given by Štepánek and Koňak.[216]

PCS is really only suited for measurement of most types of particles smaller than about 1 μm. If the particles are larger than 1 μm, the speed of movement due to Brownian motion becomes slow and difficult to determine accurately and sedimentation starts to become significant, making the movement of the particles no longer random.

PCS had been used to measure particle size for several years before the first commercially available purpose-built instrument was described by Gähwiller.[217] Providing average particle size, Lines and Miller verified its performance by using it to size latex particles previously measured by electron microscopy.[218] A correlation coefficient of 0.997 was obtained with 30 different latexes covering the range of 90 nm to 3.5 μm.

Since then, the technique has evolved, together with technology, such that modern instruments can provide reasonable size distribution information. This information is extracted from the correlation curve by a mathematical inversion process. Here, PCS again mirrors Fraunhofer diffraction since each of the manufacturers uses their own particular inversion solution and one might again expect results to disagree to some extent between units from different manufacturers. Again, these algorithms are kept proprietary, with the possible exception of the COULTER® N4 range, which utilizes the CONTIN algorithm first described by Provencher.[219]

Various people have investigated the different data reduction options available. Stock and Ray compared a number of analysis methods.[220] Simulated data, including added "noise", together with experimental data from latex standards, were used to investigate the so-called cumulants, histograms, exponential sampling, nonnegatively constrained histograms, and

Provencher's methods of analysis. The Provencher method was found to give accurate values, but required much computer memory, in contrast to the exponential sampling linear-least-squares method and the nonnegatively constrained histograms, which gave accurate values and were easily implemented on a microcomputer. Later work by the same authors investigated the incorporation of a Mie calculation in Provencher's algorithm and the modification of nonnegative least squares.[221,222] They concluded that the mass distribution of particle size could be obtained without the separate measurement of intensity and that averaging over several scattering angles is sometimes more accurate than obtaining data over the same time period at a single angle. This work was along lines similar to that of Bott,[223,224] who also described the incorporation of a Mie calculation into the Provencher method.

A rational method for comparing analysis schemes was described by Edwards et al.[225] Their method depended upon the maximum likelihood estimation or least-squares methods for *a priori* estimation of measurement errors. It was admitted that it was a practical impossibility to reconstruct an arbitrary particle size distribution in any detail.

A generalized exponential (GEX) approach was outlined by Vaidya et al.[226] They compared their method to the constrained regularization method of Provencher and the polynomial subdistribution method, using generated data. The authors found that the GEX method gave results that were the most consistent with the input distributions and was more operator independent than the Provencher approach. It should be noted, however, that several of the input distributions were GEX generated.

Combining nonnegatively constrained least-squares analysis and multiple pass analysis on a single set of data was found to improve the resolution of particle size distributions.[227]

Taylor et al. used the PCS data to arrive at relative particle number distributions from the measured intensity information.[228] They pointed out that, although accurate representations of the intensity distributions can be achieved, this does not guarantee accurate recovery of the number distribution. The authors concluded that an adequate conversion is not always possible and is limited by the width of the distribution.

The analysis of multiexponential decays by a linear programming method was described by Zimmerman et al.,[229] who believed that this method offered improvements over the different types of least-squares methods. An alternative maximum entropy method of analyzing multiexponential data was described by Livesey et al.[230]

Such detailed and complex investigations have helped the particle size analyst to have a clearer idea of the careful way in which some PCS measurements have to be made and results interpreted.

Weiner and Tscharnuter detailed the uses and abuses of PCS as a method of particle sizing[231,232] and pointed out that it is best for narrow-range size distributions. They also reasoned that, providing the limitations are understood, PCS can provide very useful information on broad-range samples. Resolution of peaks separated by a diameter ratio of less than 2:1 are unlikely to be resolved unless *a priori* assumptions are made. They also explained that, for broad distributions, several hundred linearly spaced correlator channels are advisable, although nonlinear sample time spacing is superior. Bott described in detail the advantages of a "multi-Tau" correlator.[233]

Various commercial PCS devices have been presented by manufacturers,[234,235] although other instrumentation has also been described. Nash and King detailed their own design of a heterodyne photon correlation spectrometer which provided ease of alignment and long-term stability.[236] A fully automated apparatus was described by Ganz and Boeger, who used a robot to carry out the sample changing step, with a computer controlling the light intensity, scattering angle, and correlation parameters.[237] Oka et al. discussed their own PCS apparatus.[238]

Chowdhury et al. showed that PCS could also be applied to moving Brownian motion systems by using a flowing suspension of latex particles,[239] while Itoh and Takahashi de-

scribed the use of PCS for aerosol measurements.[240] They claimed that PCS offers advantages over the usual methods of aerosol measurement because of its higher sensitivity and its *in situ* capability.

PCS also offers the possibility of obtaining information on the shape of particles. Rarity calculated the intensity cross correlation from ellipsoids rotating under Brownian motion.[241] He obtained good agreement with results from electron microscopy of cross-linked latex particles with low axial ratios. He pointed out that characterization of particle size and shape could be done without prior knowledge if both field-correlation-intensity cross correlations were known. Resolution of prolate from oblate ellipsoids was achieved in systems having low polydispersity.

Aragon and Percora gave a theoretical discussion of the dynamic light scattering of cylindrical symmetrical particles[242] and evolved exact solutions which were compared to other theoretical approaches for dilute systems of arbitrary shapes.

The uses of PCS tend to be more in the biomedical field than in industrial particle size analysis. Structural studies of casein micelles have been carried out[243] and a number of other workers have used it to assess drug delivery systems.[244-250] Guterman et al. used the method to study the dissolution effects of hydrochloric acid upon mixed gels of aluminum and magnesium hydroxides and upon Magaldrate, a commercial product of similar constitution.[251] Herb et al. studied the formation and stability of submicrometer oil/water emulsions.[252]

In the future, it is anticipated that improvements in the technique will allow the measurement of particle size distributions with greater confidence and precision than is currently possible.

VIII. CHROMATOGRAPHY AND FIELD-FLOW FRACTIONATION

These are two families of separation methods whereby the original liquid suspension of particles is classified into size fractions, which must later be quantified in order to produce a particle size distribution. In chromatographic techniques, particles are separated according to size within a flow channel by their passage through a stationary phase in a manner similar to conventional chromatography or simply by their passage through a long capillary, while in field-flow fractionation, the particle retention is induced by an external force, such as a centrifugal, electrical, or thermal gradient. The large particles travel faster than the small ones. All of these separation methods are suited to the low and submicrometer particle size range and the subject has been comprehensively reviewed by McHugh.[253]

There are three major chromatographic methods:

1. Hydrodynamic chromatography (HDC), which was developed by Small of the Dow Chemical Company[254] and is now commercially available from the Micromeritics Instrument Corporation. In this method, the particles are passed through a packed bed of nonporous column material. Their rate of transport depends on the size of the particles making up the bed and the flow rate and ionic strength of the eluting solution, as well as the particles' own sizes.[255] The technique's range of applicability seems to be to particles of some 20-nm to 2-μm diameter and to high molecular weight polymers.[256] Langhorst et al. were able to measure the molecular weight distributions of partially hydrolyzed polyacrylamides up to about 6×10^7 Da.[257] Van Gilder and Langhorst reported particle size distributions of latex polymer emulsions[258,259] and Leitzelement et al. studied milk casein micelles, acrylic polymer latex, cement dust, formazine precipitate, and lymph chylomicrons.[260] Secchi et al. reported that latex particles were not efficiently recovered at sizes above some 0.2 μm and found that, by repeatedly injecting samples of the same latex into the bed, the accuracy for larger sizes could be improved.[261,262] The commercial device is intended for the polymer latex industry and has been shown to give excellent sizing ability.[263,264]

2. Size exclusion chromatography (SEC) is claimed to be an improvement over HDC since porous particles are employed in the column and the flow through them imposes an extra separation effect by steric exclusion.[265,266] Again, an electrolyte solution is necessary, but this time there may be no lower boundary of measurement. Hence, the detection limit may, in effect, be where the particle stops being a particle and becomes a molecule. Since its upper limit is about 400 nm, it seems that SEC may be more suitable for molecules, while HDC may be more suitable for particles. Latex particles have been used to evaluate the capabilities and calibration of SEC.[267-269]
3. Capillary particle chromatography (CPC) is an extension of HDC.[270] It was found that a packed particle bed was not essential to provide separation; a very long, narrow capillary tube can be as effective.[271] The tube is typically some 100-m long and 250 to 500 μm in internal diameter. Particle transit time is a logarithmic function of the particle's diameter. Pressures of up to 30,000 Pa are required and its separating range seems to be around 0.2 to 200 μm, so it overlaps and extends HDC. De Jaeger et al. investigated CPC and reported that it seemed to offer advantages over HDC for the measurement of real particulate systems, where HDC often resulted in clogged beds.[272]

In field-flow fractionation methods,[273] DuPont has commercialized a centrifugal sedimentation version.[274] Fractionation occurs within closely spaced parallel plates, engineered as a spiral hollow-channel ribbon and housed within a high-speed centrifuge to develop the required force field. The particles are caused to roll or tumble along the outer wall to produce size segregation. It is claimed that the technique can be used to separate particles ranging in size from 10 nm to 1 μm, as well as soluble polymers in the molecular weight range of 10^6 to 10^{13} Da.[275] Giddings and Schure have derived correction factors to account for the viscous flow at the channel edges,[276] thereby improving the resolution of the method, and Jahnová et al. tested several methods for correcting the zone spreading.[277]

Kirkland et al. showed that particle shape has little or no effect on sedimentation field flow fractionation (SFFF) retention until the aspect ratio becomes quite large, greater than some 50 or 100:1.[278] In such cases, very small flow velocities can be used to minimize the effect.

Reinjection techniques to improve sizing response were developed by Giddings and Yang,[279] and fragile colloids, such as emulsions and virus particles, have been analyzed with no signs of degradation during measurement.[280,281]

Aoki et al. have developed a new separation method by using a rotating tube with alternate flow, which was recommended for separating unstable biological particles, such as blood cells.[282]

Whatever the separation techniques used in these methods, it is still necessary to measure the concentration of the particle fractions in order to produce the size distribution. Hamielec described many available detection methods.[283] Zarrin and Dovichi used a light-scatter detector to provide the particle counting after CPC separation.[284] One detection method is to use the theoretical calculation due to the Mie theory of scattered light, for spheres within its applicable size range, in which case the effects of particle and eluant refractive indices, light absorbance, and particle shape need to be considered and appropriate mathematics developed. In addition, considerable computer power is needed to control the instrument's operation and to deconvolute the raw separation data to account for detector response and separation-zone spreading. Calibration is best performed using known sized standards.

IX. MISCELLANEOUS OTHER METHODS

If suspended nonspherical particles are subjected to an electrical field, they will align according to that field. Turning off the field causes them to be returned to random orientation

and the rate of the decay to random orientation has been used as a method of particle size analysis, called electrical birefringence. Parslow and Jennings reported that, by analyzing the rates of decay from a series of pulsed electrical fields, even a bimodal size distribution could be measured in the submicrometer range.[285]

Lenn exploited radiation-scattering theory, but used ultrasonic waves to produce an instrument capable of measuring *in situ* both mean size and concentration of particulate suspensions.[286] It was verified that sieve fractions of sand could be characterized and even wide-range fractions with mean sizes as close as 120 and 150 μm could be distinguished. The method was said to be applicable to any "acoustically hard" material; that is, any material whose relative density and velocity of sound transmission is greater than the surrounding medium in which it is suspended.

Sound was also used by Hidaka et al.,[287] who analyzed the frequency spectrum of the noise of a flow of powder on an inclined plane to allow the simultaneous measurement of the mean size and flow rate of the particles. The transient sound of one pair of particles colliding was analyzed theoretically and the estimated pressure-wave form produced by multiple particle collisions was shown to compare well with that generated in practice.

Photoacoustic spectroscopy was used by Kitamori et al.[288] A laser beam was used to illuminate particles in suspension, causing their heating. The time required for these heated particles to dissipate their heat into the suspending medium fluctuates according to the intensity of the illuminating beam pulse, causing an acoustic wave to be created with a phase shift which is detected by a piezoelectric signal detector. The sensitivity of measurement of the phase shift was such that submicrometer latex particles could be sized and, in addition, by selecting a suitable modulation frequency with respect to their heat releasing time, the particle concentration could also be determined.

The turbidity spectra produced from the scattering of light from an ensemble of particles in liquid suspension was used by Gulari et al. to determine, with high resolution, the particle size distributions of latexes.[289] The range studied, 0.5 to 7 μm, makes the method complementary to PCS at the lower end and to FDA at the higher end. The technique requires knowledge of particle shape, which is preferably spherical, and of the r.i. of the particles at several wavelengths.

A chemical method (oxidation rate) has been used by Roebuck et al.[290] They gave an example of tungsten carbide particles being oxidized to tungsten trioxide, the change in mass being detected in a thermogravimetric analyzer. The basis of the method is that fine particles oxidize faster than coarse ones because of their larger surface area. Differences in mean sizes of <0.1 μm could be found between different batches of material.

Sieving continues to be of importance, although novel discoveries are rare. To obtain representative, but small, samples of sieved powders, Kaye and Clarke combined a spinning riffler with a series of miniature (1/2 in. diameter) woven wire or electroformed sieves.[291,292] After sampling into the sieve holders, the riffler could be disconnected and vibration applied to the sieves to allow the fines to pass into collectors. The aperture diameter distributions of the sieves were measured by a Doppler image analyzer and the flow rate through the mesh was enhanced by the addition of 0.1% Cab-o-sil flowing agent to reduce humidity and electrostatic effects within the powder.

Meloy and Clark found that, while 5 min of sieving time was sufficient for spherical and rounded material, the increased time necessary for other particle shapes could be determined by an examination of the rate of passage through the mesh.[293] To do this requires the sieving rate constants, and it was said that these could be obtained from the literature or from the use of the Sieve Cascadograph, a device intended to measure particle shape from the time taken for a particle to pass through a vibrated stack of identical sieves.[294]

Errors in test sieving also include the properties of the test sieve itself, such as the aperture width distribution. Müller et al. described in detail the German FIA methods for inspection

and calibration of sieves, recommending the use of test powders for calibration since this combines the effects of several potential errors.[295]

Every particle size analysis method is associated with errors, some of which are systematic (e.g., inherent in the method used) and some of which are random (e.g., sampling). According to Leschonski and Legenhausen,[296] the former can be minimized by standardizing the instrumental method used, while the latter can be evaluated by taking a sufficient number of repeat measurements. If a grade efficiency curve is required as a means of quantifying a separation process, the errors continue since the curve is calculated from the size distributions of the feed material, as well as from the separated coarse and fine fractions. The authors show that, for a known error in particle size distribution, the grade efficiency curve can be corrected by a statistical method. For example, error spectra generated for sedimentation and diffraction methods of analysis were used to help correct the grade efficiency curves obtained.

A new use for sieves was introduced by Hunt et al.,[297,298] who showed that the particle count of a contaminated oil sample could be obtained by monitoring the pressure change across a filter as the mesh became blocked. The method was suitable for on-line use since the contaminated oil flow could be automatically reversed to clean and present the cleaned face of the mesh for subsequent measurements. The size distribution of the particles could be obtained by using meshes of different aperture sizes. A prototype for a commercial device has been described.[299]

X. HYBRIDIZED METHODS

Given that any one principle of particle size measurement measures its own "size" parameter, which is not necessarily the same as that obtained from another principle, and given that each method has limitations in its effective sizing range, then not even spherical particles need be sized in the same way by different methods. However, a combination of two or more methods can extend the size range analyzed or provide extra information from the particles. For instance, results from sedimentation and ESZ can give a crude estimation of particle shape.[300] Heidenreich proposed using two sensors, light blockage and ESZ, to share a common electrical assembly,[82,83] while light scattering, fluorescence, and ESZs have been successfully used together in commercial flow cytometers to help identify cell types. The hybridization of two or more methods into one instrument has advantages over using the methods separately; such combined technologies are in their early days.

Plantz described a forward-angle and 90° light-scatter dual-optical system which can be used to supplement the limited data obtained below 3 μm from Fraunhofer diffraction.[301] Tate and Raper combined data from Fraunhofer diffraction and PCS analyzers to help produce size distributions over the range 0.1 to 80 μm.[302] This was not an ideal combination since PCS only gave the average particle size of the sedimented (mainly) submicrometer size fractions, rather than size distribution. This meant that an extrapolation of the Fraunhofer diffraction analysis into the submicrometer range could be created by locating the fines to that one PCS point, rather than providing a fully analyzed particle size distribution. The location point was taken from the average mass mean size of size fractions <1.52 and 1.06 μm taken from the Andreasen pipet. It was noted that agreement was not as good as expected, perhaps because of the presence of particles above 1 μm settling in the PCS cell. It also seems likely that the assumption that Stokes diameter is equivalent to diffraction or PCS diameters is another complication.

Bayvel et al. have combined the techniques of Fraunhofer diffraction and the extinction of light caused by the ensemble of particles to provide an optical device for monitoring size distribution in the range of 0.1 to 1000 μm.[303] The mathematical basis for the analysis of the optical information is given, and the developed software provides the best-fit size-

distribution data results to standard distribution functions, as well as, of course, a visual display of the size distribution curve.

Oka et al. combined Rayleigh light scattering at 5 and 150° with PCS to allow the measurement of molecular weights and particle size in the micrometer region.[238] Light blockage and image analysis have also been combined.[304] A laser beam, focused down to 1.2 μm, scans a liquid or gaseous suspension of particles in 600-μm diameter circles at a constant velocity. A particle present in the focal zone casts a shadow on a photodiode detector, creating a pulse, the duration of which is a function of the particle's size. An internal microscope camera is simultaneously focused onto the measuring zone so that the particles can be displayed on a TV screen for direct observation or processed for shape and analysis.

Caldwell et al. have combined SFFF, as the size separation method, with PCS, as the particle-sizing method.[305] If particle relative density is known, SFFF can give particle sizes. PCS can give an accurate average size only if the dispersity of sizes present is not great. The methods were shown to agree well if the particle density is known, as is the case for lattices. If the particle density is not known, fractions produced from the SFFF can be sized by PCS and the density calculated. Measurement of a size distribution over a wide range was not studied: this would require the mass of each of the fractions to be determined, as well as their mean particle size.

Xu et al. used a combination of Rayleigh light scattering and electrical birefringence to determine the structural characteristics of disk-shaped bentonite particles in suspension.[306,307] PCS measurements gave the average "size" from the average of the translational and rotational diffusion coefficients. Electrical birefringence, coupled with PCS, allows the electrophoretic mobility of particles to be measured.[308]

In the future, more hybridized methods can be expected, perhaps because of their potential promise and because they are more readily possible now with cheaper and faster computer power, or perhaps because they will offer a major breakthrough toward the ultimate particle size measurement device. That might be one that measures from 1 nm to 1000 μm, or more, requires no specific knowledge of the properties of the particles to be analyzed, gives real-number and real mass-size distributions and concentration, characterizes particle shape, requires no specific sample preparation, is simple and foolproof to use, has high accuracy and size resolution, is virtually instantaneous in its response, and, as a market survey might also show, would cost the user only one or two thousand dollars to buy! These are the manufacturer's targets; time will tell how effectively the manufacturers will respond.

XI. COMPARISONS OF METHODS

Comparing results from two different methods, such as the average sedimentation (Stokes) diameter and the average volume (Coulter) diameter, can be interpreted as deriving a "shape" ratio. The mean sizes produced by these methods were used to obtain a sphericity value for lime and mud samples,[309] as are used in paper pulp dewatering. Lines had reviewed other data produced over the years to determine if a crude estimate of average particle shape could, indeed, be achieved.[300] He found that, in general, spheres and fairly regular, but angular, particles tended to give settling-to-volume diameter ratios close to the expected value of unity, while flaky particles gave values of around 0.5.

Many publications show results from the same material analyzed by a variety of techniques, but often no interpretation of the similarities or differences between them is made. In fairness, it is often difficult to draw any conclusions other than that the results differ for unknown reasons, but just attributing the differences to "the effects of particle shape" is usually too simple an explanation.

BCR supplies powdered quartz reference materials which have been well characterized

for particle size distribution by gravitational sedimentation (the Andreasen pipet).[310] Clearly, they are useful for interlaboratory control purposes when using the same method and can also be used to obtain data from a variety of methods under different conditions and in different locations. Harfield et al. used these materials to compare results from the Andreasen pipet, Micromeritics' MIC 5000 D Sedigraph, Malvern's 3600D, and Cilas' Granulometer 715 Fraunhofer diffraction analyzer, and a COULTER COUNTER® model TAII.[208] Clearly, exact equivalence with these nonspherical particles cannot be expected because of the differing size parameter being measured, but the materials' fairly regular, if angular, nature should allow any major differences in performance to be seen. Generally, the COULTER COUNTER® analyzer results were in close agreement with the reference sedimentation data, as had already been reported by Wilson,[311] as well as the Sedigraph results, but the diffraction data were dissimilar by an amount which did not seem to be related to the different size parameter being detected. In addition, the Cilas 715 and, to some extent, the Malvern 3600D data showed more fines (<10 μm) than expected in several cases. By using latex and pollen particles with no significant amount of fines, this overestimation was shown to be a characteristic problem.

Arakawa et al. used mica flakes as an extreme shape of material for their comparisons, as well as the fairly regularly shaped corundum and ground calcium carbonate.[312] Results were shown for optical microscope, sedimentation balance, photosedimentometer, COULTER COUNTER® and Microtrac diffraction instruments. Their rather unsurprising conclusion was that methods which are more sensitive to the orientation of particles give a greater spread of size distribution results than are obtained from more regularly shaped materials.

Sedimentation, diffraction, and sieving results on tungsten powders were compared by Halldin.[313] The results, of course, varied, partly because the ends of the distributions were truncated by the different methods. Sedimentation was preferred for powders with a significant mass below 2 μm, while diffraction was preferred if little or no mass existed below 2 μm since it was faster.

Švehlová and Svěrák provided results on the same samples as measured by microscope, Sedigraph, COULTER COUNTER® instrument, and Andreasen pipet, as well as by Joyce Loebl centrifuge, Microtrac, and Malvern FDAs.[314]

Koehler and Provder analyzed a series of PMMA latexes by disk centrifugal photosedimentometry, SFFF, hydrodynamic chromatography, PCS, transmission electron microscopy (TEM), and turbidity.[25,26] For small monodisperse latexes, the average particle sizes agreed more closely than for larger, less monodisperse, latexes. The light-scattering methods gave the largest apparent particle sizes and TEM the smallest, while DCP and SFFF were in the center of the range.

Gulari et al. compared the advantages and disadvantages of three light-scattering methods — PCS, multichannel turbidity spectra (TS), and FDA — in their overlap region of 0.5 to 5 μm by using latexes.[315] PCS and TS results compared well, but it was found that FDA cannot accurately measure such particles below 2 μm. PCS was the most difficult one to use.

Roebuck and Almond analyzed ultrafine tungsten carbide samples by the Fisher Sub-Sieve Sizer, the COULTER COUNTER® instrument, gas adsorption, X-ray sedimentation, Fraunhofer diffraction, image analysis, and oxidation.[316] The latter method appeared to be very useful for these materials having a mean size of around 0.3 μm.

Holtan and Pickard found that the Malvern 3600 FDA showed a second population of particles where microscopy did not.[317] In view of the often-reported anomalies in FDA results below some 4 μm, it is unclear whether the second population discovered was true or false.

That three different diffraction analyzers give different results is again shown by Blackford and Bartholomay[140] and Slangen,[318] the Leeds and Northrup, Cilas, and Malvern results being contrasted. Slangen also showed results from image analysis, Sedigraph, sedimentation

balance, sieving, Bahco sifter, light-blockage and light-scattering counters, and Sympatec and COULTER COUNTER® instruments, using a range of different materials.

Five techniques were used by de Yong and Wilson:[319] sieving, diffraction, light blockage, image analysis, and air permeametry. The advantages and disadvantages of the methods for pyrotechnic materials were reviewed and care was taken to present each set of analysis data on a volume basis. The differences seen were enough to restrict comparisons only to the central part of the distributions; even so, the conclusion was that it was difficult to directly compare the results from the different techniques. Curiously, the authors saw the need for calibration as a disadvantage. It can be argued that the ability to properly calibrate a device, rather than rely on the manufacturer's calibration or claim that it does not need calibrating, or the device's long-term stability, is an advantage.

Tüzün and Farhadpour evaluated their results thoughtfully.[199] The Malvern diffraction analyzer was found to give size distributions within ± 10% of those obtained from scanning electron microscopy, image analysis, and ESZ for a 1- to 10-μm crystalline silicalite of fairly uniform particle shape. Since the diffraction results were not expected to be reliable for sizes close to the wavelength of light, the agreement was shown to be due to a rather fortunate combination of the light absorptive nature and polydispersity of the particles.

When measuring particulate contamination in parenteral solutions, Montanari et al. found, as others have, that the particle counts from a COULTER COUNTER® instrument were usually higher than those from a HIAC instrument, when at the 2- and 5-μm size levels.[320] As noted by Haynes-Nutt,[321,322] this may, in part, be caused by the differences in size response to nonspherical particles between the two methods due to particle shape and surface texture, but it is also likely to be, in the case of the light-blockage technique, a function of the wavelength of the incident light, the r.i. of both particle and liquid, and reflection and diffraction. In cases where the refractive indices are similar, the particles will be invisible or of an apparently reduced size to such an optical method, but will be measurable by the ESZ technique. The authors believed that the optical effects were the major cause of the discrepancies in the results.

A HIAC particle counter was compared with an Ortho flow cytometer as a means of monitoring particulate contamination in deionized water; both were found to give more or less comparable results, although the accuracy of the numbers recorded was said to be questionable.[323]

XII. EPILOGUE

The continued proliferation of particle size analysis instruments, together with the movement toward more and more reliance on the manufacturer's software — details of which are rarely given — means that standardization, particularly for results from nonspherical particles, is perhaps the most important requisite in the future. A strong plea for full standardization, for example, has been made by Davies.[324] He indicated that the current needs, at least in the U.S., were for more effort in preparing particle standards and reference materials and in addressing the needs of newer technologies, more international cooperation, and a greater understanding of what optical methods measure. It is our opinion that the industry can no longer make do with the attitude that all methods measure different parameters of the particle and so must give different results. Independent and thorough evaluations of particle-size analyzers, performed by competent and respected authorities, are required internationally. However, no suitable bodies seem to be available at present to do this.

Until that time comes, the value of the national groups will be to help bring about a fuller awareness of the various techniques and their respective advantages and limitations. This is not a new requirement, but, as more and more workers enter the field of particle size analysis and manufacturers introduce new instrument models with increasing frequency, the need is becoming much more urgent.

No exciting technique, which will solve everyone's problems, is just around the corner or even expected. Relatively minor, but frequent, advances in the existing methods will continue for the foreseeable future. The hybridization of existing techniques will offer some advantages.

Nevertheless, the former trend of operator convenience, when users only required "black-box" results, is beginning to return to the primary requirement of accuracy and resolution. Advances in the understanding of all of the methods involved, along with today's enhanced data processing capability, should allow particle size measurement to become an even more powerful and useful tool in the future.

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