THE LANGUAGE OF PARTICLE SIZE

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KEY POINTS

The following key points are discussed:

- Knowledge and understanding of particle size data are vital to practitioners in the pharmaceutical, mining, environmental, paints and coatings, and other industries.
- The vocabulary of particle size is unique and complex. Clear understanding of terminology is necessary for correct interpretation of data.
- Graphical representation of particle size distributions by histogram and / or cumulative distributions is fundamental. Distributions may also be expressed by various percentile notations.
- Laser light scattering and other instrumentation report particle size distribution data in terms of equivalent spherical diameter.
- Data from various instruments may be expressed as a number distribution or a volume distribution.
- A listing of relevant particle size terminology and definitions is provided.
- Important details associated with the interpretation and understanding of particle size data are discussed.
- Correct interpretation of particle size analyses is rooted in an understanding of distributions and the associated statistical descriptive terminology.

INTRODUCTION

Most practitioners in the pharmaceutical, mining, environmental, paints and coatings, and other fields have reason to know the sizes of particles in a given powder or slurry sample. While many technologies exist to describe that collection of sizes, the reports delivered by those technologies are written in their own vocabulary. This particle size lexicon can convey a tremendous amount of information as long as the terms and their definitions are clearly understood and their underlying assumptions are fully considered. This discussion introduces the common values encountered on a typical particle size report and provides references for deeper mathematical interpretations. With this information in hand, the reader will be well-equipped to judge compliance.

THE PARTICLE SIZE DISTRIBUTION AND ITS REPRESENTATION

A fundamental concept to understand is that any accumulation of particles larger than molecular scale actually contains many different sizes of particles (1). Thus the term distribution is applied. In this way, it is acknowledged that a collection of particulate contains a continuous range of sizes. A collection of particles having a single size is only attainable with meticulous classification effort.

In order to represent the size range, a frequency diagram or histogram is typically produced. The histogram is a bar graph wherein the x-axis represents the particle size.

The vertical height of the bars (the y-axis) represents the relative amount of matter contained at that size, or the frequency of occurrences. ISO 9276-1:1998(E) (2) describes the plotting procedure in detail.

A sieve analysis demonstrates the concept. A free-flowing powder sample is introduced to the top of a stack of six sieves having graduated mesh sizes, closed by a solid pan at the bottom. After completing the requisite agitating methodology, some portion of the original sample rests on each sieve, with the finest portion falling all the way through to the pan at the bottom. Hypothetically, the data could resemble Table I.

TABLE I. SIEVE RESULTS

Sieve Size (Length Units)	Amount Retained on Respective Sieve (Weight Units)	Incremental Weight % Retained
60	0	0/220 = 0%
50	5	5/220 ≈ 2%
40	30	30/220 ≈ 14%
30	150	150/220 ≈ 68%
20	30	30/220 ≈ 14%
10	5	5/220 ≈ 2%
Pan	Trace	0/220 ≈ 0%
	Sum = 220	Sum = 100%

The sieve sizes are plotted on the x-axis, while the calculated Incremental Weight % Retained on each sieve governs the height of each bar (y-axis point). In this case, convention is to plot the height at the center of the size bin, i.e. 68% weight between 30 length and 40 length, at 35 length units. Instrument software can often be customized, however, so it is important to check the output settings. The Beckman Coulter laser diffractors, for example, give the option to print data at the left, right, or center of the size bin. As a result, this should be kept in mind when evaluating results with respect to Certificates of Analysis specifications, or when cross-comparing two datasets from different labs.

The histogram for the Table I sieve dataset above follows in Figure 1.

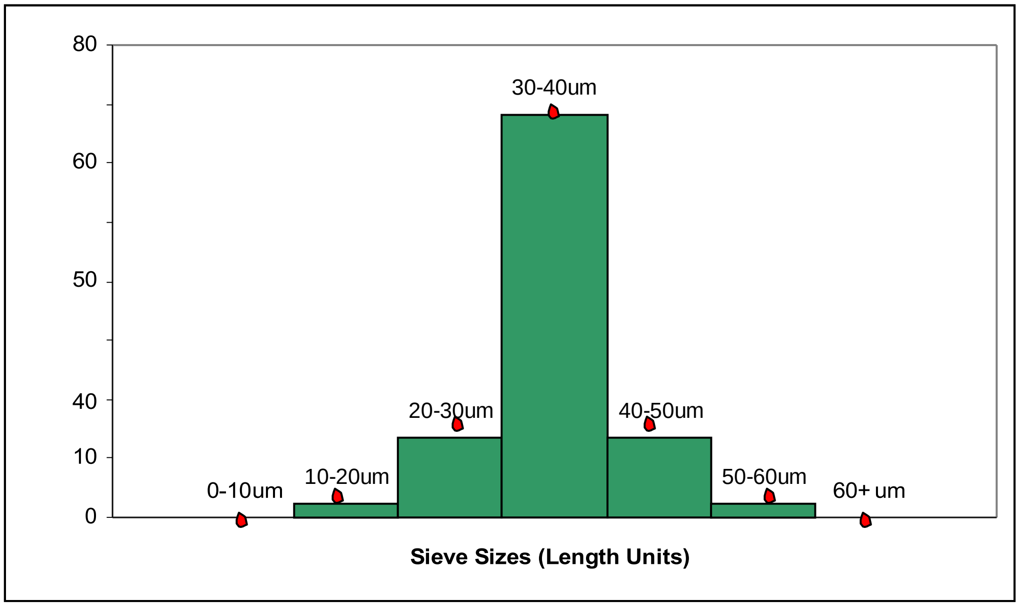


FIGURE 1. Histogram based on Table I.

Note there exists an amount of material between two sieve sizes. This size range is called a size bin. Bins are represented by the width of the bars in the histogram. In an instrumentation output, the size bins (or channels) are typically predefined and numbered consecutively. Each detected occurrence is “filed” into the appropriate section (3). The number of bins or channels in the output indicates the resolution of the instrument.

The size bins may be wide or narrow, depending on the resolution of the data. Increasing the resolution in this example would be the equivalent of inserting more sieves into the stack. The overall size range remains the same, but the number of data points collected within that range increases. As the number of data points increases, the bins narrow smaller and smaller and the graph tends toward a smooth line. To obtain a graph made up of only points on a smoothed line, calculate the Cumulative % Retained as in Table II. The resulting Cumulative distribution is shown in Figure 2 (1).

TABLE II. SIEVE RESULTS, INCLUDING CUMULATIVE CALCULATIONS

Sieve Size (Length Units)	Amount Retained (Weight Units)	Incremental Weight % Retained	Cumulative Weight % Retained	Cumulative Weight % Passing
60	Trace	0/220 = 0%	0	100-0 = 100%
50	5	5/220 ≈ 2%	0+2 = 2%	100-2 = 98%
40	30	30/220 ≈ 14%	2+14 = 16%	100-16 = 84%
30	150	150/220 ≈ 68%	16+68 = 84%	100-84 = 16%
20	30	30/220 ≈ 14%	84+14 = 98%	100-98 = 2%
10	5	5/220 ≈ 2%	98+2 = 100%	100-100 = 0%
Pan	Trace	0/220 = 0%	100+0 = 100%	100-100 = 0%
	Sum = 220	Sum = 100%		

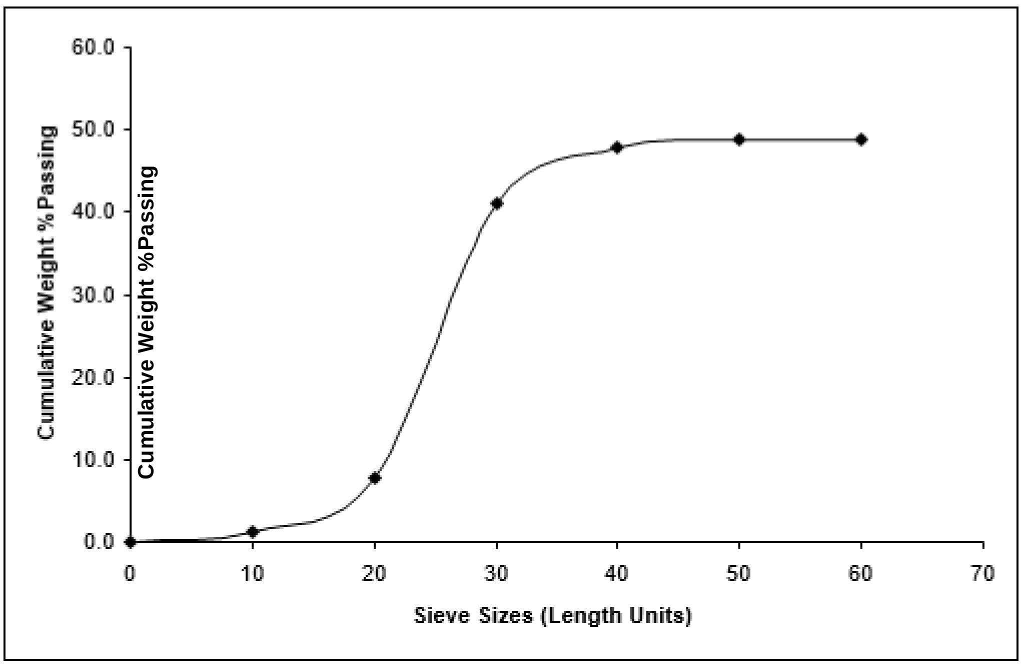


FIGURE 2. Continuous Cumulative Curve.

In order to convert a cumulative curve back to a continuous incremental distribution, take the derivative of the cumulative curve with respect to size (2). Figure 3 shows the result of this process, including higher resolution. Here, the bins are aligned at the left-hand side with each x-axis value.

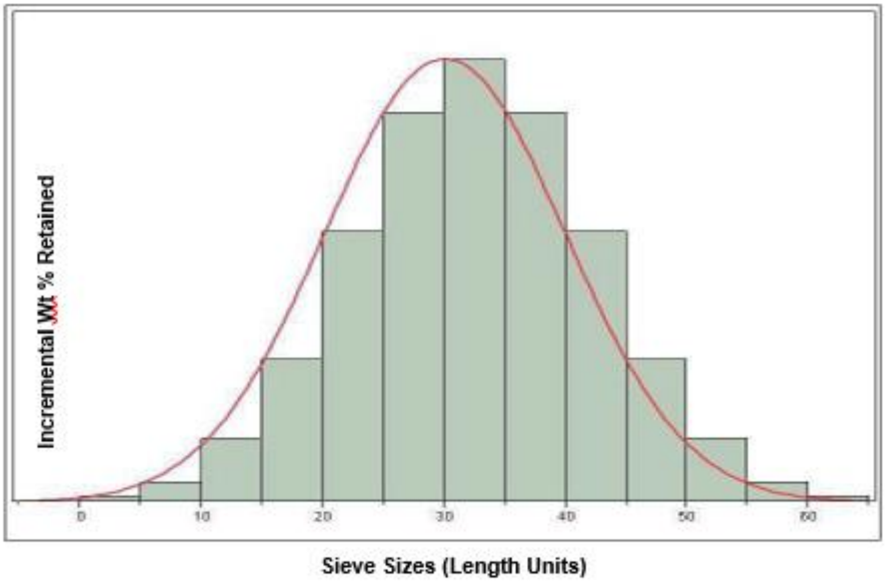


FIGURE 3. Continuous Incremental Distribution: Derivative of the Cumulative Distribution.

Reviewing Figures 1-3 shows that all data have been plotted on linear x-axes. Some readers may have encountered particle size data plotted with the x-axis on a log scale. The log scale adds convenience for several reasons. According to Brittain, applying a log scale to the x-axis helps to convert leaning or skewed linear histograms into a more normal or Gaussian shape (1). Also, the equal distance spacing between size bins on a linear scale can produce cumbersome graphical representations of the widely distributed data often encountered in particle size measurements. Use of a log scale thus manageably compacts the data presentation (2).

EMBEDDED MEANING IN THE NOTATION

Particle size reports use notation specific to the field that may not be intuitive. The following are common terminologies associated with particle size data presentation.

Percentiles are of utmost importance. The shorthand is usually written as 'd' or 'x' with a subscripted number referring to a percent. For example, d50 or x50 refers to the 50th percentile, meaning the diameter of a sphere at which 50% of the particles in the sample are smaller. ISO 9276-1:1998(E) (2) specifically indicates that d is interchangeable with x. Other terminology for the same value is D(v, 0.5). The v represents a volume weighted basis, in this example.

Similarly, d10 = x10 = the 10th percentile = the diameter of a sphere at which 10% of the particles in the sample are smaller; on a volume basis = D(v, 0.1), and so on.

Other details in the notation can change as well. D(n,0.1) = the diameter of a sphere at which 10% of the particles in the samples are smaller on a number basis. The 'n' indicates the basis.

Most instruments default to a percent smaller (or "<" or "less than") basis. However, this can be typically changed by the operator depending upon the desired output. Keep this in mind when evaluating results for comparison to specifications or other datasets.

EQUIVALENT SPHERICAL DIAMETER

Particle size results from an assortment of instruments are reported in the form of a histogram. However, the graphs are developed more indirectly than the direct weighing technique described earlier in the sieve example. A very commonly used output is that of laser light scattering (laser diffraction). This technique, along with numerous others described in detail by Allen (4), defaults to reporting in terms of Equivalent Spherical Diameter [or Volume Weighted **Equivalent Spherical Diameter** for laser diffractors]. This phrase is critically important to assess the possible subtleties underlying a particle size measurement result.

- Particles reported using this assumption will pass through the same sized aperture as the equivalent sphere (sieving)
- Will settle at the same velocity as the equivalent sphere (sedimentation)
- Will scatter light at the same intensity at the same angle as the equivalent sphere (laser diffraction)
- Will displace the same volume of liquid as the equivalent sphere (electrosensing zone).

The reason the concept is so common in the field is due to the extreme programming requirements of the electronics used and the extensive dataset that would be generated if information could be collected on all possible dimensions. Visually, the human eye can distinguish several dimensions within a single irregularly- shaped particle (see the diagrams by Brittain [1]). However, the end user is expecting a “short answer.” How can a rod, for example, with one long axis and one short axis, or even corner-to-corner within the rod, be defined in a single number?

The custom is to describe a singular feature of the particle which can be mathematically converted back to the dimensions of a sphere, the only three-dimensional shape which has truly one measurement in all directions— its diameter (d). Some such singular features are weight, surface area, or volume of the rod. Each can be described with one value regardless of how different the axes are from each other. As such, the volume (for example) of a rod (or cylinder) is

$$V_{rod} = \pi r^2 h$$

where r is the radius of the end circle (r is half of the circle’s diameter, or d/2), h is the height of the rod, and V is the volume. Instead of needing to know how wide and high the rod is, one can simply determine V (say 33.5 µm3), then equate that to the volume of a sphere

$$V_{sphere} = \frac{4}{3}\pi\left(\frac{d}{2}\right)^3 = V_{rod}$$

By doing so, one eliminates the two variables r and h, and obtains a single value for the diameter (d = 4 µm in

this example). This diameter is that of a sphere having the same volume as the original rod, which had several different linear dimensions. The programming and reporting becomes far more manageable. Rawle (6) thoroughly describes the concept and all its implications in his technical paper.

The primary message to take away is to know something about the shape of the measured particulate. This will help with interpretations of the measurement technique results and their effect on the detected size. Shape information is usually evaluated using a microscope or by image analysis.

The National Institute of Standards and Technology (NIST) gives an exhaustive list of definitions of diameters delivered by different measurement techniques (7). The differences are subtle but important in data interpretation. An example is that the flow paths the particles follow during certain analyses will tend to align elongated particles, thereby presenting only maximum dimensions to the detectors (which normally assume tumbling in random orientation). This can bias the results large when considering the back-calculation to equivalent spherical diameter.

NUMBER DISTRIBUTIONS VS. VOLUME DISTRIBUTIONS AND OTHERS

The sieve example at the beginning of the article reported results in terms of weight. This directly-measured reporting basis, however, is uncommon for most modern analysis techniques. The frequently encountered terminology is either volume basis or number basis. Laser light scattering (laser diffraction) defaults to a volume reporting structure, as does sedimentation. A histogram produced in this way reads as “x% of the particles at the detected size occupy this much volume.” The histograms typically resemble a bell-shaped (normal or Gaussian) curve in which a majority of the volume is occupied by the mid-range sized particles. It may be difficult to conceptualize, but it has become standard language due to the direct output of the instruments.

Laser diffraction, sedimentation, and several other forms of particle sizing techniques do not count or assign size to individual particles. These techniques look at a measured property via a cloud or assemblage of particles, and are thus termed “ensemble analyzers.”

Other techniques such as electro-sensing zone (Coulter) and light obscuration are designed to truly count particles one by one and report the size of each. In this way, an actual number distribution is developed. A typical number distribution genuinely shows the huge amount of fines present in the system, and it often grows exponentially to be cut off by the y-axis at the technique’s lower detection limit. This is important to note when evaluating data. An abrupt end to a distribution does not typically indicate an absence of particulate below or above the designated size (unless, for example, it has been sieved) but generally indicates a detection limit of the instrument or technique.

Computerized instruments are programmed to convert from their base outputs (microscope = number, laser diffraction = volume) to the other presentation formats as detailed mathematically by Stintz (8). These conversions should be regarded with caution, as the exponents in the equations are also applied to the inherent error in the measurements, multiplying the error quickly (9).

To visualize a practical example of the difference between a number-based distribution and a volume-based one, start by imagining a fruit basket. Only one huge juicy watermelon will fit in it, but plenty of small round grapes can nestle into the nooks and crannies. The number distribution counts far more grapes (fines) than watermelons (coarse), but the volume distribution clearly shows that the watermelon occupies far more space than the entire collection of grapes that are scattered around, fitting in where possible. Giving these fruits some dimensions, it can be said it only takes a single particle of 100-micron diameter to occupy the same space as one million particles of 1-micron diameter!

$$1 \times (100\mu m)^3 = 1{,}000{,}000 \times (1\mu m)^3$$

On a volume-based distribution, the coarse particulate volume far overshadows that of the fines in a normally distributed sample, so the fines can easily be overlooked. A particle counter, which provides a number-based distribution, will report the true story if fines are of critical import. Once again, this concept is of vital importance when setting specifications, interpreting data, or investigating processing issues.

DEFINING TERMS GIVEN BY THE INSTRUMENT OUTPUTS

The values above can be categorized in terms of their exponent: linear (first dimension or number) and cubic (third dimension or volume.) Area would be square (second dimension.) These have great importance in mathematically describing all typical terms reported by particle sizing instruments. A basic statistics text could describe all of the following in terms of mathematical formulae.

The most basic terms describing the key points of a distribution curve are as follows:

- **Mode** – the most commonly occurring signal or size, also known as peak diameter.
- **Median** – the signal or size at which exactly half of the responses are below and half of the responses are above. On a cumulative distribution, d_{50} is the median.
- **Mean** – the average.

A **normal** (or Gaussian) **distribution** has identical values for mode, median, and mean. It is also possible to find two completely different shaped curves having the same values for mode, median, and mean.

Many different means can be calculated:

- **Arithmetic Mean** is the first dimension average, the one learned in grade school. It is the sum of all values divided by the total number of values.

$$\textbf{Arithmetic Mean} = \frac{\sum_{i=1}^{n} x_i}{n} = \frac{x_1 + x_2 + \ldots + x_n}{n}$$

- **Geometric Mean** uses multiplication instead of addition as in the arithmetic mean, so a root must be taken to return back to a base value. Geometric means are most appropriate when data is highly skewed (as in most particle size distributions) because they tend to dampen the effect of extremes in the data (10). They are especially apt when a change in data occurs relative to a change in some other factor (e.g. the amount of particulate on a filter relative to the flow rate through the filter). Data on a log scale (as in particle size reports) is a giveaway that the statistics are given in geometric terms in many instances.

$$\textbf{Geometric Mean} = \left(\prod_{i=1}^{n} x_i\right)^{1/n} = \sqrt[n]{x_1 \times x_2 \times \ldots \times x_n}$$

Weighted Means (Moment Means), the basis on which the data are presented (i.e. Number, Area or Volume) can influence the mean value relative to a traditional arithmetic mean. Examples are as follows:

$$\textbf{Number [Population] Mean = Arithmetic Mean} = D[1,0] = \frac{\sum d}{n} = \frac{\sum d^1}{d^0}$$

$$\textbf{Surface [Area] Weighted Mean} = D[3,2] = \frac{\sum d^3}{\sum d^2} = \text{Sauter Mean}$$

$$\textbf{Volume Weighted Mean} = D[4,3] = \frac{\sum d^4}{\sum d^3} = \text{default output from laser diffraction}$$

The numbers within the brackets are translated to variables p and q in the literature and are the generally accepted terms by the International Organization for Standardization (ISO). The abbreviated notation D[p,q] is defined by assigning values to p and q that correspond to the exponents in the formulae. When the difference between p and q is equal to 1, an arithmetic mean is represented. When (p – q) > 1, the mean is geometric.

Weighted means are measures of central tendency, meaning they behave like a center of gravity: the weighted mean is the centerpoint around which the distribution would rotate (6,8). It is interesting yet intuitive with practice to note that the volume mean is always greater than the number mean, unless one is dealing with a perfect Gaussian curve. Also, the broader the distribution, the greater the difference between the two values (11). Rawle gives a thorough and easy-to-understand description of various means, when they are applicable, and which instruments report them (12).

The following are other definitions to describe the shape of the distribution curve:

- **Standard Deviation** – an indication of the spread of the curve about the mean.

- **Variance** – the square of the standard deviation; therefore also an indication of the spread of the data points. When two factors act together to cause variability in a distribution, their standard deviation is a square root function. Squaring it to obtain a value is therefore convenient in certain applications (13).

- **Coefficient of Variation** – another indication of the spread of the data, this one being normalized so it can be used to compare datasets having very different means. Coefficient of variation is defined as the ratio of the standard deviation to the mean. Sometimes the ratio is multiplied by 100 to report the coefficient as a percent; in any case the value is always dimensionless. When reported as a percentage, it is commonly called the **Percent Relative Standard Deviation** or %RSD.

- **Skew (Skewness)** – an indication of how far the distribution deviates from symmetry. A normal (Gaussian) distribution has 0 skew. A distribution that "leans" to the right with a long tail at coarse sizes and with mean > mode has positive skew, and the value will increase with increasing lean. A distribution that "leans" to the left with a long tail at fine sizes and with mean < mode has negative skew (see Figure 4.)

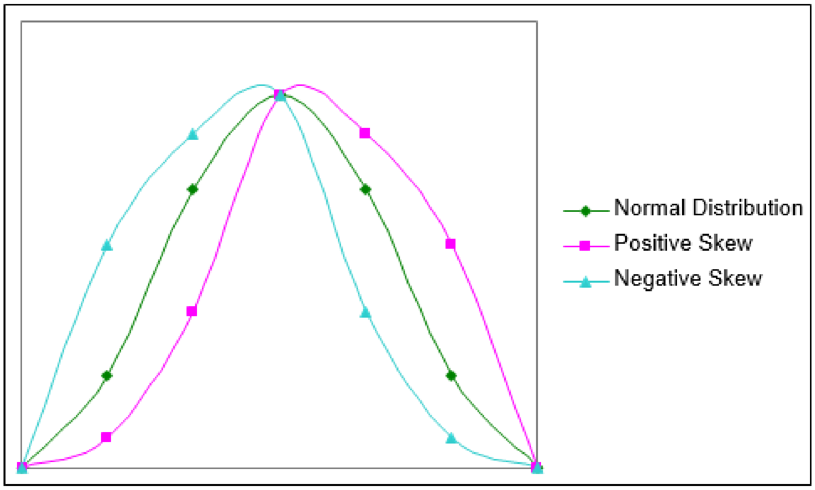
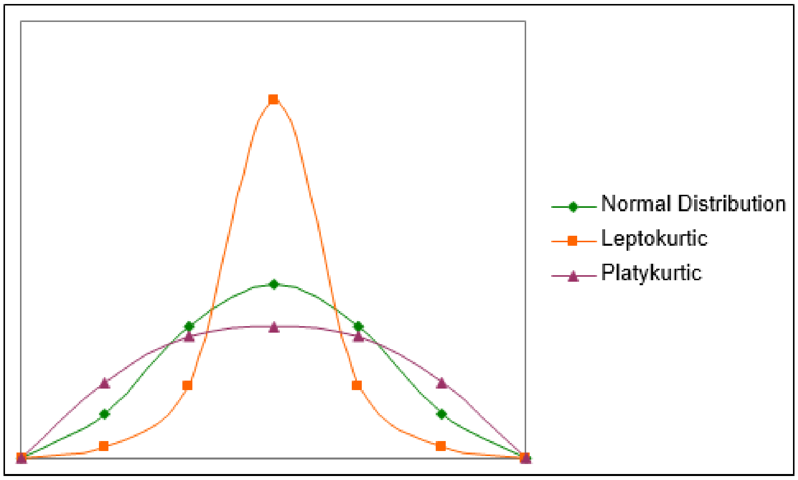


Figure 4. Examples of Skew.

Kurtosis – an indication of how sharply peaked the distribution plot is compared to a normal (Gaussian) distribution. If the peak is very narrow and sharp with most particles having a size close to the mean, the distribution is **leptokurtic** and the kurtosis is large. If the peak is broad, flat, and shaped like a plateau, the distribution is **platykurtic** and the kurtosis is small (14) (see Figure 5).



Span – an indication of the width of the distribution. Span is the distance between two points equally spaced from the median. A commonly reported span is as follows:

$$Span = \frac{d_{90} - d_{10}}{d_{50}}$$

Uniformity – usually grouped with span, a ratio of the absolute distances between data points to the distribution stretch from the median.

$$Uniformity = \frac{\sum V_i |d_{50} - d_i|}{d_{50} \sum V_i}$$

APPLYING THE LESSONS

Allen reminds all practitioners to use a measurement technique that reports a result having properties relevant to the application anticipated for the material of interest (4). Recalling that the equivalent spherical diameter reported by various instruments may be based upon settling, aerodynamic movement, or area of a shadow being cast, it becomes very important to consider that, although sizes are being reported in terms of equivalent spheres, they may not actually behave as spheres in the particular application or processing environment. A catalysis application should focus on a surface area weighted result, for example. An evaluation of contamination will use information related to number. Knowing and understanding the basis behind the reports is, as they say, half the battle.

DETAILS TO REMEMBER

The following details are important to remember:

- The alignment of the data point with the left, right, or center of each bar in the histogram can be changed by the operator in some software platforms. It implies whether the result is below or above the corresponding size.

- The x-axis in most instrumental particle size reports is logarithmic largely because it allows for a greater range of sizes to be represented; the log means that all statistical calculations are delivered on a geometric basis in most cases.

- The equivalent spherical diameter concept allows for complex shapes to be represented in single- value terms. It also makes the computer programming far more manageable.

- Because the particles being measured are not typically spheres, they may not behave as spheres would in a manufacturing process, ascension up a smokestack, or analysis method. Therefore, the particle size measurement report should include caveats describing possible areas of discrepancy due to influences of shape where applicable.

- True Number (or population) distributions grow exponentially toward the fines in most sample types unless they are classified or intentionally produced. They can never actually show all particles present because the lower detection limits of particle counters restricts the level of measurement.

- Particle size analyzers (ensemble analyzers) that are not true counters can only convert a distribution mathematically from volume or area to number, so the resulting number distributions are incomplete with a high degree of error. As a result they should not be used as a basis for specification. If number-weighted statistics are required, a direct particle counting technique should be used.

- While interpreting volume distributions, it is important to remember that the fine particulate can be overwhelmed by the coarse, so the fines may not be seen at all in the histogram. Conversely, if an amount of fines are discernible in the distribution, it indicates that a significantly large amount of fines are present in the sample in order to command a presence alongside the coarse.

- Unless otherwise indicated, the statistical measures reported on the data as d90, x50, etc. represent the particle size at which i% of the population of particles are smaller or less than that size.

- Understand the critical properties needed for your application, and then choose the measurement technique that is best suited to deliver that answer.

CONCLUSION

The successful study of particle size analysis is rooted in an understanding of distributions and the statistical terms describing them. A report can give a wealth of information on a single page. It is important to understand the assumptions behind the descriptions, as well as the inherent features of the measurement techniques, in order to choose the appropriate particle size measurement for your application. After the analysis is complete and the numbers are presented, every detail is important. From these, an astute evaluator can determine whether the material indeed complies with the established specifications.

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