



Analytical Series

Particle Size Distribution, Measurement, and Assessment: Principles, Features, Limitations, and Benefits

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The field of particle size distribution (PSD) characterization and measurement has experienced a renaissance over the past 40 years. These changes have been driven by advances in electronics, computer technology, and sensor technology in conjunction with the market pull for PSD methods embodied in cost-effective, user-friendly instrumentation. These changes can be characterized by at least four activities: (1) End user innovation exemplified by techniques such as hydrodynamic chromatography (HDC), capillary hydrodynamic fractionation (CHDF), and field flow fractionation methods (sedimentation, flow, and thermal fields, respectively SdFFF, FIFFF, and ThFFF); (2) Revitalization of older instrumental methods such as gravitational and centrifugal sedimentation; (3) Evolution of research-grade instrumentation into low-cost, routine, user-friendly instrumentation exemplified by dynamic light scattering (DLS); and (4) The attempt to meet extremely difficult technical challenges such as: (a) providing a single hybrid instrument with high resolution over a very broad dynamic range (4+ decades in size; e.g., Fraunhofer/Mie; photozone

sensing/DLS); (b) PSD measurement of concentrated dispersions (acoustophoretic, dielectric measurements, fiber optic DLS (FOQELS)); (c) in-situ process particle size sensors (in-line or at-line, e.g., FOQELS); (d) routine measurement of particle shape and structure (e.g., image analysis). Instrumental methods resulting from these activities are discussed in terms of measurement principles and the strengths and weaknesses of these methods for characterizing PSDs. Business and societal driving forces will impact customer perceived instrumentation and knowledge needs for the future and the ability to meet the specific difficult technical challenges in particle size distribution characterization mentioned above. Anticipated progress toward meeting these technical challenges in particle size distribution characterization mentioned above is discussed.

INTRODUCTION

Over the last 40-plus years, newer coatings technologies, such as high solids, powder, waterborne, and radiation-curable coatings have had significant market share growth. These coatings technologies have been developed to meet the challenges of: (a) governmental regulations in the areas of ecology (volatile organic compounds (VOC) emission); (b) long-term increasing

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costs of energy and petroleum based solvents; (c) more active public consumerism; and (d) the continual need for cost-effective high-performance coatings in a highly competitive and global business environment. These new coatings technologies require the use of water as the major solvent with water-soluble or high molecular weight latex polymers or the use of strategically designed low-molecular weight polymers, oligomers, and reactive additives which, when further reacted, produce high molecular weight and crosslinked polymers. This has led to a need for improved methods of materials characterization in diverse areas, which include molecular weight distribution analysis, particle size distribution (PSD) measurement and assessment and characterization, rheology of coatings, film formation and cure process characterization, morphological surface and bulk characterization, and spectroscopic analysis, as well as a need for improved methods for modeling and predicting materials properties and processes.

Concurrent with the major technological changes in the coatings industry was the significant increase in the rate of change in instrumentation technology. This change was driven by significant advances in electronics and computer and sensor technologies to produce computer-aided, more user-friendly, reliable, and cost-effective instrumentation. The advances in instrumentation and computer technology are filling the need for improved polymer and coatings characterization methods in the context of the newer coatings technologies.

The newer coatings technologies have driven the need for improved methods of PSD assessment and characterization for each of the coatings technologies in terms of size ranges and component particulates as follows:

Waterborne coatings (0.01–50 μm)

- Latex
- Pigments (size and shape)
- Emulsions and dispersions

Powder coatings (0.1–100 μm)

- Resin-pigment composite particle:
 - (a) dry powder;
 - (b) wet concentrated dispersions
- High solids
- Pigment grind particle size analysis (0.1–100 μm)

The particle size assessment and characterization needs resulting from the challenges presented by the newer coatings technologies and their component materials leads to the following measurement requirements:

- Wide dynamic particle size range
- Improved resolution
- Measurements made in the concentrated dispersion regime
- Assessment of dispersion stability
- Description of structural and textural morphology

The changes in the field of PSD characterization and measurement, aided by the advances in electronics computer and sensor technologies, can be characterized by at least four activities:

- End user innovation
- Revitalization of older instruments
- Evolution of research grade instrumentation into low-cost, user-friendly instrumentation
- Attempts to meet extremely difficult technical challenges

The advances in PSD measurement methods will be discussed in the context of the four above-mentioned activities in terms of measurement principles and the strengths and weaknesses of these methods for characterizing PSDs.

END USER INNOVATION— COMMERCIAL DEVELOPMENT

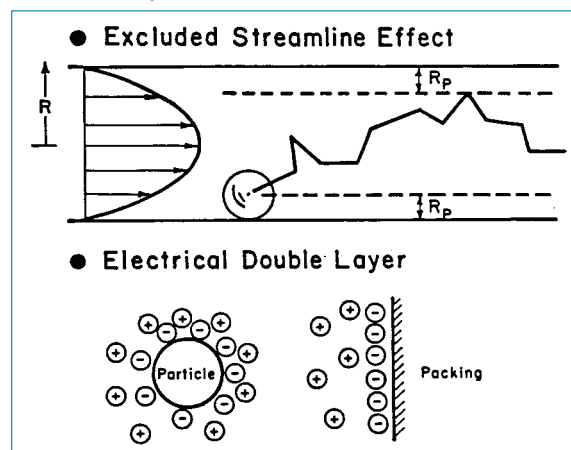
The first activity in the changes in PSD characterization and measurement is the commercial development of instrumental methods originally developed in a few academic and industrial laboratories by individuals with high levels of skill and expertise. Innovations in instrumentation and methods usually are driven by the customers who are the technological and scientific leaders and prototype developers, while the instrument vendors are the technological followers who have the engineering skills to do cost-effective commercial development. Examples of such methods are hydrodynamic chromatography (HDC), capillary hydrodynamic fractionation (CHDF), and field flow fractionation methods involving the use of sedimentation, flow, and thermal fields (e.g., SdFFF, FIFFF, and ThFFF).

Hydrodynamic Chromatography (HDC)

HDC, first reported in 1976, was invented in an industrial laboratory by Hamish Small¹ to fulfill an analysis need of The Dow Chemical Company. It took 10 years to be transferred from a laboratory method requiring a high degree of skill into a commercial instrument requiring a moderate degree of skill. The commercialization was carried out by Micromeritics Corporation. However, the commercialization failed in the marketplace because of technological limitations inherent in the method and because of competitive market pressures.

HDC instrumentation is comprised of a liquid chromatograph with an accurate and precise pumping system. Detection was accomplished with a sensitive fixed wavelength ultraviolet (UV) detector. Fractionation and separation of particles occurred in a column packed with uniform, non-porous beads. The separation of particles by size took place in the interstices between the beads and was primarily a function of the bead size and the ionic strength of the medium. The separation mechanism is shown in *Figure 1*. The interstices between the beads can be treated as capillaries of varying

FIGURE 1—Schematic of hydrodynamic chromatography separation mechanism and operative forces.



sizes. Larger particles ride higher up on the parabolic flow profile and are eluted first while some smaller particles hug the walls of the capillary experiencing slower flow streamlines and exit later. Other contributing factors to the separation mechanism include electrical double layer effects and Van der Waals attraction. The fatal technical flaw in the methodology was the unpredicted occurrence and amount of particle deposition, which took place in the packed columns. The overall features, benefits, and limitations of this methodology are shown in *Figure 2*.

Capillary Hydrodynamic Fractionation (CHDF)

The “Tubular Pinch Effect” mechanism operative in CHDF was first discovered by Segre and Silberberg² in 1962 and applied to particle size analysis in 1979 by Regnier and Ball³. However, it did not develop into a viable commercial instrument until innovative experimental and theoretical work was carried out by Silebi and Dos Ramos.^{4,5} The commercial embodiment of CHDF had become available from MATEC Applied Sciences. CHDF instrumentation is quite analogous to HDC in that a liquid

FIGURE 2—Features, benefits, and limitations of hydrodynamic chromatography for PSD analysis.

Features and Benefits

- Large Representative Sample Used (10^9 Particles)
- Samples Measured in Dispersion (No Particle Shape Change)
- Results are Independent of Particle Density
- Apparent PSD Directly Obtained
- Routine Methods for Plant Quality Control can be Developed (Equipment is Easy to Set Up)

Limitations

- Particle Deposition in Packed Columns Probable
- Operating Conditions Somewhat Specific to Type of Samples Being Analyzed
- Calibration of Size Scale with Standards Required
- Detector Response Corrections Needed (Mie Scattering)
- Band Broadening Corrections Needed
- Complex Mathematics Required for Absolute PSD Analysis

chromatograph with precise, accurate, and reproducible flow is required. In this instrument, the separation does take place in capillaries of defined dimension using split-flow injection. The mechanism of this separation method is essentially the same as that postulated for HDC. However, now the column is an empty capillary, so there is much less propensity for the particles to deposit in the column. The factors influencing the particle size fractionation are shown in *Figure 3*, and the associated features, benefits, and limitations of CHDF are shown in *Figure 4*.

Field Flow Fractionation (FFF)

Field Flow Fractionation methods were invented by J. Calvin Giddings and co-workers and reported in 1967.⁶⁻⁷ The technology transfer of FFF methods from an academic laboratory method to viable commercial instrument has taken a minimum of 20 years to occur. The DuPont Instrument Company commercialized a sedimentation FFF instrument (SdFFF) in 1986 based upon the pioneering work of J. Calvin Giddings and the subsequent research of Kirkland and Yau.⁸ Unfortunately, the DuPont Instrument Company’s SdFFF instrument was a commercial failure and unavailable by 1991. However, a small entrepreneurial company known as Fractionation,

FIGURE 3—Operational factors and data analysis considerations influencing CHDF PSD analysis.

Capillary

- Particle Radius/Tube Radius
- Tube Length

Eluent

- Liquid Viscosity (Temperature)
- Surfactant Type (Anionic, Ionic)
- Molecular Weight of Surfactant
- Ionic Strength
- pH
- Temperature
- Flow Rate
- Accuracy
- Constancy

Detection

- UV (Turbidity)
- Viscometer

Data Analysis

- Response Factor Correction
- Band Broadening Corrections

Inc. began making SdFFF instruments commercially available in 1988, followed by FIFFF (flow FFF) instruments in 1991 and, more recently, ThFFF (thermal FFF) instruments.

Field flow fractionation is a form of one-phase chromatography. The instrument is a liquid chromatographic system in which the separation takes place in a flat, narrow channel (typically 100 to a few hundred micrometers in width). A parabolic flow profile is created in this narrow channel by the mobile phase. An external field is applied across the face of the channel such that the field extends over the channel’s thin dimensions and is perpendicular to the flow field. Particles are driven toward the accumulation wall of the channel and form a diffuse cloud, which has an exponential concentration distribution as a result of Brownian motion acting against the field. For particles less than 1–2 μm , smaller particles are displaced farther from

FIGURE 4—Features, benefits, and limitations of CHDF for PSD characterization.

Features and Benefits

- Large Representative Sample Used (10^9 Particles)
- Sample Measured in Dispersion (No Particle Shape Change)
- Apparent PSD Directly Obtained
- Routine Methods for Plant QC for Specific Products Easy to Develop
- High Resolution
- Very Little Sample Information is Required
- Results are Independent of Particle Density
- Analysis Time is Under 8 Minutes
- High Sample Throughput with Unattended Automatic Sample Injection
- Separation on Basis of Particle Surface Chemistry is Possible but Not Implemented

Limitations

- Possibility of Particle Deposition and Plugging of Capillary
- Operating Conditions Somewhat Specific to Type of Sample
- Calibration of Size Scale with Standards is Required
- Detector Response Corrections Needed (Mie Scattering)
- Band Broadening Corrections Needed
- Complex Mathematics Required for Absolute PSD Analysis
- Dynamic Size Range ~ 1.5 Decades for Particles Less Than $1.0\mu\text{m}$

the accumulation wall. When the flow field is turned on, the smaller particles, which ride higher on the parabolic flow profiles elute first. The fields that have been used include SdFFF, ThFFF consisting of a temperature gradient across the channel walls, cross flow (FIFFF), electric (ElFFF), and magnetic (MFFF). Commercial instruments are available to perform SdFFF, ThFFF, and FIFFF.

A schematic of the instrumentation separation mechanism and some channel configurations are shown in Figure 5. When the particles are greater than 1 μm , effects of Brownian motion become negligible, and the larger particles ride higher on the parabolic flow streamlines because the velocity-dependent lift forces increase relative to the driving forces produced by the perpendicular external field. In the $\sim 1\text{--}100\ \mu\text{m}$ size range, the larger particles elute first, analogous to CHDF. This mechanism is termed

the steric mode of FFF (StFFF). In the commercially available instrumentation, field programming options are available for extending the size separation range, reducing the analysis time and optimizing the resolution per unit of time. Examples of separation by SdFFF, FIFFF, ThFFF, and StFFF are shown in Figure 6. The features, benefits, and limitations of FFF chromatography methods are shown in Figure 7. For a review of FFF applied to particle characterization, the reader is referred to the many papers and review articles of Giddings and co-workers.⁹

The commercialization of the instrumental techniques of HDC, CHDF, and FFF have attempted to address the market pull by many industries for PSD analysis methods, primarily in the $0.01\text{--}1.0\ \mu\text{m}$ size range. The coatings industry material characterization needs, as a result of the growth of waterborne coatings technology for improved particle size distribution

analysis of latex, pigments, and emulsions, is a component of the overall market pull for these techniques.

REVITALIZATION OF OLDER INSTRUMENTAL METHODS

Gravitational and Centrifugal Sedimentation

The second activity in the renaissance of PSD characterization and measurement is characterized by the revitalization of older instrumental methods such as gravitational and centrifugal sedimentation methods. Redesign, modernization with advanced electronics, and user-friendly computer-aided analysis have extended the instrument product life cycle. A good example is disc centrifuge photosedimentometry (DCP).^{10,11} The basic technology has been around since the late 1950s and was embodied into a commercial instrument in the 1960s by the Joyce Loebel Company. During the 1970s, the Joyce Loebel Disc Centrifuge Photosedimentometer was the only commercially available instrument for obtaining PSD information by the DCP technique. This technique was particularly well suited for the particle size analysis requirements of the coatings industry for the analysis of latexes, pigments, and emulsions.¹²⁻¹⁴ However, it had deficiencies that made it unsuitable as a plant quality control instrument. Over a period of about 10 years, industrial scientists at The Glidden Company developed an improved instrument¹¹, method of use^{15,16} and user-friendly data analysis system. The Glidden Company's DCP technology was licensed to the Brookhaven Instruments Corporation in 1986, which made additional engineering improvements and successfully commercialized the enhanced and revitalized DCP technology. The current instrument can operate in both the line start and homogeneous start modes.

In addition, Brookhaven Instruments Corporation extended the technology by developing an X-ray detection system that facilitated the analysis of heavy small inorganic particles. The X-ray disc centrifuge photosedimentometer (X-DCP) became commercially available in 1991 and was based upon a prototype developed by Terry Allen at DuPont. The X-DCP can operate both in the gravitational and sedimentation modes.

FIGURE 5—Schematic of FFF instrumentation, separation mechanisms, and channel configurations for SdFFF, FIFFF.

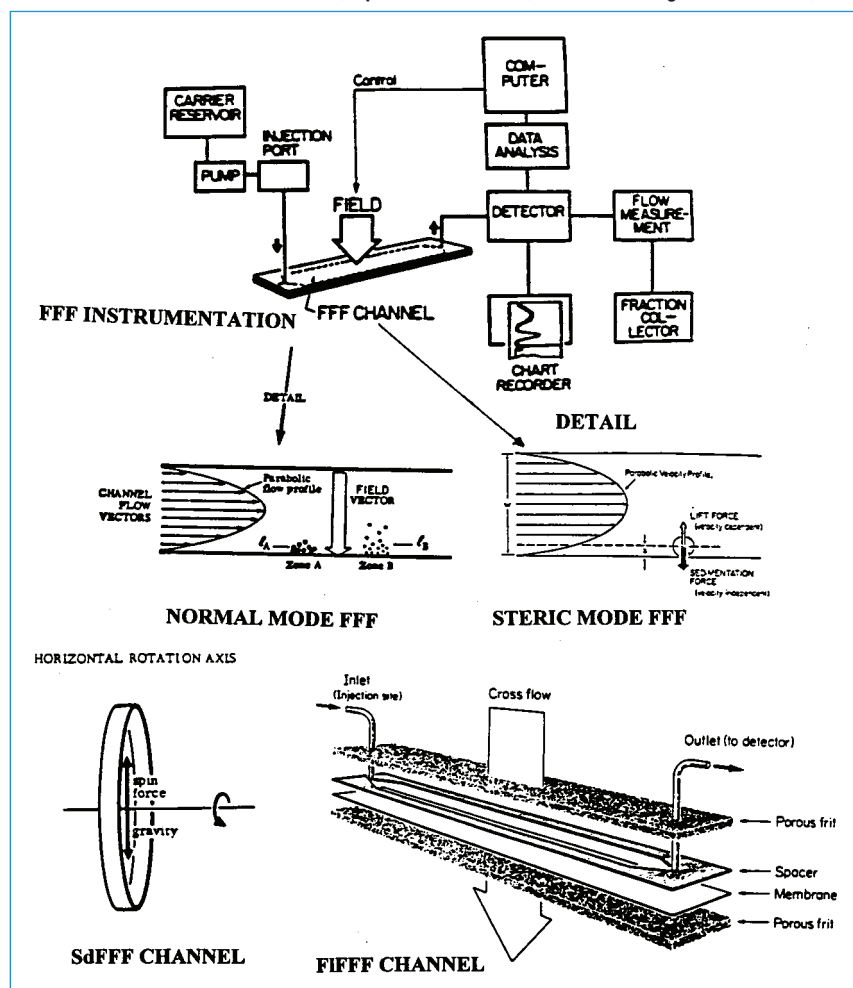


FIGURE 6—FFF separation of mixtures of monodisperse latex beads. a) Field programmed SdFFF with rpm = 10,000 at $t = 0$. b) FIFFF With polypropylene membrane at 42.9 ml/min. c) ThFFF in acetonitrile with $\Delta T = 170$ °C. d) StFFF at 38 ml/min and 1100 rpm.

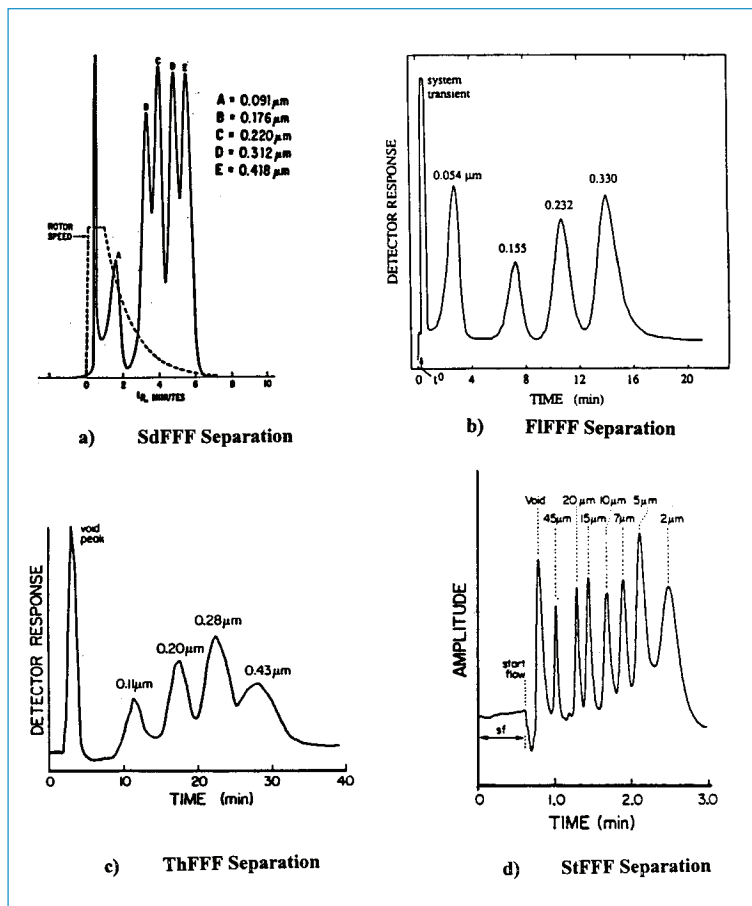


FIGURE 7—Features, benefits, and limitations of FFF (SdFFF, FIFFF, ThFFF, and StFFF) for PSD characterization.

Features and Benefits

- Large Representative Sample Used (10^9 Particles)
- Samples Measured in Dispersion (No Particle Shape Change)
- Particle Density can be $>$ or $<$ Mobile Phase Density
- Apparent Particle Size Distribution Obtained Directly
- Retention (Particle Size) is Predictable
- Wide Dynamic Particle Size Range Achievable (.01–10 μm for SdFFF, FIFFF, ThFFF, \sim 1–100 μm for StFFF)
- PSD Calculations are Simple

Limitations

- FFF Channel Difficult to Construct with Precise Control Over Geometry
- Correction for Detector UV Response Needed (Mie-Scattering Correction)
- Upper Limit to Particle Size Range = 1 μm Unless Steric FFF Mode is Invoked
- Particles Must Be Spherical for Accurate Data Analysis

The range of variations in sedimentation instrumentation mode, detection, and experimental method is shown in *Figure 8*. Also shown in *Figure 9* are Stokes' laws for gravitational and centrifugal sedimentation, which govern the fractionation of particles by size in a gravitational or centrifugal force field. The line start mode^{11,12} can produce very high resolution separations. An example of such a separation is shown in *Figure 10* for a mixture of nine Duke polystyrene latex standards covering a size range of 107–993 nm in approximately 100-nm increments. Baseline resolution was achieved in seven out of the nine standards. Another major advance in the method of operation is protecting the aqueous meniscus from evaporative cooling and disruption of the density gradient in the fluid by sealing the surface with a small amount of dodecane (usually 1 ml of n-dodecane, injected a few minutes after the density gradient has formed, in about 15–20 ml of an aqueous spin fluid). The sealing of the fluid surface inhibits evaporative cooling and thereby maintains a stable density gradient for several hours and extends the analysis size range. The homogeneous start mode is faster, covers a wider dynamic size separation range, but has less resolution than the line start mode for multi-modal separations. The features, benefits, and limitations of sedimentation methods are shown in *Figure 11*.

An instrument designed for particle size analysis by sedimentation in a gravitational field was patented by Oliver, Hicken, and Orr and commercially embodied, in 1969, by Micromeritics into an instrument known as the Sedigraph. This instrument produces a cumulative distribution of particle sizes and has been used heavily for the analysis of pigments such as titanium dioxide. Starting in 1988, the Sedigraph's design and function were revitalized by adding an automatic sample introduction system for unattended operation as well as improving the data analysis system.

EVOLUTION OF A RESEARCH INSTRUMENT INTO A ROUTINE USER-FRIENDLY INSTRUMENT

Dynamic Light Scattering (DLS, PCS, QELS)

The third activity is the evolution of a research instrument into a low-cost instrument that requires a minimum

degree of skill to use. An excellent example of this process is the transformation of research-grade photon correlation spectrometers into low-cost, easy to use, limited-function instruments for routine analysis applications.

Dynamic light scattering (DLS) was first known as quasielastic light scattering (QELS) derived from the fact that when photons are scattered by mobile particles, the process is quasielastic. This gave rise to the acronym DLS, since QELS gave information on the dynamics of the scatterer. Since measurements are made with a digital correlator, the acronym PCS (photon correlation spectroscopy) is widely used. The first QELS measurements were made in 1964 by Cummins et al.¹⁷ The first commercial instruments were available circa 1976 and only suitable for use by experts. The early measurements were concerned with obtaining translational diffusion coefficients of macromolecules and particles. The technique was used to gain information about particle size by relating the diffusion coefficient to particle size through the Stokes Einstein equation for spheres.¹⁸

By the early 1970s, the fundamentals had been established. From the mid-1970s onward, improvements occurred in the technology for digital autocorrelators as well as in automation and integration of advances in microprocessors and laser technology. From the early 1980s onward, the PCS instrumentation was increasingly used for particle size analysis. By 1985, low-cost routine 90° instruments were commercially available for routine analyses. The PCS instrumentation was made more automatic and

FIGURE 8—Variations in sedimentation instrumentation and operational factors.

Gravitation large sizes, high density	➔	Centrifugation small sizes, low density
X-Ray Detection no optical corrections	➔	Light Detection optical corrections
Scanning Detector faster run, less resolution	➔	Fixed Detector slower run, high resolution
Line Start slower run, high resolution	➔	Homogeneous Start faster run, less resolution

FIGURE 9—Equations of motion and Stokes' law for gravitational and centrifugal sedimentation.

<p>Gravitational Mode (Rock in a Pond)</p> $m_p \cdot d^2x/dt^2 = m_p \cdot g - m_f \cdot g - F \cdot dx/dt$ <p style="text-align: center;">↓① ↑② ↑③</p> $t = (18 \cdot \eta \cdot x) / (g \cdot \Delta \rho \cdot D^2)$ <p>Where</p> <p>① = Gravitational Force ② = Buoyancy Force ③ = Frictional Force ④ = Centrifugal Force</p> <p>$F = 3 \cdot \pi \cdot \eta \cdot D$, sphere $\Delta \rho = \rho_p - \rho_f$ t = appearance time at detector D = Particle Size Diameter X = Sedimentation Distance to Detector Position</p>	➔	<p>Centrifugal Mode (Rock in a Spinning Pond)</p> $m_p \cdot d^2r/dt^2 = m_p \cdot \omega^2 \cdot r - m_f \cdot \omega^2 \cdot r - F \cdot dr/dt$ <p style="text-align: center;">↓④ ↑② ↑③</p> $t = [18 \cdot \eta \cdot \ln(r/s)] / \omega^2 \cdot \Delta \rho \cdot D^2$ <p>M_p = Mass of Particle M_f = Mass of Fluid ρ_p = Density of Particle ρ_f = Density of Fluid η = Viscosity of Fluid g = Gravitational Constant ω = Rotational Speed of Disc r = Radius of Photodetector Position s = Initial Radial Position of Particles determined by spin fluid volume</p>
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FIGURE 10—Line start separation of a nine-component mixture of polystyrene latex standards (107, 220, 298, 496, 597, 705, 895, 993 μm.)

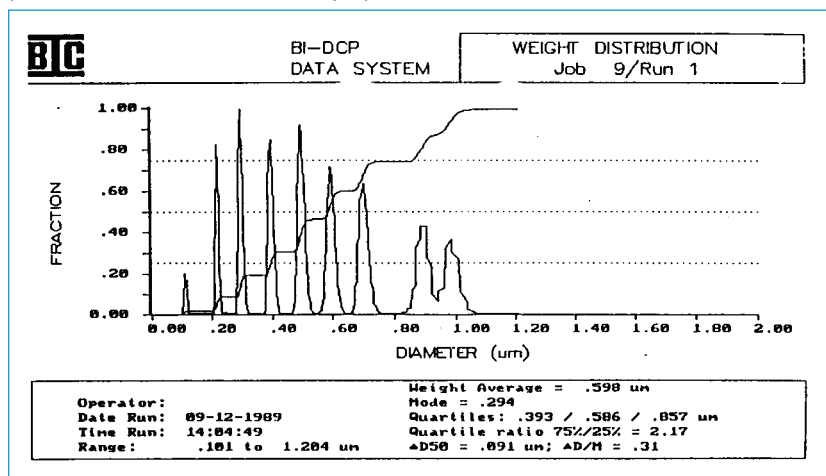


FIGURE 11—Features, benefits, and limitations of sedimentation methods for PSD characterization.

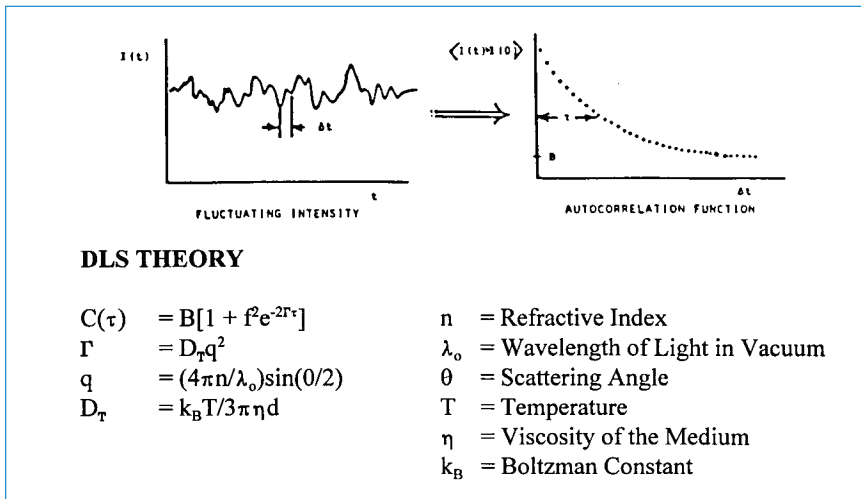
Features and Benefits

- Large, Representative Sample (10⁹ Particles)
- Samples Measured in Dispersion (No Particle Shape Change)
- Scanning Detector, Fast Measurements Possible
- Fractionation Leads to High Resolution
- Wide Size Range, 10nm–100 μm
- Particle Size Predictable from Stokes' Laws
- PSD Calculations are Straightforward

Limitations

- Particle Size Limits Depend on Density, Viscosity
- Hydrodynamic Instabilities: Gradients
- Very Broad Distributions Require Long Measurement Times

FIGURE 12—Simplified representation of scattering intensity $I(t)$ and corresponding autocorrelation function $C(\tau)$.



useful for the analysis of particle size and estimating PSD with the commercialization of an automatic sample dilution system invented by Nicoli and Elings.¹⁹

The DLS method utilizes the fluctuations in light scattering intensity observed over a range of time intervals. The autocorrelation function of light scattering intensity at time t is compared to time zero, $C(\tau) = (I(t) - I(0))$, for a range of Δt intervals. The autocorrelation function can be described by an exponential decay function of Δt . This process is schematically shown in Figure 12. For a monodisperse sphere, the correlation function is represented by an exponential decay function as shown in Figure 12 where D_T is the translational diffusion coefficient, q is the scattering wave vector. The particle

size d is related to D_T through the Stokes-Einstein equation as shown in Figure 12. It has been shown that particle sizes obtained on monodisperse spheres are accurate, precise, and highly reproducible. In addition, the PCS instrument is fast and has high throughput.

A schematic of a PCS instrument with auto-dilution is shown in Figure 13. This type of instrument also has been shown to have potential for online measurement of particle size for an emulsion polymerization reactor.²⁰

For polydisperse distributions, an average size and estimate of dispersity can be obtained from the method of cumulants. Inversion of correlograms to obtain PSDs for multimodal distributions has had limited success. If particle

size modes are in a ratio of 3:1 or greater, then it should be possible to extract the peak modes from the data. This is a low-resolution method compared to techniques such as CHDF, FFF, or sedimentation in a centrifugal force field.

The features, benefits, and limitations of DLS are summarized in Figure 14.

ATTEMPTS TO MEET EXTREMELY DIFFICULT TECHNICAL CHALLENGES

The fourth activity characterizing the changes in PSD characterization and measurement methods involve attempts to meet extremely difficult technological challenges as a result of advances in electronics and computing and sensor technologies. These technological challenges will be discussed below and can be cataloged as follows:

- Measurements in concentrated dispersions
- Wide dynamic particle size range measurement capability in a single instrument
- On-line and at line analyses
- Structural and textural morphology characterization of particle shape

Concentrated Dispersion Measurements

Fiber Optic Quasi-Elastic Light Scattering (FOQELS)

The need to measure particles in concentrated dispersions has led to the development of fiber optics QELS, given the acronym FOQELS by Brookhaven Instruments, for making measurements in concentrated dispersions up to 40% by

FIGURE 13—Schematic diagram of a DLS particle sizing instrument, including auto-dilution (NICOMP Model 370).

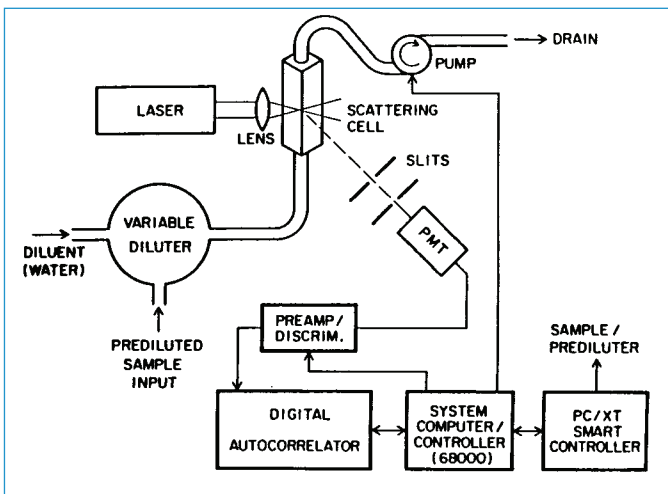


FIGURE 14—Features, benefits, and limitations of DLS for PSD characterization.

Features and Benefits

- Fast and Automatic
- Reproducibility
- No Calibration
- Large Size Range (3 nm–~3 μm)
- Versatility

Limitations

- Low Resolution (~3:1 Modal Separation)
- Intensity-Weighted
- Not Counting Particles (Ensemble Method)
- Dust in H₂O
- Limited Shape Information

weight. This commercial development is based on the work of Dhadwal et al.^{21,22} Visible light from a laser diode is focused into the sample by a monomode fiber, and the scattered light is collected by a second monomode fiber at an angle of 153°. The fluctuations in scattered light are analyzed by the photon correlation technique. As long as the dispersion has observable fluidity, translational diffusion coefficients can be measured and transformed into particle size information. The fiber optics technology enables remote measurement of processes. For small particles less than 100 nm, accurate measurements of size in concentrated dispersion can be obtained. As the particle size increases, deviations from absolute size are observed as the concentration increases due to multiple scattering effects. The precision, reproducibility, and size range of measurement associated with PCS measurements applies to the FOQELS measurements. FOQELS applications reported include particle size growth in emulsion polymerization, nucleation processes in metallic oxide manufacture and monitoring protein crystal growth.²³

Laser Light Diffraction

Over the last 30 years, there has been intense activity to revitalize Fraunhofer light diffraction technology to measure concentrated dispersions over a wide dynamic particle size range (0.1–800 μm) by combining Fraunhofer diffraction technology with light scattering detectors to generate a hybrid instrument. There are at least 10 instrument vendors involved in this marketplace. The market pull for this type of instrument has been

the need to provide particle size distribution information above and below 1.0 μm with a single instrument. Fraunhofer diffraction physics dates back to 1840. The advent of laser technology coupled with advances in computer technology has made this a viable commercial method of measuring particle size since 1972. The measurement is fast and can be used with dry powders and often the instrument of choice for powder coatings PSD measurements. Combining Fraunhofer diffraction with light scattering detection via Mie theory has enabled measurements to be made down to 0.06 μm, as reported by some vendors. The technique is a moderate to low-resolution technique for extracting multimodal distribution information. Below 2 μm, one has to carefully check the validity of the specific instrument vendor's software to extract multimodal distributions.

Electroacoustic Efforts

There have been at least three vendors (Matec Applied Sciences, Sympatec, and Malvern Instruments) that have produced instruments which take advantage of electroacoustic techniques in concentrated dispersion to measure both the particle size and the electrophoretic mobility distributions. These techniques are well suited for dense, inorganic materials such as titanium dioxide.²⁴ Exploratory experimentation has been underway to evaluate the technique for organic (low-density) dispersions. The technique is limited with respect to bimodal or multimodal distribution analysis in the same way as is the DLS technique.

Other Methods

Dielectric spectroscopy has some promise for particle size characterization in concentrated colloids, as reported by Sauer et al.²⁵ The authors showed that unique Cole-Cole plots could be obtained as a function of concentration and ionic strength for monodisperse latex particles.

Rheological flow curve analysis using the Cross equation for concentrated dispersions shows correlations of one of the rheological parameters to particle size and distribution.

Both dielectric spectroscopy and rheological flow curve analysis merit further study as possible methods for characterizing the PSD of concentrated dispersions.

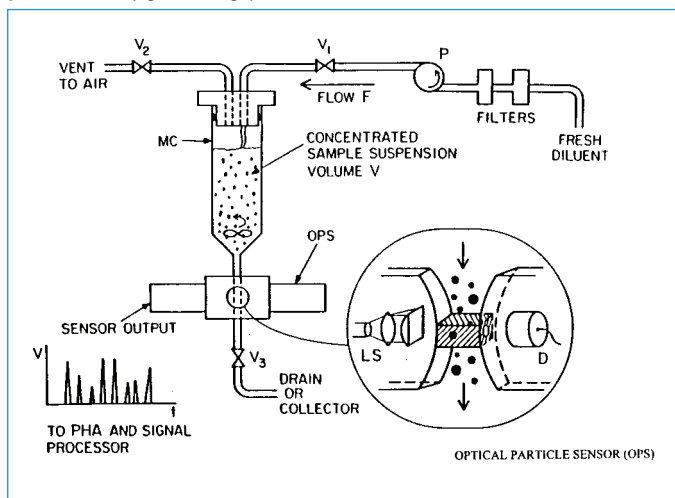
Wide Dynamic Particle Size Range Measurement Capability

There has been a lot of activity in developing this capability manifested by the development of hybrid instruments to cover a broad particle size range, some of which has been previously mentioned.

- Fraunhofer Diffraction/Mie Scattering (0.06–8000 μm)
- High resolution gravitational/centrifugal sedimentation (0.05–100 μm)
- Combination of FFF modes (e.g., StFFF with FIFFF or SdFFF)
- Single-particle optical sensing/DLS (0.1–300 μm)

The combination of single-particle optical sensing (SPOS) with DLS offers the possibility of analyzing a broad particle size range conservatively from 0.1–300 μm. The single particle optical sensing method is a photozone sensing method in which particles are counted by their ability to obscure light as they move through an orifice. This technique is automated through an auto-diluter. The sensing size range of SPOS is from about 1–300 μm. The SPOS technique is a high-resolution technique with respect to extracting multimodal distributions and is extremely sensitive to low levels of large particles in the presence of small particles (contaminant analysis). A schematic of the auto-dilution SPOS apparatus is shown in Figure 15 with a separation of a hexamodal mixture of monodisperse particles shown in Figure 16 to demonstrate the resolution of the method. When coupled with DLS, this hybrid instrument can characterize the full PSD of particulate systems in which the main contributor to the PSD are small particles.

FIGURE 15—Schematic diagram of the auto-dilution apparatus and optical particle sensor (light blockage).



DLS provides characterization of the small particles while SPOS characterizes the small level of larger particles, barely discernible in the DLS size distribution. An example of this type of analysis is shown in Figure 17.

On-Line, At-line Analysis

The main techniques available for on-line and at-line analysis of particle size distributions have been discussed to some degree. These techniques are:

- Fiber optic QELS (FOQELS) for concentrated dispersions
- Automatic dilution PCS
- Automatic dilution turbidity analysis
- Laser sensor-backscatter measurements

Angular scattering and absorbance measurements as a function of wavelength with photo diode array instruments and automatic dilution coupled with sophisticated mathematical analysis of PSDs is revitalizing the classical turbidity measurement and has been the subject of research by Prof. Luis Garcia-Rubio at the University of South Florida at Tampa.²⁶⁻²⁸

Lasentech has developed a laser backscatter instrument to measure effective particle size (chord length across a particle) in concentrated dispersion from several microns to larger sizes and has found practical application for monitoring particle size changes in many processes.

Structural and Textural Morphology Characterization of Particle Shape

The need for structural and textural morphology information has led to cost/performance improvements in automated image analyzers that now provide shape information using signature wave form characterization and fractal dimension characterization of shape and texture.²⁹

CONCLUSIONS

As we look forward toward the future, we can expect further advances in PSD characterization and measurement. It is anticipated that additional hybrid type instruments will be produced to cover a wide dynamic particle size range with improved resolution. The quest for PSD analysis methods for concentrated dispersions with good resolution over a wide dynamic range will continue and will be extremely difficult to achieve. However, advances will continue to be made in providing structural and textural information as a result of

FIGURE 16—Separation of a hexamodal mixture of monodisperse particle size standards by SPOS.

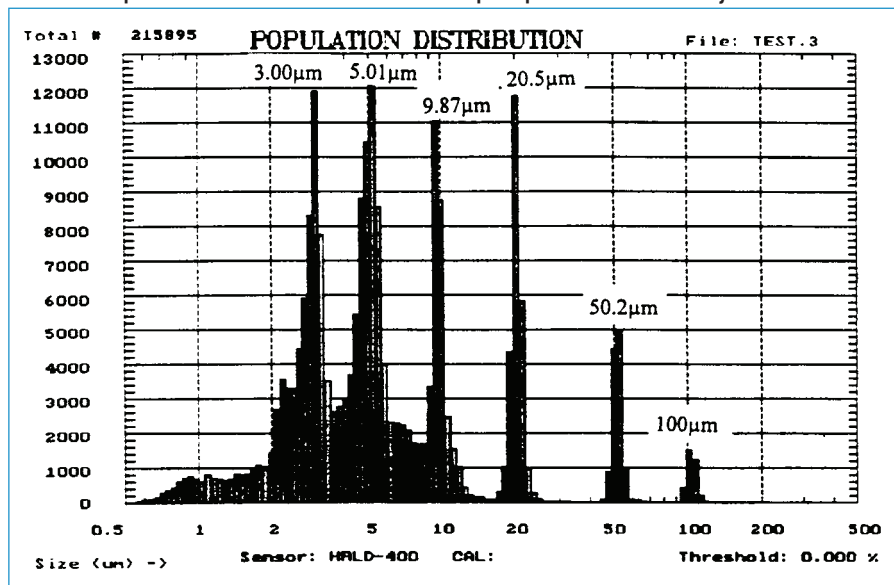
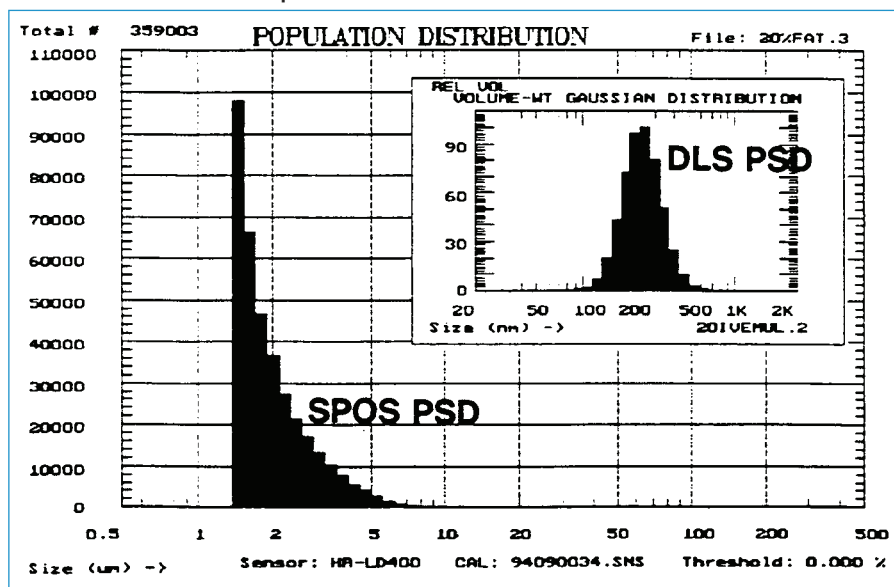


FIGURE 17—Combined SPOS/DLS particle size distribution.



advances in computer technology. Another major technical challenge which will probably be met is the development of in-line or in-situ particle size monitoring technology for latex reactors.

In addition, we expect the instruments to be more user-friendly, easier to use, more automated and smarter with respect to programmed intelligence.

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