Evaluating a Laser Diffraction Instrument for Accuracy

Introduction

Before selecting a particle size analyzer, or any other measurement device, several questions must be answered. Is the instrument accurate? Are the measurements it makes reproducible? What is the precision of the device? How will the company selling the instrument support the product? And of course, is it easy to use? Other issues may be more or less important depending on the specific requirements, such as: will it be possible to make a meaningful correlation between measurements made with this instrument and those in a company's historical database? In this article, the accuracy of a Beckman Coulter® LS™ Series analyzer, LS 13 320 is determined. This instrument has a range from 0.04 micron to 2000 microns and can measure across the entire range in a single analysis.

Laser Diffraction

Before directly addressing the question of accuracy, it is worth spending a little time discussing the laser light scattering technique and how it works. The laser light scattering method, generally referred to as laser diffraction (LD), is the fastest growing technique for sizing particles from submicron sizes to a few millimeters. The reasons include its huge dynamic range of measurement, excellent reproducibility and ease of use. Many applications that were formerly the domains of sedimentation, sieving and microscopy are now routinely handled using light scattering, including ceramics, clays, cement, foodstuffs and others. Its flexibility in handling samples dry or wet, in any transparent fluid including organic solvents, make it the perfect choice for laboratories characterizing a wide range of materials.

In contrast to single particle counters and sizers, such as the electrical sensing zone method (the Coulter Principle), or optical particle counting, the light diffraction method interprets a signal received from an entire ensemble of particles. This method of measuring particle size takes advantage of an optical effect: small particles in the path of a light beam scatter the light in characteristic patterns. Given a certain pattern of scattered light intensity as a function of angle to the incident beam, the distribution of particle sizes can be deduced. Knowledge of the refractive index of the sample particles increases accuracy for particles in the lower end of the range, so in this evaluation the refractive index of the materials used is applied.

The simplest scattering pattern, from a monomodal dispersion of spheres, consists of a central bright spot (known as the Airy disk), surrounded by concentric dark and bright rings, whose intensity diminishes further from the center of the pattern, that is, at higher scattering angles. The scattering angle at which the first dark ring, or diffraction minimum, occurs depends on the size of the particles; the smaller the particle, the higher the angle of the first dark ring (or,

alternatively, the larger the size of the Airy disk).

These scattering patterns obey the rule of linear superposition. In other words, the pattern from a mixture of two (or more) monomodal dispersions of particles can be constructed by adding the intensity functions of the constituent particles in the mixture. It is therefore possible to determine the intensity contribution to the measured scattering pattern from each particle size class in the sample, which can then be converted to the volume percentage of these size classes in the sample. In this evaluation, the accuracy with which the instrument recovers volume percentages is examined.

To make a measurement, a suspension of particles in air or liquid is passed through a sample cell situated between a laser source and a detector array. As the particles pass through the sample cell, the patterns of scattered light are measured by the detector array and are time-averaged over the course of the analysis to produce an intensity vs. angle function representative of the distribution of particles in the sample. This function is then mathematically converted to the size distribution. Figure 1 shows a laser diffraction instrument.

Figure 1. a Beckman Coulter® LS™ Series particle size analyzer, LS 13 320

These instruments are generally referred to as "laser diffraction" analyzers because the early models used only the Fraunhofer diffraction approximation to convert the scattering function to the size distribution. This model treats particles as opaque, circular obstructions in the beam of light and mimics the true scattering of light by three-dimensional particles only for non-transparent particles much larger than the wavelength of the light and only for small, scattering angles.

PIDS TECHNOLOGY

Most commercial instruments today use optical models in their analysis algorithms based on the Mie theory. The Mie theory is a complete solution to the problem of light scattering by a smooth and homogeneous sphere. When used with red lasers common to the industry, a Mie optical model permits accurate sizing down to about 0.5 micron, below which scattering patterns become too similar to resolve differences in size.

The Beckman Coulter LS Series laser diffraction instruments incorporate two enhancements to basic light scattering technology: resolution across the range is increased by using greater numbers of detectors per unit angle than other instruments using this technology, and measurements of particles smaller than 0.5 micron are substantially improved by a patented technology called polarization intensity differential scattering (PIDS).

The PIDS technology uses three wavelengths of light, filtered for polarization in the vertical and horizontal planes. Six detectors (in addition to the 126 detectors used for measuring scattered laser light) are positioned at around 90 degrees to the direction of the light path to measure the differential intensity between scattered light of vertical and horizontal polarizations. A total of 36 measurements are made at six scattering angles and three wavelengths, each at two polarizations.

The combination of multiple wavelengths and two polarizations provides information that differentiates

between submicron particle sizes and dramatically increases resolution. Although PIDS uses a second light source split into six "flavors," the scattering of these light beams by particles is described by the same Mie theory, so all scattering information is converted to particle size using the same algorithm in a single operation. The resolution and accuracy of PIDS was tested using a mixture of particle sizes in the submicron region.

TESTING MATERIALS

Many reference materials are now available for particle size characterization. These materials are either Standard Reference Materials (SRMs) produced by the National Institute of Standards and Technology (NIST, US) or the Bureau of Community Reference (BCR, UK), or materials whose characterization is traceable to SRMs (NIST- or BCR-traceable). By measuring a series of SRMs and NIST-traceable materials, the accuracy of the instrument can be evaluated. All materials used were spherical to avoid any shape-dependent bias since the theory underlying laser diffraction instruments is based on the assumption of spherical particles, as are the theoretical underpinnings of most particle sizing instrumentation.

A series of nine NIST-traceable microspheres from Duke Scientific (now Thermo Fisher, Fremont, CA) were measured. Eight of these consisted of polystyrene latex spheres (either pure polystyrene, PSL or polystyrene divinylbenzene, PSDL) and one consisted of glass spheres (GS). All of the NIST-traceable materials have very narrow particle size distributions. In addition, SRM 1003b, a broad distribution of glass beads from NIST, was measured.

Two of the NIST-traceable materials were selected to test the accuracy of the volume percentage recovery of the instrument by mixing various proportions of the two materials. If an instrument does not correctly recover volume percentages, then little confidence can be placed in results that indicate the presence of secondary populations of particles that can have important consequences for the performance of a material.

The two materials chosen for this part of the evaluation were selected using two criteria: that their diameters were relatively close together, allowing a simultaneous test of resolution, and that they were packaged dry, allowing more accurate proportions by weighing than is possible with materials suspended in water. Finally, submicron resolution and the ability to recover correct volume percents for a mixture of submicron particles were tested using a trimodal mixture of NIST-traceable particles from Duke Scientific.

ACCURACY ANALYSIS

Table 1 lists the results for the NIST traceable samples analyzed by the laser diffraction instrument (LD) individually. Since the certified mean diameters are uncertain by a specified quantity, any results within the uncertainty limits are listed as ‘in’ for in-specification in Table 1. The error for results that fall outside the uncertainty limits is calculated from the nearest uncertainty limit. Of the nine materials, the LS 13 320 recovered mean diameters within the uncertainty limits for seven. The recovered mean for the 1.034 micron polystyrene spheres was 2.37% outside the lower uncertainty limit, and the recovered mean for the 274 micron polystyrene divinylbenzene spheres was 1.62% outside the upper uncertainty limit. Overall, results emphasize the effectiveness of the Beckman Coulter LS Series instrument to measure particle size accurately.

Materials	Traceable Diameter		LD Result	
	d(µm)	±(µm)	d(µm)	in/out
304nm PSL	0.304	0.006	0.306	in
503nm PSL	0.503	0.004	0.506	in
1µm PSL	1.034	0.020	0.99	2.37%
10µm PSDL	10.0	0.3	10.14	in
40µm GS	40.0	2.8	41.52	in
116µm PSDL	116	2.3	116.8	in
167µm PSDL	167	3.4	167.8	in
274µm PSDL	274	5.5	284.1	1.62%
539µm PSDL	539	11	550	in

Table 1. The LD results for NIST traceable samples

Table 2 lists the results for the volume-percent-recovery test using three mixtures of 167 micron and 274 micron spheres, indicated in the first column for the approximate ratio of 167µm:274µm PSDL. The second column lists the actual volume percentage of 167µm PSDL added. The LS 13 320 recovered within 2% (as a percentage of the total volume) of the added volume percentages (the third column), which indicates that the LS 13 320 has excellent resolution for an instrument of this type given that the ratio of the mean diameters is only 1.64. Again, if an instrument cannot correctly recover volume percentages, it is difficult to base decisions on particle size distributions.

	added	recovered		
Ratio	V_{167}%	V_{167}%	d_{167}(µm)	d_{274}(µm)
1:1	50.35	51.50	166.8	283.6
2:1	66.57	68.55	168.6	282.8
1:3	25	23.67	166.7	279.1

Table 2. Information recovered of mixtures of PSDL. The right two columns are the mean sizes recovered from the particle size distribution peaks.

The mean particle diameter and the uncertainty limits of the NIST SRM 1003b material were calculated from the certified cumulative-percent-less-than values, the upper limits of the certified values and the lower limits of the certified values. Table 3 shows that the mean diameter and standard deviation recovered by the LS 13 320 are within those calculated for the upper and lower limits, and deviate from those of the certified values by only 1.3% for the mean and only 0.9% for the standard deviation.

parameter	Calculated from certified values			LD
	lower limit	mean	Upper limit	mean
d(µm)	36.53	37.09	37.66	37.59
SD(µm)	8.953	9.048	9.112	8.967

Table 3. Particle Size Distribution of NIST SRM 1003b

Table 4 lists results for the submicron trimodal mixture, including the recovered means and volume percentages for the three modes. The size distribution as measured by the LS 13 320 is displayed in Figure 2 and a SEM photo showing the particles is accompanied in Figure 3.

$d_{certified}$(nm)/V%	d_{LD}(nm)	$V\%_{LD}$
83±2.7(nm)/50%	74	55
204±6(nm)/25%	218	24
503±4(nm)25%	504	21

Table 4. Results for submicron trimodal mixture

Clearly the accuracy for complex samples is not as high in the submicron region as it is for larger particles. The recovered volume percentages are skewed towards the 83 nm component, and the two smaller components show errors in mean diameter that are larger than any errors found for single mode standards or the large-particle mixtures. The mean diameter of the 503 nm component was recovered without error. Historically, however, laser diffraction instruments have not been able to distinguish the separate modes in submicron samples such as these, but the PIDS system in the LS 13 320 now permits successful analysis of complex submicron distributions.

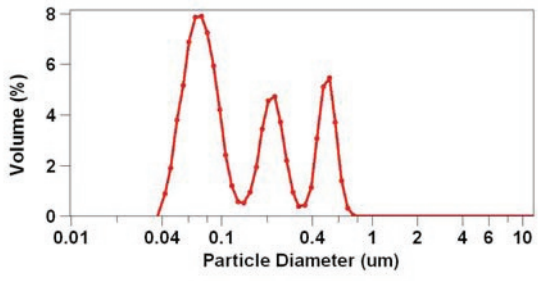

Figure 2. Trimodal mixture of NIST traceable PSL analyzed on the LS 13 320

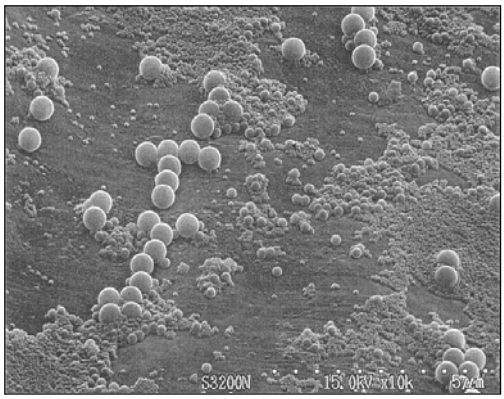

Figure 3. An SEM picture of the trimodal sample

TRACEABLE DATA

The expanding implementation of quality systems is evident in the upsurge of IS0 9000:2000 registrations within industry throughout the world. Quality policies dictate validation and verification of both instruments and products. When considering the purchase of a particle size analyzer, the accuracy of the instrument is therefore of paramount concern. Never before has it been so critical that data measured with analytical instruments be traceable to standard reference materials. The availability of particle size standards traceable to national and international standards makes testing an instrument for accuracy a relatively easy task.

Although the cost of traceable standards may seem high relative to non-traceable alternatives, the difference is small compared to the cost of a particle sizing instrument, and completely insignificant compared to the cost of purchasing an unreliable instrument with the implications unreliable measurements have for end-product quality. The performance of the Beckman Coulter LS 13 320 relative to traceable standards indicates that the instrument can be used with confidence, and that the particle size distributions it produces accurately reflect the sample material.

REFERENCE

Xu R. Reference Materials in Particle Measurements, in *Liquid and Surface Borne Particle Measurement Handbook*, Eds. J. Knapp, etc., Marcel Dekker, New York, 1996, Chapter 16, p709-720

Xu R. Particle Size Analysis Using Laser Scattering, in *Liquid and Surface Borne Particle Measurement Handbook*, Eds. J. Knapp, etc., Marcel Dekker, New York, 1996, Chapter 18, p745-777

USA, Fullerton, CA (1) 800 742 2345 **USA, Miami, FL** (1) 305 380 3907 **Email** pc-sales@coulter.com
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