10

Field scanning methods of particle size measurement

10.1 Introduction

Field scanning methods are those in which the size distribution of an assembly of particles is inferred from the interaction between the assembly and a measurement probe. In the simplest systems, the powder (or slurry) is probed or classified in order to generate a single point on the distribution curve. For example, one might monitor the 100-mesh percentage oversize from a mill in order to control a continuous milling operation. If the percentage increases, the residence time in the mill is increased in order that the product size remains unchanged.

It is commonly found that comminution shifts the whole distribution to a finer size distribution, to form a homologous family of curves, and plotting particle size against milling time on a log-log scale generates a straight line. Knowledge of two points on the distribution curve allows one to generate the whole distribution. An alternative method for plotting such distributions is the Gaudin-Schuman plot where the cumulative weight finer than a given size is plotted against that size, with each scale on a logarithmic basis. For the majority of milled material the relationship between the two variables is linear except at the coarse ends of the distributions. The distribution is characterized by two parameters; a distribution modulus, \( n \) (slope), and a size modulus, \( k \). Again, \( n \) remains constant for consecutive grinding of the same material.

Djamarani and Clark [1] state that many industrial processes are defined by a coarse \( (C) \) and a fine fraction \( (F) \), for example, oversize and undersize. In their example they use sieve sizes of 1400 \( \mu \)m and 180 \( \mu \)m that they fit to a Rosin-Rammler distribution. They define a curve of \( C+F \) against \( C/F \) from which the Rosin-Rammler constants can be read.

Field scanning instruments are ideally suited to on-line analysis. Rapid control of crystal size from a crystallizer; granule size from a granulator;
product size from a milling operation; particle size from a reactor etc. can yield enormous dividends in terms of less wastage (i.e. more material in specification) and superior product quality.

One problem associated with implementing this technology is the need to build an interface between the process and the measuring instrument. This often requires a dilution step that may alter the size of the particles. In the case of crystallizer control, for example, it may be necessary to remove two streams from the crystallizer and filter one so that the mother liquor can be used as the diluent.

Process streams often operate at high flowrates and these have to be split in order to obtain an acceptable flowrate in the measuring device. This reduction has to be carried out with care in order to minimize sampling errors. Ideally, the whole of the process stream should be examined. Inserting a probe directly into a process line is usually not feasible due to servicing and downtime problems. It is therefore preferable to use a side-stream that can be isolated from the process stream.

A sophisticated on-line analyzer can cost around $100,000 and the interface can easily double this cost. However, a 1% increase in yield can pay back this investment inside a year, making on-line size analysis very attractive. At the present time retroactive fitting of size analyzers is often necessary and one is often faced with space limitations. Designing these units into new process lines greatly reduces cost and makes their introduction more attractive.

10.2 Single point analyzers

10.2.1 Static noise measurement

This technique has been applied to the measurement of the average size of milled silica powder (size range 2 to 5 μm) suspended in air [2]. A continuous sample is drawn from the product stream into a sampling probe and diluted with an air injector that also provides the driving force. The sample stream is then passed through a 'uni-flow' cyclone that splits the sample into two streams; a low concentration ‘fine’ stream and a high concentration ‘coarse’ stream. As the relative mass flow rates of the two streams depend strongly on the size distribution of the feed (at a given flow rate), an average size may be found from a measure of the two concentrations.

Most particles suspended in air carry an electric charge, particularly if they have passed through a highly turbulent process. A probe inserted into the stream will detect this charge as an AC voltage that is strongly
dependent on concentration. The system was calibrated by feeding in samples of known mean sizes and recording the signals these generated for comparison with signals from unknown samples.

10.2.2 Ultrasonic attenuation

The attenuation of ultrasound by a slurry depends upon the particle size distribution and concentration of the solid phase. In order to separate these two variables it is necessary to carry out analyses at two different wavelengths, one of which is strongly dependent on concentration and the other on particle size distribution. The attenuation is also dependent on the spacing of the transmitter and receiver and other physical parameters in a predictable manner [3,4].

The first commercial ultrasonic on-line particle size analyzer was developed in the 1970’s and was based on the measurement of ultrasonic attenuation at two frequencies with an empirical model to predict particle size and concentration [5]. Instruments based on this patent are available as the Denver Autometrics PSM-100, 200, 300 and more recently 400. These are pre-calibrated for the selected mesh size (100, 200, 300 and 400) and the mesh read-out is proportional to the mass percentage less than this. These instruments can operate at extremely high concentrations, up to 60% by weight, and have found their widest application in mineral processing plants for improved grinding circuit control.

A major problem in the early development of the Autometrics’ system was that traces of air could lead to substantial attenuation losses. The air must be stabilized or removed to allow accurate measurement of particle size. Removing the air with a device that utilizes a combination of centrifugal force and reduced pressure solved the problem. The need to remove air increases the cost of the overall system significantly and makes it an expensive instrument when compared with other instrumentation often installed in grinding circuits. Nevertheless, it appears to be perfectly compatible with other approaches when its inherent reliability and long-term stability as an accurate size analyzer is taken into account. Several articles have been written describing applications of the PSM systems [6-9].

The limitations of the system 100 are: (a) the percentage solids should be less than 60% by weight (b) the particle size distribution should be within the range 20% to 80% less than 270 mesh and (c) the slurry particles should not be magnetized. The PSM systems 200 and 400 are later instruments designed to overcome these limitations.
10.2.3 β-ray attenuation

Instruments have been described that employ β-ray attenuation [10-15]. The accuracy of these devices is limited by their sensitivity to changes in feed density [16]. In order to calibrate it is necessary to re-circulate slurry samples in a closed loop at a number of dilutions for each slurry system, sieve analyses being carried on representative sub-samples. The signals from a scintillation counter can be used to control mill feed rate in order to compensate for changes in feed ore, grindability and feed particle size. Accuracies of 2% to 3% have been reported on Cornish granite, nepheline systems and copper and iron pulps in the size range 20 to 105 μm [17,18].

10.2.4 X-ray attenuation and fluorescence

This sensor is based on the comparison of the absorption of two x-ray beams, one of which is sensitive and the other insensitive to variations in particle size [19-21]. Each sensing head is specific to a particular system since the relationship between the two beams is dependent on the composition of the solids in the slurry stream. The technique is limited to x-ray opaque material.

Von Alfthan [22] describes an on-stream x-ray fluorescence system that consists of two flow cells through which the slurry passes. In the classifying flow cell, the slurry flows in a straight path behind a window; it then strikes an obstacle that causes slurry mixing as it enters a turbulent flow cell. X-rays excite the slurry in both cells and the resulting fluorescent radiation is a measure of particle size. The system, sold as the Courier 300, measures both x-ray scattering and x-ray fluorescence and is intended primarily as a composition monitor. The measured data can be analyzed to give chemical composition, solids content and maximum particle size.

10.2.5 Counter-flow classifiers

Two instruments have been developed for on-line measurement of flowing powders coarser than 100 μm in size [23-26]. In the first instrument a side stream of solid particles from a process line is fed into an air elutriator that separates it into an oversize and undersize stream. The particle flow rate into the elutriator is measured and the cut size for the elutriator adjusted so that the flow of oversize particles out equals 50% of the inlet flow. The elutriator cut size is then equal to the average size of the powder. In the second instrument the flow rate is varied and the signal ratio of the two
flowmeters is inputted as the y-axis of an x-y recorder. The x-axis is reduced to the cut size for the elutriator. A sweep time of 40–60 s at flow rates of 2.4–3 g s\(^{-1}\) gives a cumulative distribution in the size range 100-700 \(\mu m\).

10.2.6 Hydrocyclones

An ideal on-stream sizing device would sample the whole of the stream and not include any special instrumentation. The nearest approach is to use a classifying hydrocyclone as these are easily installed and often form part of an industrial plant. By measuring the flow rates and pulp densities, and assuming a size distribution law for the feed, a computer program can be written to give the modulus and index of the feed. Under normal operating conditions the present state of the theory of cyclone operation renders this impracticable [27] although it can be used under favorable conditions [28].

Lynch et. al. [29] proposed that the percentage less than some chosen mesh size in the cyclone overflow could be related directly to the \(d_{50c}\) parameter of the cyclone, provided that the size distribution of the feed to the cyclone does not change appreciably. In closed production circuits there may be marked changes in the size distribution of the cyclone feed and an empirical relationship has been developed [30]. The application of this technique requires very thorough analysis of the circuit and repeated checking of empirical equations. An alternative approach has been to accept the inherent difficulties of sampling and install smaller, more precise, classifiers alongside the production classifiers [31]. Tanaka has also investigated the use of hydrocyclones for on-line analysis [32].

10.2.7 The Cyclosensor

This is a batch size analyzer [33] (Figure 10.1). An extremely dilute sample of milled ore is introduced, at a constant flow rate, to a coarse separator in the form of a tangentially fed cylindrical screen. The coarse fraction is allowed to settle and the fine fraction is further separated with an efficient hydrocyclone into a fine and a very fine fraction. The very fine fraction is discarded and the fine fraction is allowed to settle. The ratio of the times taken to fill the coarse and fine fraction collection vessels to indicated levels can be related directly to the particle size distribution. The cyclosensor has a sensitivity whereby a change of ±1.8% passing 100
mesh can yield a 7% change in the ratio of the settling times. The reproducibility is such that for the same feed rate of the same solids the ratio of times remains constant to better than 1% and an increase in feed rate of 30% has no effect on the ratio.

A patent has been issued on an instrument operating in a similar way [34]. It consists of a particle suspension sampler, a settler and a weight or volume sensor. Particle size distribution is determined from sensor output and the time for the settling particles to pass the sensor.

10.2.8 Automatic sieving machines

This automatic wet sieving machine determines a single point on the size distribution curve in a few minutes without the need to dry samples [1, 16]. The sieving vessel is first filled with slurry and topped up with water to a precise level to allow accurate determination of the mass of solids added \( w_l \) by application of Archimedes' principle. The fine fraction is next removed from the vessel through a discharge valve. Screening is hastened by propeller agitation and with ultrasonics to maintain the sieve mesh free
of pegged material. The weight of the residue ($w_2$) is determined by further application of Archimedes' principle, and the fraction coarser than the screen size is given directly by ($w_2/w_1$). It is interesting to note that the capacity of the rapid wet sieving device, expressed as screen charge mass per unit screen area, is more than an order of magnitude higher than that normally recommended for conventional dry test sieving [16].

A description has been given of a technique using a two-cell compartment divided by a screen [35]. The slurry density in the two compartments is determined using nuclear gauges to provide a single point on the distribution curve. A fully automatic sieving machine that can determine seven points on the size distribution curve has also been described [36]. In this technique a pulsating water column is used with the application of ultrasonics and the charges are dried and weighed automatically.

10.2.9 Gas flow permeametry

Air, whose pressure varies sinusoidally with a specific amplitude and frequency, is forced through a moving bed of powder [37-40]. At a known height in the bed the attenuated and retarded air pressure is tapped by a pressure transducer, so that the amplitude and pressure drop are measured after being separated into the pulsating and steady flow components. The amplitude attenuation of the pulsating pressure is related to bed porosity and specific resistance. Using the Carman-Kozeny permeametry relationship the average size of particles can be evaluated. The bed is packed into a test cylinder and discharged by a vibratory feeder at the bottom after measurements have been taken. This enables a new bed to be packed and measured within minutes.

Air permeability has also been used to determine the surface area of cement [41]. A porous piston compresses the sample of cement into a cell. Air is passed through a bottom porous plate, through the sample and porous piston, into the atmosphere. The inlet pressure is automatically adjusted and recorded to give a known air flowrate and the surface area is evaluated from the inlet pressure. The cell is emptied automatically becoming ready for the next test.

Weiland [42] used a similar idea but based on the Blaine permeability method. An automatic weigher produced a packed bed of powder, of known voidage, in a standard cell. Air was drawn through the bed by the passage of water from one reservoir to another. After a certain volume of air had passed through the bed, measured by a certain volume of water flowing, the time required was converted to an electrical proportionality
signal. The measurements were repeated every 4 min and the signals used to control the feeder to a grinding mill.

10.2.10 Correlation techniques

Correlation techniques can be used with signals from the attenuation of radiation, such as light, but these are mainly used for low concentration systems. The signals from two sensors in close proximity, situated in a flowing stream of slurry, are cross-correlated to give an autocorrelation function. Stanley-Wood et al. [43,44] found that this function obtained from alternating current transducers, initially designed to measure mass flow rate, gave a measure of the particle size of a sand/water mixture. A measure of mean size could be achieved by allowing the normalized signal from a correlator to be divided in two and passed through either high or low pass filters. This results in an inequality, due to variations in frequencies from large and small particles; the ratio of this inequality can be used to determine mean size after calibration. The particle size was between 70 and 2000 μm with a concentration between 10% and 30% by weight.

Fig. 10.2 Interaction of a ray of light with a spherical particle.

10.3 Light scattering and attenuation

10.3.1 Introduction

When light strikes a particle, some of it is absorbed, some is refracted, some diffracted and some transmitted (Figure 10.2). The amount absorbed depends upon the optical properties of the particles and surroundings and
is also a function of the cross-sectional area of the particles. The absorption, or turbidity, can be used to determine a mean particle size and, in conjunction with sedimentation, a size distribution. For very small particles however, the laws of geometric optics no longer hold and a correction has to be applied in the form of an extinction coefficient, \( K \), which is defined as the effective particle cross-section divided by its geometric cross-section.

This may be determined theoretically over the whole particle size refractive index domain using Mie theory or, over limited ranges, with modified theories. Other interactions between the particles and the incident radiation, such as state of polarization, light flux at a fixed angle to the direction of the incident beam and angular spectra can be used for particle size determination.

Interaction between the incident and diffracted radiation gives rise to interference phenomena with characteristic maxima and minima in intensity [45]. In order to describe fully the scattering pattern it is necessary to assume that the particles are optically homogeneous and spherical and, in order to give independent, incoherent scattering, in a dilute random arrangement.

10.3.2 Turbidity measurements

Turbidity has been widely used for determining the particle size distribution (PSD) of particles in suspension, since it is experimentally simple, can be used over a wide size range and does not disturb the system under investigation. It is also fast, reproducible and inexpensive.

If a light beam falls on an assembly of macroscopic particles the attenuation is given by:

\[
I = I_0 \exp(-anL)
\]  

(10.1)

where \( I \) is the transmitted intensity when a light beam falls on a suspension of particles of projected area \( a \) and number concentration \( n \) and traverses it by a path of length \( L \); \( I_0 \) is the transmitted intensity when no particles are present. Turbidity gives a measure of the attenuation of a beam of light passing through a suspension. More generally, equation (10.1) may be written:

\[
I = I_0 \exp(-KanL)
\]  

(10.2)
where the extinction coefficient, \( K \), may be evaluated theoretically thus permitting the determination of particle size. If \( c_v \) is the volume concentration:

\[
c_v = \frac{\pi}{6} nd_v^3
\]  

(10.3)

where \( d_v \) is the mean volume diameter.

The projected area \( (\alpha = an) \) of an assembly in random orientation is:

\[
\alpha = \frac{\pi}{4} nd_s^2
\]  

(10.4)

where \( d_s \) is the mean surface diameter; Hence:

\[
I = I_0 \exp\left( - \frac{3Kc_vL}{2d_{sv}} \right)
\]  

(10.5)

where \( d_{sv} \) is the surface-volume mean diameter. Hence:

\[
I = I_0 \exp\left( - \frac{1}{4} Kc_vS_vL \right)
\]  

(10.6)

\[
I = I_0 \exp(-\tau L)
\]  

(10.7)

where \( \tau \) is the turbidity.

For a suspension of non-spherical, non-monosize non-adsorbing, isotropic particles, in the absence of multiple scattering:

\[
\tau = \frac{3Kc_v}{2d_{sv}}
\]  

(10.8)

The surface volume mean diameter for a suspension of spherical particles is given by:

\[
d_{sv} = \frac{\sum_{0}^{\infty} d^3 f(d) dd}{\sum_{0}^{\infty} d^2 f(d) dd}
\]  

(10.9)
Equation (10.8) can be written in the form:

$$\tau = \frac{\pi}{4} \int_{0}^{\infty} K d^2 f(d) dd$$

(10.10)

This is a Fredholm integral equation of the first kind. The regularized solution to this equation has been applied to the measurement both for the moments and the size distribution of a wide range of latices [46]. $K$ has been given by van de Hulst [45] in terms of particle size/refractive index domain. Mie theory applies to the whole domain but in the boundary regions simpler equations have been derived.

For dilute suspensions of particles smaller than 0.04 μm in diameter, the turbidity can be calculated from the equation:

$$\tau = \frac{32\pi^3 (m-1)^2}{3N\lambda_m c^2} f$$

(10.11)

c is the mass concentration, $N$ is the Avogadro Number and $f$ is very nearly equal to unity [45 p396]. Turbidity measurements have been carried out on non-uniform latices and it is suggested that this is one of the most useful of the light scattering techniques for average size determination [47]. PSD can be estimated from the turbidity at different wavelengths provided the other variables are known. Kourti et. al. [48] assumed a log-normal PSD and observed that the parameters of the estimated distribution were so highly correlated that an infinite number of distributions could explain the data. However, all the alternative solutions were found to have the same weight average (surface-volume mean) diameter.

With turbidity ratio, the ratio of the turbidities at two wavelengths, one of which is chosen as basis, is used. This has been successfully applied with large particles [49], (0.65<D<1.3) μm, but it is not applicable to smaller particles or for small values of $m$ ($m<1.15$) [50].

The controversy over whether turbidity is capable of giving a true size distribution has been fully discussed by Kourti and MacGregor, who conclude that in many cases it can, and much of the controversy arises due to unjustified extrapolation from one regime to another [51].

Zollars [52] described an on-line turbidity system for the estimation of particle size distribution, refractive index and solids concentration. In a review and simulation of turbidimetric methods of on-line analysis Brandolin and Garcia-Rubio [53] state that this method is suitable only for
mono-modal distributions. Turbidity has also been used on-line, in conjunction with an Anton Paar vibrating tube densitometer for measuring concentration, in order to determine the particle size distribution of polyvinyl acetate. Samples were withdrawn from the process line using a Bristol Engineering Isolock sampler and a dilution system. Turbidity measurements were carried out using a Bausch and Lomb Single Beam Spectronic 20 [54].

Raphael and Rohani [55] developed a method for on-line estimation of solids concentration or mean size of crystals in a crystallizer. The method was only applicable to slurries in the absence of background particles. Later, an on-line double-sensor turbidimeter was proposed [56]. The technique is based on measuring the transmittance of an infrared light beam through the suspension, once in the presence of soluble particles and a second time when the particles have been dissolved.

Crawley et al. [57] applied the above equations to determine particle size distributions from turbidity measurements. The problems arise in finding a particle size distribution from the measured extinction coefficient due to the ill-defined inversion problem. Scholtz et al. [58] focused on the problem of analyzing spectra of colloidal solutions, for which the size distribution was known from other methods like electron microscopy and light scattering; they termed this 'transmission spectroscopy'.

Turbidimeters can be used to determine the product of particle concentration and particle size. Small measuring zones additionally allow measurement of the standard deviation of the fluctuating extinction signal. For monodisperse particles the particle size and particle concentration can be calculated from the measured mean and standard deviation of the extinction signal [59,60]. Variation in the size of the measuring light beam influences the standard deviation of the extinction signal and allows the determination of the particle size distribution. This can be effected by the use of a small angle photometer with the variation in the size of the light beam being realized by an axially shiftable flow cell in combination with a convergent laser beam [61]. An alternative approach is to use two light beams and a flowing suspension [62].

10.3.3 Transient turbidity

Transient turbidity is an optical technique for measuring the size of magnetic particles [63,64]. It does this by aligning particles in an electric field, removing the field, and following their return to random orientation induced by Brownian motion. Their relaxation is measured by turbidity and this can be related to particle size distribution if assumptions are made
536 Powder sampling and particle size determination

about the particle geometry and the shape of the size distribution. The technique is rapid (less than a second) and reproducible. Its most serious limitation is that the specific conductance of the sample must be less than 100 μmho cm⁻¹. Transient electrical birefringence operates in a similar manner.

10.3.4 Holography

Conventional methods of sampling aerosols are frequently unsatisfactory because they are too slow to monitor dynamic aerosols which results in the collection of non-representative and modified samples. Hologram systems, which overcome these objections, record and reconstruct large volumes of aerosols containing particles in the size range 3-100 μm. These holograms are called far-field or Fraunhofer holograms [65-67] because they are recorded at a distance from the object, effectively in its far field. The effective sampling depth is \( 49(D^2/\lambda) \) that, for 50 μm particles and a ruby laser, gives a depth of 18 cm, which is over 3 orders of magnitude greater than a microscope. Prototype instruments based on the use of Fraunhofer holograms have been described [68-70].

Visual comparison of the holographically recorded radiation pattern of a particle with Mie theory has also been used for particle sizing [71]. Holography has also been used to locate sub-micron particles in a 3-dimensional volume [72] and, in conjunction with an image analyzing computer, to size the droplets in sprays [73].

In-line holography has been used to characterize the spray produced by a commercial rotary device; a description of the optical system used to record and reconstruct the images has been given [74].

A simple method of laser diffractometry has been described for sizing droplets with radii greater than 1.5 μm [75]. Under partially polarized laser illumination, at a 90° angle to a camera receiver, well-focused droplets appear as small circular dots. Out of focus droplets give large diffraction haloes crossed by a row of dark, parallel stripes, the number of which is indicative of particle size.

Yule et. al. [76] suggest these holographic techniques offer no significant advantage over the relatively simple two-dimensional spark photography technique for measuring particles in sprays. Tyler [77] has reassessed the application of Fraunhofer holography to particle size determination.
10.3.5 State of polarization of the scattered radiation

When a system, containing isotropic and monosize spherical particles of diameter \( D \), is irradiated with unpolarized incident radiation of wavelength \( \lambda_m \) the horizontal and vertical components of the scattered radiation are, in general, functions of the three parameters; refractive index \( m \), angle of observation \( \theta \) and \( x = D/\lambda_m \). The scattered intensity increases with the square of the particle size for vertically polarized light whereas it increases linearly for horizontally polarized light. If the intensities of the horizontal and vertical components are, respectively, \( H \) and \( V \), then the polarization ratio \( R = H/V \) is a function of \( m \), \( x \) and \( \theta \). For fixed \( m \) and \( x \), \( R \) depends only on \( \theta \), hence particle size can be determined from the positions of maxima and minima.

For Rayleigh scattering \( R = 0 \) at \( \theta = 90^\circ \). As \( R \) increases, theory shows that \( x \) is a periodic function of diameter for monosize particles, and this has been used to measure particle size [78] specifically the size of aerosols in the size range 0.1 to 0.4 \( \mu \text{m} \) [79]. It has also been used to determine the sizes of sulfur solutions [80]: In this work, transmission and polarization methods yielded results in accord with high order Tyndall spectra (HOTS) for sizes in the range 0.365 to 0.62 \( \mu \text{m} \). In the limited region where \((0.45<d<2.8) \) \( \mu \text{m} \) and \((1.06<m<1.12) \) the fluctuations in \( R \) at \( 90^\circ \) are smoothed out and the following identity results [81].

\[
\bar{R} = 1.89(m - 2)^2 \pi \frac{D}{D_m} \quad (10.12)
\]

where

\[
\bar{D} = \frac{\int_0^\infty D^{7/2} n(D) dD}{\int_0^\infty D^{5/2} n(D) dD} \quad (10.13)
\]

where there are \( n(D) \) particles in the beam in the size range \( D \) to \( D + dD \). Maron, Elder and Pierce [82] review and extend earlier work on \( R \) measurements at \( 90^\circ \) on monodisperse polystyrene latices and found appreciable differences between theoretical and experimental values. They showed that the discrepancy is due to inherent anistropy in the latex particles believed to be due to non-random orientation of the polymer chains in the colloidal latex particles. The size range of applicability they give to this technique is 0.135 to 1.117 \( \mu \text{m} \).
This procedure has been used to determine droplet size in sprays. Oscillations in the curve relating \( x \) and \( D \) can be smoothed out by the use of an incident laser beam having a broad spectral bandwidth [83]. An accumulation of independent scattering intensities from multiple scatterers can be used to measure the mean droplet size of a group [84]. This procedure has been applied to water sprays and the experimental data confirmed by phase Doppler anemometry [85]. The applicability of the polarization ratio technique is strongly influenced by the complex refractive index of the dispersed media and is limited to media having a relative refractive index below about 1.44 [86].

![Fig. 10.3 Design of the fiber optic FBR-sensor](image)

**10.3.6 Forward/backward intensity ratio (FBR)**

The physical principle of FBR is the increasing lack of symmetry in the spatial intensity pattern of light scattered in the forward and backward directions which becomes significant outside the Rayleigh region. Depending on the sensor configuration and the light source a size range from 0.05 to 10 \( \mu \text{m} \) can be detected and sized in a matter of milliseconds. This technique is highly pertinent in processes where changing particle size needs to be monitored with a high time resolution.

A prototype instrument (Figure 10.3) has been described using the ratio of light scattered at 60° and 120° from the direction of the incident light using a collecting angle of 10° [87]. For a realistic upper volume concentration level of 0.1% numerous particles are present in the measuring volume and the derived size is the mean size for these particles.
A simple calibration has been carried out with latex spheres and a practical application on time dependent growth of calcium carbonate [88]. A further experiment was carried out to monitor the wet grinding of submicron color pigment using diluted, extracted samples. Further work was proposed to investigate the effect of particle shape.

A redesign of the FBR-sensor was performed to reduce the measurement volume and increase the upper volume concentration level to 1%. The improvements also permitted a low number concentration to be monitored (<10^5 particles cm^{-3}) so that the instrument could be used in a stream-scanning mode and as an in-line counter to monitor particles in gases.

10.3.7 Optical back-scattering

The mixing process of pesticide dispersion in a spray tank mounted on a tractor was monitored using optical back-scattering probes mounted in the tank [89]. A granulated powder was fully dispersed in 20 s whereas a powder product took 4 min.

10.3.8 Transmission fluctuation spectroscopy

A transmission signal measured on a flowing suspension of particles shows significant fluctuations which contain complete information on particle size and concentration. Details have been published in three parts [90-92]. In parts one and two the basic properties were studied for a beam of uniform intensity. The theory was extended in part three to a Gaussian beam with experimental tests to follow.

10. 4 Light scattering theory

10.4.1 The Rayleigh region (d << \lambda)

In the Rayleigh region the intensity of the scattered radiation in a direction making \theta with an incident beam of unit intensity is given by [45]:

\[ I_\theta = |\alpha|^2 \left( \frac{2\pi}{\lambda_m} \right)^4 \frac{\left( 1 + \cos^2 \theta \right)}{2r^2} \]  

(10.14)

where \alpha is the particle polarizability, r is the distance from the particle to the point of observation and \lambda_m is the wavelength of the incident radiation in the medium surrounding the particle.
The intensity is the sum of two terms:

\[ I_v = |\alpha|^2 \left( \frac{2\pi}{\lambda_m} \right)^4 \frac{1}{2r^2} \quad \text{and} \quad I_h = |\alpha|^2 \left( \frac{2\pi}{\lambda_m} \right)^4 \frac{\cos^2\theta}{2r^2} \]

which refer respectively to the intensities of the vertically and horizontally polarized components. For spheres:

\[ \alpha = |\alpha|^2 \frac{3(m^2 - 1) \frac{V}{(m^2 + 2)^4}} \]

Equation (10.15) has been applied to very small particles but is more relevant to the size determination of molecules. For \( m - 1 \rightarrow 0 \)

\[ \alpha = (m^2 - 1) \frac{V}{4} \approx 2(m - 1) \frac{V}{4} \quad (10.16) \]

where \( m \) is the refractive index of the particle relative to that of the surrounding medium and \( V \) is the volume of the particle.

10.4.2 The Rayleigh-Gans region (\( D < \lambda \))

The Rayleigh-Gans equation for the angular dependence of the intensity of the scattered light is given for spherical particles of low refractive index by the equation [45]:

\[ I_0 = I_0 \left[ \frac{k^4V^2(m-1)^2}{8\pi^2 r^2} \right] \left[ \frac{3}{u^3} \left( \sin u - u \cos u \right) \right]^2 \left( 1 + \cos^2 \theta \right) \quad (10.17) \]

Again, the two terms in the final brackets refer respectively to the intensities of the vertically and horizontally polarized components, \( I_0 \) is the intensity of the incident beam, \( D \) is particle diameter and:

\[ u = \frac{2\pi D}{\lambda_m} \sin \left( \frac{\theta}{2} \right) \quad \text{and} \quad k = \frac{2\pi}{\lambda_m} \quad (10.18) \]

Equation (10.17) reduces to equation (10.14) when the middle term is equal to one. The scattering pattern is however modified by this term, thus
enabling a size determination to be carried out in the Rayleigh-Gans region. Differentiating equation (10.17) with respect to \( u \) and putting \( dI/du = 0 \), for minimum intensity gives:

\[
\sin u - uc\cos u = 0 \tag{10.19}
\]

and, for maximum intensity:

\[
3uc\cos u - u^2\sin u - 3\sin u = 0 \tag{10.20}
\]

The first minimum is at \( u = 4.4934 \) radians corresponding to:

\[
\frac{D}{\lambda_m} \frac{\sin \theta_1}{2} = 4.4934 \Rightarrow \frac{\lambda_m}{2\pi} = 0.715 \tag{10.21}
\]

Similarly the first maximum occurs at:

\[
\frac{D}{\lambda_m} \frac{\sin \phi_1}{2} = 0.916 \tag{10.22}
\]

A graphical solution for all maxima and minima has been determined by Pierce and Maron [93] who, together with Elder [94,95] extended equations (10.21) and (10.22) beyond the Rayleigh-Gans region, \((m - 1 \rightarrow 0)\) to \(1.00 < m < 1.55\), deriving the following formulae:

\[
\frac{D}{\lambda_m} \frac{\sin \theta_1}{2} = 1.062 - 0.347m \tag{10.23}
\]

\[
\frac{D}{\lambda_m} \frac{\sin \phi_1}{2} = 1.379 - 0.463m \tag{10.24}
\]

These equations give the positions of the first intensity minimum and maximum respectively.

The range of validity of these equations has been investigated by Kerker et.al. [96]. The angular positions determined experimentally were found to depend on concentration hence it is necessary to take reading at several concentrations and extrapolate to zero concentration. This concentration dependency has also been noticed with depolarization and dissymmetry methods becoming negligible only when particle separation exceeds 200 radii [97].
10.4.3 High order Tyndall spectra (HOTS)

When a dilute suspension of sufficiently large, mono-disperse, spherical particles is irradiated with white light, vivid colors appear at various angles to the incident beam. The angular positions of the spectra depend on \( m \) and \( D \), hence they may be used to determine particle size in colloidal suspensions.

Since the red and green bands predominate it is usual to observe the ratios of the intensities of the vertical component of the red and green light in the scattered radiation as a function of \( \theta \). When these ratios, \( R = \frac{I_{\text{red}}}{I_{\text{green}}} \) are plotted against \( \theta \), curves showing maxima and minima appear, the maxima being the red order, the minima the green. Smaller particles yield only one order but the number of orders increases with increasing particle size.

HOTS have been studied extensively in monodisperse sulfur solutions by La Mer et al. [98-101], by Kenyon [102], in aerosols by Sinclair and La Mer [103], in polystyrene latices by La Mer and Plessner [105] and in butadiene latices by Maron and Elder [106]. The following equations derived by Maron and Elder for the angular positions of the first red and green order, \( \theta_{r1} \) and \( \theta_{g1} \) are particular examples of equation (10.22).

\[
D \sin \left( \frac{\theta_{r1}}{2} \right) = 0.2300 \quad (10.25)
\]

\[
D \sin \left( \frac{\theta_{g1}}{2} \right) = 0.3120 \quad (10.26)
\]

Pierce and Maron [107] show that the angular positions of the red orders are identical with the angles at which minima occur in the intensity of the scattered light when the incident light has a wavelength of \( \lambda_g \). Similarly, the angular positions of the green orders coincide with the angles at which minima occur with incident light of wavelength \( \lambda_g' \). Consequently, for the same effective incident wavelengths, minimum intensity and HOTS represent equivalent measurements. For equations (10.25) and (10.26), solving with equation (10.23) with \( m = 1.17 \) gives:

\[
1.062 - 0.347(1.17) = 0.2300/\lambda_g
\]

\[
\therefore \lambda_g = 0.3506 \, \mu m \, (0.4673 \, \mu m \, \text{in vacuo})
\]
$1.062 - 0.347(1.17) = 0.3120/\lambda'$

$\therefore \lambda' = 0.4756 \mu m (0.6340 \mu m in vacuo)$

This method is qualitative unless $\lambda'$ and $\lambda_g$ are known.

The above equations yield weight average diameters. With increasing $m$ the evaluation of $D$ becomes more difficult due to reduction in the intensity of the maximum and broadening of the peak. The method has been used for the size range 0.26 to 1.01 $\mu m$ [108].

10.4.4 Light diffraction

The far-field diffraction pattern of an assembly of particles yields information concerning their size distribution. For particles dispersed on a transparent slide the geometrically scattered part of the incident beam may be eliminated by coating the slide with aluminum and then removing the particles. The particle size distribution of the particles can then be determined from the resulting far-field diffraction pattern [109-112]. This effect was utilized in the Talbot diffraction size frequency analyzer (DISA) [113] that used a series of interchangeable filters to determine the number size distribution of the resulting apertures. Talbot later described a filter that transmitted amounts of light proportional to particle volume [114]. He also incorporated the principle in a slurry sizer, the Talbot Spacial Period Spectrometer [115,116].

Gucker et al. [117] developed equations from the Lorentz-Mie theory relating the size of the Airy points to particle size. Davidson and Haller [118] applied these equations to 0.07 to 0.50 $\mu m$ latices deposited on microscope slides and obtained poor agreement that they attributed to strong particle-slide interaction. Robillard et al. [119,120] used Mie scattering at two wavelengths and a similar set up to determine the mean diameter, the polydispersity and the refractive index of a Dow latex. The experimental intensity curves were in good agreement with theory.

10.4.5 Early commercial light scattering equipment

Most of the equipment described in the preceding section has been individually designed but commercial equipment was also developed.

The Sinclair-Phoenix aerosol photometer brought the light to a focus at the sample cell, with a diaphragm stop placed in the optical path so that a diverging cone of darkness encompassed the light-collecting lens of the
photomultiplier housing. Hence the only light reaching the detector was that scattered by the aerosol under test. Solids concentrations as low as $10^{-3} \, \mu g \, l^{-1}$ were detected, the mass concentration being displayed on a meter or recorder.

The *Differential light scattering photometer* was designed for the study of monosize particles in suspension [121]. A cuvette containing the particles in suspension is illuminated by monochromatic light and a scanning detector system records the intensity of the scattered light as a function of scattering angle. The light scattering patterns are matched against computer generated curves available as an Atlas of Light Scattering Curves [122]. The analytical approach is described in [123,124].

The *Brice-Phoenix light scattering photometer* and the *Absolute light scattering photometer* were designed for the measurement of attenuation, dissymmetry and depolarization. The former has also been used to determine the particle size distribution of an aerosol at various levels in a flowstream through a column [125].

The *Brice-Phoenix model 7 photo-nephelometer* received light at two photocells at right angles to the incident beam whilst the model 9 had a third photocell to measure the transmitted light.

### 10.5 Multi angle laser light scattering; (MALLS)

Early instruments employed low (forward) angle laser light scattering (LALLS) but these have been replaced by multi-angle instruments. MALLS instruments use Lorenz-Mie (often referred to as Mie) theory or Fraunhofer diffraction theory.

Mie theory is the classical theory relating light scattering to particle size. Major assumptions in the derivation include plane light waves and spherical particles [126,127] but the theories of light scattering are continuously being upgraded [128]. Mie theory requires knowledge of both the real and imaginary (absorption) parts of the refractive index. Fraunhofer theory is limited to particles that are opaque or large compared with the wavelength of light and, since only diffraction is considered, no knowledge of the particle refractive index is needed. The diffracted interference pattern is large compared with the geometric image with smaller particles diffracting the light through larger angles than larger particles. The optical system is arranged on an optical bench whose length, therefore, needs to be greater for large particles than for small ones. Assemblies of monosize, spherical particles give enhanced diffraction patterns. Azzopardi [129] states that this phenomenon was used for particle sizing more than 180 years ago, in what was called Young’s
eriometer, and in 1918 a commercial instrument was developed for sizing blood cells [130,131].

Refractive index consists of two parts, a real part that describes the refracted light and an imaginary (complex) part that describes absorption. In the case of very small particles, or particles where the complex part of the refractive index is near zero, light is transmitted through the particles and interferes with the diffracted radiation. The interaction between the transmitted and diffracted radiation results in ‘anomalous scattering’ and can be catered for in the Fraunhofer theory if both parts of the refractive index are known.

Non-spherical particles are measured over all orientations and this causes a broadening in the measured size distribution. Textured particles tend to give enhanced weighting to the fine end of the distribution.

The measurement volume is controlled by the width of the laser beam (10-25 mm) and the path length in the sample cell. The number of large particles in a broad distribution is low, which requires an extended measurement time in order to obtain an accurate estimate of their frequency. Since large particles are present in a small number of “sweeps” they are lost in the averaging process. They can, however, be distinguished by comparison of the sweeps using cross-correlation and principle component studies [132].

Synthetic fibers have been found to give a bimodal log-normal distribution using MALLS and rod shaped particles a trimodal log-normal distribution. Mühlenweg and Hirleman [133,134] found that surface roughness had little effect on measurements; in contrast to this a particle's deviation from sphericity, i.e. an elongated or a flattened shape, greatly affects the measurement result. Laser diffraction data has been inverted to provide size and shape distributions. The method was investigated using simulated diffraction patterns of elliptical particles; the limitation is that all particle sizes need to have the same shape distribution [135]. Other investigations of the response of MALLS to anisotropic particles have been carried out [136].

MALLS instruments collect light, scattered from particles in a collimated laser beam, by an array of detectors in the focal plane of the collecting lens. Early instruments used forward scattering angles up to 14° which limited the lower size to about a micron. Later instruments allowed angles up to about 40° through the use of converging incident beams and larger lenses, which extended the lower size to 0.1 μm. Some instruments incorporate additional information, such as polarization ratios and intensities at higher angles using extra detectors, in order to improve the characterization of particle size in the sub-micron size range, with
extension down as low as 0.04 μm. The optical system of the Helos acts as a telescope, which extends its upper size to 3,500 μm while retaining a lower size limit at the sub-micron level.

Samples may be introduced directly into the laser beam, as is the case with aerosols and metered dose inhalers, passed through a sample cell whose windows are transparent to the laser beam, or suspended in a cuvette under agitation. Dry powders are either blown through the beam or allowed to fall through it under gravity whereas particles in suspension are recirculated through the beam via a pump.

![Diagram](image_url)

**Fig. 10.4** The principle of low angle laser light scattering instruments.

The basic instrument consists of an analyzer that includes an optical bench that has a low-power visible wavelength laser, a lens train, a photodetector, a receiver and an amplifier/analog-to-digital converter linked to a microprocessor and monitor (Figure 10.4). Misalignment of the photodetector and incident laser beam is found to have severe effects on results [137]. If the inclination is limited to < 2.5° and the beam eccentricity to less than 0.10 μm the resulting error is less than 0.5%.

The possible size range of a MALLS instrument is linearly dependent on the wavelength $\lambda$ and the focal length of the Fourier lens $f$. The lower limit for a He-Ne 632.8 nm source is 0.1 μm and this can be extended to 0.05 μm with a 325 nm He-Cd source; however this is 30 times more expensive. At the upper limit, a He-Ne laser at a wavelength of 1152 nm
extends the size limit to 6 mm. A discussion of the various alternatives has been presented by Witt and Röthele [138].

10.5.1 Theoretical basis for MALLS instruments

The angular intensity distribution of scattered light \( I(\theta,\mu) \) at angle \( \theta \), for particles of diameter \( d \) and refractive index \( \mu \) is given by Mie scattering theory. For a polydisperse distribution:

\[
I(\theta,\mu) = \frac{I(0)}{\theta^2} \int_0^\infty h(\alpha,\theta,\mu) \alpha^2 n d\alpha
\]  

(10.27)

which is also known as a non-homogeneous Fredholm equation of the first kind. \( I(0) \) is the intensity of the incident beam, \( n(\alpha) \) is the number of particles in the laser beam with sizes between \( \alpha \) and \( \alpha + d\alpha \), where \( \alpha = \pi D/\lambda \), \( \lambda \) is the wavelength of light in the surrounding medium. The solution depends on the exact form of the kernel function \( h(\alpha,\theta,\mu) \).

For a ring detector the scattered light arriving at the \( i \)th ring of the detector is given by:

\[
I(\theta_i,\mu) = \frac{I(0)}{\theta_i^2} \int_0^\infty h(\alpha,\theta_i,\mu) \alpha^2 n d\alpha
\]  

(10.28)

Similar equations apply to each ring of the detector. This results in a linear set of \( i \) equations with \( k \) (discrete size classes) unknowns. The vector of scattered energy can be expressed as a matrix equation:

\[
S = CW
\]  

(10.29)

where \( S \) is the real vector of scattered energy, \( W \) is the real vector of size distribution of particles with diameters between the limits for the discrete size classes and \( C \) is the coefficient matrix of \( i \) rows and \( k \) columns. The element \( cik \) indicates that unit mass of particles in the \( k \)th size interval produces a scattering signal on the \( i \)th ring of the detector. For this reason the particle sizes are divided into \( k \) discrete size classes that are determined by the following equation [139]:

\[
\alpha \theta_m = 1.357
\]  

(10.30)
where $\alpha = \pi D k / \lambda$, $\theta_m = r_m / f$, is the maximum radius of each ring of the detector and $f$ is the focal length.

Equation (10.30) indicates that the maximum of scattered energy is reached only in one position of the detector, for representative diameters of each size class. The scattering matrix depends upon two parameters, the focal length of the receiving lens and the relative refractive index. Equation (10.30) is ill-posed so that the scattering matrix $C$ is highly ill-conditioned. This implies high-frequency oscillations in the solution $W$. Thus more sophisticated methods are required in order to find a solution. Integral transformations are used successfully [140] giving close solutions to equation (10.30). Alternatively a function constrained inversion in which the size distribution is assumed to follow a given form with two degrees of freedom or a model independent function can be employed.

Alvares et. al. [141] successfully applied a method known as the Tikhonov Regularization method and L-curve criterion to generate data in close accord with the Malvern software.

Fraunhofer theory applies to the scattering of light in the near forward direction by large particles. The scattering pattern for a single spherical particle consists of a series of light and dark concentric rings that decrease in intensity with increasing angular position. These rings are produced through constructive and destructive interference of light diffracted from the edge of the particle with changing light path length. The angular distribution of light flux $I(\theta)$ for a single opaque spherical particle, as given by the Fraunhofer equation, is shown in equation (10.31) in terms of the first order spherical Bessel function $J_1(\theta)$.

\[
I(\theta) = I(0) \left[ \frac{2 J_1(\alpha \theta)}{\alpha \theta} \right]^2
\]  

(10.31)

For a distribution of particle sizes this becomes:

\[
I(\theta) = I(0) \int_0^\infty \left[ \frac{2 J_1(\alpha \theta)}{\alpha \theta} \right]^2 f(D) dD
\]  

(10.32)

Figure 10.5 presents a two-dimensional graph of the pattern for latex beads in air ($\lambda = 1.55$) of diameter 50 and 25 $\mu$m. The diffraction pattern is independent of the optical properties of the particles and is a unique function of particle size being defined by the size parameter $\alpha = \pi D / \lambda$, where $D$ is the particle diameter. The scale of the curve on the vertical
Fig. 10.5 The forward intensity distributions for single particles: note that 84% of the energy lies within the first minimum.

Fig. 10.6 Intensity distribution from three particles of size 10, 60 and 200 μm. The intensity scale is times 1 for the 200 μm particle, times 100 for the 60 μm particle and times 105 for the 10 μm particle [142].
axis decreases with increasing particle size, compressing to smaller angles on the horizontal axis, so that the 50 µm particle results in a curve compressed by a factor of two compared to the 25 µm particles. Over a particle size range of 1000:1 the scale changes a thousand fold.

Figure 10.6 shows the relative intensities from three opaque particles, in air, of sizes 10, 60 and 200 µm; this illustrates how the scattered flux in the forward direction falls off rapidly with decreasing particle size. The effect is also illustrated in Figure 10.7a together with the resulting diffraction pattern for a monosize distribution (Figure 10.7b).

Information on the particle size distribution can be found by measuring the scattered light flux at several radial locations to characterize the series of annular rings from the particle's diffraction pattern. It is then necessary to invert the relationship between the scattering pattern and the particle size distribution. This can be done using iterative methods or analytical inversion techniques.

In early instruments, the detectors consisted of a series of half rings [143,144] (Figure 10.8) so that a matrix equation developed. Sliepcevich and co-workers [145,146] inverted this equation to obtain the particle size distribution. The equation was solved by assuming the distribution fitted a standard equation and carrying out an iteration to obtain the best fit. A matrix inversion was not possible due to the large dynamic range of the coefficients and experimental noise that could give rise to non-physical results. An inversion procedure that overcame these problems was developed by Philips [147] and Twomey [148] that eliminated the need to assume a shape for the distribution curve.

**Fig. 10.7 (a)** Particle size determines diffraction angle (b) the diffraction pattern from a monosize distribution.
Fig. 10.8 Representation of a typical photosensitive silicon detector. The thin lines represent insulating gaps.

The mathematics of the single-event Fraunhofer diffraction of an on-axis laser beam by a sphere was used in the development of this technique [149]. The assumption of single scattering is adequate for accurate measurement so long as the light obscuration by the particle field lies within the range 5-50%. Although measurement at low concentration is desirable it is not always possible; with industrial sprays, for example, size measurements may have to be made for light obscuration values in the range 90-99%. The more that multiple scattering occurs, the more the particle size distribution is biased to smaller sizes if single event theory is wrongly used.

Boxman et. al suggest that more information can be obtained if the fluctuations in the signals from each detector are examined together with the mean values [150]. They note that this approach can identify whether the inaccuracy is due to insufficient sampling of the detector array or imperfections in the optical model. More recently Knight et. al. [151] developed an analytical inversion method that gave improved resolution and accuracy in size distribution measurement.

Considerable differences exist between instruments, both in hardware and software, so that there is a lack of agreement in data generated by different instruments.

A commercially used means of measuring the scatter pattern is with a logarithmic line array detector, which has detector elements in a geometric size progression with each element larger than the preceding one by a constant multiple. The important feature of the logarithmically measured scatter pattern is that for two different particle sizes the shape of the elements remains the same but the position on the ln(θ) axis is shifted. This shift invariant function $f(x)$ permits the use of iterative deconvolution
to determine the particle size distribution from the scatter pattern measurement. Typically, the pattern is measured 1000 times in 20 s and the results averaged. Mathematically, a coordinate transformation converts the linear scatter function $f(\theta)$ to the logarithmic scatter function $f(x)$. This function is a convolution of the volume distribution of particles and the single sized shift invariant response functions for each size shifted according to the size.

A method of solving the deconvolution is to divide the particles into size intervals and assume that each one will generate a diffraction pattern according to its average size, the intensity of which depends upon the number of particles in that size range. The diffraction pattern can then be manipulated by matrix methods to yield the size distribution. The measured data always contain random and systematic errors which have to be accounted for in the deconvolution step. Several mathematical procedures have been developed which can generate different solutions using the same initial data [148,152].

10.5.2 Commercial instruments

Several instrument manufacturers have applied this principle (Table 10.1). A low power laser illuminates a suspension of particles to be examined. The scattered light is focused by a convergent optical system on to a multi-element, solid-state detector that usually consists of 32 semi-circular rings or a linear array. An additional detector at the center is used to align the laser and measure the intensity of the unscattered light. The electrical output of the rings is proportional to the amount of light flux falling on them and the signals can be interrogated to obtain the size distribution generating them. A total size range of 0.1 \( \mu \text{m} \) to 3600 \( \mu \text{m} \) can be measured, though only a part of this range can be measured at one time. The measurable size range can be extended by the use of off-axes detectors and white light sources with 90° detection of polarized light.

The powder to be measured is dispersed in a bath, where it is stirred or/and ultrasonically agitated whilst being circulated through a glass measurement cell. The cell is illuminated with a laser beam and the forward scattered light is focused on the multi-element detector with a Fourier transform lens. The signal that is derived from each detector element according to the intensity of the light falling on it is collected and digitized for high speed computer processing. Each instrument uses its specialized software to generate the size distribution from the signals and, since the algorithms differ, the size distributions generated also differ.
<table>
<thead>
<tr>
<th>Instrument</th>
<th>Size Ranges (μm)</th>
<th>Number of Intervals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beckman Coulter LS100Q</td>
<td>0.40 - 948</td>
<td>84</td>
</tr>
<tr>
<td>Beckman Coulter LS200</td>
<td>0.40 - 2000</td>
<td>92</td>
</tr>
<tr>
<td>Beckman Coulter LS230</td>
<td>0.04 - 2000</td>
<td>116</td>
</tr>
<tr>
<td>Cilas 920, (U.S. agent, Quantachrome)</td>
<td>0.70 - 400</td>
<td>100</td>
</tr>
<tr>
<td>Cilas 940</td>
<td>0.50 - 2000</td>
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</tr>
<tr>
<td>Cilas 1064</td>
<td>0.10 - 500</td>
<td>100</td>
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<tr>
<td>Cilas &quot;2 in 1&quot; dry/wet</td>
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<td>Fritsch Analysette 22 (U.S. agent, Gilson)</td>
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<td>Horiba LA-300</td>
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<tr>
<td>Horiba LA-900</td>
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<td>Malvern Insitec ESPA systems</td>
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<td>Sympatec Helos</td>
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<td>31</td>
</tr>
</tbody>
</table>
Since one lens is only suitable for a limited range of particle sizes, several lenses are usually available to encompass a wider range. The technique can be used to analyze powders in suspension, liquids, droplets and particles dispersed in air. The radial symmetrical diffraction pattern can be measured in other ways, for instance by a rotating optical filter with windows at different radial distances, such as was used in the Microtrac Small Particle Analyzer [153]. Some instruments combine MALLS with 90° scattering at three wavelengths and orthogonal polarities to extend the size range to a lower size than is usually assumed possible for forward light scattering alone. Others use off-axis lasers and detectors to extend the size range.

**Beckman Coulter LS** series uses a dark-field reticule having an array of 500 µm holes for automatic alignment purposes. The LS uses reverse Fourier lens optics incorporated in a binocular lens system to optimize light scattering over the widest dynamic size range. Results are calculated from either Fraunhofer or Mie theories. An application of this instrument to the measurement of micro-silica mixtures has been presented [154].

**Beckman Coulter LS 200** uses 118 detectors to measure particles from 0.4 to 2000 µm in a single scan, using 92 channels, without changing optics or settings with a resolution into 116 size channels.

**Beckman Coulter LS 230** has eight more detectors in its diffraction arrays with an additional 42 data points provided by the polarization intensity differential scattering (PIDS) system which extends the lower size limit down to 0.04 µm. The PIDS system uses three wavelengths at two polarizations, obtained by filtering light from an incandescent bulb at 0.450, 0.600 and 0.900 µm. Measurements are made at several scattering angles at both polarizations. The difference in scattered intensity between the two polarizations is highly sensitive to particle size, wavelength of light and angle of measurement.

**Beckman Coulter LS 13 320** is new to the series designed to meet the requirements of ISO Standard 13320-1[155]. It comes with an “Autodock” system that enables switching between modules in seconds together with a number of functions that simplify the measurement process.

**Aqueous liquid module** is a fully automated module, for large sample volumes, with high sample throughput and an optional auto-prep. station.

**Universal liquid module** is designed for operating with water or organic solvents. It incorporates full auto-rinse and fill capability, minimizing fluid usage.

**Tornado dry powder system** uses a “hypersonic” high shear system to ensure maximum dispersion without sample attrition. This system is stated.
to be preferable to positive pressure systems that tend to offer poor control and a tendency to mill the sample.

*Micro liquid module* has a 15 ml capacity and is ideal when sample is at a premium or when hazardous material is being analyzed.

In a series of lectures, the improvements effected using the Coulter double lens system and PIDS are discussed [156]. Scattering intensity falls off rapidly as $\theta$ increases; the effect of this is reduced using PIDS which also enables the lower limit of measurement to be reduced to 0.05 $\mu m$. PIDS system has been applied to size determination of several pigments [157]. The importance of the imaginary part of the refractive index, in calculation of particle size distribution, was stressed.

Ancillaries include a micro-volume module, a hazardous fluid module and a dry powder module. Their small volume module uses less than 125 ml of diluent. The micro volume module has a total volume of 12 ml; this has an internal stirring mechanism to keep particles suspended during analyses. The automatic hazardous fluids module can be supplied with a microtip eight power ultrasonic probe to keep the particles dispersed. The dry powder module analyzes both free flowing and cohesive powders covering the size range from 0.375 $\mu m$ to 2000 $\mu m$.

*Cilas 920* measures suspensions or dry powders in the size range 0.3 to 400 $\mu m$ without changing the optics. It includes automatic feeding and analyses of up to 28 samples and has the capability for displaying particles in the 10 to 400 $\mu m$ range using a CCD camera.

*Cilas 1064* has high resolution, giving information over the size range 0.04 to 500 $\mu m$ for suspensions and 0.3 to 500 $\mu m$ for dry powders in one shot, due to a double sequenced laser system (two lasers at different incident angles) and 64 separate silicon detectors to give 100 size channels of data. The benefits of such a system include coverage of a wide size range with a small optical bench structure. The diffraction pattern is compared to a known powder and the size distribution calculated.

*Cilas 1180* covers the size range of 0.04 to 2,500 $\mu m$, for both wet and dry systems, using three lasers with a custom silicon detector and a CCD camera, with fast response and high resolution. A wide range of accessories includes free fall, small liquid volume unit, alcohol recirculator, integrated Windows base and particle visualization.

*Coulter LSI00* uses (PIDS) to extends the lower limit to 0.1 $\mu m$ and 126 detectors to measure the scattered light. Multiple optical trains and a wide-angle detector array are used so that the instrument can simultaneously capture light diffracted at high angles from small particles and at small angles by large particles. Measurements from 0.1 to 1000 $\mu m$ can be made in a single run [158].
Fritsch Analysette 22. The outstanding feature of this instrument is its convergent laser beam, with the broad measurement range of 0.16 to 1250 μm that can be covered in a single pass with no need to change optical elements. Moreover, by moving the measurement cell in the beam the complete range can be divided into over 400 individual size ranges starting at 0.16 to 23.7 μm. The instrument is available in four versions; A(dvanced), C(onvenient fully automated), E(conomical) and P(rofessional).

Horiba LA-300 is a compact instrument with a built-in auto-alignment function. This feature not only maintains ideal operating conditions but self-calibrates with the touch of a button. Measurements are performed using a 650 nm laser diode, six wide-angle detectors and a 36 channel ring-shaped silicon diode array detector.

Horiba LA-700 is a more sophisticated instrument that employs side and back scattering detectors as well as forward scattering detectors. By using a tungsten lamp in conjunction with a He-Ne laser the lower limit is reduced to 0.04 μm to cover the range 0.04 μm to 262 μm with no change in lens.

Horiba LA-900 extends the upper range to 1000 μm by the use of a long focal length lens to cover the range 0.04 to 1000 μm with no need to change lenses.

Horiba LA-910 extends the lower size limit down to 0.02 μm with no optical changes. Small angle light intensity is measured using a condenser lens to condense the light on to a ring-type detector. Detectors are located at the side and rear to measure light scattered at larger angles. The measurable range is extended with the use of a short wavelength tungsten lamp in addition to the He-Ne laser beam. Up to three different dispersing media can be stored in the analyzer's reservoir unit that automatically injects the right amount of dispersant into the sample. It employs an auto-cycle agitation, ultrasonic dispersion, circulation and measurement. The analyzer uses an iterative deconvolution method to calculate the size distribution. The results are displayed in an 80-channel histogram.

Horiba LA-920 has the functionality of the LA-910 with improved software. It has a ring shaped detector in 75 sections together with 12 wide-angle detectors to give 87 sensing elements that extend the upper size limit to 2000 μm. The optical system includes a He-Ne laser for large particles together with a shorter wavelength tungsten lamp for small particles. The unit comes with a computer, printer, monitor and Windows-based operator interface.

Horiba PowderJet Dry Feeder can be teamed up with the LA-910 or LA 920 to disperse and de-agglomerate powders by subjecting them to a
high shear rate where high and low velocity air meets at the nozzle exit followed by expansion in a low pressure region. An optional vacuum sample cell is available for friable powders. A high performance industrial vacuum is also included.

*Horiba Autoreservoir*, available for the LA-910 and LA-920, is a three-chamber tank with a built-in pump. The unit supplies liquid to the analyzer in response to commands. Concentrated surfactant solutions can be added to two of the tanks and then automatically diluted during the fill sequence. This automates the supply of dispersant solution for fill, sample dilution and rinses.

*Horiba Autofill or Autoreservoir* supplies liquid to fill the pumping system. The system then circulates the dispersant solution and records the baseline.

*Horiba Autosampler or Slurry Sampler* then supplies the sample to the analyzer. Built-in ultrasonics aid in dispersing the sample. The concentration is checked and diluted until it is in the optimum range before measurement begins. After the results have been calculated, the data is saved or printed. The sample dispersion is then drained and rinse cycles prepare the system for the next sample. The Autosampler can make continuous measurement of up to 24 different samples. Minute quantities of material can be analyzed in the optional *Fraction Cell*. The unit includes a *PowderJet* dry feeder capable of feeding millimeter size powders and dispersing cohesive powders to sizes below 1μm. Horiba claim a higher resolution than similar devices by using repetitive calculations instead of the more conventional matrix method.

A description of the Horiba instruments and a discussion of the requirements and physical basis for carrying out particle size measurements with these instruments have been presented by Boeck [159].

*Insitec EPCS* is covered in detail in section 10.7. They are laser-based instruments for in-line particle measurements that provide information on particle volume concentration and size distribution. Unlike other instruments operating on this principle, the EPCS can perform direct measurements of particle-laden gas flow stream provided the concentration is within operating limits.

*Lecotrac-LT-100*, manufactured by Leco Corp, uses three lasers and two detector arrays to measure light intensities from 0 to 160 degrees. Lasers are self-aligning and the instrument uses Windows based software.

*Lecotrac-LT-150* is a basic cost-effective analyzer with a more limited size range.

*Lecotrac-LT-200* is designed to analyze coarser particles than the *LT-150*. 
Fig. 10.9 Low angle on-axis and high angle off-axis array as used with the Microtrac Full Range Analyzer.

The *Leco* units handle dry or wet samples and an automated small volume recirculator with autosampler permits unattended particle size analysis.

*Microtrac SRA 150* (Standard Range Analyzer) is a low cost instrument which covers the size range of 2 to 700 μm using either a small volume (250 ml) recirculator or a dry powder feeder (10-20 g min⁻¹).

*Microtrac FRA* (Full Range Analyzer) has extended the lower size by using an off-axis low angle array with a separate collector lens in conjunction with the logarithmic line array detector (Figure 10.9).

*Microtrac X100* system uses three lasers to measure scattered light at angles up to 160° with resolution from 0.04 to 704 μm. The use of three lasers provides superior resolution in the sub-micron region so that modes smaller than 0.5 μm can be more readily detected and resolved. An automated small-volume re-circulator accessory provides efficient sampling.

*Microtrac Ultrafine Particle Analyzer* operates using photon correlation spectroscopy in the controlled reference mode, extends Microtrac’s lower size to 0.003 with an upper limit of 6.5 μm.

*Microtrac S3000* is available in a number of upgradeable configurations to satisfy a wide range of application requirements. A photograph of this instrument is presented in Figure 10.10. The modular design provides the ability to update and expand a system inexpensively. The S3000 uses a Tri-laser source and logarithmic array detectors for high accuracy and
Fig. 10.10 The Leeds and Northrup Microtrac X3000

consistency. Conversion from a wet system to a dry powder system is accomplished in seconds. The instrument is designed to occupy the minimum of bench space.

There are two types of Mastersizer instruments; the Mastersizer Micro and the Mastersizer E, which are low cost instruments for repetitive analyses; and the modular series of Mastersizer S and Mastersizer X, the ultimate in resolution and dynamic size range, which are required when samples in the form of aerosols, suspensions and dry powders need to be measured. Mastersizer X provides a selection of small size ranges using a variety of interchangeable lenses whereas the Mastersizer S provides a wider dynamic size range covered in a single measurement. For powders which are to be suspended in a solvent, emulsions, suspensions and particles in liquids there are small volume cells which require as little as 15 ml of dispersant. Where a material is either valuable or toxic the Malvern Small Volume Flow Cell, with a sample volume of 50-80 ml and full sample recovery, can be used. The X-Y sampler is a 40-sample accessory
for either dry or wet samples. Malvern also offer a free fall dry powder feeder, a dry powder feeder, an automated dry powder feeder and an aerosol mounting unit.

The Malvern lower size limit is extended to the range 0.01 to 3 µm with the addition of the Autosizer, which operates using fixed angle photon correlation spectroscopy, and this is extended to 0.001 to 5 µm with the more sophisticated System 4700.

_Malvern Mastersizer E_ is a fixed configuration model to lower cost. A range of small volume accessories are available along with the standard Mastersizer E tank that is suitable for volumes of 1 liter. The wide size range of 0.1 µm to 600 µm makes it ideal for routine analysis and quality control.

Earlier versions comprise the Series 2600 and 3600 and Mastersizer R/IP on-line particle size analyzer. The Malvern 2200 was a droplet and spray particle analyzer and the Fibersizer 600 was designed for fast automatic measurement of fibers in the 4 to 64 µm size range with a resolution of 0.25 µm.

_Malvern Mastersizer X_ operates in the size range 0.1 to 2000 µm. A wide choice of modules can handle dry powders, suspensions, emulsions, aerosols and sprays in manual or fully automatic mode.

_Malvern Mastersizer S_ uses Mie theory to cover the size range 0.05 to 900 µm using a single lens, and up to 3500 µm with an extended range system. Scattering angles from 0.01° to 150° are detected in order to cover this wide size range. The system handles measurements of particles, droplets or gas bubbles.

_Malvern Mastersizer Micro_, which uses a 'folded optics' configuration, is the most compact MALLS instrument presently available. In its basic form it has a size range of 0.3 to 300 µm.

_Malvern Mastersizer Microplus_ extends this range to 0.05 to 550 µm. This instrument is intended where low sample throughput, a limited size range or well-defined user needs makes the flexibility of the more sophisticated versions unnecessary. Roberts has presented a discussion of low cost sizing using these two instruments [160].

_Malvern Mastersizer 2000_ uses a standard operating procedure to eliminate user variability. A redesigned optical system has removed the need for adjustments between samples. An integrated optical system covers the full size range from 0.02 µm to 2000 µm. Reverse Fourier optics, using wide angle dual wavelength detection system provides improved resolution and extended range, have been enhanced by additional
forward and back scattering detectors, combined with a high-stability monochromatic blue light source.

Malvern Spraytec droplet size analyzer measures size and concentrations in continuous sprays, aerosols and dry powder inhalers. The multi-scattering algorithm allows the unit to measure higher concentrations than with laser diffraction. Sampling is carried out every 0.4 ms. Measurements can consist of a single detector scan or averages of multiple scans.

Micromeritics Saturn DigiSizer 5200 measures in the size range 0.1 to 1000 \( \mu \text{m} \). A light beam from a solid-state laser is coupled to a beam splitter that directs a portion of the light on to a reference photodiode. The remainder of the light is directed by fiber optics on to a collimator and thence to the sample cell. A Fourier lens intercepts the scattered light, projecting a fraction of the scattering pattern on to a CCD array.

The CCD array is composed of over 1.3 million detector elements that accumulate electrical charge in proportion to the intensity of the light on its surface and its exposure time. The operating software scans the detector array and determines which element contains the center of the beam. The software then maps all the other pixels according to their angular position. This eliminates the need for accurate optical alignment.

The range of light intensity in a scattering pattern can scan more than 10 orders of magnitude which is greater than the dynamic range of any light detector. To compensate for this, multiple exposures are taken at each CCD position using different quantities of light and different exposure times.

After the first set of measurements, the scattering pattern is shifted by increasing the angle of incidence relative to the sample cell, thereby exposing the CCD to a new range of angles. The software re-maps the CCD array accordingly. Another series of exposures is taken, the series normalized, and the angle of incidence again increased. The process continues until the scattering pattern is determined. The result is a digital representation of the scattering pattern expressed as intensity versus scattering angle. The resolution gained by this system is such that modes spaced as closely as 1.1 and 1.3 \( \mu \text{m} \) can be resolved.

The MasterTech 052 Autosampler can line up 18 samples to run consecutively without operator involvement.

Nitto LDSA-1300A covers the size range 1 to 2000 \( \mu \text{m} \) and the LDSA-2300A covers the size range 1 to 500 \( \mu \text{m} \).

Seishin PRO-7000 laser micron sizer operates in the measurement range 1 to 192 \( \mu \text{m} \) with ancillaries for dry powder feeding and automated
analyses on 20 samples. The PRO-8000 is an on-line system for either wet or dry processes.

*Shimadzu SALD 201V Model 1* is a compact unit, consisting of the analyzer and a batch cell, covering the size range 0.4 to 50 μm and featuring reliable analyses with small (2 ml) samples.

*Shimadzu SALD 201V Model 2* also has a flow-through cell and provides a wider measuring range of 0.4 to 200 μm.

*Shimadzu Sald 2001* covers the size range from 0.03 to 700 μm using a 76 element sensor to capture the forward scattered light while side and back-scattered light is captured by three other sensors.

*Shimadzu Sald 3001* covers the size range from 0.1 to 2000 μm.

*Shimadzu Wingsald* measurements and data processing software allows flexible test parameter set-up and real-time monitoring of sample dispersion. Windows 95 software features 3-D graphing and a superimposed comparison of up to 12 graphs.

*Sympatec Helos* is available in 4 configurations. BF: 0.1-875 μm, KF: 0.1-8750 μm, Vario: 0.1-8750 μm, Mytos: 0.5-1750 μm. Ancillary modules permit the sizing of aero-dispersions, suspensions and sprays. The measurements are carried out using a multi-element detector consisting of 31-semi-circular elements with the beam auto-aligned on the central element. Sample couplers are available for on-line use.

The ancillary *Rodos* is a unique dispersing system for both cohesive and free-flowing dry powders [161]. The powder is fed from a hopper into a rotating channel where the excess is skimmed off and the remainder compacted. It is then transported into an eductor using suction and a rotating brush. Impacting the powder against inclined targets in the eductor can carry out further dispersion. The brush disperser has been compared with a pin mill disperser with sub-micron powder feed [162].

**Ancillary Equipment:** Most instruments are based on the analysis of circulating wet suspensions. This set-up is unsuitable for brittle material and many manufacturers provide agitator cells to reduce breakage. Waste disposal is a major problem with some materials and this is reduced by the use of small volume cells (<125 ml). Cells are also provided for corrosive liquid systems. Instruments can be set up to analyze falling streams of dry powders; this is particularly suitable for brittle or soft (wet granules) materials. Deagglomerators are often provided for sticky dry powders.

**Activity Software** imports data from Micromeretic’s Sedigraph 5100, Leeds and Northrup's Microtrac and Cilas Model 920. In operation data such as particle size distribution, surface area, filler costs or other properties are entered into the software. Target values are next assigned to the data components with the values scaled to reflect each component's
importance. Software automatically analyzes the data and displays the result as a table or a graph.

10.5.3. Discussion

MALLS are being used increasingly for rapid off-line and also on-line size analysis. The latter requires an automatic sampling device that takes part of the process slurry (or powder) and dilutes it to the required concentration for the analyzer. The dilution unit can be quite complex; when the instrument is hooked up to a crystallization unit for example it is necessary to filter some of the mother liquor and use that as the diluent. The Mastersizer on-line analyzers, the MS200/IP series have the same 0.1-600 μm overall and sub-ranges as the laboratory analyzers. For a wider overall range the MS200/IP systems extend from 0.1 to 2000 μm. Sympatec manufacture an on-line system extending from 5 to 3500 μm or more. A cell has also been described for measuring the fines outlet in an air classifier [163]. The instruments tend to be easy to operate and yield highly reproducible data. Data presentation varies from instrument to instrument and generation to generation, each new model being an improvement on its predecessor [164,165]. The general tendency with non-spherical particles is to oversize the coarse end of the distribution and assign an excess of particles to the fine end and, in so doing, broaden the distribution. The instruments are particularly useful with powders that are difficult to disperse since such powders can be incorporated into a liquid containing a dispersant and close loop circulated whilst undergoing ultrasonic probing. Analyses are taken every few minutes until the measured size distribution stabilizes.

In an examination of glass beads sieved into five fractions in the size range 70 to 400 μm it was found that the accuracy of the determined medians was good. The distribution widths and the resolution of binary mixtures were compared with image analysis. These showed some discrepancies for both mono- and bi-modal distributions with undersizing in both cases [166].

Comparison tests between the PSS Accusizer 770 (light blockage), API Aerosizer (time of flight) and MALLS instruments (Malvern Mastersizer and Coulter LS) indicated that the MALLS instruments gave results that differ from each other and from microscopy whereas the other two instruments gave results in agreement with each other and with microscopy [167]. The choice of the Fraunhofer or Mie theory model affected the calculated size distribution in an unpredictable manner and the use of Mie
theory did not assure more accurate results. For glass microspheres 10-95 μm in diameter the Mie model with the Mastersizer yielded results closely matching the Aerosizer but not the Coulter instrument, three other irregularly shaped powder systems were also examined and gave disparate results. [168].

Kaye et al. [169] compared sieving, image analysis and MALLS using four ferrite powders and discussed the causes of observed differences. They found that the particle size distribution by MALLS was larger than by image analysis and much larger than by sieving. In particular they found large particles that were not present using image analysis; they ascribed this to artifacts from the data processing deconvolution.

In a comparison with an x-ray centrifuge (XRC) it was found, predictably, that the XRC determined mixing ratios of bimodal mixtures with small errors: The errors with the Sympatec were larger but the reproducibility was higher [170].

The shape of the detector disc in the Malvern Mastersizer X allowed it to be used in an innovative way. Particles are aligned in the flow cell hence the scattering pattern differs in the vertical and horizontal plane. The detector is an annular disc divided into 32 light sensitive segments radiating outwards. This can be rotated and the two sets of signals compared to generate data on fiber length distribution. [171].

The effect of multiple scattering has been studied by several researchers [172,173]. Solutions, in the form of empirical equations, have been provided for Rosin-Rammler and log-normal distributions [174]. This has since been extended to a 'model-independent' case [175]. Fraunhofer theory does not apply if the refractive indices of the particles and the fluid are similar. Fraunhofer theory applies when a plane wave front of monochromatic light is diffracted by an opaque particle, much larger than the wavelength of light, and focused by a lens on to a detector. For low relative refractive indices it is possible for light to pass through the particle and the transmitted light then interferes with the diffracted light to produce the so-called 'anomalous diffraction patterns'. If no correction is applied an erroneously high percentage of small particles will be predicted. Experimental and theoretical verification of this effect has been reported [176]. An experimental study has also been carried out on the on-line monitoring of clear and opaque particles. [177].

Jones discussed ISO 13320 [178] and stated that application of this guideline ensured high reproducibility and highlighted the weakness of Fraunhofer theory as opposed to the Mie theory [179].

The need for maintaining constant temperature was emphasized since this affects the length of the light path in the measurement cell and the
particle. Considerations such as this are particularly important when studying crystal growth [180].

A standard test method for calibration verification of laser diffraction particle sizing instruments using photomask reticules has been introduced by the American Society for Testing and Materials [181-183]. The test sample consists of a two dimensional array of thin, opaque, circular discs deposited on a transparent disc. The test method is designed to verify instrument performance on an ongoing basis, to compare one instrument performance with that of another and to provide error limits for the instrument tested. These photomask reticules have been tested to determine the effect of having overlapping images as opposed to non-overlapping images [184].

Seselj [185] reported on the use of wet and dry laser light scattering to determine the size distribution of magnetic material. Muehlbacher [186] used a tri-laser system to determine accuracy and reproducibility with +0.022 μm polystyrene samples.

Classically, the particle size distribution of soils and sediments are determined by sieve for the coarse fraction and Andreasen pipette for the fine fraction. From the point of view of laboratory efficiency MALLS is deemed superior. Although MALLS data for standard material were in good agreement with certified measurements; tests on the mean diameters of sediment, except for the sub-μm mean diameter, showed poor agreement. Platey clay particles, for example, were 2 μm in median size by pipette and 8 μm by laser light scattering. The authors discuss the possibility of calibrating the laser instrument to give similar data to traditional data [187].

Veran stated that in industry, measurements are usually carried out by x-ray sedimentation and laser diffraction and they hardly ever agree. He compared the CILAS 1064, the x-ray Sedigraph 5000ET and 5100 and found that the application of an extinction coefficient brought the laser diffraction into agreement with photosedimentation [188].

Bordes et al. [189] reported experimental results on the use of the Turbiscan On-Line Formal action particle analyzer for monitoring a wet grinding process.

Many manufacturers have large data banks using, for example, sieve analysis and they need to continue generating data in the same form. To cater for this need, some manufacturers of MALLS instruments install a conversion program, so that the instruments provide data that can be compared with historical data. However, Austin [190] compared sieve analyses with Sedigraph and Microtrac data and found that the conversion
from Microtrac to sieve size depends not only on a mean shape factor but also on the size distribution being measured.

Laser diffraction not only provides a particle size distribution by volume but it can also be used to provide a value for volume concentration. Since laser diffraction assumes that all particles are spherical, for plate-like particles, this leads to an overestimation of volume concentration. Particle thickness and aspect ratio can be derived using this information [191].

The Sympatec has been applied on-line to the analysis of a polymer in a styrene/water suspension [192].

A recent review contains 35 references and covers fundamentals, sample preparation, operations and evaluation of results [193].

Figure 10.11a illustrates the installation of a low-angle laser light scattering instrument in a pan granulation process. A major problem in retro-fitting equipment such as this is the dearth of suitable installation positions. In cases where there is insufficient room for a commercial sampler, a special unit has to be designed (Figure 10.11b). Since segregation is almost certainly present it is necessary to design a system that takes the whole of the stream for very short time intervals. This ‘bite’ is fed to a hopper and thence to the analyzer via a vibratory feeder such that the complete sample is fed through the system in about 20 s. The sampler senses when the concentration is adequate and commences analyzing; when the concentration fell below the required level the analysis is terminated. During the measurement time several hundred analyses are carried out; the instrument generates a weighted average and stores the data.

In this illustration, six parameters were forwarded to the control room for display; the 10%, median and 90% sizes, the mass percentage within specification, the mass percentage oversize and the mass percentage undersize. Figure 10.9c and 10.9d show a process going out of specification due to generation of excess fines. An increase in yield of 1% can be worth hundreds of thousands of dollars per year and pay-back is rapid. Using laboratory type equipment to measure the dried product gives a time lag of hours. Minute by minute control of such variables as the slope of the pan, the amount of water and the positions of the sprays maximizes the yield. The use of the Sympatec for on-line particle size distribution of fines in an air classifier outlet has also been reported [194].

It is well known that free-flowing powders segregate, but not so widely recognized that cohesive powders may segregate during manufacture and need to be mixed prior to assay. A ceramic paste, used as a dielectric in electrical capacitances, needed a median size by MALLS of between 2.8 and 3.2 μm. Too fine a distribution caused blistering during sintering and
Field scanning methods

too coarse a distribution led to electrical leakage. The paste was ball-milled then dried and 16 samples taken from the dried powder had a mean size and standard deviation of (3.1±0.17) μm. The selection criterion was that if any three consecutive samples fell outside the range of 2.8 μm to 3.2 μm the batch was rejected and on this criterion there was a 50% chance of this happening. After mixing the standard deviation fell to 0.012 μm. It was conventional to mill for 145 hours to reach the desired end-point. The implementation of these rapid response instruments permitted the extraction of samples after 8 hours and 12 hours and plotting the measured median on log-probability paper allowed one to determine the milling time required to attain the desired end-point thus eliminating wastage.

Fig. 10.11 On-line installation of particle size analyzer
Determination of refractive index is difficult for light scattering determination. A new method of refractive index determination has been proposed and applied to several powders and its usefulness confirmed [195].

10.5.4. Neural networking

Empirical methods such as neural networking can be used in place of optical methods to estimate the size distribution of concentrated suspensions. The method determines particle size distribution and suspension concentration based on measured spectra on known size distributions.

The feasibility of the inversion of laser diffraction data for size and shape distribution has been investigated by computer simulation. Size and shape density distributions can be represented by only four parameters making this technique an order of magnitude less accurate than conventional inversion techniques [196].

Three particle systems were examined by image analysis and their aspect ratio and particle size distributions were measured [197,198]. The data were then used as a reference method for neural networking using a Malvern Mastersizer X and concentrations from 2 g l⁻¹ to 60 g l⁻¹. Particle shapes ranged from an ellipsoidal cracking catalyst, needle shaped asbestos and monoclinic sucrose crystals.

Neural networking has also been applied to particle sizing of slurries by reflectance spectroscopy [199]. The method is based on measured optical reflectance spectra measurement on known size and concentration slurries.

10.6 Malvern (Insitec) Ensemble Particle Concentration Size (EPCS) Systems

Insitec now forms part of Malvern Instruments but is still based in California for process and laboratory R & D. The EPCS are laser-based instruments for in-line particle measurements that provide information on particle volume concentration and size distribution. EPCS instruments are part of the larger group of electro-optical instruments (MALLS) whose principle of operation is based on light scattering from a group (or ensemble) of particles. Unlike other instruments operating on this principle, the EPCS can perform direct measurements of particle laden flow stream provided the concentration is within operating limits.
*Malvern (Insitec) EPCS-P* instrument is designed for in-line measurements in powder or spray processing systems under hostile conditions [200,201]. Applications include process powder sizing, mass emission monitoring and fossil energy combustors. It has a general capability from 1 to 500 μm at concentrations up to 1000 g m\(^{-3}\). EPCS-P has a gas-purged window with a 9 cm by 4 cm aerosol access region. The 5 mW He-Ne laser beam is approximately 1 cm in diameter. All particles in the beam, over the 9 cm length, scatter light into a logarithmically scaled solid-state ring detector. Particle measurements are based on the analysis of light scattered into each of the 32 detector rings from all particles in the laser beam.

*Malvern (Insitec) EPCS-F* is designed for powders in the size range of 0.2 μm to 1000 μm [202]. Particle measurements are made at rates up to 500 per second with immediate display of particle size distribution and characteristic diameters. Specific values or points on the particle size distribution are continuously fed back to the user or to a process control system. Particles with different refractive indices and aspect ratios up to 2:1 can be measured.

**Fig. 10.12** EPCS-F optical head installation.

The instrument consists of an optical head with a purge gas over the lenses to reduce coating by the powder stream, an interface box, computer and
software. As particles pass through the laser beam, light scattered in the forward direction is collected by the receiver lens and focused onto an annular ring detector. The detector is scanned at high speed and the signal level on each of 32 rings is measured and stored. Once a sufficient number of detector scans are acquired the software uses a non-linear inversion technique to solve for the relative particle concentration. The size distribution is determined from theory defined by the relative refractive index between the particles and carrier with no assumptions on the shape of the distribution.

Figure 10.12 shows the optical head inserted in the process line. The head is installed directly into the line, preferably via a flexible coupling for vibration isolation. The interface box is a NEMA 4.9 rated explosion proof enclosure, weighing 50 lb, which can be bolted to a wall or floor within 20 ft of the head.

![Figure 10.12 Optical head inserted in the process line.](image)

**Fig. 10.13** EPCS process control display format.

The process control display is divided into three sections. Six process control variable displays are shown at the top of the screen. Variable displays reflect the most recent measurements of the particulate. A time
history of the point values for the process control variables is displayed on the lower portion of the screen. The third portion is the system status flags, shown in the middle of the screen. The particle size distribution may also be viewed whilst in the process control mode but this can slow down the processing time considerably.

Figure 10.13 depicts the screen. The six variable display boxes are positioned at the top of the screen and reflect the current values only. The process control plot shows a time history of all six variables. The window bar is on the bottom of the time axis and shows the relationship of the current window to the total planned duration of the test. System status flags on the left light up when the control and error flags are on. The error status shows the error number if it is active. The other flags are for display only and indicate the status of the program.

Discrete data point, extracted from the log file, can be viewed. The data can also be viewed in tabular form and as a size distribution curve. Data can also be integrated over any selected range. A Statistical Process Control (SPC) option enables the file data to be viewed in standard control chart format either as an X or R chart.

*Malvern (Insitec) ECPS2* is designed to monitor and control particle size distributions from 0.5 to 1,500 μm, at concentrations up to 10,000 ppm, directly in pneumatic powder streams. Up to one thousand size distribution measurements per second are carried out at flow velocities from static to ultrasonic. Discrete data point, extracted from the log file, can be viewed. The data can also be viewed in tabular form and as a size distribution curve. Data can also be integrated over any selected range. A Statistical Process Control (SPC) option enables the file data to be viewed in standard control chart format either as an X or R chart. Various interface arrangements have been described, [203]:

- **E (external)** the transmitter and receiver units are external to the flow (sprays, pipe flows with windows, free jets *etc.*) for systems less than a meter in size and for high pressure/temperature environments.
- **P (probe)** for large-scale systems (e.g. combustion furnaces *etc*.). The probe is gas purged and can be used at high temperatures.
- **F-(flange)** is intermediate to the probe and external systems being used for production streams in the 4 to 16 inch diameter range.
- **E-(eductor)** is a slipstream or bypass system which uses a gas driven aspirator to withdraw a portion of the flow stream isokinetically, pass it through the optical system and re-inject it back into the flow stream. The system is intended for high temperature/concentration applications and multiple flow streams.
A comparison between the Insitec ensemble sizer (field scanning system) and the Insitec single particle counter showed good agreement with gas atomized zinc powder [204]. The ensemble sizer has been used successfully to characterize the atomization and dispersion of droplets and solids dispersed in a pneumatic transport device [205]. The instrument has also been used for on-line control of grinding circuits [206] and in side lines in cement plants to measure particle size [207]. The Malvern instrument has been used for on-line monitoring for process optimization with special regard to pneumatic and mechanical conveying. Control of particle size in the range 0.5 to 1000 μm was found feasible. The application of on-line monitoring led to fast system adaptation with associated risk and cost reduction [208].

10.7 Optical incoherent space frequency analysis

The method for obtaining particle size distributions using optical incoherent space frequency analysis is detailed in [209,210] and resulted in the development of a low price, robust, on-line dry powder measuring system, the Jenoptik PSI-Z, (Particle Sizing using Incoherent light) which covered 32 size intervals in the range 1.5 μm to 2 mm. This was later expanded to 0.7 to 2500 μm [211]. For particles smaller than 50 μm a dispersion nozzle had to be fitted.

The basis of the method is to replace the coherent light source used in MALLS with an infinite number of point light sources that emit light in an incoherent way with respect to each other. The intensity of radiation resulting from this two dimensional radiator is measured using a point detector located on the optical axis. This is equal to the surface integral of the Fourier power spectrum and can be measured with the aid of wedge-ring detectors in a coherent optical set-up. In this way, the incoherent arrangement consists of several switchable two-dimensional light emitters together with a single detector on the optical axis. This allows the measurement of the same intensity characteristics as in a coherent arrangement.

Figure 10.14 shows the principle set-up. The incoherent light source consists of a 25 W halogen lamp L with voltage stabilization, including condenser system O1, diffusing screen S and filter F. The variable geometry, binary two-dimensional emitter consists of an addressable liquid crystal modulator (LCD) with back lighting. The structural organization of the transparent electrodes within the LC modulator can create ring segments with transmission controlled by the help of the corresponding voltage. The response time of the individual LC segments is less than 3 ms.
when the electrically controlled birefringence of liquid crystals is utilized [212]. A photomultiplier, with a micro pinhole in front of it, serves as a point light detector with diameter variable up to 300 \( \mu \text{m} \) with a resolution of 1.2 \( \mu \text{m} \). The LCD modulator is projected on to the detector by transformer objective O2. A piezoelectric \( x \)-\( y \) stage adjusts the central segment of the LC modulator precisely on the micro-pinhole. The material is fed through the optical path with sample feeding device P.

![Fig. 10.14 Experimental set-up of PSI-Z.](image)

A personal computer (PC) controls the measuring arrangement. The evaluation algorithm in the PC calculates the ring intensity values of the percentage of certain particle size classes by comparison between measured values and predetermined theoretical values. The intensity values are converted into a size distribution by an iteration process.

The apparatus and software are described in a paper on the application of this technique to the particle size measurement of bulk material [213] and control of a grinding process [214].

10.7.1 Retsch Crystalsizer

This is a later development of the Jenoptic system described above. A high resolution liquid crystal display system makes it possible to measure free-flowing dispersible materials in the size range 0.7 to 2500 \( \mu \text{m} \). Its
measuring principle is based on the diffraction of incoherent white light by a stream of particles. The light source used is a halogen lamp whose light is modulated by a liquid crystal display (LCD). The LCD produces ring-shaped light beams with various diameters. Each diameter only results in a signal when particles of the correct matching size are found within the sample. These particles scatter the light at the right angle onto a detector. During measurement the individual rings of the LCD are switched through in rapid succession. Each ring is only active for a few milliseconds at a time. The cycle is repeated until the complete sample has been measured.

The Crystalsizer is based on the principle of incoherent light diffraction thus turning the traditional optical structure back to front. Thus the same physical effect is measured as with traditional devices, but without using coherent laser light. The size distribution is determined using Fraunhofer diffraction theory. The robust construction of the instrument makes it suitable for use ‘on-site’. Typically, samples are removed from the process and fed to the Crystallizer sequentially.

10.8 Pulse displacement technique (PDT)

PDT is based on the detection of scattered refraction and reflection pulses that sweep past a detector at different times as a particle traverses a narrow laser sheet. In conjunction with Mie scattering and time-of-flight velocity measuring technique, detailed distributions of particle size from 2 µm to 6000 µm are provided together with particle velocities from 0.5 m s\(^{-1}\) to 150 m s\(^{-1}\). A miniaturized particle size velocimeter developed by Metrolaser is the first of its kind to utilize this technique.

Particles larger than the focused laser beam are measured with PDT while smaller particles are measured by \(I_{\text{max}}\). In principle the entire size range could be measured with a single optical configuration but in most applications small particles are present in large numbers while large particles are present in small numbers. This creates incompatible probe volume requirements and number density constraints. For this reason the instrument incorporates two optical configurations for large and small particles respectively.

PDT is implemented using a single off-axis receiver that measures the intensity of the scattered light from a particle sequentially passing two laser sheets with wavelengths of 0.5145 µm and 0.4880 µm. The laser sheets have waists of 20 µm that is smaller than the diameter of the particles being measured by PDT. As a particle traverses either sheet, a set of double pulses results when the laser light is first refracted and then reflected by the particle. The two pairs of pulses are sorted according to wavelength and sent to one of two detectors. The temporal separation of
either of the two refraction or reflection pulses is proportional to the velocity of the particle. The temporal separation of the refraction and reflection pulses, each of the same wavelength, is proportional to particle size.

The $I_{\text{max}}$ technique measures diameters smaller than PDT. This technique uses a laser beam elongated in one dimension to form a sheet where the intensity along the central portion is constant. As the particles traverse the sheet a single pulse is produced the size of which is related to particle diameter by Mie theory. Hess and Wood presented detailed analytical results [215,216]. The instrument is small enough to fit in the palm of a hand and operates with negligible flow disturbance. It is rugged enough to stand harsh environments, high moisture levels, high noise and high vibration levels [217].

10.9 Small angle x-ray scattering (SAXS)

This effect depends upon the difference of electron density between particles and their surroundings, and the measured sizes are of primary particles rather than the external aggregate size. Thus samples are relatively easy to prepare and do not require pre-dispersion. The operating size range is from 1 to 300 nm and it breaks down at concentrations over about 3% due to inter-particle interference. A necessary requirement is near sphericity of the particles. The electron density also needs to be high. SAXS cannot distinguish between pores and particles and is therefore not suitable for porous particles. The theory is similar to that for MALLS, the forward scattered flux being related to the size and size distribution of the particles in an x-ray beam [218]. Three approaches have been described for calculating size distributions from SAXS data, the successive logarithmic graphical (SLG) [219,220], the dividing distribution function (DDF) [219] and Monte Carlo fitting. Monte Carlo fitting of SAXS of nanospheres was tested with several mono and bimodal distributions. [221] The method has been used extensively on metallic and ceramic powders, colloidal suspensions and precipitates.

Colloidal gold is measured conventionally by TEM which is a complex operation requiring considerable time and a skilled operator and cannot be used in-situ. Using SAXS the mean size can be estimated from the wavelength of peak absorbance using Mie theory; particle size distribution can be estimated by fitting experimental and theoretical spectrum for particles larger than 60 nm; and, for narrow size ranges, the mean size can be determined. [222].
10.10 Near infra-red spectroscopy (NIR)

NIR has been used to determine the mass median diameter of a micronized active compound contained in a lactose monohydrate at a concentration of 4% by weight and a size between 8 and 20 μm [223]. Multivariate statistical analysis was applied to zero order NIR spectra using particle size distributions by low angle laser light scattering as a reference technique. Due to its speed, simplicity and low operating costs it was demonstrated that this is a viable alternative to other methods used to carry out this type of analysis.

Merck & Co. [224] have a patent on a visible and IR spectroscopy method to monitor particle size distribution of on-line monitoring of optically dense samples.

10.11 Ultrasonic attenuation

10.11.1 Introduction

In-line measurements of particle size distributions are essential in order to maximize production capacity and product quality. Ultrasonic attenuation is emerging as a technique, with capabilities beyond those of light scattering. In addition to the needs of industry for compact, robust instrumentation, this method is capable of operating at high concentrations, thus eliminating the need for an expensive dilution step, which may alter the very properties one wishes to measure [225,226].

Originally developed as the Denver Autometric’s PSM single point device; the scope of the technique was greatly enhanced by the use of a range of frequencies to generate a series of relationships between particle size, mass concentration and wavelength. These can be solved by nonlinear mathematical programming techniques to generate the full particle size distribution. The program is linked to the PSM instrument via a computer based signal processor for on-line data analysis and graphics display and is marketed by Proassist as the SD-21.

10.11.2 Theoretical basis for ultrasonic instruments

A mathematical model, Allegra-Hawley [227,228], predicts the attenuation of ultrasonic waves as a function of frequency for each particle size distribution and concentration. Some mechanical, thermodynamic and transport properties of both phases are needed. The relationship between the size, concentration and frequency is obtained from the solution of the
ultrasonic wave propagation equations synthesized in matrix form [229]. The theory assumes spherical particles and single scattering conditions. At slightly higher concentrations (5% to 10% by volume) a multiple scattering correction has to be made [230]. In the case of even higher concentrations steric effects dominate and the scattering model fails. Coupled phase theories agree with experimental results at concentrations up to 25% by volume. An alternative approach has been to combine existing models with empirical correction factors [231].

Heat losses occur at the surface of each particle when a suspension is radiated with ultrasonics due to velocity differences between the viscous liquid and suspended particles and this results [232] in absorption of energy.

A viscous term predominates when the ratio of wavelength to particle size is so high that particles do not follow the liquid movement. The viscous losses term can be derived from Stokes' equation for the effect of viscosity on a spherical pendulum swinging in a viscous liquid.

A scattering losses mechanism is an apparent absorption of energy due to a redistribution of energy. Energy losses occur because of interference between radiated and scattered waves or simply because a scattered beam goes outside the wave path of the main beam and is not picked up by the detector. Essentially, in the diffraction region the wavelength is so small compared to particle diameter that sound behaves in the same way as light. Each particle casts a shadow so that the attenuation is proportional to the square of the particle diameter.

10.11.3 Development of commercial instruments

Proassist: Herbst and Alba [233], in developing the Proassist, measured the attenuation of the sound at ten different frequencies from 0.5 MHz to 6 MHz to retrofit five points on the size distribution instead of only one as with the original Autometrics instrument. They discretized the resulting equation for narrow size fractions and used a mathematical programming technique to find the set of fractions and concentrations which gave the best fit.

Ultraspec: Alba reported on an extension of this technology and termed it the Ultraspec particle size analyzer [234]. The prototype laboratory instrument covered the size range 0.01 μm to 1,000 μm at a volume concentration range from 0.1 to 70 employing a continuous frequency band of 1 MHz to 2000 MHz. In conjunction with the DuPont company, the technique was extended to the measure of undiluted emulsions and an online system was developed.
Further development was carried out by Scott et al. [235] who state that on-line measurement of PSD on concentrated slurries of sub-\(\mu\)m particles is a difficult challenge. First in the design of the flow cell, since the slurries heavily attenuate the ultrasonic beam, a typical design will use a small-bore flow cell that frequently plugs. Secondly is that surprisingly little information is contained in the attenuation spectrum so that it is difficult to estimate a meaningful PSD from the spectrum. The authors addressed these issues with the development of a new ultrasonic instrument that differed significantly from their earlier instrument based on Alba's design. This instrument uses a flow cell designed for reliable operation with concentrated slurries. A short wide-band pulse, that covers a wide range of frequencies, is sent to the transmitting transducer thereby launching an ultrasonic wave through the slurry. The attenuated wave is detected by a receiving transducer, amplified, digitized and Fourier transformed into its frequency components. Once the attenuation spectra is measured the PSD is estimated by a curve fitting procedure based on the Allegra-Hawley [236] model of ultrasonic attenuation. The instrument has been applied to on-line comminution studies on pigments and to droplet size studies in emulsion of chlorobenzene in water.

*Malvern Ultrasizer SV:* After the original research work Alba worked with Malvern Instruments and this led to the development of the Malvern Ultrasizer [237]. The analyzer covers the size range 0.01 \(\mu\)m to 1,000 \(\mu\)m, at a volume concentration range of 0.5% to 50% for powders and up to 80% for emulsions, employing a frequency band of 1 MHz to 150 MHz. The Ultrasizer SV features a range of interchangeable measurement cells that can be exchanged in seconds. Fixed stirred batch cells are available with capacities from 450 ml. Flow cells are available that allow the instrument to be interfaced into particle streams and reactors.

*Pen Kem System 7000 Acoustophoretic Titrator:* Pendse and co-workers used discrete frequencies in the development of the Acoustophoretic titrator. This instrument is based on the measurement of colloidal vibration potential arising from the motion of suspended solids relative to the suspending medium when subjected to a sound field, was the first commercial instrument capable of monitoring zeta potential of concentrated solids.

*Pen Kem Acoustophor™ 8000 system (now Dispersion Technology):* The system was extended for the measurement of sub-micron particle size distributions in concentrated slurries [238] which resulted in a prototype instrument, the Acoustophor™ Penn Kem 8000 system. This instrument consists of two flow-through cells for acoustic and electro-acoustic measurements respectively. With this system the acoustic attenuation is
measured at several discrete frequencies between 1 and 100 MHz with a variable transducer separation. This set-up makes a dynamic range up to 3,000 dB cm\(^{-1}\) attainable. At these frequencies viscous energy dissipation of the sound wave is the dominant phenomenon for sub-micron, rigid particles.

*Dispersion Technology DT-100 Acoustic Spectrometer* measures sound attenuation in suspensions with volume concentrations from 0.1 to 50% to generate size distributions from 0.005 to 100 \(\mu\)m. No information about the sample is required. A variable path length between the source and detector eliminates any need for calibration. A pulse technique, which automatically adjusts the accumulated number of pulses to reach a target signal-to-noise ratio, provides the extremely large dynamic range needed to characterize samples over a wide size range of particle size and concentration.

*Dispersion Technology DT-1200* combines the DT-100 with the DT-200 to give both size and zeta potential. Ultrasound induces a motion of particles relative to the liquid. This motion disturbs the double layer shifting a screening cloud of counter-ions. This displacement creates a dipole moment the sum of which creates an electric field that is measured by two electrode sensors. This field depends upon the value of the zeta potential which can be calculated using the appropriate theory.

*Sympatec Opus*: The OPUS\textsuperscript{TM} (Figure 10.15) is based on ultrasonic attenuation in the regime where attenuation is proportional to the total projected area concentration of the particles and the attenuation is governed by the Lambert-Beer law. For this to be valid, the particles must be considerably larger than the wavelength of the incident radiation. The original Sympatec Opus; (Figure 10.16) system used 20 discrete frequencies in the 1.7 to 8 MHz range with typical measurement times of 2 to 5 min to cover the size range 5 \(\mu\)m to 3000 \(\mu\)m at volume concentrations from 1% to 40%. The measurement range has now been extended to 0.01 \(\mu\)m to 3000 \(\mu\)m at volume concentrations from 1 to 70%. The early flow-through cuvette for on-line analysis had to be arranged in a bypass but a new sensor, called the OPUS Probe, is now available which can be installed in a pipe or vessel [239].

Riebel and Löffler [240] obtained an acoustic attenuation spectrum with one transducer pair to infer the particle size distribution. Solids concentrations and particle size distribution were obtained using both the Phillips-Twomey algorithm (PTA) and the relaxation method. The PTA gives a least squares solution by simple linear matrix operations to yield a numerical inversion from the attenuation spectra to the size distribution.
Fig. 10.15 Schematic representation of the experimental apparatus for ultrasonic spectroscopy.

Fig. 10.16 Simplified presentation of the Sympatec Opus.
and concentration. This works well in the presence of systematic errors such as concentration fluctuations whereas errors arising from inaccurate extinction data often give negative values. Iterative solution algorithms use a priori knowledge to correct for this. However, Riebel and Löffler showed that the relaxation method, though slow, gave the most reliable results but that its use on-line requires a larger computing capacity. Narrow and broad size ranges of glass beads were analyzed. They found that concentration effects were less important than with laser diffraction with little deviation from linearity until the volume concentration exceeded 10%. If results are plotted in terms of the surface-volume diameter, even fibers give good agreement with microscopy.

In later papers they extended the theory to cover multiple scattering effects [241, 242]. They also investigated neural network recognition of particle size distribution by ultrasonic spectroscopy [243] for measuring high concentration suspensions. This work formed the basis for an on-line ultrasonic size analyzer (OPUS) which is available from Sympatec (Figure 10.15).

The problem reduces to finding the size distribution and the solids concentration given measurements of the total attenuation. The problem is difficult because of inherent instabilities in the inversion of the transform.

10.11.4 Discussion

Data, using the Malvern Ultrasizer has been presented from two applications, chemical mechanical polishing slurries used in the semiconductor industry and monitoring a crystallization growth system [244].

The technique has been extended to measurement of undiluted emulsions [254] and the on-line system has also been tested [246]. The flow cell for the on-line system consists of two transducers, one stationary and one that can be moved to give different acoustic path lengths. Three distinct concentration regimes were found. For concentrations below 5% by volume the attenuation at each frequency, from 2 to 50 MHz, was found to be proportional to slurry concentration. In the intermediate regime, 5 to 10% by volume, the observed attenuation was higher than expected. A third regime, at greater concentrations, was found to have attenuation significantly lower. Although the attenuation spectra could be predicted using the A-H model, it was found necessary to assume a log-normal
particle size distribution to determine the particle size from the attenuation data [247].

The originators of the Penn Kem system claim that it is capable of measuring particle size distributions in the size range 0.01 to 100 μm for slurry concentrations at volume concentrations as high as 50%. They report experimental work with an on-line system using titanium dioxide at volume concentrations from 3.5% to 42.3%. Quantitative comparison of data was carried out at eighteen frequencies and eleven concentrations by volume [248,249]. Theoretical work resulted in the development of a unified coupled phase model which successfully predicted the experimental data for suspensions, emulsions and aerosols [250].

To illustrate the capability of this instrument, two high-purity alpha aluminas having log-normal distributions were analyzed separately and as a 50:50 mixture. Results clearly demonstrated the ability of this technique to resolve the original component distributions from a mixture of the two powders [251].

A high-density system (silica spheres) was examined by image analysis using an SEM, by sedimentation, laser diffractometry, dynamic light scattering and ultrasonic attenuation using the Acoustophor. Image analysis and acoustic attenuation both gave narrow distributions whereas the other techniques gave wider distributions, the widest being with laser diffractometry (MALLS) [252]. A comparison between the Matec Acoustosizer and the Acoustophor with DuPont R900 titanium dioxide gave median sizes of 0.300 and 0.311 μm respectively. These compare well with typical DuPont values, obtained with the Brookhaven x-ray centrifuge, of 0.308 μm.

Dukhin and Goetz [253] found a non-linear attenuation spectra for rutile titanium dioxide dispersions in the volume concentration range 1% to 42% and developed a theory to account for this. Dukhin et al. [254] state that viscous losses are dominant in high density contrast dispersions e.g. rutile whereas thermal losses are dominant in low-density contrast dispersions e.g. latices. A report of two years experience of operating this instrument was reported by Hinze et al. [255].

A personal computer (PC) controls the measuring arrangement. The evaluation algorithm in the PC calculates the ring intensity values of the percentage of certain particle size classes by comparison between measured values and predetermined theoretical values. The intensity values are converted into a size distribution by an iteration process. Ultrasonic measurement has also been used to determine the particle size distribution in emulsions down to 20 nm in size. The attenuation was measured in the frequency range 100 kHz to 185 MHz with computer
controlled small volume cylindrical resonators and computer assisted VHF and UHF pulse send-receive apparatus. Concentrated (25% w/v) aqueous emulsions of F-dimethyladamantane-trimethyl-bicyclononane, among others, were studied as well as perfluorochemical emulsions [256]. For a review of ultrasonic particle sizing readers are referred to a paper by Riebel and co-workers [257]. A comparison with x-ray sedimentation showed good agreement for nominal 1 μm silica [258]. In a comparison between the Acoustosizer and the AcoustoPhor it was found that both instruments were capable of zeta potential measurement. Good agreement was found between the techniques for particle size measurement and also between measurements made with diluted and concentrated suspensions. This was expected for monodisperse spherical particles but excellent agreement was also found with non-spherical particles and broader distributions [259]. The potential of ultrasonic spectroscopy for in situ measurement of a crystallization process has also been examined [260].

Babick et al. [261] compare sound spectroscopic determination of particle size distributions of sub-micron emulsions with dynamic light scattering and laser diffraction using olive oil in water droplet suspensions at volume concentrations from 1% to 60%.

An experimental method has been developed to measure the intrinsic attenuation spectra for polystyrene latex using the Malvern Ultrasizer [262].

![Fig. 10.17 Matec AcoustoSizer Measurement cell schematic](image)
10.12 Matec Acoustosizer (ACS)

Matec [263,264] in collaboration with the University of Sydney introduced the Acoustosizer™ ESA-8000, in which the sound waves are generated by the particles themselves as they are exposed to a high voltage alternating electric field. When an alternating electric field is applied across a sample, the double boundary layer surrounding each particle is distorted, so that the particles are displaced relative to the liquid. This motion represents a pressure wave, which is detected by ultrasonic transducers. The amplitude of the wave depends on surface potential, the electrical double layer around the particles and particle size. The phenomenon is called the ESA effect, an acronym for electro-acoustic size analyzer, and yields the average particle size (0.1 to 10 μm), breadth of distribution and zeta potential at volume concentrations from 1% to 40%. ACS measurements provide a means of investigating moderately concentrated suspensions directly without changing the surface equilibria and hence the state of agglomeration. The measurement cell contains about 400 ml of suspension and two electrodes that are used to apply the electric field to the sample. Behind the electrodes there are two glass rods that serve to guide the sound waves to the transducers (Figure 10.17).

When comparing results with other methods it is often necessary to dilute the suspensions without changing their state of agglomeration. Despite this, under electrokinetically stable conditions, excellent agreement was found in a comparison with the Mastersizer S, the Ultra Fine Particle Analyzer, the Sedigraph 5000D and scanning electron microscopy [265]. It was stressed however that sample preparation procedure was important.

The original Acoustosizer used a single frequency whereas a later development has a range of 13 frequencies between 0.3 and 13 MHz. This allows the measurement of the dynamic mobility spectrum and the determination of the zeta potential and particle size. In order to invert the mobility spectrum into a size distribution a log-normal distribution of particle size is assumed. A comparison with photon correlation spectroscopy for determining particle size and laser Doppler anemometry for particle charge confirmed the results using ACS [266]. These and additional sedimentation measurements confirmed that changes in particle size and zeta potential due to dilution effects are likely to occur in aqueous and non-stabilized systems.
10.13 Ultrasonic attenuation and velocity spectrometry

For liquids, the velocity of ultrasound depends on the compressibility and density of the liquid. For suspensions, the velocity depends also on the drag of particles in the liquid under the influence of the ultrasonic wave. At low frequencies, small particles tend to move in phase with the liquid and the ultrasonic velocity may differ widely from that in the pure liquid. As particle size and ultrasonic frequency increases, the particles tend to lag more and more behind the movement of the liquid and the ultrasonic velocity approaches that of the suspension acting as a uniform fluid. There is a transition frequency range between complete entrainment and no entrainment of the particles that can be used to obtain particle size information. The hydrodynamic model of Harker and Temple [267] can be used to calculate ultrasonic velocity. This model takes into account the effects of fluid viscosity, of concentration, density and elastic modulus of both particles and fluid and can predict ultrasonic velocities accurately for volume fractions between 5% and 20%. Ultrasonic velocity measurements in the 50 kHz to 50 MHz can be used to determine particle size distributions in the range of about 0.1 to 30 µm.

In a comparison between ultrasonic velocity and attenuation measurements Harkins et al. [268] reported excellent agreement between predicted and measured values for the former and discrepancies for the latter.

CSIRO Minerals has developed a particle size analyzer (UltraPS) based on ultrasonic attenuation and velocity spectrometry for particle size determination [269]. A gamma-ray transmission gauge corrects for variations in the density of the slurry. UltraPS is applicable to the measurement of particles in the size range 0.1 to 1000 µm in highly concentrated slurries without dilution. The method involves making measurements of the transit time (and hence velocity) and amplitude (attenuation) of pulsed multiple frequency ultrasonic waves that have passed through a concentrated slurry. From the measured ultrasonic velocity and attenuation particle size can be inferred either by using mathematical inversion techniques to provide a full size distribution or by correlation of the data with particle size cut points determined by laboratory analyses to provide a calibration equation.

A resonant technique has been applied to the measurement of phase velocity and attenuation of acoustic waves in water suspensions. Results were compared with theoretical predictions from three different approaches and with data from the Microtrac X100. A tri-modal titanium dioxide (due to aggregation of 0.3 µm primary particles) and a mono-
modal alumina were examined at a frequency of about 75 kHz and at a volume concentration of 10%.[270].

Aeration in a slurry cause large ultrasonic attenuations making accurate particle size measurement impossible. Aerated slurry can be fed to a holding tank and ultrasonic measurements made once the aeration level has dropped low enough to allow meaningful measurements. Clearance times were found to be short enough for a baffled tank passive de-aeration system to be feasible.

The method was used, in combination with a gamma ray transmission technique, for particle size applications in alumina plants [271] and has been tested on a variety of mineral and paint slurries giving good agreement with laser diffraction measurements.

For composite samples the method discriminated separate TiO₂ and CaCO₃ components and accurately determined their proportions. In addition, in combination with ultrasonic attenuation measurements, the size fractions of iron ore slurries below 10 and 30 μm were determined to within 1.3% and 1.0% respectively when compared with laser diffraction measurements [272]. According to Coghill et. al. velocity measurements are complementary to attenuation methods but better suited to the finer size fractions. A description of the analyzer and the results of plant feasibility tests and on-line installation has been presented [273].

10.14 Photon correlation spectroscopy (PCS)

10.14.1 Introduction

Particle sizing of sub-micron powders can be performed on a routine basis using photon correlation spectroscopy. The success of the technique is based mainly on the facts that it provides estimates of average size in a few minutes, no severe sample preparation procedure is required and user-friendly commercial equipment is available. The main drawback is its low resolution. In order to partially overcome this problem, advanced data inversion procedures are required. Other limitations of the technique are; the need to use low concentrations in order to avoid multiple scattering, which results in too low an estimate of particle size; and the conflicting need for high concentrations in order that the number of particles in the measurement zone is sufficiently high for statistical significance. There are also reservations about its ability to separate accurately multimodal distributions and determine wide size distributions. Its strong point is the accuracy with which narrow size distributions may be determined on an
Fig. 10.18 Block diagram of a fixed angle photon correlation spectrometer [284]

absolute basis, i.e. without calibration, in only a few minutes. The technique is also referred to as quasi-elastic light scattering and dynamic light scattering [274].

10.14.2 Principles

The technique involves passing a collimated laser beam into a dilute suspension and measuring the radiation scattered at an angle $\theta$ (usually $90^\circ$) with respect to the incident beam (Figure 10.18). Particles in a fluid are in constant motion as a result of collisions with molecules of the suspending medium. As the particles become smaller the movement becomes more rapid and gives rise to the phenomenon known as Brownian motion. The incident light is of wavelength $\lambda$ whilst the scattered light is of wavelength $\lambda + \delta\lambda$, where the frequency shift is an (optical) Doppler shift the magnitude of which depends upon the velocities of the particles and the angle of observation. The Doppler shifts are too small to be measured directly and are sensed from the interference of light scattered from pairs of particles and summed over the whole distribution. The velocity differences between the paired particles, ranging from a few microns to thousands of microns per second, generate 'beat' frequencies ranging from 1 to 10,000 Hz.

The signal generated by the detector resembles a noise signal due to the constantly changing diffraction pattern caused by destructive and
constructive interference as the particles change their position. Analysis of the intensity fluctuations yields a diffusion coefficient that is related to particle size.

The basic technique is only applicable to dilute suspensions where multiple scattering does not occur and this technique is sometimes referred to as through dynamic light scattering. The introduction of the controlled reference method has extended it to more concentrated systems [275].

In the through sample technique the low frequency signal is deconvoluted using the autocorrelation function, whereas in the controlled reference method the signal is transformed into a frequency spectrum and the particle size determined from iterative deconvolution of the spectrum. This greatly simplifies photon correlation for process control since the remote sampling, dilution and wash cycles are eliminated. The signal is fed to a correlator and the autocorrelation function of the scattered intensity is interpreted in terms of average particle size and polydispersity index.

10.14.3 Through dynamic light scattering

The autocorrelation function of the scattered intensity $G(t)$ is defined as the product of the light intensity at the detector at time $t$ and at a short time later $t + \tau$:

$$G(\tau) = \langle I(t)I(t + \tau) \rangle$$

where $t$ is effectively zero at the commencement of an analysis. The symbol $\langle \cdot \cdot \cdot \rangle$ refers to an average value of the product $I(t) \times I(t + \tau)$ for a large number of times $\tau$.

The normalized first order autocorrelation function $G(\tau)$ can be calculated from the measured function:

$$G(\tau) = A + B \exp(-2\Gamma \tau)$$

where $A$ and $B$ can be considered as instrument factors with $B < A$.

The ratio $B/A$ is often designated as the intercept, as a percentage merit or as a signal to noise ratio.

The decay rate $\Gamma$ is linked to the translational diffusion coefficient $D$ by:

$$\Gamma = K^2D$$
The modulus of the scattering vector, $K$, is defined as:

$$K = \frac{4\pi n}{\lambda_0} \sin \frac{\theta}{2}$$

(10.36)

where $n$ = refractive index of liquid medium, $\lambda_0$ = wavelength of light in vacuum. Note, that with PCS the diffusion coefficient $D$ is determined and not the particle size. The latter quantity can only be determined by relating the diffusion coefficient to the particle size. There is no general relationship that applies to all situations and the frequently used Stokes-Einstein expression only applies to non-interacting, spherical particles.

$$D_0 = \frac{kT}{f_0} = \frac{kT}{3\pi \eta x}$$

(10.37)

where $D_0$ is the diffusion coefficient for a single particle in an infinite medium; $T$ is the absolute temperature; $k$ is Boltzmann constant; $\eta$ is liquid viscosity; $x$ is particle size ($x$ is used in this section to avoid confusion with diffusion coefficient) and $f_0$ is the friction coefficient for a single particle.

10.14.4 Particle size

For homogeneous spherical particles, which are small compared to the wavelength of light, the average diffusion coefficient is the $z$ average $D_x$. However the diameter calculated from this ($x_m$) is not a $z$ average but a harmonic $z$ average i.e. an average intermediate between the volume-moment and the $z$ average [276].

$$x_z = \frac{\sum n_i x_i^7}{\sum n_i x_i^6}$$

(10.38)

$$x_m = \left(\frac{1}{x_z}\right)^{-1}$$

(10.39)
so that:

$$x_m = \frac{\sum n_i x_i^6}{\sum n_i x_i^5}$$  \tag{10.40}

where $n_i$ represents the number of particles of size $x_i$.

### 10.14.5 Concentration effects

The particles must scatter independently; otherwise the diffusion coefficient, and particle size, cannot be determined unambiguously from the decay rate of the autocorrelation function. The net effects of multiple scattering are that the instrument factor $B/A$ decreases, and the autocorrelation factor decays faster, leading to too low an estimate for particle size. Thus, multiple scattering limits the application of the technique to low concentration dispersions ($< 0.01\%$ by volume), although techniques have been developed to overcome this condition.

### 10.14.6 Particle interaction

Since most colloidal dispersions are stabilized by particle interactions, the use of equation (10.51) may lead to biased estimates of particle size that are often concentration dependent. The effect may be taken into account by expanding the diffusion coefficient to a concentration power series that, at low concentrations, gives:

$$D_c = D_0 \left(1 + kDc\right)$$  \tag{10.41}

The equation reduces to the Stokes-Einstein equation for spherical particles. Since the friction coefficient for a non-spherical particle always exceeds the friction coefficient for a spherical particle, over estimation of particle size will occur if equation (10.41) is applied.

The virial coefficient $kD$ is positive for repulsive particle interaction and negative for attractive interaction. Thus if particle interaction is neglected the apparent size will be concentration dependent, increasing with increasing concentration for attractive interactions and decreasing with repulsive interactions. In such cases, the diffusion coefficient should be determined at a range of concentrations and $D_0$ determined by extrapolating to zero concentration.
The effect of particle interaction is proportional to the average interparticle distance that, for a fixed volume concentration, decreases with particle size. Hence, the effect of interaction reduces as particle size increases. However, small particles scatter much less light than large particles and it is necessary to use a higher concentration for reliable PCS measurements. In these cases the concentration needs to be increased to volume fractions up to 0.1% and, again, particle sizes can only be determined from extrapolations to zero concentration.

10.14.7 Particle size effects

PCS relies on uneven bombardment of particles by liquid molecules that causes the particle to move about in a random manner and this limits the technique to particles smaller than 2 or 3 μm.

In order to avoid bias due to number fluctuations, it is necessary that there is at least 1000 particles present in the measuring volume and, for a typical value of the scattering volume of $10^{-6}$ cm$^3$, effects of number fluctuations are to be expected for particle diameters greater than around 0.5 μm. Number fluctuations lead to an additional time decaying term in the autocorrelation function. Since the characteristic decay time of this additional term is usually much slower than the decay attributed to Brownian motion, the average particle size, which is proportional to the average decay time, will be overestimated if the effect of number fluctuations is neglected [277].

Loss of large particles due to sedimentation effects can usually be considered negligible. Stokes' law predicts that a 1 μm particle of density 3000 kg m$^{-3}$ sediments in water at a rate of about 1 μm s$^{-1}$ so that, in 3 min, there will be no particles larger than 1 μm at a depth of 0.2 mm below the surface. Since the measuring volume is usually situated several mm below the surface, this effect is only important for unduly protracted measurement times.

10.14.8 Polydispersity

For monodisperse samples, a plot of $G(\tau)$ against $\tau$ gives a straight line with a constant slope which is inversely proportional to particle size. For polydisperse samples, the relationship is multi-exponential and a plot of $G(\tau)$ against $\tau$ acquires curvature, the degree of which increases with increasing polydispersity [278].
The autocorrelation function for a polydisperse system represents the weighted sum of decaying exponential functions, each of which corresponds to a different particle diameter. For such a system:

\[
G(\tau) = \int_{-\infty}^{0} F(\Gamma) \exp(-\Gamma \tau) d\tau
\]  

(10.42)

\(F(\Gamma)\) is the normalized distribution of decay constants of the scatterers in suspension. Given \(G(\tau)\) it is necessary to invert equation (10.42) in order to determine \(F(\Gamma)\). Unfortunately, the inversion is ill-posed in that there are an infinite number of distributions which satisfy this equation within the experimental error to be found in \(G(\tau)\). A large number of algorithms have been suggested for the inversion and an evaluation of their performance can be found in Stock and Ray [279].

The autocorrelation function can also be analyzed by the method of cumulants. In this approach \(G(\tau)\) is fitted to a low order polynomial. For a third order cumulants fit:

\[
G(\tau) = -\bar{\Gamma} \tau + \left( \frac{1}{2!} \right) \mu_2 \tau^2 + \left( \frac{1}{3!} \right) \mu_3 \tau^3
\]  

(10.43)

An average particle size is obtained from the average decay rate \(\bar{\Gamma}\) using equations (10.41-10.43) and an indication of spread (or polydispersity) is given by \(\alpha_2\).

An advantage of the cumulants approach is that it is computationally very fast. A chi-squared fitting error parameter serves to test whether the assumed Gaussian shape in diffusivities is reasonable. The calculated values of mean size and polydispersity are reasonable (chi-squared approaching unity) for approximately symmetrical distributions having a coefficient of variation within 25% of mean size.

Commercially available instruments usually employ both approaches. For highly skewed distributions or distributions having more than one mode, an inversion algorithm must be used [280] whereas for narrowly classified mono-modal distributions the cumulants approach is satisfactory.

The relative second moment, \(K_2/\bar{\Gamma}^2\), a dimensionless quantity, is a measure of polydispersity. It is the intensity-weighted variance divided by the square of the intensity-weighted average of the diffusion coefficient distribution. The relative second moment is also called the polydispersity.
index that characterizes the spread of the decay rates and hence the spread of particle size about the average value.

Most inversion methods (e.g. Contin [281] and maximum entropy method) [282], require prior knowledge of the distribution.

The singular value analysis and reconstruction method (SVR) reduces the inversion problem to a well-conditioned problem, thus eliminating the need for prior knowledge [283].

Other methods of translating the polydispersity index into size distribution information have been proposed [284]; but the reliability of the transformations is in question. Finsey details these procedures in a review containing 67 references [285]. A later review contains 292 references [286].

10.14.9 The controlled reference method

In the controlled reference method laser light is guided into the sample cell by an optical waveguide. Particles within 50 \( \mu \text{m} \) of the tip of the wave guide (a fiber optic probe) scatter light, some of which is reflected back into the fiber and transmitted back through the guide. The reflected light from the interface between the guide tip and the suspension is also transmitted back. If these two components are coherent they will interfere with each other and result in a component of signal that has the difference or beat frequency between the reflected and scattered components. The difference frequencies are the same as the desired Doppler shifts. The received signal resembles random noise at the output of the silicon photodiode as a result of the mixing of the Doppler shifts from all the particles scattering the laser light. The photodiode output is digitized and the power spectrum of the signal is determined using fast Fourier transform techniques. The spectrum is then analyzed to determine the particle size distribution [287,288]. The iterative deconvolution of the frequency spectrum used with this technique supplies more detail about complex distributions than is possible with autocorrelation analysis. The controlled reference method has been shown to give a more constant measured size, over the concentration range 1 to 1,000 ppm, than the through dynamic method and has also been operated successfully with polystyrene at a concentration of 25% [289].

For a single particle size the power function takes the form of a Lorenzian function. The \( a_0 \) term depends inversely on size so the power spectrum plots for different sizes show a shift to higher frequencies as the particle size decreases. In terms of the Brownian motion, smaller particles move more rapidly than large ones. An assembly of particles will have a
power spectrum $P(\omega)$ which is the sum of Lorenzian functions weighted by the volume concentration of each size (equation 10.44). An additional weighting occurs since the scattering efficiency $S(\alpha)$ is size dependent. The analysis routine must deconvolute the combined power spectrum to determine the volume distribution. The optical properties of the particles and the suspending medium together with the viscosity and its temperature coefficient must be known.

$$P(\omega) = S(\alpha) \frac{2\omega_0}{\omega^2 + \omega_0^2}$$

(10.44)

$$\omega_0 = \frac{8\pi kT}{3\lambda^2 \eta a}$$

$\eta$ = viscosity; $\lambda$ = wavelength in fluid; $T$ = absolute temperature and $a$ = particle radius.

One advantage of this system over conventional PCS is that since the light is reflected back rather than transmitted through the suspension, higher concentrations can be monitored.

Measurement of bimodality for mixtures of sizes ranging from less than 0.1 \(\mu\)m to sizes greater than 0.1 \(\mu\)m is difficult because of the rapid decrease in scattering efficiency as the size decreases. Broad distributions can be measured accurately.

A laboratory made fiber optic dynamic light scattering instrument has been described together with a description of its use to study the kinetics of aging processes in emulsions [290]. The method is particularly useful for this purpose since it permits measurements in concentrated emulsions.

Weiner et. al. [291] determined the particle size distribution as a function of concentration for a number of colloid suspensions. The results showed the advantage of using single mode fiber optics as a practical tool. A comparison made between this and a previous design was presented and several limiting features summarized. A recent review with 54 references covers basic physics, and experimental methods [292]. Applications of the technique to the determination of mean particle diameter, polydispersity and higher order moments are discussed.

10.14.10 Multi-angle measurements

The resolution of PCS can be improved by the simultaneous analysis of data collected at more than one scattering angle, combined with the
additional constraint of the angular dependence of particle scattering power [293]. The basic idea behind multi-angle measurements is that, although the particle scattering power for a monodisperse sample varies over several orders of magnitude as a function of scattering angle, the decay time of the intensity autocorrelation constant remains constant and is proportional to particle size. Consider a mixture of particles, some with a particle size comparable to the wavelength of light and others of a smaller size, e.g. 500 nm and 100 nm respectively. In this case the decay time at small angles will be characteristic of the larger particles, whereas the decay time at larger angles will be characteristic of the small particles. Both features of the size distribution can be recovered from the simultaneous analysis of the autocorrelation functions collected at several angles. Experimental multi-angle PCS results [294-297] indicate that this technique is an excellent tool to detect minor amounts of relatively large particles in the presence of small ones. On the other hand equivalent or better results can be obtained from multi-angle static light scattering data [298,299].

Multi-angle instruments are also available to generate the angular variation of scattered light intensity for derivation of molecular weight, radius of gyration, translational and rotational diffusion coefficients and other molecular properties [300].

The utility of combining Static Light Scattering (SLS), i.e. single angle, with Dynamic Light Scattering (DLS), i.e. multi-angle for obtaining more robust and reproducible particle size distributions, has been demonstrated. The results were excellent but the measurements were tedious and the method required high quality photometer equipment. Bryant [301] combined SLS measurements with only a few angles of DLS data, and also recording DLS data at many angles and iteratively reconstructing the SLS data during the data analysis. The results, by doing DLS at only ten scattering angles and perhaps as few as five, were as good as those obtained with simultaneous multi-angle DLS and SLS. The advantages of this approach are shorter measurement times and a lower quality photometer system.

An instrument has been described which performs zeta potential measurements via electrophoretic light scattering (ELS) and particle size distribution using multi-angle dynamic light scattering. The device uses a single optical fiber/collimetro and a high resolution stepping motor [302].
Table 10.2 Commercial photon correlation spectroscopy equipment

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Multi-angle</th>
<th>Fixed angle</th>
<th>Multi-angle</th>
<th>Fiber optics</th>
<th>Dual angle</th>
<th>Forward scatter</th>
<th>Fiber optics: multi-angle</th>
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<th>Fixed angles</th>
<th>Fiber optics</th>
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<th>Back Scatter</th>
<th>Controlled reference method</th>
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</table>

10.14.11 Commercial equipment

Commercial particle sizing equipment usually operates at a fixed angle of 90° (Table 10.2). Multi-angle instruments generate two moments of the size distribution that renders direct evaluation of size distribution possible, provided a suitable model (e.g. log-normal) can be selected [303]. Multi-angle goniometers using different wavelengths increase flexibility.

Amtec spectrophotometers are designed to measure angular dependent intensity and correlation function either separately or concurrently. The photon correlation option enables sizing to be carried out from 5 nm to 3 μm. Rotation is continuously variable between 10° and 160° with angular resolution of 1/60° in the manual model and 1/100° in the step motor version.
Beckman-Coulter Model N4 Plus system operates in the 3 nm to 3 μm size range, determining average particle size, standard deviation and diffusion coefficient, typically in 1 min. For complete size distributions, the Size Distribution Processor analysis resolves the components of polydisperse sample and reports results in intensity % or weight % as a function of particle diameter or molecular weight. The intensity of scattered light depends on both particle size and angle of observation therefore multiple angles lead to greater sensitivity and increased size range. To take advantage of this the N4 Plus uses six fixed angular positions.

Brookhaven BI-90 is designed for routine sub-micron particle sizing in quality control. Operation of the instrument is fully automatic and a series of repeat measurements including data processing can be set up easily.

Brookhaven ZetaPlus is an electrophoresis instrument with the capability of particle sizing by photon correlation spectroscopy.

Brookhaven BI-200SM is a multi-angle instrument that yields more information on particles and molecules.

Brookhaven 90 Plus sub-micron particle sizing instrument is a dual-angle instrument with measurements at 15° and 90° to generate size distributions in the 10 nm to 1 μm size range together with zeta potential determinations.

Brookhaven BI-200SM goniometer system is a precision instrument designed for macromolecular studies and sub-micron particle sizing. It is based on a special turntable to measure angular intensity and photon correlation measurements.

Horiba LB-500 operates in the size range from 0.003 to 6 mm, at concentrations up to 20%. The focal point of the lens is positioned on the inner wall of the cell concentrating maximum light in order to measure high concentration suspension. In addition a pinhole filter removes errant
beams assuring that only light scattered from the focal point will be sent to
the detectors. The LB-500 can be combined with the LA-910 and 920 to
extend their size range.

**Lecotrac LTU-150** operates in the 0.003 to 6.5 μm size range using the
controlled reference method.

**Lecotrac LTU-251** Coupled to an external probe, this analyzer allows
fast in-line measurement. The external probe is constructed of rugged,
flexible steel and can be attached to a process line via a 3/8-inch NPT pipe-
thread mounting hardware. The probe tip consists of a sapphire window
embedded in a stainless steel sleeve using Teflon® seals.

**Leco Tri-laser** uses 3 angular detectors to cover the size range 0.02 to
2000 μm.

**Leeds and Northrup Microtrac Ultrafine Particle Analyzer (UPA)** uses
the controlled reference method, using a sapphire tipped waveguide that
collects back-scattered light within 100 μm of probe tip, to cover the size
range 0.003 to 6.5 μm.

**Leeds and Northrup Microtrac Series 9200 Ultrafine Particle Analyzer**
Model 9230 operates in the 0.003 μm to 6 μm size range (Figure 10.19)
and gives reproducible results in the concentration range 2 to 2000 ppm
(2%).

**Malvern Autosizer Hi-C.** Particles in suspension scatter light emitted
from the tip of the launching fiber (Figure 10.20). Scattered light
backtracks to the fiber and is collected again and passes to the detector via
the directional coupler. This prevents light from the source reaching the
detector directly. Some light is reflected back from the tip of the fiber
without being emitted. This acts as a reference signal that is mixed with
the scattered portion. Since the particles in the sample are in random
motion due to Brownian motion the light they scatter is frequency shifted
due to the Doppler effect. This shift is revealed by comparison with the
reference signal resulting in a low frequency spectrum that is related to
particle size. The instrument covers the size range 0.015 to 1 μm at solids
concentrations from 0.01% to 50%. One reported application [306] was
the measurement of casein micelles in cheese making as they grew in size
from 200 to 1200 nm.

**Malvern System 4700** comprises a variable angle spectrometer with
computer controlled automatic operation, combining photon correlation
spectroscopy and angular intensity measurements with full Mie theory
calculations to give accurate size distributions in the 1 nm to 5 μm size
range.
Field scanning methods

Fig. 10.19 Line diagram of the Microtrac Ultrafine Particle Analyzer (UPA).

Fig. 10.20 The optical unit for the Malvern Autosizer Hi-C.

Malvern Auto-sizer 4800 is a sensitive, high performance multi-angle light scattering spectrometer designed for both static and dynamic light scattering measurements operating in the size range 1 nm to 5 μm.

Malvern Zetasizer II consists of a light scattering spectrometer and digital autocorrelator with integral microcomputer. In addition to measuring electrophoretic mobility the movement of charged colloidal particles under the influence of an applied electric field the Zetasizer II also determines particle size by Brownian motion. The Zetasizer III combines both photon correlation spectroscopy and angular intensity measurements with full Mie theory calculations to give accurate size distributions in the 2 nm to 3 μm size range.

Malvern Zetasizer nano zs uses non-invasive back-scatter technology to measure particles in the 0.6 nm to 6 μm size range together with molecular weight and zeta potential measurements.
Malvern High Performance Particle Sizer (HPPS) combines high sensitivity with a high concentration capability using dynamic light scattering with back-scatter optics. The HPPS covers the size range 0.6 nm to 6 µm at concentrations from 0.00001 vol% to 20 vol% at speeds up to 20°/s.

Malvern Compact Goniometer System (CGS-3) is a multi-angle light scattering spectrometer. The detector scans a sample cell from an angle of 12° to 152° with an angular resolution of 0.025°.

Nicomp380/DLS Submicron particle sizer uses dynamic light scattering with a size range of 0.003 to 5 µm with unique modular options. An Autodilution unit that eliminates the need for manual dilution of concentrated samples [307]; an Auto-sampler that permits automatic batch analysis of as many as 76 samples; high-power laser diodes, multi-angle options and zeta-potential accessory.

Nicomp Model 780/SPOS provides two analysis modes, Gaussian and Nicomp’s proprietary algorithm. This algorithm enables the instrument to analyze complex multi-modal distributions with high resolution and reproducibility. Its capabilities can be enhanced by adding one or more accessory modules including a zeta potential analyzer with multi-angle particle sizing capability.

Nicomp Model 380/MA is a multi-angle option that uses a precision stepper motor to vary the scattering angle (0.9 degrees per step). This capability permits an improved analysis of polydisperse distributions of larger particles (>0.1 µm).

Nicomp Model 380/L is designed for on-line monitoring either by itself or in combination with the Particle Sizing System AccuSizer. These instruments are available from Particle Sizing Systems.

Otsuka Photal is a dynamic light scattering spectrophotometer that provides sub-micron sizing in the 3 nm to 3 µm size range and also provides information on the shape of polymers.

Wyatt QELS is a compact add-on instrument that can be connected to a Dawn® Eos or a miniDawn Tristar in order to determine particle sizes and their distributions. The combined system gives the ability to size very small particles (under 10 nm), as well as very large particles on-line after they have been separated by some kind of fractionation. The Wyatt QELS comes with the ability to measure the correlation function at 18 angular positions.

In the microliter batch mode, the system collects data from small samples that have been injected into special blackened cuvettes. Unfractionated samples produce complex correlation functions whose
departure from exponential decay arises from the presence of heterodisperse components in the suspension.

In the flow mode, the instruments may be used to collect, simultaneously, the dynamic and classical light scattering data from which the molar mass and root mean square radii are calculated from each slice (See section on fractionation).

For the mini-Dawn Tristar, dynamic light scattering signals are only collected from the 900 location, whereas for the Dawn Eros dynamic light scattering signals can be collected at any one of its 18 detector locations.

10.14.12 Discussion

The basic theory and discussion of results are covered in papers by Thomas [308], who uses a Brookhaven Instrument Fiber Optics Quasi-Elastic Light Scattering System (BI-FOQELS) with dynamic light scattering obtained using the BI-DLS and diluted samples.

An autodilution unit has been described to analyze on-line particle growth during a polymerization process [309]. The results compared favorably with off-line dynamic light scattering and on-line turbidimetric data [310].

Several data analysis software packages are available and average sizes generated by these are not comparable [311-313].

De Jaeger et al. [314] carried out inter-laboratory tests using polystyrene lattices with particle sizes ranging from 30 nm to 2 μm. They concluded that reliable particle sizes could be obtained for diameters less than 0.5 μm. In the range 0.5 to 1 μm this was only possible within a very narrow range of concentration. For the largest size investigated (about 2 μm) the measurements were less reliable. In comparison tests, using standard latex particles, it was found that DLS gave data that is approximately 0.005 μm larger (0.064 μm) than electron microscopy and light turbidity methods, i.e. 0.059 ± 0.002 μm.

In a comparison between the Coulter N4 and the Malvern Autosizer it was found that both instruments gave good results with monodisperse latices [315]. For bimodal distributions, the two modes were not always detected and, if they were, the locations of the modes were incorrect [316].

Koehler and Provider [317] sized monodisperse PMMA latices with a range of instruments: Disc centrifugal sedimentation (DCP), sedimentation field flow fractionation (SFFF), hydrodynamic chromatography (HDC), photon correlation spectroscopy (PCS), turbidimetry and transmission electron microscopy (TEM). TEM gave the smallest sizes, DCP and SFFF were in fair agreement in the center and PCS the highest sizes.
In an evaluation of a range of instruments Lange [318] stated that turbidimetry appeared the most reliable approach to average size determination, whereas ultracentrifugation, DCP and TEM with image analysis were superior for determining size distributions and polydispersity.

Lee et al. [319] compared FFF, PCS and TEM for sizing acrylic latexes. They stated that FFF is a useful tool for accurately determining mean size and size distribution due to its simplicity and ease of operation. PCS provided reasonable data for small diameters and narrow distributions but suggested that multi-angle analysis was needed for larger particles and broader distributions.

Multi-angle PCS was also preferred by Bryant et al. [320,321] for measuring multi-modal PSD's, and they showed that accuracy increased with increasing number of angles.

Four instruments were evaluated using eight polystyrene latexes, ranging in size from 0.039 to 0.804 μm, from Duke Standards [322]. The instruments were: Matec CHDC-2000, Brookhaven BI-DCP, Coulter N4-Plus (PCS) and Hitachi H-7000 FA (TEM). TEM gave average sizes close to nominal values, CHDF gave values slightly larger than nominal except for the lowest size where it gave a value of 0.046 μm, PCS and DCP gave reasonable values. The measurement time was unduly protracted with the DCP for the finest fraction, the generated size being 0.70 μm for a run time of 2 hours reducing to 0.056 μm when this was extended to 6 hours. It was found that both PCS and CHDC gave much broader distributions than DCP and TEM. For polydisperse (bi- and tri-modal) CHDF and DCP provided the most accurate distributions whereas PCS failed to capture the whole distribution.

Photon correlation spectroscopy measurements for growth rate, together with a quartz crystal microbalance for mass deposition, have been integrated into a single platform to permit simultaneous in-situ real time measurement at times and temperatures representative to those found in aviation fuel systems [323].

Kroner et al. [324] compared DLS with static light scattering for determining soot particle size in a premixed flame. They concluded that static is preferable to dynamic since the latter procedure requires detailed information about the flame.

10.14.13 Spectral turbidity

Beckman DU 7500 spectrophotometer has been used to determine the size distribution of “monodisperse” latex in the size range 200 to 800 nm, to
study agglomeration during crystallization and attrition of potassium sulphate. A polychromatic light beam from a uv source passes through a silica fiber to a sensor immersed in the suspension. After crossing the measurement zone the transmitted light passes through a fiber to a holographic grating that splits the light into a spectrum that falls on to a 256 photodiode array. Using Mie theory the spectral turbidity yields the particle size distribution of the powder in suspension [325].

10.14.14 Diffusion wave spectroscopy (DWS)

DWS addresses dynamic light scattering in the multiple scattering concentration range. Pine et. al. [326] describe the theory for the technique and it has been applied to the determination of mean size and polydispersity [327,328]. The method has also been used for on-line measurement of concentrated suspensions [329].

10.14.15 Photon migration

In photon migration, an intensity-modulated light beam is launched into the sample and the photons diffuse through the sample and are detected [330]. The transmitted signal is attenuated and phase shifted relative to the incident beam. Measurement of the phase shift and attenuation as a function of modulation frequency yields scattering coefficient and particle size. Mie scattering theory is applied to generate particle size. The theory can be extended to higher concentration regimes. The particle size distribution is determined by determining the scattering coefficient at one wavelength over a range of known particle concentrations.

10.15 Turbo-Power Model TPO-400 in-line grain size analyzer

Nisshin developed this instrument for the cement industry. At preset times it automatically samples a few kilograms of material and feeds it into a turbo classifier. The fines are fed into a micron line that determines the Blaine number for the powder.

10.16 Concentration monitors

Monitek instruments measure the concentration of suspended solids in a liquid by shining a light through the stream and detecting the amount of light that is scattered by the suspended solids. The scattered light is seen as turbidity hence the name turbidimeters. Suspended solids scatter light
in all directions so that there are many potential viewing angles; 90° side-scatter instruments are called nephelometers. Forward scatter instruments sample a more representative cross-section of a process stream and can monitor as wide range of particle sizes from 0.01 to 100 μm. For accurate measurement Monitek uses a ratioed forward scatter intensity where the scattered intensity is divided by the direct beam signal.

10.17 Shape discrimination

The morphology of particles is an important characteristic that can seriously affect powder handling and end-use properties. Off-line techniques are often not suitable for monitoring industrial processes since extracting the particles from the process can alter their shape, e.g. particles taken from a crystallizer may fracture or aggregate.

To resolve the problem an in-line camera, capable of imaging crystals produced in a commercial crystallizer, was developed [331]. The instrument is based on a borescope and video camera that fits inside the housing of a laser backscatter probe, which installs in a standard ball valve. A strobe light is used to "freeze" crystal motion. Crystal features seen directly include shape, surface roughness, inclusions and transparency.

The information content of the uv/vis spectrum of sub-micron and micron size particles yields information on the size, chemical composition and shape of the particles [332]. The angular dependence of the scattered intensity is given by the Rayleigh-Gans-Debye (RGD) theory. The form factors for various particle shapes were calculated as a function of the angle of observation θ and wavelength λ of the incident light. Comparison of the scattering intensities for particles with different shapes showed that each differently shaped particle had a unique surface pattern thus suggesting the possibility of selecting combinations of λ and θ to enable shape discrimination.

10.18 Miscellaneous

10.18.1 Back-scatter intensity

A relationship has been derived between average particle size and concentration and the back-scatter intensity of a light beam entering a slurry of non-transparent particles [333]. Concentrations used were 0.3 to 2.5% and the average sizes were 40 to 1200 μm. The light source and detector were built into one tube that was mounted on the wall of a 1 liter
vessel that contained an agitated suspension of the particles under test. The derived relationship took the form:

\[ i_{bt} - i_{bw} = (I_{bm} - I_{bw}) \exp\left(\frac{k c^p d^q}{\lambda}ight) \]  \hspace{1cm} (10.45)

The suffixes refer to the back-scatter intensity from; \( b_t = \) total, \( b_w = \) container walls, \( b_m = \) maximum possible. For aluminum silicate, experiment yielded \( p = 0.77, q = 1.67, k = 0.20 \).

In a second paper [334] the technique was extended to on-line. A similar technique to the above, but using ultrasonics, has also been described [332,336].

10.18.2 Spectroscopy photo-acoustic (PAS) and photo-thermal (PTS)

The surface of a specimen may become heated through irradiation, the degree of heating depending on the material's absorption coefficient at the particular wavelength of radiation. A wavelength scan across a suitable part of the electromagnetic spectrum thus causes temperature changes that reflect the adsorption spectra at the point of illumination.

In PAS the heating serves to increase the pressure inside a small chamber in which the sample is situated, being irradiated through a window. A recording of the pressure variations versus wavelength of illumination reflects the absorption spectrum of the material.

In PTS one records the increase in thermal emission from the sample induced by irradiation. PAS techniques require samples to be placed in a spectrophone for analysis. PTS methods allow constant free on-stream inspection at a distance. Particle size may be inferred from the signal level. Since specific surface increases with decreasing size the signals also decrease. A discussion of these techniques has been presented by Kanstad and Nordal [337].

10.18.3 Transient electric birefringence

A dilute suspension of electrically and optically anisotropic colloidal particles becomes birefringent when subjected to an electric field. In random orientation the suspension is optically isotropic but when the grains align with a uniform electric field the suspension becomes anisotropic; in particular the effective refractive index of the ordered suspension parallel to the field direction differs from its refractive index.
perpendicular to the field. This double refraction, or birefringence, has been used for evaluating the size distribution of sols in solution.

Experimentally, a colloidal system, in random orientation, is illuminated with polarized light. The system is subjected to an electric field that aligns the particles due to the interaction between the field and any permanent dipole or electrical polarizability of the particles. The birefringence grows as the particles align; when the field is removed the birefringence decays as the particles revert to random orientation.

For a monodisperse suspension the decay rate can be described by a first order rate equation. For a polydisperse suspension the decay rate is a sum of exponentials. Measurement of the decay rate permits computation of particle size [338].

Haseler and Hinds used this procedure to determine the size distribution of anisometric silver halide crystals using an instrument that they developed called an electric field birefringece. They found that the technique was capable of good accuracy and high precision [339].

10.18.4 Crossed lasers

A description of a crossed laser beam technique for particle sizing and its application to shock tube experiments was presented by Waterson and Chou [340].

10.18.5 Frequency domain photon migration

A method for on-line monitoring of particle size distribution and volume fraction in real time using frequency domain photon migration measurements (FDPM) has been described. In FDPM the time dependence of the propagation of multiply scattered light provides measurement of particle size distribution and volume fraction. The technique has been applied to a polystyrene latex and a titanium dioxide slurry at volume concentrations in the range 0.3 to 1% [341].

FDPM consists of launching sinusoidally modulated light into a scattering medium at a single point source and detecting the modulated light at another point some distance away from the source. The photon density wave is attenuated and phase-shifted relative to the incident signal as it propagates through the scattering medium due to the scattering and adsorption properties of the sample. These properties can be measured by fitting the phase shift and modulation to the appropriate solution of the optical diffusion approximation, which describes the transport of light in random media. Particle size distribution and volume concentration can be
determined from multi-angle measurements of FDOM and determination of the isotropic scattering coefficient.

The technique is fast and the equipment relatively inexpensive. Moreover, since photon migration measures the time it takes for light to travel through the sample rather than the intensity of the detected signal, it is self-calibrating.

10.18.6 Laser induced incandescence (LII)

Aerosol particles are heated close to their evaporation temperature by a high energy laser pulse and start to emit thermal radiation. As the particles cool, mainly by heat transfer to the carrier gas, their thermal emission intensity decreases with time. Due to their higher heat capacity large particle cool more slowly than small ones and the cooling time can be used as a measure of particle size. Early applications mainly concentrated on average parameters for soot particles in flames [342] and this was extended to determination of a detailed characterization of the size distribution and internal structure of aerosols at room temperature [343]. The results showed good agreement with TEM and DMA data. Particle sizes were in the nanometer range at number concentrations down to 10^3 cm^-3. Other accessible parameters are the diameters of agglomerates, the volume fraction and the mean number of primary particles [344]. LII has been applied to in-situ measurement of primary particle size on the manufacture of carbon blacks [345]. The system has also been applied to the measurement of nanosize particles on soot and vehicle exhausts. Measurements on carbon black particles gave data which correlated well with product properties. Tests with titanium dioxide and metal powders were encouraging [346].

10.18.7 Spectral transmission and extinction

Cemi used spectral transmission and extinction using UV, visible and near IR to measure slurry particle size distributions with undiluted continuous flow [347]. The method uses multiple linear detector array spectrometers. It also uses multiple sample cells of different optical depths optimized for a specific spectral range, multiple optical paths and multiple linear detector arrays.
10.18.8 *Turbiscan* multiple light scattering measurements

*Turbiscan On-Line* monitors and quantifies the effects of process variables in dispersed systems. It operates in the volume concentration range from 0 to 60% and the size range of 0.1 to 5,000 µm. The vertical scan macroscopic analyzer consists of a reading head that moves along a flat bottomed cylindrical cell to scan the entire sample length. The optical sensor consists of a pulsed near-infra-red light source and two synchronous detectors: The transmission detector monitors light transmitted through the suspension and the back-scattering detector receives the back-scattered light at 135°. The optical sensors acquire transmission and backscattering signals in from 0.1 to 10 seconds, every 40 µm along the sample tube for a maximum of 80 mm, and these signals are digitized and displayed by the software indicating real-time changes in transmission and backscattering intensities. These parameters are directly related to particle size and volume concentration.

*Turbiscan Lab* measures concentrated suspensions at up to 95% by volume. The mean particle diameter can be calculated over the size range 0.05 to 1000 µm.

*Turbiscan Ma* 2000 measures the destabilization of concentrated dispersions and determines the mechanisms driving it. The ma 2000 is used to improve formulations, document stability tests and shorten stability test time.

Anisotropic particles have been measured using a variety of techniques and correlation between them was found to depend on particle morphology [348]. For cylindrical glass fibers photocentrifuge data gave good correlation with image analysis using the Turbiscan, whereas for platelets laser diffraction gave the best correlation. The correlation between Turbiscan for flake-like mica was found to be very good whereas the photocentrifuge gave better agreement with rod-like copper oxalate. In both cases some information from the image analysis data was required in order to make assumptions to simplify the deconvolution data of size and shape from the collected data.

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