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Technical Workshop Series: Introduction to the Latest
ANSI/ISO Standard for Laser
Particle Size Analysis

A Primer on
Particle Sizing by Static Laser Light Scattering

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INTRODUCTION

The number of techniques employed for particle size determination exemplifies its importance and perhaps indicates the difficulty in acquiring this information. Duke Scientific Corporation (1998) published on their web site (http://www.dukescientific.com) a list of particle sizing methods. That list is reproduced below.

Particle Sizing Methods

Microscopy Methods
  - Optical
  - Transmission Electron Microscopy
  - Scanning Electron Microscopy
  - Atomic Force Microscopy
  - Imaging Analysis

Light Interaction Methods
  - Laser Diffraction
  - Photon Correlation Spectroscopy
  - Single Particle Light Scattering
  - Multi-Angle Light Scattering
  - Single Particle Light Obscuration
  - Laser Doppler Velocimetry
  - Time Of Flight
  - Fiber Optic Doppler Anemometry (FODA)

Electrical Property Methods
  - Coulter (Electrozone) Principle
  - Differential Mobility Analyzer (DMA)
  - Electrophoretic Mobility
  - Zeta Potential

Sedimentation Methods
  - Photosedimentation
  - Centrifugal Sedimentation
  - X-ray Sedimentation

Sorting and Classification Methods
  - Fluorescence Activated Cell Sorting (FACS)
  - Field Flow Fractionation (FFF)
  - Sieving and Screening
  - Air Classification

Considering Only Light Scattering Techniques

Of the five methods and twenty-four techniques listed above, this document addresses only the light interaction method and only the laser diffraction or static laser light scattering (SLLS) technique within that category. The other light interaction methods (photon correlation spectroscopy, single particle light scattering, multi-angle light scattering, single particle light obscuration, laser Doppler velocimetry, and time of flight fiber optic Doppler anemometry) are defined in the glossary.

Additional Convergence

To fully describe light scattering phenomenon, familiarity with several supporting theories is required. That background is provided here, but only to the extent necessary to provide continuity in the discussions that follow. Detailed information is available from various sources and the reader will need to research those sources if technical details are desired. The general format of this document, then, will be to present a broad and general picture, then focus only on details pertinent to the main subject of this document which is particle sizing by deconvolution of the light scattering pattern using Mie theory.

From Theoretical Models to Practical Applications

Current scattering theory provides the foundation for building an understanding of the phenomenon, but by no means provides a mathematical solution for all situations in which scattering occurs. This is true for a great number of theories, therefore they are qualified with statements similar to, "..under the assumed conditions of..." Samuel C. Florman, in his book The Civilized Engineer, puts this reality into perspective by reminding practitioners that "*Although we are committed to scientific truth, there comes a point where this truth is not enough, where the application of truth to human objectives comes into play We are no longer considering theoretical forces and ideal substances. We are now obliged to work with materials that are real, impure, and sometimes unpredictable. Our aim is no longer to discern absolute truth, but rather to create a product that will perform a function.*"

This document will introduce the theories and the conditions under which those theories accurately predict the outcome. It then will apply those theories to the practical problem of determining, from the pattern of light scattered from an assemblage of particles, how the population of particles is distributed by size. In doing so, the effects of not working with *"theoretical forces and ideal substances "* will be revealed.

LESSON 1: Light and its Interaction with Matter

The Nature of Light

Energy transmitted by waves through a medium is called radiation or radiant energy; it includes electromagnetic, sound, and elastic waves. Electromagnetic energy includes cosmic rays, γ-rays, X-rays, light, heat, microwaves, and radio waves. This continuum of energy is called the electromagnetic spectrum. Energy residing in a specific and very narrow band of this spectrum is referred to as 'light'.

Wave theory often is used to describe electromagnetic radiation and therefore to describe light. Light waves, sound waves, water waves, etc. share some characteristics and can be studied using the same theories, but only in limited cases. Although similar in some respects, there are considerably more differences than similarities between sound waves and electromagnetic waves. The same holds true when studying details of electromagnetic waves in different bands of the spectrum; theories that apply to one band of wavelengths may not apply well to another band.

This document is concerned only with light. Even within this narrow band of electromagnetic radiation, interaction between light and matter may produce very different effects depending on the wavelength of the light or the characteristics of the material; these variables may be referred to as the conditions under which an interaction takes place. Interactions that result in what is called *light scattering* are no exception. So, any description of light scattering must be accompanied by qualifying statements that define the conditions under which the statements (theories, explanations, or conclusions) are believed to be factual. The discussions that follow hold fast to this caveat; terms are defined and statements qualified as they pertain to the theoretical discussion. These definitions and qualifications may be referred to as limitations, conditions, constraints, or boundary conditions. Regardless, they are what ultimately will separate the theoretical ideal from real-world applications of light scattering theory.

A few additional facts about light should be mentioned. The smallest bundle in which electromagnetic energy is packaged is called a *photon*. All photons of light of a specific wavelength have a specific quantity of energy. The intensity of light of a specific wavelength is a function of the total number of photons emitted (or collected per unit area) per unit time.

The study of optics also deals with light beams and light waves. A *ray* is the imaginary line that corresponds to the direction in which radiant energy flows. A *light beam* can be thought of as a group of parallel rays and as having finite thickness; a light beam also may be considered a stream of photons all moving in the same direction. To express it another way, a light ray is the limit of narrowness of a light beam. The branch of optics that is concerned with the path of light rays through optical systems is called *geometrical optics*.

Light and, in fact, all electromagnetic radiation has a dual personality. Sometimes it behaves like a particle and sometimes it behaves like a wave, the wave most often being depicted as sinusoidal. This is the particle-wave duality characteristic often attributed to photons. In this document, light will be treated either as a continuous wave or as a photon, depending on which view best serves the current technical discussion.

Interactions Between Light and Matter

Rarely do we observe light directly. More typically, we observe light that has reached either our eye or a light detection instruments by some indirect path from its source, having interacted with some object in its direct path. The study of how light interacts with matter is called *physical optics*. How the matter responds to the interaction is of minor importance in this section; that will be covered in light detection theory. How the light responds to an interaction is our principal concern in this section. Descriptions of some possible reactions follow.

intensity versus angle is called the *scattering pattern*.

Adding Constraints and Conditions

General Mie theory applies to scattering of plane waves of monochromatic light by isotropic spheres. Isotropic materials, incidentally, have properties that are independent of the direction in which they are measured. Mie theory, therefore, is constrained to these conditions. Below are listed the theoretical and experimental constraints assumed in regard to the formation and analysis of scattering patterns in an effort to extract size distribution by quantity.

Only monochromatic light is considered. Mie theory applies to formation of a scattering pattern by light of only a single wavelength.

The particle is isotropic. This is explicit in Mie theory. With such particles, it makes no difference from which direction the incident beam strikes the particle.

The particle is spherical. This is a condition of Mie theory.

The incident light is composed of plane waves. This is a condition of Mie theory.

Both scattering AND absorption are considered. These are two different phenomena and both are important in understanding how the incident light beam is affected by interacting with suspended particles. Absorption of a light beam is not 100% efficient; some photons in the beam also may be reflected or transmitted through the object. In some cases, absorption may approach 100% and few photons are reflected after impact and few transmit through the object after refraction. In this case the object is said to be opaque. This does not eliminate the diffraction component of scattering and the opaque object still scatters light due to the interaction of the wave front with the edge of the object.

Both scattering and absorption cause the incident light beam to be diminished as it is projected through an assemblage of particles, some decrease due to redirection of rays by scattering, some decrease due to loss of the photons by absorption. This reduction in the energy of the incident beam leads to the concept of extinction, which is the degree of attenuation of the incident light energy.

Extinction = scattering + absorption

where scattering = reflection + refraction + diffraction

Only single scattering is considered. Mie theory considers only the scattering of light from the primary light source, and does not include light scattered from one particle to another, which is called multiple scattering. Multiple scattering occurs when the light beam reaching a particle has been strongly attenuated by other particles. Single scattering means essentially that the radiation impinging upon each particle arrives directly from the incident source. A more rigorous definition is: *If there are N particles subjected to the incident radiation, then the scattered light intensity is N times that scattered by a single particle.* Another way of stating this is *the energy removed from the incident beam by N particles is N times that removed by a single particle*. This is another example of extinction.

Only static light scattering is considered. The scattering characteristics under consideration are independent of the motion of the particle. This is discussed in more detail later in this lesson.

No quantum effects are considered. Light scattering, as discussed hereafter, does not apply to any alteration of the wavelength of the incident light (Raman or Doppler effects).

SIDEBAR: A test to determine if multiple scattering is negligible is to double the concentration of particles and see if the scattered light doubles. If so, then multiple scattering is negligible. A more in depth understanding of the effects of particle concentration on scattering can be acquired by plotting extinction versus concentration. Particle size analyses should be performed in the linear range.

The Mechanics of Light Scattering

The amplitude of scattered light at different angles (the scattering pattern) depends not only on concentration and particle size, but also on the ratio of the refractive indices of the particles to the medium in which the particle exists. The more the particles differ from the medium (i.e. the more their refractive indices differ), the more light will be scattered by the particles. At the other extreme, if there is no difference in refractive indicies, no light will be scattered.

The diagram in Figure 1-3 illustrates the interaction of light with an isolated object. It shows incident light beams (assume intensity I and wavelength λ) in close proximity with a spherical particle. Photons in one ray are sufficiently far away from the particle to have no interaction and are unaffected by its presence. Another beam comes close enough to be diffracted by interaction with the edge of the particle. Another beam intersects the particle. Some photons are reflected; others penetrate the surface and, in doing so, are refracted. The refracted ray of photons strikes the far side of the particle. At this interface, some photons penetrate and are transmitted, while others are reflected internally. The reflected ray intersects another internal interface and is partly reflected and partly penetrates. Since there is no absorption, there is no net loss of photon energy.

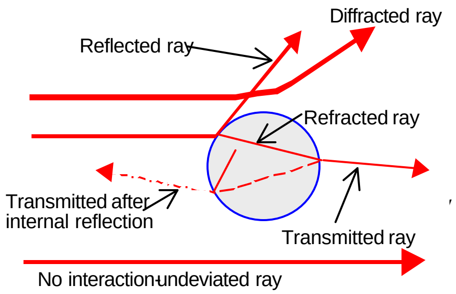

Figure 1-3. Light rays interacting with a particle.

The intensity of the scattered light is a function of the wavelength λ, the scattering angle θ, the particle size d, and the relative index of refraction *n* of the particle and the medium. Symbolically, then,

$$I_{sc} = I_{in}(\theta, \lambda, d, n). \qquad \text{(Eq. 1)}$$

Limitations and conditions as noted previously are assumed. It should be noted that θ is measured relative to the angle at which the incident light was directed. The undeviated ray in Figure 1-3, therefore, is scattered zero degrees and the diffracted ray is illustrated as having an approximately 45 degree scattering angle. This is called *forward scattering* as is any scattering at angles less than 90 degrees.

Mie theory is a powerful tool to calculate the size or refractive index of spheroids because the pattern of scattered light from particles is very sensitive to small changes in size or refractive index. Comparing the measured scattering pattern to that predicted by Mie theory allows particle size to be calculated if refractive index is known.

The theories introduced above form the theoretical bases for static laser light scattering particle size analyzers. The next lesson in this series will provide information on how various manufacturers of SLLS particle size analyzers design the optical system in order to measure the scattered light. Strengths and weaknesses of these designs will be explored.

Future lessons will focus on extracting particle size information from measurements of the scattering pattern followed by instrument-specific information and application information.

Differentiating Between Dynamic and Static Light Scattering

The definitions of light scattering as given above introduced a juncture in light scattering theory at which static light scattering (SLS) and dynamic (or quasi-elastic) light scattering (QELS) are separated. By the static light scattering technique, particle size information is extracted from intensity characteristics of the scattering pattern at various angles. With dynamic light scattering, particle size is determined by correlating variations in light intensity to the Brownian movement of the particles. Values obtained by the latter technique vary widely depending on the concentration and condition of the sample, as well as environmental factors. With both techniques, however, the scattered light has undergone no alteration in wavelength.

Other scattering methods include Laser Doppler Velocimetry (LDV) and Fiber Optic Doppler Anemometry (FODA). LDV employs a laser to measure the aerodynamic diameter of particles between 0.5 and 10 m in diameter and is independent of the particles optical properties as long as the particles scatter light. FODA is a technique that utilizes fiber optic sensors to detect and measure mass concentration in submicron particle systems. In these methods, the wavelength of light is altered by the interaction with matter.

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SUMMARY OF LESSON 1

Scattering is a process that conserves the total amount of energy, but the direction in which the radiation propagates (spatial distribution) may be altered.

Absorption is a process that removes energy from the incident light beam by converting it to another form.

Extinction (or attenuation) is the net effect of scattering and absorption and describes the effect of the interaction between the radiation and the matter upon which it impinges.

Limitations must be applied in order to describe scattering exactly. The limitations include:

- Incident light of only a single wavelength is considered.
- No dynamic scattering effects are considered.
- The scattering particle is isotropic.
- There is no multiple scattering.
- All particles are spheres.
- All particles have the same optical properties.
- Light energy may be lost to absorption by the particles.

General Mie theory rigorously describes the scattering pattern from a spherical, isotropic particle illuminated by monochromatic plane waves.

Constraints and conditions are applied to the experimental conditions under which the scattering pattern is produced. Otherwise, Mie theory may not directly apply.

LESSON 2: Mie Theory and Particle Sizing

Light Scattering Patterns

In Lesson 1, light scattering achieved under certain conditions was discussed. Some of the conditions are:

A) incident and scattered light are of a single wavelength,

B) scattering particles are separated sufficiently that they are exposed only to parallel rays of the incident light,

C) scattered light from these particles have sufficient space to form their own scattering patterns undisturbed by other particles,

D) all particles have the same optical properties, and

E) the particles that scatter the light are spherical and isotropic.

Some of these conditions are fundamental to Mie theory, others are imposed by experimental conditions to assure that the scattering pattern produced is subject to analysis by Mie theory.

An image of a scattering pattern produced under the conditions described in Lesson 1 appears as concentric bright and dark rings around a central bright spot. The image is circularly symmetrical meaning that for a given scattering pattern the intensity I of light scattered at any angle θ relative to the optical axis is the same whether it is scattered θ degrees up, down, left, right, or whatever. Therefore, a scattering pattern can be described completely in two dimensions, (θ, I).

Figure 2-1 illustrates four ways of depicting a light scattering pattern. The first illustration at the left shows how the pattern projected onto a screen may appear to the eye. Superimposed upon this illustration is the second way a light scattering pattern can be described as an X-Y plot of intensity versus scattering angle.

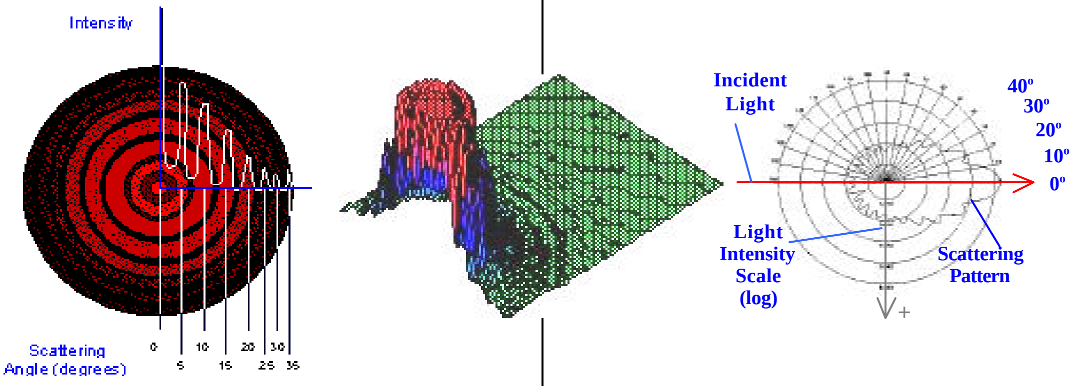


Figure 2-1. Four ways to represent a light scattering pattern. LEFT: the bull's eye pattern is what one sees when several degrees of the pattern are projected onto a screen. The overlaid plot is a graphical representation of intensity (y-axis) versus scattering angle (x-axis). CENTER: A false-color, 3-dimensional plot, the vertical projection representing light intensity. RIGHT: A plot of light intensity versus scattering angle in polar coordinates. NOTE: the four representations are not necessarily of the same light scattering pattern.

The center illustration is a three-dimensional plot of the scattering pattern where the vertical axis indicates light intensity and the position of the rings on the radius represents the scattering angle; zero angle is the center of the rings. The rightmost illustration is yet another way to illustrate a scattering pattern as a two-dimensional polar plot where light intensity is depicted by the extent of the radius and the scattering angle is represented by the angle of the radius vector.

Mie, Rayleigh, and Fraunhofer Light Scattering Theories

Gustav Mie developed a complete mathematical-physical theory of the scattering of electromagnetic radiation by isotropic spherical particles, in 1906. Mie theory predicts scattering intensity as a function of the angle at which light is scattered at the point of interaction with a spherical particle. Prior to the wide availability of fast computers, Mie theory was applied with boundary conditions (constraints) that placed limits on the range of particle size and index of refraction that a particular data reduction method could accommodate; this is illustrated in Figure 2-2. The simplest mathematical reductions and the clearest physical interpretation of the scattering formula are obtained in areas of the refractive index particle size plane that satisfy at least two of the following conditions:

$$\begin{array}{rcl} x << 1 & \text{or} & x >> 1 \\ n-1 << 1 & \text{or} & n-1 >> 1 \\ x(n-1) << 1 & \text{or} & x(n-1) >> 1 \end{array} \qquad \text{(Eq. 2-1)}$$

where n is the relative index of refraction of the particle to the medium (m_p/m_m), and x is related to particle size by

$$x = 2\pi(r/\lambda) \qquad \text{(Eq. 2-2)}$$

where λ is the wavelength of incident light. The expression x(n-1) represents the phase shift of the light ray in passing through the particle along a radius, r.

Today, with the availability of considerable computing power on one's desktop, constraints are not necessary and Mie theory can be applied as expressed by Mie with no additional constraints for the sake of simplifying the math.

The pattern of scattered light from spherical particles can be very sensitive to small changes in size or index of refraction. Refraction, as introduced in Lesson 1, is one of the light-matter interaction processes and the index of refraction is a parameter that characterizes the extent to which the path of light is bent at the interface when leaving a medium of one index of refraction and entering a medium of a different index of refraction.

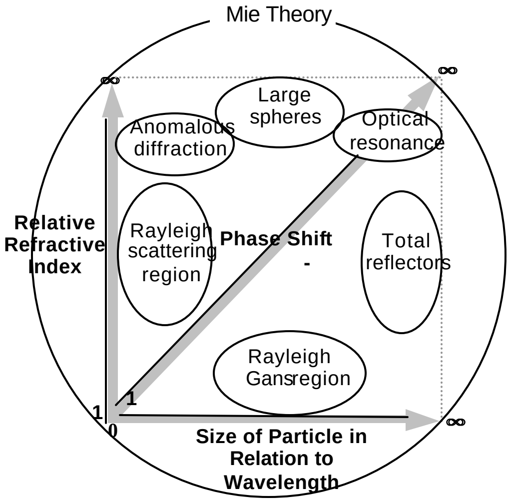


Figure 2-2. Constrained subdivisions of Mie theory for which simplified mathematical expressions were derived. These constraints were necessary to simplify hand calculations, but are no longer needed due to the availability of computers.

Fraunhofer theory predicts the diffraction of light at the edges of objects, specifically, opaque objects. Originally describing the diffraction patterns produced by light projected through an aperture, in particle sizing it relates to light bending around the edges of an opaque particle. If the particle is not opaque, then Fraunhofer scattering theory is incapable of completely describing the scattering phenomena. A Fraunhofer diffraction pattern consists of concentric bright and dark rings.

The limitations of using Fraunhofer theory are that it must be applied only to opaque or essentially opaque particles and the particles must be much larger than the wavelength of the incident light. It usually is applied when the light absorption by the particle is very high. The advantages are that the calculation is simple compared to that of Mie theory (therefore, fast) and no index of refraction is required. However, the same results can be obtained using Mie theory and therefore Mie theory is sometimes said to encompass the

Fraunhofer techniques for determining particle size.

Presenting to the Optical System the Particles to be Measured

The design of a light-scattering, particle-sizing instrument based on Mie theory must be guided by expressed conditions of Mie theory in order to produce a scattering pattern reducable by that theory. These conditions are listed, A through E, in the first paragraph of this lesson. Condition A becomes a specification of the optical design, specifically, the incident light source. Conditions B and C pertain to the sample suspension and, although can be manipulated to some extent by the design of an automated sample handler, the operator also must be involved in satisfying this condition. Conditiion D pertains to the sample material and it is the responsibility of the operator to introduce the proper sample materials to the measuring system. However, some variation on this condition is permissible and the error introduced may be insignificant. Because of the essentitally infinite variety of sample types, methods development is called upon to determine exactly how much a particular sample can deviate from ideal and still produce acceptable results. How one procedes under condition E is similar to how one deals with condition D.

Devices Used to Deliver Particles to the Measuring Zone of the Instrument

Laser light scattering instruments of concern here analyze samples in one of three methods of presentation: 1) solid particles suspended in a liquid medium, 2) widely separated solid particles that cascade in a stream either under the influence of gravity or carried in a gaseous stream, and 3) solid or liquid particles suspended in a gaseous medium (aerosols). Other types of instruments include those that size particles entrapped in a solid or gel, those that analyze bubbles forming in a medium, those that characterize dissolution of solids in a liquid, those that analyze flocculation of particles, or growth of crystals, and others.

The distribution of particles in various suspension media may differ; this can be a desirable or undesirable consequence. For example, adding dispersant to the liquid medium can prevent particles suspended in the medium from flocculating. Preventing particles from grouping together is more difficult when working with dry powders and aerosols. So, when a solid sample is cascaded or an aerosol is formed or particles are placed in a liquid, the influences to separate or to agglomerate are different and different distributions may be reported for the same sample.

From Micromeritics experience with the SediGraph, most users want to determine the size distribution of individual particles so efforts are made to keep the particles separated. But, even with the SediGraph, some experimenters are interested in measuring flocculated or agglomerated assemblages and, so, do not want to apply too much ultrasonic dispersion energy to the suspension because it will break up the clusters.

When working with laser particle sizing equipment, the user has a choice of methods for presenting the sample to the measurement zone. Why particle size is being measured will influence how best to present the sample to the analyzer. For example, if one is measuring particle size as a parameter in understanding how a solid-liquid suspension of these particles behaves during transport, then it seems reasonable that the samples should be evaluated while suspended in the same liquid. Simply because dry powder sample handlers eliminate the need to prepare dispersing liquids and may save operator time may not be sufficient reasons for their use.

Regardless of the sample presentation method, the sample material must be delivered from a source external to the instrument to the sampling zone of the instrument. The sample must be contained so it does not contaminate the sensitive optical elements and the sample must be presented in a manner that represents the bulk quantity that was introduced for measurement. How this is achieved for liquid suspensions, cascaded dry samples and gas suspensions is discussed below.

Liquid sample handlers: A liquid sample handling system must present to the incident light beam a homogeneously suspended, bubble-free liquid-solid suspension of the proper concentration. This, in the majority of applications, is accomplished by maintaining flow from the reservoir through a sample cell while data are being collected or by maintaining a stirring action within a sample cell through which is no flow.

A flow system would include at minimum: 1) an exterior reservoir with an opening to receive a pre-suspended sample, or in which to create the dispersed suspension, 2) a pump, 3) conduit to carry the suspension to the sample cell, 4) a sample cell, 5) conduit to carry the suspension back to the reservoir and 6) a means by which to drain and rinse the system.

The liquid sample handler system may have additional, convenient, but non-essential features. Examples are liquid level sensing, and automatic dilution, rinsing, and refilling.

Each of the essential subsystems, 1 through 6, may have their own special features to further enhance the utility or overall operation of the system. Each subsystem and added feature must be designed to maintain the homogeneity of the suspension (no particle trapping or segregation by size), prevent or eliminate bubbles (maintain a mixing action without pulling bubbles in from the surface), and avoid mechanically altering the particles (crushing or grinding by the pump or valves).

The flow velocity of the liquid through the cell is an important design consideration because the energy of the flow keeps large particles circulating. Flow velocity can be achieved at low flow rates by reducing the size of the liquid-carrying conduits. However, for good sampling statistics, flow rate also must be considered. The volumetric flow rate through the cell and the total cell volume determine how many times the contents of the cell 'turn over' or are swept out . The relation between sample cell sweeping and sampling statistics is illustrated by Table 2-1. For example, a flow of 100 cc/sec (6 liters per minute) through a 100-cc cell means that the contents of the cell are swept out every second. The total time during which measurements are taken multiplied by the flow rate gives the total volume passed through the cell and the maximum volume of the liquid-solid suspension that was subjected to measurement. Dividing the total system volume by this number gives the fraction of the total system volume that underwent analysis.

These are important considerations when evaluating measurement statistics; here s why. First, the volume of a sphere is

$$V = (4/3)\pi r^3 \qquad \text{(Eq. 2-3)}$$

If the size distribution of a sample of spherical particles ranges approximately from 1 to 10 µm, the range of volume is 5.24 x 10^{-1} to 5.24 x 10^{+2} µm^3, or three orders of magnitude in range. Since mass is directly proportional to volume, mass scales the same as volume. To determine how many smaller particles are required to be of equal volume or mass to one larger particle, the following relation is used:

$$n_S(4/3)\pi r_S^3 = n_L(4/3)\pi r_L^3 \qquad \text{(Eq. 2-4)}$$

where n_S is the number of smaller particles, n_L the number of larger particles, and r_S and r_L the radii of the smaller and larger particles, respectively. This leads to the general expression for number ratio,

$$n_S/n_L = (r_L/r_S)^3 \qquad \text{(Eq. 2-5)}$$

and for the specific case of r_S = 0.5 µm and r_L = 5 µm,

$$n_S/n_L = (5/0.5)^3 = 10^3.$$

Therefore, a single 10 µm diameter particle is equal in mass and volume to 1000 particles of 1 µm diameter.

Figure 2.3 in which the number and volume distributions of the same sample are shown illustrates these points. As can be seen for this distribution, about 3% of the total sample volume is 1 µm or larger, but this represents nearly 40% of the total number of particles. Likewise, about 2% of volume (thus, mass) is 10 µm and larger, but the number of particles

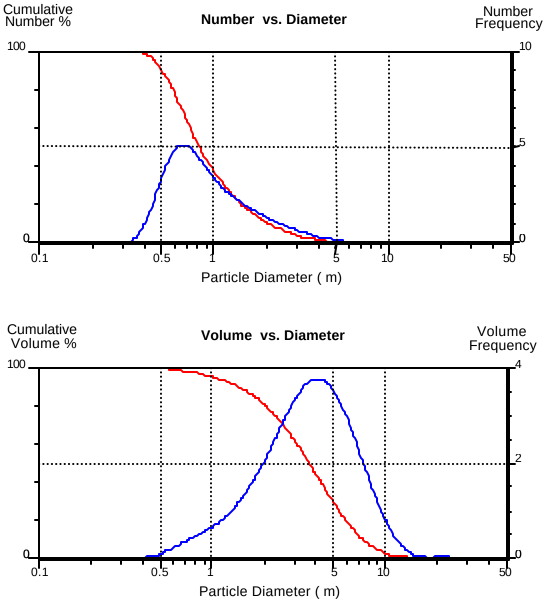


Figure 2-3. Top: Number distribution. Bottom: Volume distribution of same sample.

is far less than 1% (actually, 0.012% from the experimental data).

For the particle size analysis illustrated (garnet reference material), the mass concentration of particles in the suspension is 6.36×10^{-5} g/ml. The density of garnet is 3.87 grams per ml, therefore the volume of garnet in each ml of suspension is

(Eq. 2.6)

$$(6.36 \times 10^{-5}\ \text{g})/(3.87\ \text{g/ml}) =$$
$$1.64 \times 10^{-5}\ \text{ml of garnet per ml of suspension}$$

Since only about 2% of sample volume is composed of particles ≥ 10 µm, this means that the total volume of particles of size 10 µm and larger is 3.28×10^{-7} ml or 1.27×10^{-6} gram of these sizes of garnet particles in each ml of suspension.

Likewise, there is about 3% of sample volume contained in particles ≤ 1 µm diameter, the total volume of these particles is 4.92×10^{-7} ml or 1.9×10^{-6} grams per ml of suspension.

Assume that all large particles in this sample are 10 µm in diameter (this gives the maximum number of particles). Each particle, then, has a volume of

$$V_{d10} = (4/3)\pi(5\mu\text{m})^3 = (4/3)\pi(5 \times 10^{-4}\ \text{cm})^3$$
$$= 5.24 \times 10^{-10}\ \text{cm}^3$$

and mass of

$$m_{d10} = (5.24 \times 10^{-10}\ \text{cm}^3)(3.87\ \text{g/cm}^3) =$$
$$2.03 \times 10^{-9}\ \text{g per 10}\ \mu\text{m diameter particle.}$$

Since the total mass of ≥ 10 µm particles per ml of suspension is 1.27×10^{-6} g, the maximum number of large particles (assuming all are 10 µm particles) per ml of suspension is

$$(1.27 \times 10^{-6}\ \text{g})/(2.03 \times 10^{-9}\ \text{g/particle}) =$$
$$= 626\ \text{particles per ml of suspension}$$

However, the distribution shown in Figure 2-3 indicate the presence of large particles of at least 20 µm diameter. These each have volume of 4.189×10^{-9} cm^3 and mass of 1.62×10^{-8} g. This means that only 78 such particles can be present in the 2% sample mass per ml of suspension. If 30 µm particles are present, then only 23 of these particles account for 2% mass per ml of suspension, and only a single particle of 40 µm diameter would account for the total 2% mass per ml of suspension.

At the other extreme, there is 3% of total mass in particles ≤ 1 µm diameter in each ml of suspension, or 0.081×10^{-5} grams. Since these particles at maximum contain 2.03×10^{-12} grams of mass each, the number must be at least

$$(1.9 \times 10^{-6}\ \text{g})/(2.03 \times 10^{-12}\ \text{g/particle}) =$$
$$= 9.36 \times 10^{5}\ \text{particles per ml of suspension}$$

As can be appreciated by this lengthy exercise, the broader the distribution, the more disparity is produced between then number of large and small particles that are subjected to measurement. Very poor sampling statistics are acquired for the larger sizes in the presence of much smaller sizes unless the sampling time is long and the flow rate is high. Those two variables are the only way to increase the number of large particles that get measured and averaged. Tables 2-1 and 2-2 further illustrate this point.

Maintaining a homogeneous dispersion in a liquid sample handling system: A primary problem in maintaining continuous circulation of a homogeneously suspended sample is that

Fraction of Sample Material Measured Under Different Conditions of Flow Rate and Measurement Time
Volume of Measurement Zone: 10cc

Flow Rate (cc/sec)	Measure-ment Time (sec)	Percent of Sample Actually Subjected to Measurement	
		Sys. Vol.= 100 ml	Sys. Vol.= 1000 ml
1	0.1	0.1 %	0.01 %
1	1.0	1.0 %	0.10 %
1	10.	10. %	1.00 %
1	100.	100. %	10.00 %
10	0.1	1.0 %	0.10 %
10	1.0	10. %	1.00 %
10	10.	100. %	10.00 %
10	100.	1000. %	100.00 %
100	0.1	10. %	1.00 %
100	1.0	100. %	10.00 %
100	10.	1000. %	100.00 %

Table 2-1. The fraction of the introduced sample quantity that actually passes through the measurement zone.

Particle Mass as a Function of Size (µm) and Density (g/cm^3)

Size	Volume	ρ = 2	ρ = 4	ρ = 6	ρ = 8
0.01	5.24E-18	1.05E-17	2.09E-17	3.14E-17	4.19E-17
0.05	6.55E-16	1.31E-15	2.62E-15	3.93E-15	5.24E-15
0.1	5.24E-15	1.05E-14	2.09E-14	3.14E-14	4.19E-14
0.5	6.55E-13	1.31E-12	2.62E-12	3.93E-12	5.24E-12
1	5.24E-12	1.05E-11	2.09E-11	3.14E-11	4.19E-11
5	6.55E-10	1.31E-09	2.62E-09	3.93E-09	5.24E-09
10	5.24E-09	1.05E-08	2.09E-08	3.14E-08	4.19E-08
50	6.55E-07	1.31E-06	2.62E-06	3.93E-06	5.24E-06
100	5.24E-06	1.05E-05	2.09E-05	3.14E-05	4.19E-05
500	6.55E-04	1.31E-03	2.62E-03	3.93E-03	5.24E-03
1000	5.24E-03	1.05E-02	2.09E-02	3.14E-02	4.19E-02
5000	6.55E-01	1.31	2.62	3.93	5.24

Table 2-2. The mass of a single particle as a function of size and density.

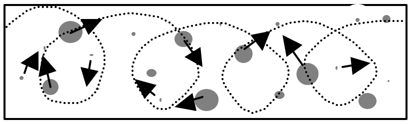
the particles tend to separate by size during circulation resulting in the smaller sizes being over-represented because they are transported more efficiently. Gravitational sedimentation is one influence on separation; another is the result of hydrodynamic effects.

To visualize what is going on during circulation, here is a thought experiment. Imagine a microscopic view through a small window in the side of the reservoir or in the tubing leading to and from the reservoir. If the liquid flow is smooth and laminar, the liquid sweeps particles of a wide range of sizes from one end of the liquid system to the other. But, particles not only move laterally following liquid flow, but also are settling. The larger particles settle faster than the smaller particles (remember Stokes law?) and the larger particles eventually settle to the lower extremes of the conduits and tumble along the lower walls. This causes resistance to motion and they move slightly slower than the liquid flow. Little by little, the large particles fall behind the smaller particles that seldom contact the walls and continue to flow along with the liquid. The smaller particles are being delivered to the sample cell more efficiently than are the larger particles. If there is a vertical section of tubing in the flow path through which the liquid flows upward, large particles move more slowly upward in this situation than do small particles, again contributing to separation.

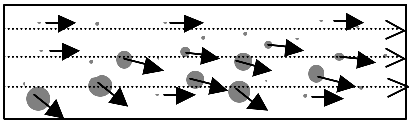
To combat the above-described effect, energy needs to be imparted to the particles to keep them uniformly integrated regardless of size. One way to accomplish this is by the introduction of fluid turbulence. Turbulent forces can overpower the sedimentation forces and cause the large particles to remain mixed with the smaller particles.

Laminar Flow versus Turbulent Flow. The long lines represents the direction of fluid flow and the short arrows represent the net direction of motion of the particles carried by the fluid. The effect in laminar flow is that the particles settle downward at rates according to size. In turbulent flow, the particles move in all directions and constantly are being mixed.

Too much turbulence, however, can hold bubbles in the liquid and, in extreme cases, can pull air from the surface into the liquid creating bubbles*. The suspension must be bubble free because bubbles are light



Turbulent Flow



Laminar Flow

scatterers and cannot be distinguished by the system from solid particles. Therefore, the circulation system must be carefully designed to control turbulence in order to achieve the dual and opposing objectives of maintaining a well-mixed liquid-solid suspension while preventing bubble induction and releasing those bubbles that do form in the liquid.

Dry powder feeders: Dry feeders may cascade the sample through the measurement zone under the influence of gravity (free-fall feeders), or drive the particles through the measurement zone by some force, typically a gas stream. Since the particles are driven by the gas and are not suspended in the gas they do not fall into the category of aerosol samplers. Fine powders (<10 µm) are difficult to disperse and being carried by a turbulent gas stream provides a means of dispersing or maintaining dispersion. In some embodiments of a gas driven system, the particles are ejected by means of gas (air) through a nozzle or carried by tubing through a sample cell. Some manufacturers configure the dry sample handler to remain on the analyzer with the liquid sample handler and require only that the appropriate sample cell with sample conduit be placed in the measurement zone.

A problem that requires attention is the accumulation of static electrical charge, which may lead to clogging of the system and separation of sample by size. According to how individual particles are charged, electrostatic effects may lead to agglomeration.

Gas jet-driven dry powder feeders use the shearing force of the air stream for dispersion. This is best accommodated by a variable gas flow rate in order to have control of the amount of energy put into the system.

Free-fall dry powder feeders are particularly important when the sample is fragile because it applies minimum forces to the sample. The only additional energy fed into the system may be vibration to keep the powder moving and to dislodge particles that tend to stick to parts along the transport route. However, these types of samplers are not as useful with fine powders (<10 µm) or larger low density materials that have a strong tendency to adhere. Another difficulty is assuring that the cascade is of low enough concentration to assure wide separation between individual particles, therefore guarding against multiple scattering.

With either type of dry feeders, abrasive samples can present a wear problem.

Aerosol samplers: An aerosol is defined as a liquid or solid particle suspended in a gaseous medium. Dry aerosols usually are not what are analyzed in a laboratory laser particle size analyzer; this type of measurement is usually relegated to environmental monitors. However, it is possible to accommodate dry aerosols in a laser particle size analyzer.

Most particle size distribution measurements of aerosols are performed on liquid droplets or spray. Most often, the device that produces the aerosol is not an integral part of the instrument system as would be a liquid or dry powder sample handler. The aerosol usually is produced by some device and what actually is under test is the capability of the device to produce aerosols of the desired size distribution. Examples are the array of familiar spray cans used in households, the less familiar devices such as automobile fuel injector nozzles or industrial spray nozzles, and pharmaceutical delivery devices, primarily respiratory inhalers. An aerosol sampler, then, is usually a means of accommodating some other device that produces the aerosol and must have the means for containing the aerosol, delivering it to the measurement zone, and disposing of the aerosol. There also may be a need to measure the size distribution at critical times in the development of the aerosol plume, for example at the initiation, during continuous production, or during cutoff. This can be appreciated by anyone who has used a can of spray paint that produces large droplets when the spray is first initiated, an undesirable effect for a spray paint applications.

* A different bubble-producing phenomenon is that of cavitation by which bubbles of the vapor phase of the liquid form due to a reduction in local pressure. This can be caused by a rapidly spinning stirrer or pump impellor.

"The Mie scattering calculations are so complex that large computers are required, particularly if the complex refractive index must be used as for metallic scattering particles. For nonspherical particles even more complex approaches are required, and special cases such as ellipsoids and rod-shaped particles have been solved by workers such as R. Gans; even more complex are mixtures of particles of different sizes. These solutions are important in the investigation of colloids, aerosols, smokes, smogs, and so on, where the particle sizes and shapes may be deduced from the light scattering behavior. "

From "**Understanding Light Scatter Artifacts In Spectroscopy Part 2: Types Of Light Scatter ", Dr. Jeffrey L. Taylor,** http://www.geocities.com/CapeCanaveral/Hangar/6386/so03007.html

WHAT DO STOKES LAW AND MIE THEORY HAVE IN COMMON?

STOKES LAW (assumes spherical particles): If the particles are not spherical, how will this affect particle settling? Particles having a density greater than that of the suspending medium will settle according to the combined influence of gravitational forces, buoyant forces, and resistive forces. The problem with non-spherical particles is that we don't necessarily know the theory that predicts exactly at what velocity the particles will settle. Since Stokes law provides an exact solution only for spherical particles, it provides only an approximation for non-spherical particles. However, since particles of a given shape, size, and relative density will settle at the same velocity every time the experiment is conducted, we can use Stokes law combined with the measured settling velocity to obtain the particle size of an equivalent sphere.

MIE THEORY (assumes spherical particles): If the particles are not spherical, how will this affect light scattering? Particles having an index of refraction different from that of the medium will scatter light according to the physical laws that govern interactions between light and matter. The problem with non-spherical particles is that we don't necessarily know the theory that predicts exactly in what direction and at what intensity the light will be scattered. Since Mie theory provides an exact solution only for spherical particles, it provides only an approximation for non-spherical particles. However, since particles of a given shape, size, and index of refraction will scatter light in the same manner each time the experiment is conducted, we can use Mie theory combined with the measured scattering pattern to obtain the particle size of an equivalent sphere.

The equivalent sphere assumption introduces error, but it introduces the same error each time we measure the same type of sample. Therefore, it has no affect on repeatability, reproducibility, and resolution. Analyzing non-spherical particles leads to a similar problem in essentially all particle-sizing techniques. So, in the same way we solve for 'equivalent spherical diameter' when working with Stokes law and the SediGraph, we solve for 'equivalent spherical diameter' when using Mie theory in laser light scattering.

SUMMARY OF LESSON 2

Light is scattered in all directions by particles, but more light is scattered at some angles that at others.

Mie theory precisely describes scattering and therefore is considered an 'exact' solution. Mie theory encompasses Rayleigh and Fraunhofer theory.

Mie theory provides an exact solution only if certain conditions or restraints are upheld: plane waves, isotropic particles, and spherical particles.

Rayleigh scattering describes scattering by particles much smaller than the wavelength of incident light.

Fraunhofer diffraction does not account for light transmitted or refracted by the particle.

A laser diffraction particle sizing instrument must be composed of, at minimum, a source of monochromatic coherent light, a particle dispersing device, an optical system that produces an image of the scattering pattern, a detector to measure characteristics of the scattering pattern, a means of reducing raw measurement data to particle size, and means to report these reduced data.

The sample handling device must be capable of assuring that particles are separated sufficiently to form a scattering pattern reducible by Mie theory (no multiple scattering).

A liquid or dry sample handling device must be capable of assuring size homogeneity of the sample presented to the measuring zone.

A laser diffraction particle size analyzer cannot distinguish scattering by bubbles, or by a cluster of particles, from scattering by a single particle.

Sampling statistics for the large end of the distribution range is negatively affected by the width of the spread in size distribution, and can be improved by lengthening the measurement time and/or increasing flow rate.

Liquid sample handlers provide considerable control over the state of the sample when presented to the measuring zone. The primary design challenges are to prevent or eliminate bubbles and to prevent segregation of particles by size.

Dry powder feeders may be gravitationally fed (free-fall feeders) or may transport the sample by gas flow. Primary design problems are to achieve and maintain dispersion, to prevent loss of sample by adhesion to internal parts, and to prevent caking and clogging. Concentration problems may also arise with free-fall (cascade) feeders.

Aerosol samplers typically pertain to liquid aerosols and the samplers usually do not produce the aerosol dispersion, but only accommodate a non-integral aerosol-producing device. The design problems are to contain and remove the aerosol and, if necessary, to synchronize measurement with certain phases of aerosol production.

Lesson 3: Measurement of the Scattering Pattern

Formation of a Measurable Scattering Pattern

The first sections of Lesson 2 described the scattering pattern. That lesson was primarily concerned with upholding conditions pertaining to the presentation of the sample material and the role of the sample handler in assuring that the conditions were upheld. Lesson 2, then, addressed the methods required to assure a scattering pattern representative of the sample introduced and resolvable by Mie theory. Attention now is returned to the scattering pattern, but in regard to interpreting from it particle size.

Light scattered by a particle is projected at all angle, that is, in all directions. It therefore produces a spherical front of scattered rays, the particle at the center. However, the intensity of light varies with the angle of scatter relative to the illuminating (incident) beam, the underlying means described by Mie theory.

Both Mie scattering and Fraunhofer diffraction from a single particle produce a light scattering pattern that is circularly symmetrical in the x-y plane. Multiple particles of the same size produce multiple scattering patterns that are shifted in space proportional to the separation of the individual particles. Measurement of the definitive characteristics of these multiple patterns is facilitated by the use of a lens that causes all rays from the scattering pattern that are directed at the same angle (and, therefore, are parallel) to converge at specific locations on the focal plane (see Figure 3-1). This is the physical equivalent of the mathematical operation of performing a Fourier transformation on the scattering (or diffraction) function g(x,y) and when a lens is used in this way it is called a Fourier lens. When the lens is placed between the sample and the detector the arrangement is referred to simply as Fourier optics; if the sample is placed between the lens and the detector, the configuration is called reverse Fourier optics.

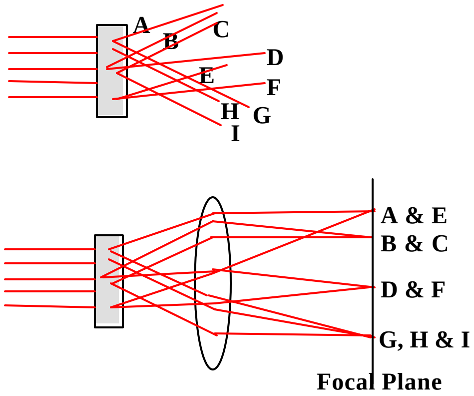


Figure 3-1. Incident light impinges upon an assemblage of particles in a sample cell. The top illustration shows a few example scattered light rays form various particles, although light rays are scattered at all angles. The bottom illustration shows the same scattered light rays being captured by a lens. Note that all parallel rays are directed to the same point in the image plane. Each ray adds intensity and the summation of all rays defines the scattering pattern.

From Figure 3-1, another characteristic of the optical system can be ascertained. Assume a single particle moving through the illuminated zone of the cell. It scatters light always in the same pattern, therefore, from position to position, the rays of the scattering pattern are parallel to the associated rays in the previous position of the particle. Therefore, the scattering pattern projected on the image plane is stationary.

The focal length of the lens and its location relative to the source of scattering determines the size of the scattering pattern (image) and therefore the range of the scattering pattern that falls upon the detector. This is the optical geometry of the instrument and the subject is sufficiently important to warrant further discussion to be certain that the design requirements are appreciated.

Optics in everyday life similar to those of a light scattering system: Relating the optical arrangement of the instrument system to something common in everyday life makes it more easily understood. A good example for comparison is a slide projector. It contains a source of incident light, something that scatters light (the slide film), and a lens that captures the scattered light and projects and focuses it onto an image plane (the screen). As the projector is positioned further away from the screen, the size of the picture becomes larger. This is because the location of the lens relative to the image plane has changed. But, the image is now out of focus, so the position of the lens relative to the slide (the source of scatter) is adjusted. The focal length of the lens and the position of the slide relative to the source has not changed.

However, when using a slide projector (or camera) with a zoom lens, changing the size of the projected image is accomplished by manipulating the focal length of the lens. This is accomplished without the need to move the relative positions of the image plane, the lens, or the source of scattered light.

Now, assume that a slide photograph of an object is being viewed and the exact size of the object needs to be communicated. One common method is to place a scale beside the object when photographed, thus providing a size reference. The projected image can be made actual size by adjusting the projector so that the image of the scale stick is exactly the size of the real scale. Only in a very specific configuration of projector lens and projection screen is the image of the scale in focus and equal in length to the real scale. Then, the actual subject of the photograph is life size and can be measured directly.

Designing a scientific instrument that depends on accurately measuring a scattering pattern presents the challenge of interpreting actual dimensions from dimensions in an image, except rather than measuring a linear size, the instrument must measure an angular size. In other words, rather than calibrating to the number of centimeters represented by the image, the instrument must be calibrated to the number of degrees of viewing angle that is represented by the image.

Understanding angular dimensions: A photograph generally depicts a view of about 35 degrees, 17.5 degrees to the left and right of straight ahead . If a scale of 0 to 17.5 is placed at the center of the photograph, then one can determine at what viewing angle any object in the photograph was relative to the camera.

Within a laser light scattering particle sizing instrument, the scattering pattern must be projected very exactly upon the image plane so that the relationship between the positions within the image plane and the associated scattering angles are known. These distances are usually fixed in a detector design, but, in some instruments, may be adjustable for calibration. Also, some instruments allow the lens to be changed for one of another focal length to allow the system to measure in more than one angular range, but there is an inverse relationship between angular range and angular resolution. This is related to the configuration of the light detectors and is explained subsequently.

The physical size of the lens (diameter) and its position relative to the sample cell are important in regard to the range of scattering angles that the lens captures and, therefore, that are included in the projected pattern. As can be imagined by looking at the lower illustration in Figure 3-1, if the lens were to be moved further away from the sample cell, then rays A and I would not be captured by the lens and these rays would not contribute to the image of the pattern.

Measuring the Scattering Pattern

The objective of the optical system is to produce a sharp image of the scattering pattern on an array of photodetectors. The detector array measures the light intensity at positions of the detector element and associates each measurement to a range of scattering angles that is calculated based on the geometry of the optical system and the physical dimensions of the active area of the photodetector. The set of intensity versus angle data is passed to the data reduction software and represents the scattering pattern. The accuracy of the angle measurement is critical to particle sizing accuracy. The number of angles at which data is taken and the range of angles encompassed by each measurement also affects accuracy, but is more important to resolution. For these reasons, manufacturers of static light scattering particle size analyzers exert great effort in the design of detectors.

Why Light Scattering Patterns are Difficult to Characterize Uniquely

Figure 3-2 shows plots from Mie theory of light scattering patterns produced by particles of 1, 10, 100, and 1000 µm. The peaks in a plot (the maxima) represent the center of a bright ring in the scattering pattern and the troughs (minima) represent the dark rings. Scattering patterns from particles of about 1 mm and smaller reveal a ’disk’ of light that is almost uniformly illuminated over the first several degrees, then the brightness diminishes rapidly. In actual experimental systems, however, there also is a very high intensity peak at the center of the pattern (zero degrees) produced by the unscattered portion of the laser beam. Of course, this peak is not considered in theory which considers all light to have been scattered.

To differentiate between, for example, scattering patterns produced by a 1 µm and by a 1.1 µm particle requires accurate measurements of the angles and intensities in the area of the knee where light intensity begins its decrease.

As particle size increases, the experimental scattering pattern develops a set of bright and dark rings around the central bright spot and the rings become more numerous, more

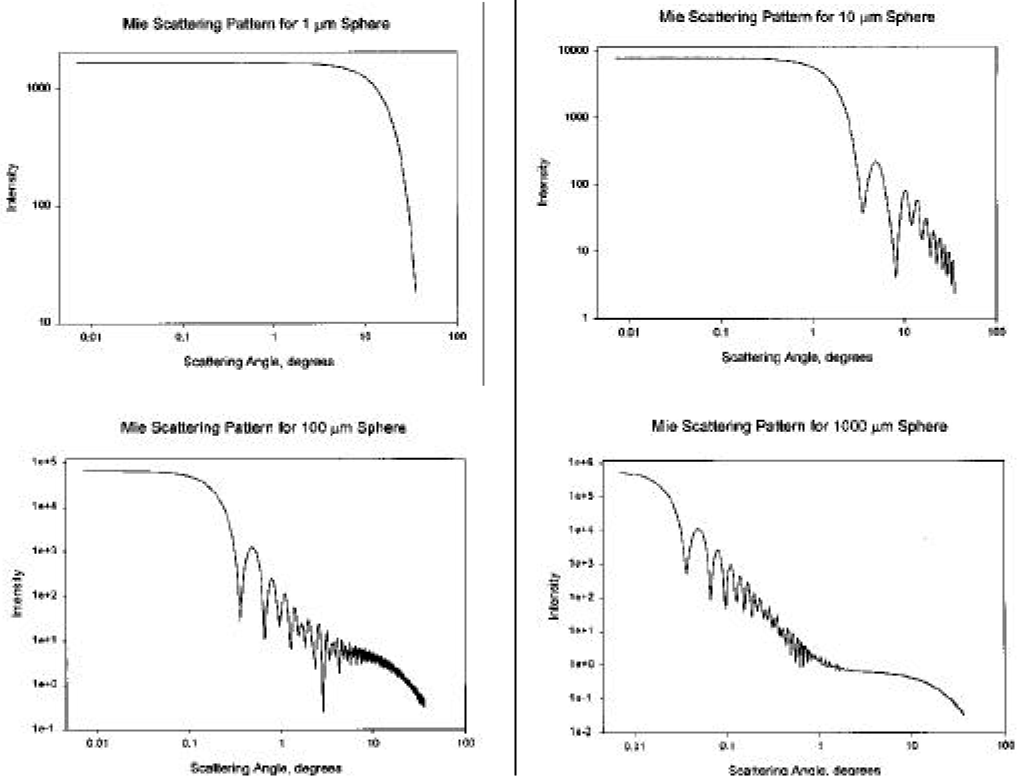


Figure 3-2. Calculated Mie scattering patterns for (form upper left to lower right) 1.0, 10, 100, and 1000 mm spherical particles.

closely spaced, and begin at smaller and smaller angles.

The above applies to narrow, monomodal distributions. When several monosized scattering patterns are summed, as is the case for broad distributions or multimodal distributions, the plot of the scattering pattern tends to smooth out and have fewer or no sharp peaks.

There can exist subtle differences between scattering patterns produced by closely sized, monomodal samples. Being able to differentiate one from the other can be quite difficult and resolution depends on this capability. Many intensity measurements at various points over the angular range of the scattering pattern must be measured to provide certainty that a pattern has been uniquely characterized and can be differentiated from all others. Ultimately, this determines whether or not the instrument can differentiate between two similar size distributions, or reliably detect a small difference between two sample materials.

Light Detectors

Detectors that react to light are called photodetectors. When a light ray (a stream of photons) strikes the surface of one of these devices (Figure 3-3), the energy of each photon liberates an electron. This is known as the photoelectric effect and is the basis of electrical photodetection. Since flowing electrons produce an electrical current, the more photons (the more intense the light), the more current. Therefore, the electrical signal is proportional to the light intensity; when the photons cease, the signal ceases.

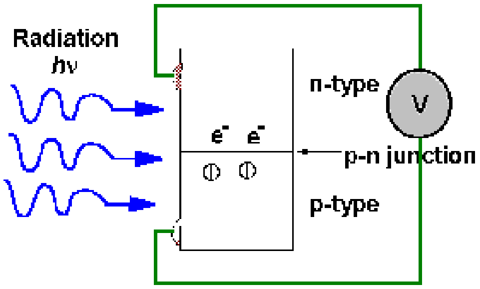


Figure 3-3. A semiconductor photodiode.

<u>Photodiodes:</u> One of the most efficient photodetectors is made of a semiconductor junction and is so configured that it is referred to as a photodiode. When a photon strikes this semiconductor device, it liberates an electron from the valence band to the conduction band producing an electron-hole pair and thereby initiating a signal proportional to the light intensity.

A photodiode array is a linear or area array of discrete photodiodes on an integrated circuit chip. A linear array refers to only one row (or one column) of detector elements; an area array refers to, at minimum, 2 columns by 2 rows of detector elements, but applies also to any arrangement of photodetectors of any shape that are distributed over an area.

The array is placed at the focal plane of the instrument and collects multiple signals proportional to the light intensity at the location of the individual detector elements. Each detector element operates by the same principle as a single photodetector device described above. One shortcoming is that as the photodiode array becomes more dense (number of detectors per unit area), area of each active element necessarily becomes smaller. The smaller the area, the less current is produced by a given light intensity. At some point, the size of the element is insufficient to produce a suitable signal-to-noise ratio.

<u>CCD s:</u> A charge-coupled device (CCD) is a photosensitive element associated with an electron accumulator that stores electrons (charge) as light energy liberates them from the light sensitive material. A CCD array is an integrated-circuit chip that contains multiple CCD elements. Unlike the photodiode that produces a current flow proportional to the instantaneous light intensity, the CCD accumulates electrons. This can be compared to photographic film that captures photons; with film, each photon causes a chemical reaction and the

results of the reaction accumulate in areas of the film where the photons strike.

With the CCD, when desired, the quantity of charge is read essentially by counting the number of electrons that were accumulated over the exposure time. This is why the CCD is considered to 'digitize' the light energy measurement, that is, convert it to a number. The CCD, also, is an integrating device since it integrates or adds up the light energy over the time interval between readings. Photographic film, too, is an integrating device accumulating more and more product of chemical reaction over the time of exposure. But, unlike the CCD, photographic film is an analog medium and the density of the reaction products is proportional to the quantity of photons that reacted with a particular spot.

CCDs are used in applications similar to other array detectors such as photodiode arrays, although the CCD typically is more suitable for measurement of low light intensities, particularly if the size of the photosensitive area is small. Being able to accumulate signal over time, the CCD can provide a suitable signal-to-noise ratio even when individual elements in the array are extremely small.

Both the photodiode and CCD are subject to threshold and saturation limitations. Neither device will produce a measurable signal or accumulate a significant quantity of charge if the photosensitive area intercepts too few photons. The photodiode can achieve only a certain signal level after which a higher intensity of light produces no additional signal and the CCD suffers a similar saturation effect.

Adapting Detector Technology to the Measurement of Scattering Patterns

Each manufacturer of LPSA products seems to have a different approach to capturing the scattering pattern and accommodating the range of light intensities. A few common designs of photodetectors used in LPSA applications are discussed below.

Ring detectors: Light scattered in the forward direction, having passed through the lens is focused onto a set of annular rings that comprise this type detector. The concentric photodetector rings increase in width from the center outward. Insulating gaps separates each ring; a hole may be placed at the center behind which is a single photodiode that measures the central bright spot in the pattern, the most intense area of illumination.

Assuming that the scattering pattern is exactly aligned with the set of rings, each ring, being of finite width, intercepts a specific and unique range of scattering angles. The signal produced by a ring is related to the average intensity over the angular range of the ring. The set of rings is scanned electronically to acquire the light measurement signals from each element.

The total number of rings found on ring detectors used in particle sizing equipment range from 18 (Horiba LA-700), to 31 (Sympatec HELOS), to 75 (Horiba LA-920).

Figure 3-4 shows the seven innermost rings of a ring detector. Below the illustration of the detector is a plot of a scattering pattern aligned with the cross-section of the ring detector to better illustrate how a scattering pattern may be projected onto a ring detector. The plot is centered on zero degrees (vertical line), that is, the optical axis and the optical axis is centered on the detector. The relationship between the bright rings and the rings of the ring detector can be seen. The importance of alignment also is evident.

As illustrated in Figure 3-2, the scattering pattern for a narrow distribution of particle sizes is composed of many peaks or bright rings. However the width and radius of each bright ring will vary if particle size is varied. It is therefore unlikely that there will be a bright ring associated with each detector ring. It is possible that a bright ring could be centered on the insulation between two rings, or that two bright peaks occupy a single ring.

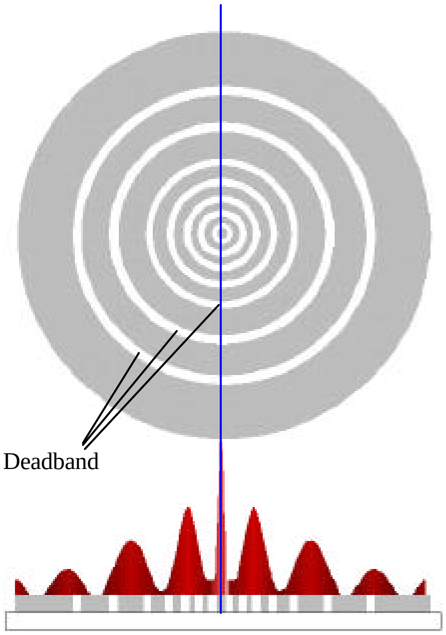


Figure 3-4. The upper illustration shows the seven innermost rings of a ring detector. Below is a plot is of a scattering pattern projected onto the ring detector, with the active elements of the ring detector shown in cross-section relative to the scattering pattern.

Since the intensity of the rings of the scattering pattern diminishes from the center outward, the light collection area of the central rings can be small compared to the outer rings. This is fortuitous because the density of detector rings can be increased near the center where rings of the scattering pattern also begin to concentrate as the particle size increases.

Each ring of the detector measures the total light intensity impinging upon the ring at any moment. Each ring spans a range of angles; therefore each ring averages the light over the range of scattering angles associated with the ring.

Ring segments: A photodiode array may be arranged in ring segments rather than continuous rings. This makes better use of the limited space, but captures less light per segment and therefore less signal amplitude. By shifting the segments (Figure 3-5), there is no 'dead area' of scattering angles such as exists with ring detectors that necessarily have insulating separations between the rings.

In the case of ring detectors, one ring may capture scattering angles A through C, but there must be some area of insulation between this and the next ring. Scattering angles C through D will fall on the deadband of insulation. The next ring will capture angles D through E, followed by a band of insulation, and so on.

When using shifted ring segments, the outer ring segment captures angles A through C, another segment captures angles B through E, another captures angles D through G, and so on, leaving no band of angles unrepresented. The fact that angle ranges overlap can be used to interpolate intensity within the overlap.

Photodiode arrays: Arrays may be linear or may occupy an area contained on a single integrated chip. Additional individual photodiodes may be placed external to the integrated circuit and at critical positions not covered by the array. Ring and ring segment detectors may be thought of as arrays and, strictly, they are. But, 'array' in the sense used here refers to an assemblige of small, usually rectangular or circular photodetectors strategically placed in the image plane in order to sample as many scattering angle bands as the designer thinks necessary to characterize the scattering pattern. With only a hundred or so detectors, however, the optimum location of

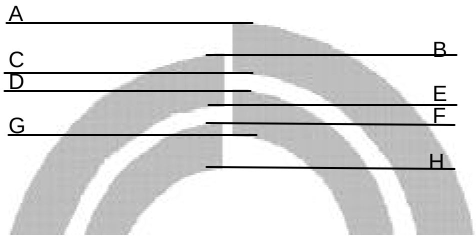


Figure 3-5. How a segmented ring detector can be arranged to avoid data loss in deadbands between active detector elements. For simplicity, only four rings in the upper half are shown. The letters indicate the angle ranges covered by the segments.

these detectors for any conceivable light scattering pattern is a trade-off. Because of the almost infinite number of light scattering patterns, the optimum position for one pattern is unlikely to be the optimum configuration for another pattern.

Few, if any, manufacturers use a detector array composed of a single geometry (rectangles, circles, rings, righ segments, etc.). A more common design of a photodetector contains a combination of variously shaped active elements.

<u>CCD arrays:</u> CCD arrays are discussed separately from photodiode arrays because they are members of a special class of detectors particularly in the manner in which they are employed. There are many types of CCD arrays available on the market ranging from consumer applications to scientific applications. The most familiar, perhaps, is the consumer type of CCD used in video cameras and digital still cameras and the applications of these devices are so widespread that they even can be found in children’s toys.

Less familiar to the average person are those CCD arrays designed for scientific use. These ’scientific grade’ devices provide the high resolution and sensitivity needed for scientific measurements. They are designed to limit, control, or eliminate certain characteristics that are permissible in consumer applications.

A primary problem that was addressed for scientific use was anti-bloom. Bloom refers to spillover of charge from one detector element in the CCD array to its neighboring elements. Although this tends to soften photographs and provide acceptable esthetic characteristics, it is intolerable in a measuring device.

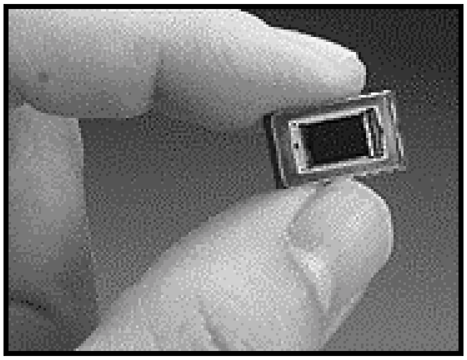


Figure 3-6. Over one million CCD-type photodetector elements are integrated into a single semiconductor chip measuring only a few centimeters square.

Pixel density in a scientific CCD typically is much greater than those used for consumer products, a matrix having greater than 1000 rows by 1000 columns of detectors being commonly found. Figure 3-6 shows a high-density CCD array. The elements in this array are 2cm/1000 by 1.5cm/1000 in dimension, or 0.02 mm by 0.015 mm.

The extreme density of CCD arrays means that measurements of light intensity are taken across very narrow ranges of scattering angles. Referring back to the lower plot in Figure 3-2 (and counting the peaks and troughs, if so inclined), one can see that it is conceivable to have a detector element at several locations on each peak.

High pixel density provides other advantages when the CCD is applied in certain ways. These advantages will be discussed in Lesson 4.

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Principal Guideline of Instrumentation Design

Whether gas sorption, mercury porosimetry, or particle sizing, one fundamental principle applies to all instrumentation design: *the quality of the raw data set is of supreme importance.* With SLLS instrumentation, the raw data set is the set of light intensity measurements at specific angles. All information about the particle size distribution is contained in that set of measurements. The measurements must by sensitive, accurate, precise, repeatable, reproducible, and accommodate a wide dynamic range of intensities. If a scattering pattern is incorrectly measured, then the reduced data will contain error.

The scattering pattern that is being measured must be sharply focused, be of known geometry and position, and must have been produced under the constraints of the physical theory by which it will be reduced. If the scattering pattern contains erroneous information, then it cannot be improved by a perfect detector system.

SUMMARY OF LESSON 3

The focal length of the lens and its location relative to the source of scattering determines the size of the scattering pattern projected onto the focal plane.

The light detector is placed at the focal plane.

The scattering pattern that is being measured must be sharply focused, be of known geometry and position, and must have been produced under the constraints of the physical theory by which it will be reduced. If the scattering pattern contains erroneous information, then it cannot be improved by a perfect detector system.

<u>All information about particle size distribution is contained in the scattering pattern.</u>

Many intensity measurements at various points over the angular range of the scattering pattern must be measured to provide certainty that a pattern has been uniquely characterized.

A photodiode produces current flow when light strikes the photosensitive surface. The electrical signal is proportional to the light intensity; when the photons cease, the signal ceases. Small photodiodes produce small signals.

A charge-coupled device (CCD) is a photosensitive element associated with an electron accumulator (capacitor) that stores electrons (charge) as light energy liberates electrons.

A CCD array contains multiple CCD elements.

Manufacturer of LPSA products have different approaches to measuring the scattering pattern as is evident by the various designs of photodetectors.

Scientific grade CCD arrays provide the high resolution and sensitivity needed for scientific measurements. They are designed to limit, control, or eliminate certain characteristics that are permissible in consumer applications.

The extreme density of CCD arrays means that measurements of light intensity are taken across very narrow ranges of scattering angles.

Lesson 4: Detector Optics and Resolution of Raw Data

Information presented in this lesson expands many subjects covered by ISO 13320-1:1999, Particle size analysis Laser diffraction methods Part 1: General Principles . The reason for this is that new technology was introduced after the introduction of the standard, specifically, the use of a Charge Coupled Device (CCD) as a detector for measuring the light scattering pattern. Therefore, this technology and its ramifications are not covered in that document. Appendix B is a summary of information pertaining to the use of a CCD and the sections of the ISO standard that are affected by this innovation.

Specific Information Pertaining to the Use of a Charge Coupled Device as a Light Detector

Lessons 1, 2, and 3 presented general information about light scattering as described by Mie theory, and how the light scattering pattern can be measured pursuant to extracting particle size information from those measurement data. Those lessons introduced some of the challenges associated with obtaining a scattering pattern that conforms to Gustav Mie's theory and the technical challenges associated with measuring the scattering pattern.

This lesson will focus on new technology that is improves the capability of measuring the characteristics of scattered light. Specifically, the design features employed in Micromeritics' Saturn DigiSizer 5200 light scattering particle size analyzer is used as the example. In this device is the unique use of a Charge Coupled Device (CCD) as the light detector. However, since the objective of this lesson only is to allow an understanding of the design concepts and ramifications, quoted dimensions generally are stated as approximations.

Optical Elements Associated with the Formation of the Light Scattering Pattern

A schematic of the DigiSizer's optical layout is shown in Figure 4-1. The DigiSizer uses a 30 mW, 687-nm wavelength solid-state laser as the coherent light source. The source is housed in a compartment separate from the image forming optics. Light energy is piped from the source to the image forming optics by a single mode optical fiber. This arrangement accomplishes several things. For one, it isolates the heat-producing components from the other optics. For another, it helps reduce the length of the optical bed, or prevents the use of a mirror or other light-redirecting element. The flexible optical fiber means that the light source can be placed almost anywhere in the enclosure. Otherwise, there would be a linear sequence of optical elements that would require a longer or deeper enclosure.

Prior to light from the laser diode entering the optical fiber, a beam splitter directs about 50% of the energy to a reference photodiode. Directly beyond the beam splitter is a movable filter that, when needed, attenuates the light energy by a ratio of 25000 to 1. The reduction in light intensity is required so that the unscattered beam and inner bright rings will

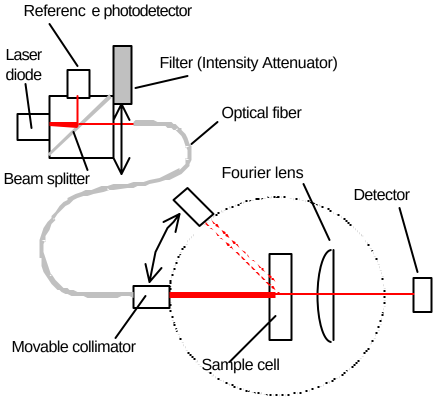


Figure 4-1. Schematic of the optical design of Micromeritics DigiSizer 5200.

not saturate the light detector.

The end of the optical fiber opposite the laser diode becomes the source and is coupled to a beam expander and collimating lens. The collimator produces a light beam of several millimeters diameter that passes through the sample cell.

The collimator is mounted on a rotation mechanism (rotating arm) whose axis of rotation passes through the cell, allowing the collimated light to be presented to the cell at various angles.

On the side of the sample cell opposite the collimator is a plano-convex Fourier lens of 200 mm focal length. All parallel light rays emanating from the cell and intercepting the lens converge (focus) at a single point on the image plane and on the detector, which lies in that plane.

At any particular position of the rotating arm, the Fourier lens intercepts only a limited band of scattering angles and only a portion of this band is actually intercepted by the detector. To cover an analytical range of scattering angles, the rotating arm is required to move to several positions.

Light Detection

Several types of light detectors for light scattering instruments were discussed in Lesson 3; the DigiSizer uses a charge coupled device (CCD). The CCD matrix used in Micromeritics' design is a 1024 x 1280 matrix containing a total of over 1.3 million detector elements. The relative size of the CCD matrix and the scattering pattern is such that the CCD intercepts only about 5 degrees of scattering angle at any time, the exact range depending on the refractive index of the suspension liquid. In order to measure the scattering pattern over the full angular range of the instrument, the position of the scattering pattern must move relative to the CCD. In fact, about 10 such moves are necessary and each step provides some overlap, that is, some of the previous scattering pattern remains on the CCD. This provides assurance that the series of segments captured by the CCD can be stitched together to form a continuum over the angular range of the measurement.

A simple example. The DigiSizer's method of capturing a scattering pattern wider than the angular view of the CCD is comparable to creating a wide-angle, panoramic photograph with a still camera that does not have a wide-angle lens. Most people have done this to capture a wide-angle view of a landscape, for example. The first picture is taken by aiming the camera to one extreme of the scene. Then, the camera is shifted slightly to the side, being careful to leave a little bit of the former section of the scene in the view finder. Another picture is taken, and the camera is shifted over a little more to capture the next image. After the sequence of photographs is developed and printed, the prints are laid side by side and lined up by using the overlap between adjacent photographs as a reference.

The same effect can be accomplished if the camera is fixed in position, always pointing the same direction, but the object to be photographed is moved. Although obviously not applicable to a landscape, it serves well for, say, a passing train. In this case, as illustrated in Figure 4-2, the subject moves to different locations in front of the camera, pictures are taken at each position, and the pictures pieced together. The DigiSizer does

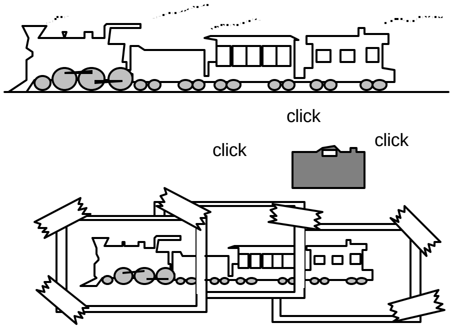


Figure 42. How to capture a photograph of a subject wider than the field of view of the camera.

exactly this; a portion of the scattering pattern moves into the 'view of the CCD, the pattern is captured, then the pattern is shifted and another measurement taken. This continues for up to 10 different locations of the scattering pattern, each having a little overlap with the former.

Accommodating Extreme Differences in Light Intensity

In the case of the DigiSizer where the scattering pattern varies so sharply in light intensity over a fraction of a degree, it is likely that some detector elements will be exposed to light either too intense or too weak for measuring, resulting in overexposure (saturation) of the element, or underexposure, respectively.

This is where the versatility of having a digitized representation of the scattering pattern is very useful. Since each exposure in the DigiSizer is taken with a CCD composed of over 1 million detector elements, the captured image, likewise, is a mosaic of over 1 million elements. The solution to extreme light intensity variations within a single exposure is to capture several exposures of the same area of the scattering pattern but at different light levels or over different exposure times. Then, use only the properly exposed elements from each image and piece them together into a new picture having no over- or under-exposed elements. However, this presents another challenge if the composite image is to be used quantitatively -- how to represent relative light intensities of a picture element in the composite.

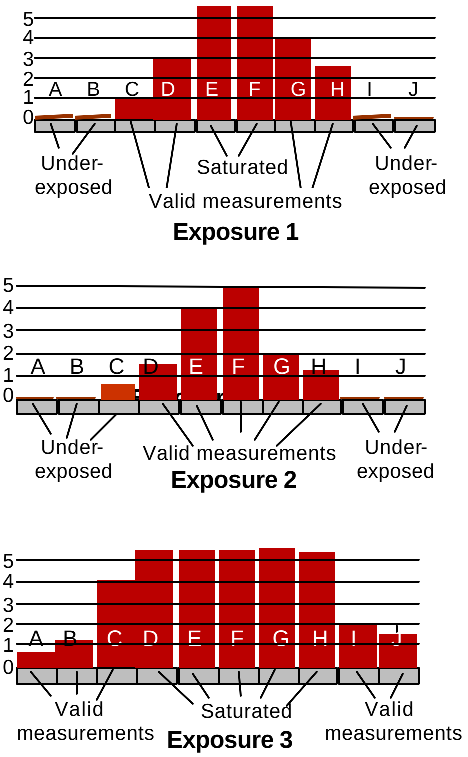
Another Simple Example To help understand how multiple exposures of the same image can be pieced together so that the range of light intensity represented in the composite exceeds the intensity range of the measuring element, a simplified illustration is used. The illustration employs a 10-element CCD, the elements being labeled A through J. Assume each element captures a 0.5 degree band of scattering angles. The three keys to being able to accurately measure the 5 degrees of scattering pattern falling upon the CCD are that 1)each element in each CCD image is digitized (represented by a number), 2) the CCD is an integrating device (accumulates over time), and 3) that the quantity of incident light is known (reference measurement).

Assume that the dynamic light sensitivity range of each photodetector element in the example CCD is 0.5 to 5.5 units. This means that light of less intensity than 0.5 is too weak to read reliably (the element is underexposed) and an intensity greater than 5 causes saturation (overexposure). However, the scattering pattern that needs to be measured has an intensity range from 0.25 to 10 units.

How this is accomplished with multiple exposures is explained below with the aid of a series of illustrations in Figures 4-3 through 4-6. Suppose that exposure #1 (Figure 4-3) is measured under the conditions of incident (reference) light intensity equaling R1 and data is accumulated by the CCD over a time period equaling T1. The results are that elements A, B, I, and J did not accumulate sufficient light energy to produce reliable data. Elements E and F received too much light and saturated. Only elements C, G, D, and H accumulated reliable data. These measurements of light intensity are designated C1, G1, D1, and H1 and stored in memory with exposure data R1 and T1. At this point, a complete 10-element digital representation of the scattering pattern has not been accomplished, so additional exposures are required in order to gather data about the scattering pattern at angles represented by elements A, B, I, J, E, and F.

To bring elements E, F on scale, light must be reduced. So, for exposure #2 (Figure 4-4), light energy is reduced by a factor of 2. Elements A, B, I, and J get even less light than before so they still produce no usable signal. The reduction in light also causes elements C, D, G, and H to be reduced. Now, elements E and F are on scale and measurable; the values of the reference measurement is R2 (= 0.5 R1) and exposure time is T2 (=T1).

To obtain valid measurements for the angular ranges of the light scattering pattern that fall upon CCD elements A, B, I, and J, more light energy is required. So, the light intensity is increased back to that of exposure #1, but the time of the exposure is increased by a factor of 4, thereby increasing the accumulated signal



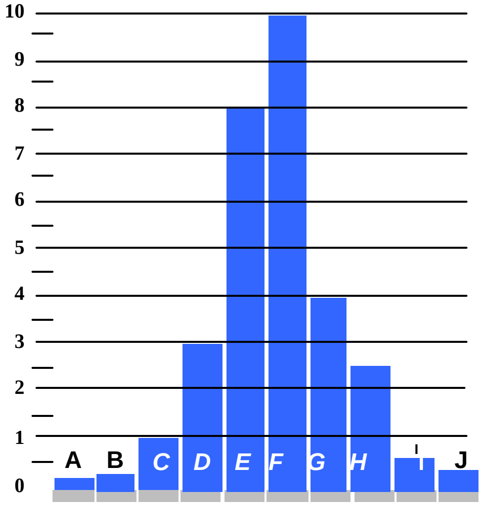


Figure 4-6. A bar graph of the normalized set of light measurements obtained from a set of three exposures of the same image. Those exposures are depicted in Figures 4-3, -4, and 5. Although the range of the detector is only 0.5 to 5.0 units of intensity, the normalized measurements span a range of

Figures 4-3, -4, & -5 (left column above) Independent detector element measurements of three exposures of the same image at different light intensities. Table 4-1 shows the raw data sets. Knowing the relative intensities of each exposure allows a normalized data set to be calculated. This is shown in table 4-2.

Table 4-1. Measured Light Intensity

		Detector Element									
Exposure	**Light Dose**	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**J**
1	8			1.00	3.00			4.00	2.50		
2	4				1.50	4.00	5.00	2.00	1.25		
3	32	0.75	1.25	4.00						2.00	1.50

Table 4-2. Light Intensity Converted to a Common Scale

		Detector Element									
Exposure	**Scale Factor**	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**J**
1	1.0			1.00	3.00			4.00	2.50		
2	2.0				3.00	8.00	10.00	4.00	2.50		
3	0.25	0.1875	0.0469	1.00						0.500	0.375
Composite		0.1875	0.3125	1.00	3.00	8.00	10.00	4.00	2.50	0.500	0.375

in each detector element by a factor of 4 compared to exposure #1. This results (Figure 4-5) in elements C, D, E, F, G, and H saturating, but elements A, B, I, and J now are onscale. The values read from these elements are designated A3, B3, I3, and J3, and the reference light intensity R3 = R1 and the exposure time T3 = 4T1.

The next step is to convert all readings to the same scale; this is similar to finding the common denominator when comparing fractions. In this example, we arbitrarily select the first exposure as the "standard scale" of light dose. The total dose of light in exposure #1 is 4 units of intensity over 2 units of exposure time for a total dose of 8 units. Light measurements in exposures #2 and #3 must be scaled by a factor of the light dose relative to the "standard dose" of exposure #1. The light intensity in exposure #2 was 2 units over 2 units of time for a total light dose of 4 units. The scaling factor is 8 units divided by 4 units or 2. Exposure #3 was performed at 4 units of intensity and 8 units of time for a total dose of 32 units. The scaling factor for exposure

#3 is 8 units divided by 32 units, or 0.25. With these scaling factors, the measurements of exposures 2 and 3 can be scaled to allow direct comparison to exposure 1. The measured data set and converted data set are shown in Tables 4-1 and 4-2 and the bar graph of converted data in Figure 4-6.

The Example Compared to Actuality

The example above is very simple compared to what happens within the DigiSizer. For example, the dynamic range of light intensity is approximately 10 orders of magnitude (in the example, light intensity varied by less than one order of magnitude). Only 10 CCD elements are used in the example, while the DigiSizer CCD has over 1.3 million detector elements. In the example, only 3 exposures were taken; the DigiSizer may require 10 exposures. Finally, only one 5-degree range of scattering angles was measured in the example; the DigiSizer measures up to 10 different 5-degree, overlapping bands.

Reducing the Volume of Raw Data

As you can imagine, the DigiSizer's CCD produces a massive number of measurements, as many as ten sets of exposures of 1.3 million element per 5-degree band. However, for each 5-degree band, these data are reduced to a single, normalized 1.3 million element exposure. The (up to) 10 normalized exposures that cover the angular range of the instrument are stitched together to represent a continuous representation of the scattering pattern from 0 to 36 degrees. This still represents several millions of data points that are further processed as described below. The scattering pattern is a circularly symetrical pattern projected onto a rectangular matrix of detector elements. Furthermore, the scattering pattern covers a much larger area than does the CCD array. The physical situation is approximated in Figure 47. As this figure illustrates, several detector elements are at the same angle. This provides one way of reducing the number of data points-- all elements at the same angle could be summed and averaged. But, since the angle range covered by a single CCD element is only a few thousandths of a degree (5^o divided by 1024 elements), even with averaging, the number of 0.005-degree angular increments over 36 degrees is still greater than 7 thousand. (*By the way, 0.005 degrees is the approximate maximum angular resolution of the optical configuration.*) This is an impractical quantity of data for computational purposes due to time and the fact that the particle size information at some level of resolution does not improve directly as a function of angular resolution; other factors may come into play. Therefore, a range of angles is used that typically is wider than a single CCD element.

Ultimately, the Saturn DigiSizer 5200 divides the total angular range into about 465 smaller ranges logarithmically distributed and averages the intensity of all CCD elements located in each angle class. The result is 465

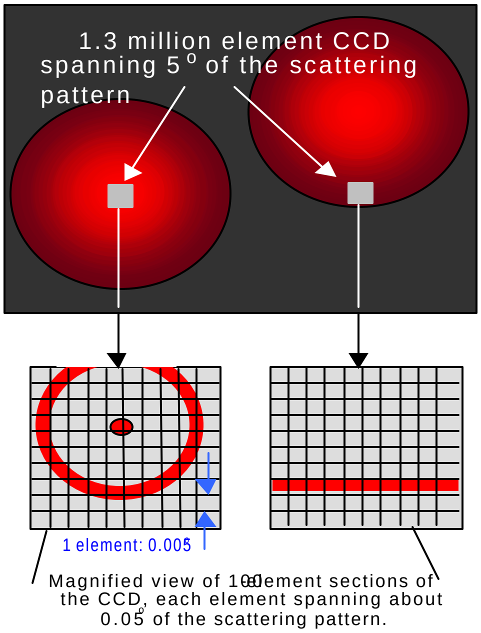


Figure 4-7. Very small sections of the CCD array magnified to show what a 0.005 degree wide band of scattering pattern might look like when projected upon it. Whether the center of the scattering pattern falls upon the CCD array as in the left illustration, or whether wider angle arcs of the pattern are intercepted, several detector elements are exposed to the same scattering angle.

ordered pair of angle class versus average intensity values. This number of points is sufficient that, when plotted, the points produce a smooth curve representing the Mie scattering function. This number of data points, incidentally, is about 4 times the number of data point collected by the highest resolution LPSA system currently on the market.

Selecting The Appropriate Density of Detectors to Accurately Represent the Scattering Pattern

The following series of examples illustrate how increasing the number of detectors per angle of scatter permits measurements capable of resolving definitive details of scattering patterns. In another sense, it shows why a limited number of detectors cannot provide the necessary data to discriminate definitive characteristics of a scattering pattern.

<u>10 Detectors per Decade of Scattering Angle (40 total):</u> The effect of the number of data points (level of resolution) is illustrated first in Figure 4-8 for a relatively low resolution measuring instrument. The figure shows two plots of the Mie scattering curve for a 100 μm spherical particle. The curve, shown in red, is calculated, so it is essentially continuous. The first plot illustrates how well an instrument with 40 detectors might reproduce the curve. In all fairness it must be pointed out that the plot points in the example are connected by straight lines making it jagged in appearance. A cubic spline fitting routine would round out the peaks and troughs providing a smoother appearance and almost any instrument manufacturer that displayed such data woud probably connect the points using a smoothed curve. Regardless of how the points are connected, there is no straight line connection or smoothing routine that can determine if peaks exist where there is no data such as is the case in the angle range greater than about 1 degree in the illustration.

<u>50 Detectors per Decade of Scattering Angle (200 total):</u> The next plot, Figure 4-9, shows the capability to reproduce the scattering pattern if the system has 200 detectors *(this number of detectors is larger than any known commercial LPSA system other than the DigiSizer).* The system in this case fails to recognize details of the scattering pattern at angles greater than about 7 degrees.

<u>100 Detectors per Decade of Scattering Angle (400 total):</u> The third plot, Figure 4-10, shows how well a system with 400 detectors or 400 data points can be expected to reproduce the scattering pattern. Here it is seen that the calculated Mie scattering pattern is accurately reproduced over the extent of the measurement range. *(DigiSizer plots contain 465 points, therefore are of higher resolution than shown in the illustrations.*

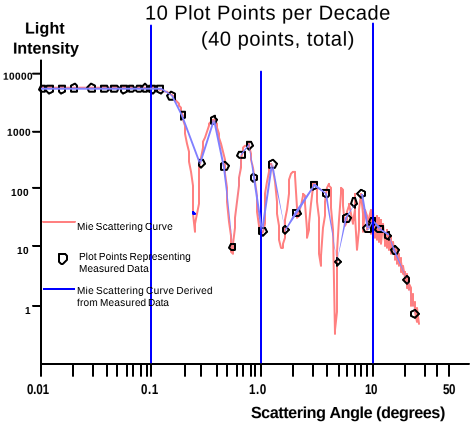


Figure 4-8. Example of a plot of 10 points per decade angular resolution Note that in the angle range greater than 1.0° the number of plot points is insufficient to accurately reproduce the scattering pattern.

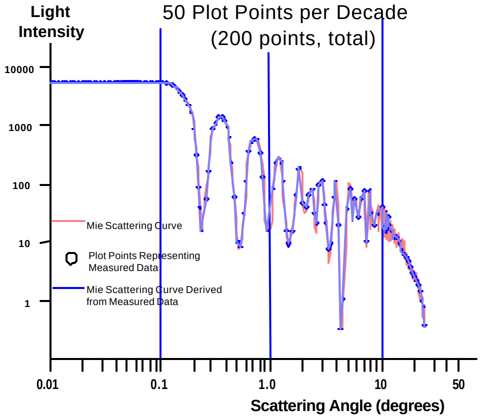


Figure 4-9. Example of a plot of 50 points per decade of angular resolution. In this example, the number of data points is still insufficient to reproduce the calculated plot when the scattering angle exceeds about 7°.

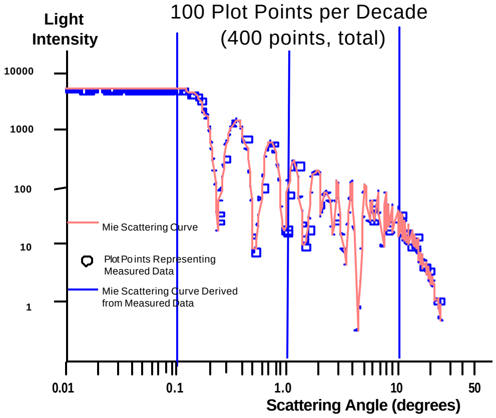


Figure 4-10. Example of a plot of 100 points per decade angular resolution. In this example, the resolution is sufficiently high to allow accurate reproduce the Mie plot even in the areas where there are closely spaced peaks. With such high resolution, slight variations in scattering patterns due to small size differences are detectable.

Figures 4-8, -9, and -10. This series of illustrations shows continuous line plots of 0 to 36° of the intensity versus angle scattering pattern calculated by Mie theory for a 100 mm sphere. Superimposed onto the Mie plot are measured data points depicting various resolutions of angular detection.

Review of Lesson 4

DigiSizer's optical design features a 30 mW, 687-nm solid state laser as the source.

The source beam is split into two components, one is directed to the reference photodetector and the other is directed toward the sample cell.

Prior to illuminating the sample cell, the light beam passes through a zone in which an attenuation filter can be placed when needed. The attenuation of the intensity of the light beam is approximately 25000:1.

A fiber optic cable carries the light energy to a collimating lens. The expanded and collimated beam is passed through the sample cell.

Some portion (a certain range of angles) of the forward scattered light from particles in the sample cell impinges upon a lens that redirects all scattered beams having the same angular scattering characteristics to the same point on the image plane. The lens, used in this manner, is called a Fourier lens.

A light detector is located in the focal plane. The angle subtended by the detector is 5^o.

The light detector is a 1024 x 1280 element Charged Coupled Device (CCD) having a total of 1,310,720 detector elements (also called pixels).

The CCD is an integrating device. It continues to accumulate charge as long as light contacts the active surface (that is, it accumulates over the time of exposure).

To determine the quantity of light energy detected by a CCD element, the number of accumulated electrons are counted-- thus, the light measurement is digitized (represented by a number).

The total angular operating range of the instrument is 36^o when water is used as the liquid medium.

The scattering pattern is moved relative to the CCD so that a wide angular range of the scattering pattern can be measured by the narrow-angle CCD.

Changing the angle of the incident beam relative to the sample cell moves the scattering pattern.

Because the light scattering pattern can vary in intensity by as much as 10 orders of magnitude, and because the CCD does not operate over the same range, multiple exposures of the same 5^o-angle band are measured.

Each exposure delivers a different dose of light energy.

Light energy doses are varied either by changing the time of exposure, or by changing the intensity of the incident light beam, or by using both methods simultaneously.

The measurements of the multiple exposures are normalized and a light intensity value is determined for each element in the CCD array.

As many as 10 overlapping angular positions in scattering pattern are measured, then stitched together to form a continuous 36^o band of the scattering pattern.

The 36^o band of the scattering pattern is divided into 465 log-spaced angle classes.

The resulting 465 intensity versus scattering angle data points are sufficient to reproduce a smooth curve representing the Mie scattering function, including details of the closely spaced peaks (maxima) and troughs (minima) in the plot. This defines the raw data set.

Lesson 5: Data Reduction by the Method of Model Fitting

Extracting Particle Size Information from Scattering Patterns

Convolution of Scattering Patterns

convoluted \ ’k n-v -l t -ed \ *adj* **1:** rolled or wound together with one part upon another

Scattering patterns, formally known by scientists as flux patterns, obey the rule of linear superposition which works as follows. Assume that there has been collected a set of (intensity, angle) experimental data pairs from the scattering pattern from a monomodal distribution of particles of size A. Assume, too, that a second experimental data set was collected at the same scattering angles for a different monomodal distribution of particle size B. If the two samples are mixed to form a bimodal distribution and then analyzed, the experimentally collected scattering data at each angle would be the sum of the intensities measured for the individual samples A and B at that angle. The data and plot of the mixture represents the convolution of data (or plots) of A and B.

This is the key to deconvoluting experimental data from multi-modal distributions. Before delving further into details about deconvolution and data reduction, it is necessary first to fully understand the combined or convoluted data set. The simple example in Table 5-1 and Figure 5-1 should be sufficient to illustrate what the convoluted data set represents. Remember the statement above about superposition while looking at the illustration and table of data that follow. *(Only 18 data points are used in the illustration to represent the scattering pattern. In actual practice, a considerably larger number of data points would be needed to achieve even moderate resolution. For example, in the angular data range of 0.01 to 1.0 degrees, Micromeritics’ Saturn DigiSizer 5200 would have about 150 angle vs. intensity data points)*

	EXPERIMENTAL DATA		
Scattering Angle (Degrees)	Intensity, Sample A (arbitrary units)	Intensity, Sample B (arbitrary units)	Intensity, Mixture of Samples A & B
0.01	1000	2000	3000
0.017	1000	2000	3000
0.028	1000	2000	3000
0.040	600	400	1000
0.043	55	45	100
0.053	130	26	156
0.065	10	600	610
0.10	130	7	137
0.11	7	40	47
0.13	43	2.3	45.3
0.205	1.2	10.3	11.5
0.30	60	1.8	61.8
0.40	1.2	10.3	11.5
0.52	1.7	1.1	2.8
0.62	3.5	2.3	5.8
0.72	1.15	1.1	2.25
0.80	0.6	1.8	2.4
1.0	0.5	0.8	1.3

Table 5-1. A table of light intensity at several scattering angles up to 1 degree for three simulated light scattering patterns. The first is for sample A, the second for sample B, and the third is the result of mixing equal portions of sample A and Sample B.

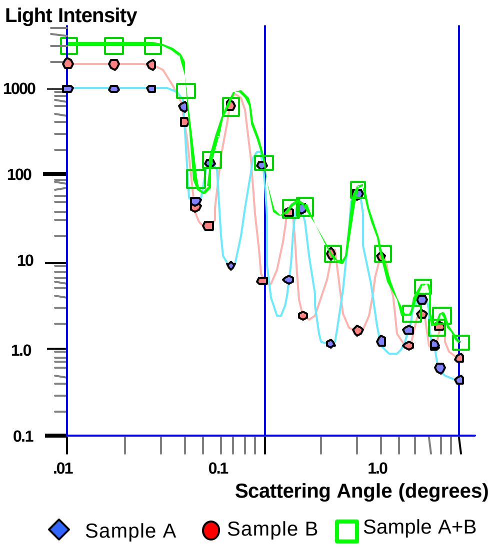


Figure 5-1. Plot of intensity versus scattering angle for Sample A (diamonds), Sample B (circles), and Sample A+B (squares). The plot of sample A+B represents the convoluted scattering data.

Deconvolution of Scattering Patterns

The scattering angle and intensity columns in Table 5-1 or, in fact, for any narrow, monosized distribution of spherical particles, represent a Mie scattering pattern model for that size distribution of the material in the same suspension medium. The table contains two models, one for particles of size A and the other for particles of size B. Assume that it also contained models for sizes C through Z. If an analysis of an unknown sample produced a data set similar to that in the right column, the problem of deconvolution (determining what mixture of sizes would produce the convoluted data set) could be solved by working backward from the mixture to the components of the mixture. By trial and error, and preferably with a computer, all possible combinations of samples A through Z could be summed until the unknown data set was reproduced. The solution would be the set of size models that, when summed, reproduce the experimental data set.

However, deconvolution as just described has some shortcomings. First, the example model in Table 5-1 is of low resolution, only about 8 points per decade of angle, and this is too small to discern small changes in the scattering pattern. Second, the data set does not cover a very wide range of scattering angles, only 0.01 to 1.0. As we know from previous lessons, for some distributions, no unique details of the scattering pattern are found at these low angles. Next, models A and B were derived experimentally with physical samples; this is impractical for several reasons, the principal two being: 1) narrow size distribution reference materials for a continuous set of models over a wide range of sizes don't exist, and 2) even if they did exist, model sets would have to be created for all material types to be analyzed. Last, the illustrated models do not take into consideration the concentration of each component in the mixture. So, additional design work must be done in order to have a universal model set that can be used to deconvolute experimental data with high resolution over a wide range of sizes, concentrations, and materials.

Designing a Method for Deconvoluting Scattering Patterns into Size Information Based on the Micromeritics DigiSizer

The size range of Micromeritics' Saturn DigiSizer 5200 is from 0.1 to 1000 µm or four orders of size magnitude. Each order of magnitude is divided into 40 size classes, so the total number of size classes is 161. This number of classes will be used in the example. A broad size range typically is represented on a logarithmic scale, so the size classes also are logarithmic. Figure 5-2 shows the arrangement of the scale.

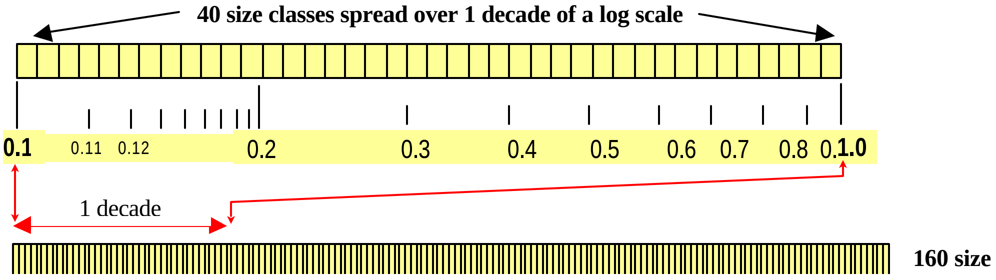


Figure 5-2. From bottom to top: The lower scale shows 4 decades or particle size from 0.1 to 1000 µm with 161 size classes shown directly above. The middle and upper scales are expanded views of 1 decade showing in more detail how size classes relate to the log scale.

Rather than measuring actual particles to determine the Mie scattering pattern, the patterns are calculated directly from Mie theory. Since the deconvolution method must determine a distribution based on the 161 size classes, a model must be calculated for each class. But, since the Mie scattering pattern varies considerably with materials of differing index of refraction, a model set of 161 light scattering patterns must be calculated for every different index of refraction of materials to be analyzed. This collection of multiple, 161-model sets is called a model library.

As stated above and in preceding lessons, the amplitude of the scattered light is proportional to the quantity of scatterers. Expressed another way, the shape of the scattering pattern for a specific, narrow distribution of particles remains the same as particle concentration varies, only the amplitude of the light intensities (the overall brightness) in the pattern changes. So, for sample A in Table 5-1 and Figure 5-1, if the number of particles in the sample had been different, then the amplitude measurements would have been different, but the positions of the peaks and troughs and their relative amplitudes in the pattern would remain the same.

In consideration of what was stated above about relative concentration, not only will the deconvolution routine be required to combine various models in order to determine the correct size mix, it will have to combine different ’concentrations’ of each size model.

A simple example of convolution and deconvolution of scattering patterns.

A simplified example will be used to illustrate more complex functions within the instrument. The simplified model, which begins with Figure 5-3, will illustrate how deconvolution by model fitting is accomplished. The four plots, A through D, are intensity (y-axis) versus scattering angle (x-axis) plots for light scattering patterns from equal concentrations of four different monomodal distributions of the same sample material. Each plot (and scattering pattern) is unique because each is for a different size. Scattering pattern models used in deconvolution routines are calculated from Mie theory. In the DigiSizer 5200, a seperate model is calculated for 465 angles classes and these angle classes coincide with the angle classes for which the much higher resolution, angular measurements were actually collected (see Lesson 4).

In Figure 5-3, the plot associated with particle size C shows how the plot (and the scattering pattern) is affected by changing the particle concentration by a factor of 2 and of 3. For example, the standard

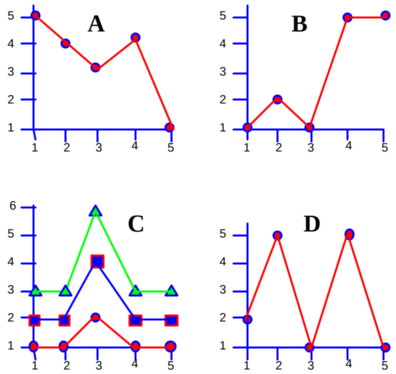


Figure 5-3. Plots of light intensity (y-axis) versus scattering angle (x-axis) for 4 simple scattering pattern models.

concentration at angle 2 produced light intensity of 2 units. When the concentration was tripled, the light intensity at every point tripled, so the intensity at angle 2 became 6 units.

The four models can be expressed in shorthand notation. For example, the three concentrations of size C could be expressed as

C1 = 1 x [1,1,2,1,1] = [1,1,2,1,1],

C2 = 2 x [1,1,2,1,1] = [2,2,4,2,2], and

C3 = 3 x [1,1,2,1,1] = [3,3,6,6,3].

The letter, of course, stands for the model identification and the number directly to the right is the concentration multiplier. On the right side of the equal sign is a shorthand method of showing more detail. The number is the multiplier (or concentration scaling factor, or weighing factor or weight) and x, of course, is the multiplication operator. Note that 1 equals 100% of the standard concentration, 2 represents 200%, and so on, not excluding values less than 100% such as 0.5 (50%) or 0.025 (2.5%). Within the brackets are the light intensity values. By convention, the order of intensity numbers corresponds to the order of angles in the data table, in this example, $[1^o, 2^o, 3^o, 4^o, 5^o]$.

The next illustration, Figure 5-4, represents experimental data from an analysis of an unknown distribution of particles. As can be read from the plot, the experimental scattering pattern was measured to be

	Intensity			
	Model			
Angle	A	B	C	D
1^o	5	1	1	2
2^o	4	2	1	5
3^o	3	1	2	1
4^o	4	5	1	5
5^o	1	5	1	1

Table 5-2: Tabulation of intensity versus angle data for scattering models A through D.

X1 = [9,13,6,19,12]

where X1 stands for experimental data and the numbers in the brackets stand for the light intensity measured at angles 1 through 5. No concentration multiplier is shown because notation of multiplication by 1 is not needed. How do we know the concentration is 1? Because the sample represents 100% of the quantity of the sample.

The deconvolution routine must scale and sum models until a solution is found that best fits the experimental data. It may be interesting to note that a scaling factor of zero may be used, but no negative scaling factors are allowed because negative concentration is a non-physical condition -- you cannot have less than zero quantity of material. That is why the method of finding the best fit to the experimental data is called a non-negative, least squares method.

In the case of the example in Figure 5-4, the solution is found to be

X1 = A1 + B2 + C0 + D1.

This can be confirmed by adding the corresponding elements of the solution as shown below:

`A1 = 1x[5,4,3,4,1] = [5, 4,3, 4,`

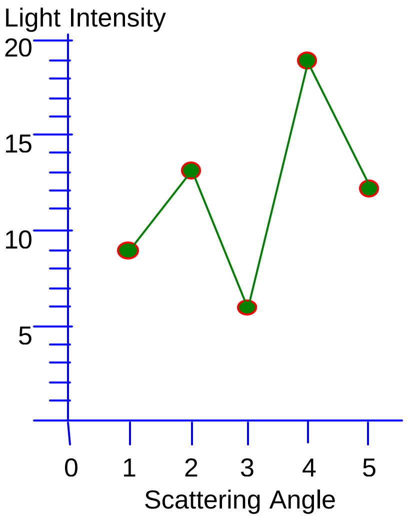


Figure 5-4. Plot of scattering pattern for measurement of an unknown distribution of particles. This is the raw data plot from which particle size and relative concentration must be extracted.

```
1]

B2  =  2x[1,2,1,5,5]  =  [2,
4,2,10,10]

C0 = 0x[1,1,2,1,1] = [0, 0,0, 0,
0]

D1  = 1x[2,5,1,5,1] = [2, 5,1, 5,
1]

X
[19,13,6,19,12]
```

The non-zero models indicate which particle sizes are present, their weights indicate the relative concentrations. So, the sizes and relative concentrations are determined by simply deconvoluting the scattering pattern. A report of the reduced data is presented in Figure 5-5.

In the example, five light intensity measurements are taken in the range 1 to 5 degrees. These raw data are used to determine the relative quantity distribution of particles over four size classes. In comparison, Micromeritics DigiSizer 5200 determines light intensity at up to 465 angles from near zero to 36 degrees. This raw data set is used to determine relative quantity distribution over 161 size classes from 0.1 to 1000 µm.

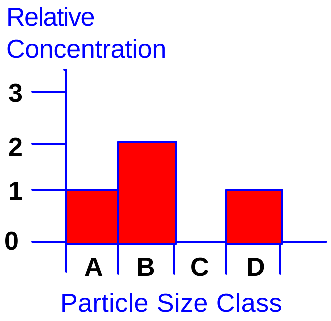


Figure 5-5. The particle size distribution of sample X1.

- END OF LESSON 5 -

REVIEW OF LESSON 5

Each size spherical particle (of the same material and in the same medium and illuminated by the same wavelength light) produces a different scattering pattern.

If two or more scattering patterns superimpose (are projected onto the same image plane), the resulting light at each point is the sum of the contribution of each pattern.

The above rule holds for many patterns from many particles of the same size (the pattern is the same; it simply gets brighter), or for many patterns from many different size particles (the patterns overlap or superimpose and create new composite patterns). These patterns are said to be convoluted.

Since each particle size produces its own unique pattern, convoluted scattering patterns must be composed of building blocks.

Even if the sizes are identical, a different set of building blocks is required if either the index of refraction of the scattering particle, the index of refraction of the suspension medium, or the wavelength of incident light changes.

Once the building blocks are known the pattern can be reproduced by selecting the correct set and number of patterns. Finding that set is called deconvolution.

Closing Remarks

Real Samples Produce Real Data

This document ends where it began with Samuel C. Florman s quote given in the introduction: "*Although we are committed to scientific truth, there comes a point where this truth is not enough, where the application of truth to human objectives comes into play We are no longer considering theoretical forces and ideal substances. We are now obliged to work with materials that are real, impure, and sometimes unpredictable. Our aim is no longer to discern absolute truth, but rather to create a product that will perform a function.*"

The deconvolution example in Lesson 5 relies on an imaginary sample and fabricated data, so it works out perfectly -- the models are perfect and the simulated experimental data set is perfect, so the solution is perfect-- everything fits. Real samples are not this cooperative.

The non-negative least squares method of model fitting to experimental data relies on scattering pattern models calculated from Mie theory for spherical particles suspended in a medium, and with values of indices of refraction entered to three decimal places. The deconvolution method, then, compares something theoretical to something real. When the instrument presents its reduced results (the best fit of theoretical models to real scattering patterns), it is reporting the particle size distribution of spherical particles that, from Mie theory, produces a scattering pattern that most closely matches the measured scattering pattern.

This, in essence, is the same a done by the X-ray SediGraph technique-- reporting the size distribution of spherical particles that have the same settling velocities as those measured for the sample material. Likewise, the electrozone sensing technique (Elzone) reports particle diameters based on spheres having equivalent volume as that displaced from the orifice tube by the particle being measured. Whether comparing light scattering patterns, settling velocities, or displacement volumes, what is reported is an equivalent spherical size based on comparing a real particle to a theoretical particle model.

What this leads to is the realization that particle sizing by the light scattering technique can be no more or less accurate than the SediGraph (X-ray sedimentation) or Elzone (electrozone sensing) techniques. What is important is that the person interpreting the analysis results knows how the data relate to particle size by way of the theoretical model and the data reduction method employed.

Additionally, the analyst must be aware that with light scattering particle sizing instruments, although the same analytical technique may be used and the same theoretical model employed, data reduction methods may differ from one instrument make and model to another. When comparing measurements of particle size obtained by different analytical techniques, light scattering to X-ray sedimentation for example, understanding the basis of the measurement is even more important .

In regard to various makes and models of static light scattering instruments not producing the same results is supported by information presented by the lessons in this document. The differences result for various reasons, including, but not limited to

a) the quality of the scattering pattern produced by the optics and projected on the image plane (focus, alignment on detectors, absence of optical aberrations),

b) the quality of the scattering pattern measurement (angular range, resolution and accuracy, intensity range, resolution and accuracy),

c) the assumptions used in the data reduction routine (refractive indicies, particle shape, wavelength of light),

d) assumptions about the sample material (shape compares to model, isotropic, homogeneous), and

e) assumptions about the sample distribution (homogeneous, single scattering).

When Sample Materials Do Not Behave Like Perfect Scatterers

First, what is a perfect scatterer in regard to Mie theory? It is a particle or system of particles that meet the conditions and conform to the restraints outlined in Lesson 1. Some of these conditions pertain to avoidance of multiple scattering; so, to simplify things, assume a single particle. What characteristics does a single particle need to be a perfect Mie scatterer? It needs to be spherical and of uniform index of refraction (homogeneous or isotropic). Do all real particles have these qualities? No. The index can depend on the orientation of the light beam to the crystal lattice (as with talc, for example). The refractive index also is affected by impurities that may be integral to the sample material or it may be a surface coating, so textbook values may not be accurate. The refractive index may not be known at all.

What about applications in which the sample materials are not spherical? When asked this question pertaining to the sedimentation, the intuitive reply is that since the particle settles, regardless of whether it is a sphere or not, it has a settling velocity. For any real value of settling velocity, there is a real value of particle size that can be calculated from Stokes law, and for every real value of particle size, there is a real value of Stokes settling velocity (whether or not such particles or velocities can exist in reality). In other words, there is a continuum of solutions (particle sizes) for a continuum of input variables (settling velocities) when using Stokes law.

Similarly, in regard to light scattering, non-spherical particles scatter light, but does this mean that a Mie size can be determined? No, because substituting every possible particle size into the Mie equation will not produce every possible pattern of intensity versus angle. In other words, there are intensity versus angle scattering patterns for which there is no Mie solution. Stated yet another way, for many scattering patterns, there is no size of spherical particle nor any distribution of spherical particles that will produce certain scattering patterns. These aberrant patterns are produced for any of several reasons already given, but, in general, because the particle system does not conform to the assumptions of Mie theory.

In these cases, solving for equivalent Mie particle size cannot be accomplished by an exact fit of theoretical data to experimental data. The residual, the difference between the experimental data and theoretical data, is manifested as artifacts in the distribution. High-resolution measurements of the scattering pattern and high-resolution scattering models provide small building blocks with which to build matching patterns. Therefore, residuals are less likely to be significant, but are also unlikely to be non-existent. The only way to get a perfect fit is to measure the scattering pattern of a perfect Mie scatterer.

At the extreme, there are sample materials that produce quite disorderly light scattering patterns. This may be due to shape factors that vary from particle to particle, high aspect ratios, or mixtures of refractive indices within the sample. This often leads to poor repeatability, significant residual quantities, and quantity distributions with many sharp peaks across the size range. For this class of sample materials, light scattering may not be a suitable technique for sizing purposes.

In some cases, poor repeatability is caused by slight differences in the scattering pattern from analysis to analysis (recall from Lesson

2 that Mie theory in the range of about 1 μm and larger is quite sensitive to variations in particle size and index of refraction). The high-resolution model-fitting routine detects these differences in the scattering pattern and assembles a different set of models each time in order to maximize the goodness of fit between the sum of the models and the experimental data. To remove the noise in the data, the model fitting routine can be instructed to relax the requirement to determine fine detail. This tends to smooth the calculated particle size distribution by not requiring the software to fill every slight deviation with a small quantity of this or that size particle. This reduction in sensitivity to details, of course, leads to reduced resolution as does all smoothing, but it also leads to more repeatable data. So, the operator has a choice between data with many inflections that don't repeat (high uncertainty), or data that suppresses fine detail, but is repeatable. Neither of these data sets is of higher quality or contains more information than the other.

The general rule in particle sizing is the same as for all analytical measurements: use the technique that produces the best data for the application. (Of course, the analyst must be able to evaluate data quality-- that is the principal message of this epilogue.) There is no single particle sizing technique that produces the best data for all sample types, but there probably is a single technique that consistently produces the best data for the range of sample materials analyzed for a particular application in a particular laboratory. The light scattering technique is not the end-all technique in particle sizing, it is just another technique and another way to view the size related properties of the material. Understanding what a technique actually measures, how it measures it, and how measurements relate to particle size are the first steps in determining if one technique should be used in place of another technique for a specific sample and application.

- END -

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APPENDIX A: Terminology Associated with Light Scattering

A

Absorbance

The product of absorption coefficient and optical path length.

Absorption

The conversion of incident light into heat within the absorber (particle or medium), thereby reducing the intensity of the light beam.

Absorption coefficient

An exponential coefficient which represents the degree of light attenuation, due to absorption, per unit path length, expressed in units of inverse length.

Absorption cross section

The product of absorption efficiency and particle geometric cross section normal to the axis of incident light.

Absorption efficiency

The amount of light absorbed by a particle, divided by the total amount of light geometrically intercepted by that particle.

Absorption index

The ratio of the imaginary to the real part of the complex refractive index.

Absorptivity

The fraction of the flux incident which is absorbed by a particle(see Absorption efficiency).

Acceptance angle

Angular field of view of detector in the scattering plane.

Airy disk

Diffuse central disk of light, due to diffraction, formed by an optical system imaging a point source of light.

Albedo

For single scattering by a particle, it is the fraction of energy lost from the incident light beam due to scattering only. Also, the ratio of scattering efficiency to extinction efficiency.

Angular intensity functions

(see Angular irradiance functions).

Angular irradiance functions

The functional dependence between the scattered irradiance per unit incident irradiance and scattering angle.

Anisometric particle

A particle having a preferred dimension (i.e., elongated or flattened).

Anisotropic scattering

Light scattering by particles exhibiting anisotropy.

Anisotropy

The optical property of a particle whereby its scattering behavior varies as it is rotated around its axis of symmetry.

Anomalous diffraction

Light scattering by a sphere whose diameter is much larger than the incident wavelength and whose refractive index approaches unity.

Anomalous extinction

Extinction by particles exhibiting anomalous diffraction.

Asymmetry factor

Equal to the mean of the cosine of the scattering angle weighted by the angular irradiance function. It is a measure of the asymmetry between forward and backward light scattering by a particle.

Avalanche Photodiode (APD)

A photodiode that exhibits internal amplification of photo current through avalanche multiplication of carriers in the junction region.

Axial ray

The ray of a light beam perpendicularly incident on a spherical particle, and which passes through its center (for dielectric particles), or is back reflected (reflecting particle).

Azimuthal angle

For linearly polarized light illumination, the angle between the scattering plane and the plane of polarization of the incident beam.

B

Backscatter

The light scattered back towards the incident direction, i.e., scattering of light at a scattering angle of 180 °. Sometimes meant as scattering at an angle larger than 90 °.

Backscatter efficiency

Ratio of backscattered irradiance to that which would be obtained if a sphere scattered all incident light isotropically.

Beer-Lambert-Bouguer law

The irradiance of a beam of radiation in an attenuating medium (e.g.,a solid-liquid suspensioin) decreases exponentially with path length (also called Bouguer-Lambert-Beer law).

Bidisymmetry

Property of non-spherical particles whereby their angular scattering pattern is asymmetric in two orthogonal planes (e.g., scattering by a rod illuminated at normal incidence).

Birefringence

Optical property of a particle whereby the refractive index depends on the polarization state of the incident light beam.

Bouguer-Lambert-Beer law

(see Beer-Lambert-Bouguer law).

Boundary conditions (electromagnetic)

The electric and magnetic fields at the interface between one body or medium and another.

Brewster angle

The angle of incidence (on a transparent plate) at which a polarized light beam, whose electric field component is parallel to the plane of incidence, is transmitted with no reflection loss.

C

Cabannes factor

The factor by which the Rayleigh ratio of an anisotropic particle is enhanced over that for an isotropic sphere (of equal volume).

Cauchy dispersion formula

A semiempirical formula that relates refractive index and wavelength of light.

Christiansen effect

The absence of light scattering by dielectric (non-absorbing) particles whose refractive index equals that of the medium which surrounds them.

Circular polarization

Polarization of an electromagnetic wave whose electric vector is of constant amplitude and, at a fixed point in space, rotates in a plane perpendicular to the direction of propagation with constant angular velocity (see Elliptical polarization).

Coaxial scatter sensing

Light scattering configuration wherein the axis of detection coincides with the illumination axis. (See Off-axis scatter sensing).

Coefficient of Variation

Relative measure (%) for precision: standard deviation divided by mean value of population and multiplied by 100 (for normal distributions of data the median is equal to the mean)

Coherence

Condition of correlation between the phases of two or more waves, so that interference effects may be produced between them.

Coherence length

The average length of the lines passing through all points in a particle in all directions and terminating on its boundaries (a measure of irregularly shaped particles).

Coherent scattering

Scattering in which there definite phase relationship between incident and scattered light.

Coincidence

The concurrent passage of two or more particles through the sensing volume of a particle counter.

Coincidence error

The counting error resulting particle from coincidence.

Collimated radiation

A beam of radiation whose rays are nearly parallel so that the beam does not converge or diverge appreciably.

Complex refractive index

The refractive index of light absorbing materials, expressed as a complex number. The real part represents the refractive component, and the imaginary part, the absorption.
Defined by its chemical composition;
real part , n, is responsible for scattering.
imaginary part, k, is responsible for absorption. If k is equal to 0 at a given wavelength, a particle does not absorb radiation at this wavelength.

Refractive index of a particle, consisting of a real and imaginary absorption) part: Np = np   i.kp

Creeping wave

Surface light wave that travels around a particle produced by grazing incident rays.

D

Dark Current

A small value current that flows in a photodiode while reversed biased, due to thermal generation of carriers and surface leakage with no incident light (also called leakage current). Range: a few pA to
10 m A

Deconvolution

A mathematical procedure whereby size distribution of a particle ensemble is inferred from measurements of their scattering pattern

Debye-potentials

Two scalar potentials in terms of which one can express the electric and magnetic fields resulting from radiation or scattering of light by a distribution of localized sources in a homogeneous isotropic medium.

Dependent scattering

Light scattering under the condition that the distance between two or more neighboring particles becomes sufficiently small to affect the scattering behavior of each individual particle.

Depolarization

In scattering of light, the decrease in the degree of polarization of incident polarized light. A characteristic behavior of a particle suspension composed of nonidentical particles.

Depolarization factor

For Rayleigh scattering, the ratio of parallel to perpendicular polarized components of scattered light at a scattering angle of 90°. It is equal to 0 for isotropic spheres, and 0.042 for air.

Depolarization ratios

Ratios between the horizontally polarized scattered irradiance for horizontally polarized incident light and the vertically polarized scattered irradiance for vertically polarized incident light, on one hand, and between scattering irradiances with oppositely polarized incident light. A measure of particle anisotropy.

Detection volume

(see Sensing volume).

Diffraction

The bending of light waves around the edge of an obstacle (e.g., a particle), or an orifice. Spreading of light around the contour of a particle beyond the limits of its geometrical shadow with small deviation from rectilinear propagation

Diffraction analysis

Particle size distribution determination by the measurement of the diffraction pattern of scattered light.

Dipolar scattering

(see Dipole scattering).

Dipole scattering

Rayleigh scattering modeled as the electromagnetic radiation by an electric dipole.

Dissymmetry

The ratio of the scattered irradiance at two scattering angles symmetrical about 90 °. It can be used for particle sizing.

Dynamic light scattering

Scattering of light by particles undergoing Brownian motion. Also called Quasi-elastic light scattering. It is characterized by a Doppler broadening of the incident light wavelength.

E

Elastic scattering

Light scattering wherein the wavelength of the incident radiation is preserved.

Electro-optical sensing

Detection and characterization of particles by light scattering in the presence of an electric field (usually time-varying).

Elliptical polarization

State of polarization of light in which the electric field vector at any point in space describes an ellipse in a plane perpendicular to the direction of propagation.

Emission (electromagnetic)

Any radiation of energy by means of electromagnetic waves.

Extinction

The attenuation of light in its passage through a particle suspension due to (light) scattering and absorption.

Extinction coefficient

An exponential coefficient which represents the degree of light attenuation due to the combined effects of (light) scattering and absorption. , per unit path length, expressed in the units of inverse length.

Extinction cross section

The product of extinction efficiency and the particle geometric cross section normal to the axis of light incidence.

Extinction efficiency

The sum of absorption efficiency and scattering efficiency.

Extinction paradox

The property of particles, whose size is comparable or larger than the wavelength of light, of exhibiting an extinction efficiency greater than unity. This is due to diffraction whose effects extend beyond the particle geometrical boundaries.

F

Fabry-Perot interferometry

Optical technique used for quasi- elastic light scattering measurements. It provides a direct measurement of the spectral distribution of the scattered light.

Far field

A distance from a scattering particle much larger than the ratio of particle area to the wavelength of illumination.

Fiber

Dielectric material the guides light; waveguide.

Fiberoptic Cable

A cable containing one or more optical fibers.

Forward scattering

Light scattered at small scattering angles, i.e., near the direction of the luminating beam.

Forward scattering nephelometer

A nephelometer that senses forward scattering. Used principally for field measurements of visual range.

Fraunhofer diffraction

Diffraction of light by particles observed in the far field.

Fresnel diffraction

Diffraction of light observed in the near field.

G

Gain

The ratio of irradiance scattered at a given angle to that which would be scattered into that direction if the angular scattering function were constant.

Gaussian beam

A beam of light (usually from a laser) whose cross-sectional irradiance distribution follows a Gaussian function (TEM(0,0) mode).

Geometric scattering

Light scattering by particles whose size is much larger than the wavelength of the illuminating light beam.

Geometrical optics

Optical behavior of particles whose size is much larger than the wavelength of light.

H

Higher-order Tyndall spectra

The colors that appear when a monodisperse suspension is illuminated with white light, when observing the scattered light at varying angles. (see Owl).

Holography

Optical imaging technique whereby an interference pattern is generated by mixing the coherent components from light scattered by particles and from a reference source. Applied to the study of particles larger than 5 μm.

Huygen’s principle

The principle that each point on a light wavefront may be considered as a source of secondary waves, the envelop of these secondary waves determining the position of the wavefront at a later time.

I

Incident irradiance

The irradiance of the beam of light illuminating an object.

Incident power

The total power of electromagnetic radiation intercepted by a particle.

Independent scattering

Light scattering under the condition that the distance between neighboring particles is sufficiently large such that the scattering behavior of individual particles remains unaffected (see Dependent scattering).

Index of refraction

(see Refractive index).

Inelastic scattering

Light scattering by particles wherein the incident wavelength is not preserved (e.g. Raman scattering) (see Elastic scattering).

Intensity

Radiant flux per unit solid angle (in the units of W sr-1). Often confused with irradiance.

Intensity fluctuation spectroscopy

(see Quasi-elastic scattering).

Interference

The variation with distance or time of the amplitude of a wave which results from the superposition of two or more waves having the same frequency.

Irradiance

Radiant flux per unit area (in the units of W m-2). Often confused with intensity.

Isometric particle

A particle having no preferred dimension (i.e., is not elongated or flattened).

Isotropic scattering

Scattering of light whose irradiance is equal in all directions.

K

L

Lambert-Beer law

(see Bouguer-Lambert-Beer law).

Laser light

Light generated by a laser. Usually in the form of a monochromatic light beam, highly collimated in the case of gas lasers.

Laser light scattering

Scattering of laser light by particles.

Laser particle counter (LPC)

An optical particle counter which uses laser light as the source of illumination.

LDV (laser Doppler velocimeter)

Light extinction

(see Extinction).

Light scattering

The deflection of light impinging on a particle, due to the combined effects of refraction, reflection and diffraction. Term applied to electromagnetic radiation ranging from the ultraviolet to the infrared.

Light scattering photometer

(see Nephelometer).

Linear polarization

Polarization of an electromagnetic wave in which the electric vector at a fixed point in space remains pointing in a fixed direction, although varying in magnitude. Also called plane polarization.

Lightwaves

Electromagnetic waves in the region of optical frequencies. The term "light" was originally restricted to radiation visible to the human eye, with wavelengths between 400 and 700 nm. However, it has become customary to refer to radiation in the spectral regions adjacent to visible light (in the near infrared from 700 to about 2000 nm) as "light" to emphasize the physical and technical characteristics they have in common with visible light.

Lorenz-Lorentz formula

An equation that relates the refractive index of a gas with the number of molecules per unit volume.

Lorenz-Mie scattering

General theory of light scattering by spherical particles. Term commonly applied to particles whose size is comparable to the wavelength of the incident electromagnetic radiation (see Transition regime). Also called Mie scattering.

LPC (laser particle counter)

M

Maxwell s equations

The set of four differential equations which relate the electric and magnetic fields to electric charges and currents, and form the basis of the theory of electromagnetic waves.

Mean free path, optical

The inverse of the extinction coefficient.

Mie (particle size) parameter

A dimensionless size parameter defined as the ratio of the circumference of a spherical particle and the wavelength of illumination (see Size parameter).

Mie resonances

Characteristic peaks in the extinction of light as a function of the Mie parameter. The amplitude of these peaks increases with particle refractive index.

Mie scattering

(see Lorenz-Mie scattering).

Mie theory

The general theory of the scattering of light by spherical particles.

Monochromatic light

Light wave composed of a single wavelength (e.g., as generated by a laser).

M ller matrix

A general 4 x 4 matrix of parameters that fully defines all polarization properties of the light scattered by a particle. It is often used for the optical characterization of particle shape.

Multiple scattering

Scattering by dense particle suspension wherein the incident light is scattered more than once before being detected.

Subsequent scattering of light at more than one particle, causing a scattering pattern that is no longer the sum of the patterns from all individual particles (in contrast to single scattering)

N

Nephelometer

A photometer designed to measure the light scattering irradiance within its sensing volume. Also known as Tyndallometer.

Nephelometry

Light scattering photometry of suspended particles. It is a multiple particle sensing technique (as contrasted with single particle counting) which provides a measure of the local scattering coefficient.

Nonspherical particles

Particles whose shape differs from that of a sphere.

O

Oblate spheroid

Particle shape generated by rotating an ellipse about one of its axes so that the diameter of its equatorial circle exceeds the length of the axis revolution. Also known as oblate ellipsoid.

Obscuration

(see Extinction).

Percentage or fraction of light that is attenuated due to extinction (scattering and/or absorption) by the particles, also known as optical concentration

Off-axis scatter sensing

Light scattering configuration wherein the detection axis differs from the illumination axis. (See Coaxial scatter sensing).

Opacity

A measure (usually in percent) of light extinction, defined as one minus the transmittance of a particle cloud. Used to assess the obscuration by suspended particles.

OPC (optical particle counter)

(see Optical particle counter).

Optical equivalent diameter

The diameter of an arbitrary particle as measured by an optical particle sizer calibrated with a reference material of known particle diameter (e.g., polystyrene latex spheres).

Optical anisotropy

(see Anisotropy).

Optical concentration

(see Obscuration).

Optical constants

The real and the imaginary parts of the complex refractive index. Somewhat misleading term since these parameters vary with wavelength.

Optical density

The logarithm (base 10) of the reciprocal of the transmittance.

Optical model

Theoretical model used for computing the model matrix for optically homogeneous spheres, with if necessary- a specified complex refractive index, eg Fraunhofer diffraction, anomalous diffraction, Mie scattering.

Optical particle counter (OPC)

A single particle detection and sizing instrument based on sensing the transient passage of each particle by means of light scattering. The detected pulses (one for each particle) are counted (to obtain number concentration), and classified by magnitude (related to particle size). Used mainly for clean room monitoring.

Optical particle detection

Detection of supended particles by optical techniques (mainly light scattering).

Optical particle sizing

Particle size distribution measurement by optical techniques (mainly by means of optical particle counters).

Optical path

For a ray of light traveling between two points (e.g., source and detector), it is the integral, over elements of length along the path, of the refractive index. Also known as optical distance or optical length.

Owl

A light scattering device used to measure particle size of monodisperse particles using white-light illumination and visual observation of the angular position of higher-order Tyndall spectra.

P

Particle counter

A direct-reading instrument for measuring the number concentration and size distribution of suspended particles. Term often used for optical particle counter.

Path length

In transmissometry, the distance between the light source and the detector.

Phase function

The angular dependence of the light scattered by a particle or a suspension of particles.

Phase shift parameter

The difference between the phase shift which the central ray undergoes passing through the particle diameter and that obtained in the absence of the particle. It is an optically normalized measure of particle size.

Photo-acoustic sensing

A technique for the detection of light-absorbing particles based on the photothermal heating effect.

Photodetector

An optoelectronic tansducer, such as a pin photodiode or avalanche photodiode.

Photoelectron emission

Emission of an electron (or electrons) from the surface of a particle due to electromagnetic irradiation whose energy is sufficiently high to overcome the surface barrier potential of the particle.

Photoemission

(see Photoelectron emission).

Photometer

An instrument for the measurement of light irradiance. Sometimes (but incorrectly) used synonymously with nephelometer (see lightscattering photometer).

Photometry

The measurement of light irradiance.

Photomultiplier tube (PMT)

A phototube with one or more dynodes between its photocathode and anode. The electron stream from the photocathode elicits secondary emissions at each successive reflection at a dynode resulting in large amplification of the signal.

Photon correlation spectroscopy

(see Quasi-elastic light scattering).

Photorefractivity

Optical property exhibited by photorefractive materials (e.g.,barium titanate) whereby their refractive index is altered due to an incident light beam.

Photothermal emission

The enhanced thermal emission of electromagnetic radiation (generally at infrared wavelengths) by absorbing particles illuminated by high irradiance light.

Photothermal heating

Heating that light-absorbing particles undergo when illuminated by high irradiance light.

Pin Photodiode

A photodiode having a large intrinsic layer sandwiched between p-type and n-type layers.

PMT (Photomultiplier tube)

(see Photomultiplier tube).

Polar nephelometer

A nephelometer capable of measuring scattering irradiance as a function scattering angle.

Polarizability

The electric dipole moment induced in the molecules of a particle by the electric field component of incident light, a phenomenon underlying refraction and (light) scattering.

Polarization (optical)

Light whose transverse oscillations follow a defined pattern, or occur in a defined plane.

Polarization ratio

The ratio of the irradiance of the horizontal to that of the vertical component of the light scattered by a particle or a suspension of particles.

Polarization, degree of linear

The ratio of the difference and the sum of the vertical and the horizontal component of the light scattered by a particle or a suspension of particles.

Polychromatic light

Light whose spectrum is spread over a range of wavelengths.

Prolate spheroid

The ellipsoid obtained by revolving an ellipse about one of its axes so that the equatorial circle has a diameter less than the length of the axis of revolution. Also known as a prolate ellipsoid.

Propagation constant

A characteristic number of an electromagnetic wave equal to 2π divided by the wavelength (also called wave number).

Q

Quasi-elastic scattering

Light scattering of suspended particles undergoing Brownian motion, and characterized by spectral broadening of the incident radiation.

R

Radiation pressure

Pressure exerted by light impinging on a particle.

Raman scattering

An inelastic scattering phenomenon whereby the incident light undergoes a change in wavelength and a random alteration in phase as it passes through a transparent particle, due to a change in rotational or vibrational energy of the scattering molecules.

Rayleigh gain

The gain for a particle exhibiting Rayleigh scattering.

Rayleigh ratio

The scattered irradiance from a unit volume of suspended particles at a given scattering angle, per steradian, when the suspension is illuminated with unit irradiance of unpolarized light.

Rayleigh scattering

Scattering of electromagnetic radiation by independent particles whose size is much smaller than the wavelength of the incident radiation (e.g., scattering of visible light by air molecules).

Rayleigh-Debye scattering

An approximate theory for the scattering of particles of arbitrary size and shape having a relative refractive index close to unity.

Rayleigh-Gans approximation

(see Rayleigh-Debye scattering).

Reflection (light)

Redirection of a light beam by interaction with the particle surface. This scattering component applies mainly to light absorbing (i.e., electrically conductive) particles.

Return of radiation by a surface, without a change in wavelength

Refraction

Redirection of a light beam caused by differences in the refractive index along the light path, either within a given medium (e.g., air), or when passing from one medium into another (e.g., particle to air). A scattering component which applies to both conductive and dielectric particles.

Change of direction of light determined by the change in the velocity of propagation in passing from one medium to another; in accordance with Snell s Law

Refractive index

A complex number whose real part is defined as the ratio of the speed of light in vacuum to the phase velocity of light within a medium (e.g., a particle), and whose imaginary part is directly proportional to the product of the absorption coefficient of the medium and the wavelength.

Relative refractive index

The ratio of the velocity of light in one medium to that in another medium. Also, the ratio of the refractive index of one medium (e.g., a particle) to that of another medium (e.g., air).

Complex refractive index of a particle, relative to that of the medium: m = Np/nm

S

Scattering

General term describing the change in propagation of light at the interface of two media

Scattering angle

The angle between the direction of the incident light beam and the direction or axis of observation, with the scattering particle at the vertex of the angle. By convention, zero scattering angle describes the case where the observer (or detector) looks into the light source.

Scattering coefficient

An exponential coefficient which represents the degree of light attenuation due to scattering, per unit path length, expressed in the units of inverse length (see Extinction coefficient and Absorption coefficient).

Scattering cross section

The product of scattering efficiency and the geometric cross section of a particle normal to the incident light beam.

Scattering efficiency

The total energy of the light scattered by a particle divided by the energy of the light geometrically intercepted by that particle.

Scattering form factor

In Rayleigh-Debye scattering theory, a factor which represents the modification of the scattered irradiance due to the finite size of the particle and to its deviation from sphericity.

Scattering Pattern

Angular or spatial pattern of light intensities (l(q) and l(r) respectively) originating from scattering, or the related energy values taking into account the sensitivity and the geometry of the detector elements

Single Scattering

Scattering whereby the contribution of a single member of a particle population to the scattering pattern of the entire population is independent of the other members of the population.

Scattering plane

Plane defined by the axis of the incident light beam and the axis of observation (or detection). This plane contains the scattering angle.

Scattering ratio

At a given scattering angle, the ratio of scattered irradiances when a polarizer, placed within the incident beam, transmits the parallel and perpendicular components, respectively.

Sensing volume

Term usually applied to optical sensing instruments. For light scattering devices, it is the intersection between the source beam and the field of view of the detector. For light attenuation devices, the volume of the source beam within the sensing path.

Single scattering

Scattering under the assumption that the particle is exposed only to the light of a direct beam, i.e., the light scattered by other particles contributes a negligible amount to the illumination.

Hence, the irradiance of the light scattered by a particle cloud is linearly related to particle number concentration (for constant size distribution) (see Multiple scattering).

Size parameter

In particle sizing by light scattering, the dimensionless ratio of the particle (sphere) circumference to the wavelength of the incident light.

Snell s law

In optics, for a ray incident on the interface of two media, the sine of the angle of incidence times the refractive index of the first medium is equal to the sine of the angle of refraction times the refractive index of the second medium.

Sphericity

The degree to which the shape of a particle approaches that of a sphere.

Spheroidal particles

Particles whose shape is geometrically generated by rotation of an ellipse about one of its axes. There are prolate and oblate spheroids (also called ellipsoids) depending on the axis of rotation.

Stabilized Light Source

An LED or laser diode that emits light with a controlled and constant spectral width, central wavelength, and peak power with respect to time and temperature.

Stokes parameters

A set of parameters that completely describes the state of polarization of electromagnetic radiation.

Stray light

Unwanted light within an optical instrument, usually due to source beam reflections from internal surfaces.

T

Transition regime

Range of particle sizes between the limiting cases of Rayleigh scattering and geometrical optics. Characterized by pronounced fluctuations in scattering cross section as a function of size parameter. Also called Mie scattering.

Transmittance

The ratio of the detected irradiance to the source irradiance for a beam passing through an attenuating medium.

Transverse electric wave

An electromagnetic wave in which the electric field vector is everywhere perpendicular to the direction of propagation.

Transverse magnetic wave

An electromagnetic wave in which the magnetic field vector is everywhere perpendicular to the direction of propagation.

Turbidity

The product of the extinction coefficient and the path length through an attenuating medium.

Tyndall cone

The visible cone of light due to scattering of a diverging beam passing through a suspension of particles.

Tyndall effect

The increase in Rayleigh scattering irradiance as particle size increases.

Tyndall higher order spectra

The spectrum of colors exhibited by light scattered by a monodisperse particle suspension illuminated with white light, as afunction of particle size and scattering angle. A property previously used for particle sizing (see Owl).

Tyndall-spectrometer

An instrument designed to observe the Tyndall higher order spectra.

Tyndallometer

(see Nephelometer).

U

V

Visibility (laser Doppler velocimeter signal)

The amplitude of the modulation of the detected Doppler signal in a laser Doppler velocimeter.

W

Wave number

(see Propagation constant).

Wavelength

The distance between two points having the same phase in two consecutive cycles of a wave, along the direction of propagation. Equal to the velocity of propagation divided by the frequency.

Wedge ring detector

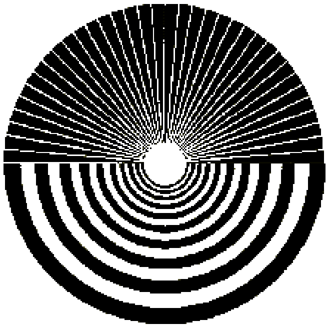
A diffraction pattern sampling unit composed of a 32-element monolithic silicon photodiode array and a readout unit. The intensity on each detector element can be separately read out by means of a control switch.

White light

Any radiation producing the same color sensation as average noon sunlight. Polychromatic light as generated, for example, by a halogen incandescent lamp.

Width of normal size distributions

Standard deviation (absolute value) or coefficient of variation (relative percentage) of the size distribution. For normal distributions about 95% of the population falls within – 2 standard deviations from the mean value and about 99.7% within – 3 standard deviations from the mean value.



A wedge ring detector

X

Y

Z

APPENDIX B: Information About Laser Diffraction Instrumentation Not Covered by ISO 13320-1:1999

Information presented in this Appendix expands subjects covered by ISO 13320-1:1999, Particle size analysis Laser diffraction methods Part 1: General Principles. New technology introduced after the publication of the standard and its ramifications are not covered in that document.

Additional Information Pertinent to Section 5 of ISO 13320-1:1999

When describing hardware and software, the document repeatably reminds the reader that the descriptions are those of a typical, usual, or general system. However, sometimes those general descriptions do not encompass a system based on CCD technology. The information that follows adds consideration of CCD technology to those descriptions.

Figure 2- Example of the set-up of a laser diffraction instrument: Although this illustration is intended to be no more than a typical set-up, it warrants differentiation from a design incorporating a CCD. For example, key item #1, the obscuration detector, typically is a fixed detector at the center of the multi-element detector array. The CCD can assign the role of obscuration detector to any element that happens to be located at the point the unscattered beam impinges upon the detector array.

Key item #7, the light source laser, is coupled by a flexible optical fiber to the system depicted by items #8, the beam processing unit, allowing items #8 to rotate in an arc centered on the sample cell while projecting the expanded and collimated laser beam.

The multi-element detector, key item #10, is a dense array of CCD elements, spaced linearly, as apposed to the apparently logarithmically-spaced elements depicted by the illustration. However, the software groups the detectors in a logarithmically-spaced arrangement, therefore the illustration shows how the signal from the CCD array is treated rather than the physical arrangement of the array elements.

Verbal description of instrument system following Figure 2: The description of the instrument system that begins on page 4 of the ISO document, being expressed in general terms, incorporates the function of the Micromeritics design until the third-to-last paragraph on page 5.

That paragraph begins, *The detector generally consists of a number of photodiodes* It should be pointed out that a photodiode is a different device from that of a CCD and produces a signal different from the *set of photocurrents* as described in the document. The CCD detector chip performs all of the described steps attributed to *subsequent electronics*.

The next sentence in the same paragraph, describes the role of the central element. In a typical instrument, the central element is discrete, defined by hardware, and always performs the same function. With a CCD, the central element is defined by software and can be any element on which the central beam happens to fall.

The paragraph continues by describing the role of the central detector(s) in alignment of the system. An optical system incorporating a CCD does not require precise mechanical alignment because the center of the scattering beam can be detected by software and the detector array remapped accordingly so that the angle associated with each detector element is known.

Section 6.6.6 Instrument location: The last sentence in the first paragraph advises how to prevent the need for frequent alignment of the optical system. A CCD-based system is far less dependent on mechanical alignment than the typical optical system. This follows from the fact that the alignment of the central beam on the detector array is software defined and not mechanically defined. Therefore, any movement of the central bright spot relative to the detector array is detected and immediately corrected by software by redefining the angular domain of each element.

<u>Section 6.3.1, subsection b): Measurement of the scattering pattern of dispersed sample(s):</u> The first sentence provides what is expressed as a general description of the method of scanning the detectors and the associated duration. Although the quoted number of sweeps and time interval may be typical for a photodiode-based detector system, it does not describe data gathering by a CCD-based system. Since the CCD is an integrating device and the photodiode is a constant current device, the scanning requirements differ considerably. The CCD accumulates information, then self-scans on demand. A photodiode provides a real-time signal when read, but provides no information about what occurred between readings.

The fourth sentence in the first paragraph states, *The magnitude of the signal from each detector element depends upon the detection area, the light intensity and the quantum efficiency.* This adequately describes the signal produced by a photodiode, but does not for a CCD. To incorporate the magnitude of the signal from each CCD element, the description would have to be appended with, ..integrated over time.

The last two sentences if the first paragraph of subsection b) describe how a typical detector system matches scattering angles to the appropriate measured intensity signals. As stated, generally, these are factory set and stored in the system computer. A CCD detector system is more flexible in that each element of the detector array does not have a factory-defined range of scattering angles associated with it. The CCD device can make that assignment on the fly by way of software. The software uses the location of the element containing the central beam as the reference position and maps all other elements by angle accordingly. The element containing the central beam is easily determined by the extraordinary magnitude of the signal.

<u>Section 6.6.6 Errors of specific parts of the procedure :</u> This section describes observation of signals from the detector elements. Because of the number of detector elements in a CCD array (thousands to millions), this procedure is performed routinely by software and any element that is found to be producing an erroneous signal is removed from the data set after reading the array. Background data are stored.

<u>Section 6.7 Resolution; sensitivity:</u> This section lists *restrictions* to resolution and claims that *these factors prevent the laser diffraction technique in <u>its usual design</u> from being a high resolution technique* The restrictions are largely based on limitations of the detection system. It should be pointed out that a CCD-based detection system does not fall under the category of usual design .

The list of restrictions include:

- ❑ *number, position and geometry of the detector elements.* The number of elements in the CCD array of the DigiSizer is about 10000 (10^4) times that of the highest density photodiode detector array being used in a commercial instrument at the time of this writing. The positioning and geometry of these elements is so closely spaced that angular increments in the order of 10^{-3} degrees can be discriminated and no angle bands are excluded.
- ❑ *Their signal to noise ratio:* The CCD, being an integrating device, can accommodate extremely low light signals by integrating the signal until the

total signal is well above the noise level of the detector element.

- *Fine structure in the measured scattering pattern:* The extremely high resolution of the CCD array allows fine structure to be measured (as exemplified in the lesson above).
- *Differences in scattering pattern between size classes:* Again, the high resolution of the CCD combined with the capability to accommodate a very wide range of light intensity allows the detection system to discriminate small differences in scattering patterns.

(How the DigiSizer deals with the last two restrictions is discussed in the next lesson.)

<u>Annex A Theoretical background of laser diffraction:</u> This section begins on page 16 and ends on page 19. The second-to-last paragraph (page 19) contains the information that requires expansion. The first two sentences express the design criteria for a high-resolution system using a large number of small detectors. The next two sentences state why using small detectors is not practical (assumingly in typical instrument designs, and definitely in photodiode-based instruments) The balance of the paragraph expands on complications associated with attempting to accomplish this task.

The root of the complication is stated as, *the signal of each detector element is the product of the intensity of scattered light, the geometric area of the element and its sensitivity*. The consequence is stated as, *any decrease of the geometric area leads to smaller signals and, thus, a lower signal to noise ratio*, and as a result, *more detectors lead to more measurement errors* and further suggest that, *this leads to some optimum situation for the number of detector elements, their size and the angular range that they cover.*

Again, what was not considered by the document was the use of a CCD detector array that overcomes the expressed complications of having a large number of small detectors. First, as previously noted, the signal strength is a function of all the cited variables, but integrated over time. Therefore, if the internal noise level of the detector is X, then the signal accumulation time can be increased until the signal is 100X or 1000X, and overcome the signal-to-noise limitation. Therefore, a CCD detector can be composed of elements of very minute active area and still provide acceptable signal-to-noise levels. It follows, then, that more CCD detectors do not lead to more measurement errors as is the case with a photodiode. Although an *optimum situation for the number of detector elements, their size, and the angular range the cover* may exist for CCD detector arrays, it is defined by a different set of criterion than for photodiodes and the optimum situation far exceeds that pertaining to photodiode detector arrays.

Summary

The ISO document was written around the currently available laser diffraction particle sizing equipment on the market and applies well to those instruments. Subsequently introduced technology is not considered in the general descriptions of instrument systems. As a result, some practical limitations as stated in the document have been overcome and superseded.

It is interesting to note that on page 20, third paragraph, forth line is the caveat, *Remember that most early designs of instruments...* and continues to describe a limitation of early designs. Since the introduction of CCD technology to the measurement of scattering patterns, this admonition applies to many statements in the document.