

Particle Characterisation

SETTING THE STANDARD – THE DEVELOPMENT OF PARTICLE SIZE REFERENCE STANDARDS

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In today's world of high precision, automated particle size analysis, it is still quite surprising that the quality of the data is often evaluated by the quality of the presentation. In other words, a high resolution colour print-out can be more believable that a hand drawn graph.

One of the first fully automated particle size analyser was the Coulter Counter, which rose to prominence in the 1950's, hitherto, results from techniques such as microscopy, sieving and sedimentation all had to be plotted by hand.

"IT'S NO USE HAVING THE BEST CAR IN THE WORLD IF YOU DON'T KNOW HOW TO DRIVE IT!"



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By the mid 1970's, particle size analysis by low angle laser light diffraction burst onto the scene and has risen to become one of the most popular methods in particle metrology laboratories today.

Laser diffraction benefited from a convergence of two important new technologies, the synergy of which caused such a dramatic impact in the field of particle size analysis.

The first was the industrial application of lasers. The excitement generated by films showing lasers cutting through steel sheet or knocking out satellites was immense.

The second new technology was the development of the personal computer. It was now possible to perform complex calculation on the laboratory bench rather than have to go to the 'computer room'. Not only were the calculations performed instantly, but tables and graphs could be beautifully printed out in seconds. And therein lay the problem.

Suddenly, financial directors rather than scientists had the final say on purchase just because the instrument looked good for visitors to the laboratory. As the old saying goes 'it's no use having the best car in the world if you don't know how to drive it'. Some of the more negative reactions were that lasers should stick to what they do best – removing tattoos!

It soon became very obvious that particle size analysers should not only look good, but they should give the right results.

Particle size standards first came into prominence with the invention of the Coulter Counter. In this technology, electrical signals from particles were sorted into channels, which had to be calibrated using narrow particle size latex particles.

The problem with latex standards for laser diffraction analysis was that they were too narrow in size distribution. While they are ideal for setting up the laser optical bench, they did not represent a realistic or typical broad distribution powder.

Recognising the limitations of the latex standards, the Bureau of Certified Reference based in Brussels developed a new set of industrial standards in 1980. These were based on crushed quartz, which was classified into fractions from about 1 micron up to 650 microns. The BCR quartz standards were analysed by a manual sedimentation process called the Andreasen Pipette.

Unfortunately, when the BCR standards were analysed by the new laser methods, large differences from one instrument to another were seen. The differences were attributed to a number of factors including: inhomogeneous optical properties in the quartz, complex scattering from the irregular particles and, perhaps most importantly unrepresentative sampling from the large weights supplied in each bottle.

The BCR therefore decided to bring out a new set of spherical reference standards to 'mirror' the original set of quartz standards but this time they were to be analysed by a number of 'primary' particle sizing methods.

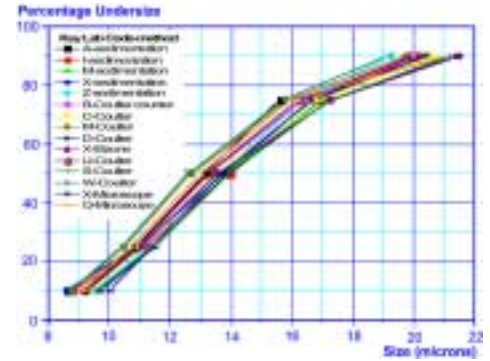


Figure 1. Primary Methods of Particle Size Analysis

A primary method is defined as one where the dimensions of length and weight are directly traceable to International Standards and do not depend on second order effects such as diffraction patterns, turbidity, elutriation, Brownian Motion or computer modelling. Furthermore, fully validated or prescriptive methodologies were developed to reduce the possibility of operator bias.

The five primary methods of particle size analysis were:

1. Optical Microscopy
2. Electroformed Sieve Analysis
3. Electrical Sensing Zone (Coulter)
4. Gravitational Sedimentation
5. Centrifugal Sedimentation

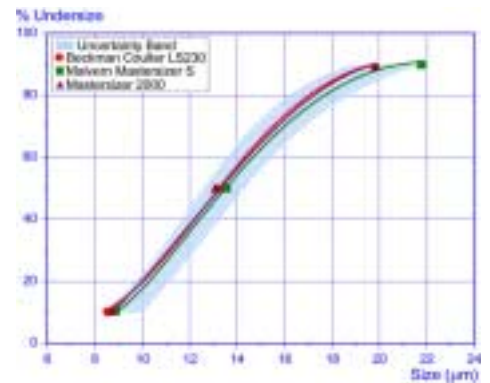


Figure 2. Laser Diffraction Analysis of a Reference Standard

In order to select the best laboratories from 40 applicants, Whitehouse Scientific produced a duplicate set of standards made from spherical glass particles. When analysed by the above 'primary' methods, very close agreement was found with all the primary methods.

There was now for the first time a precision set of polydisperse reference standards, whose size did not depend on the method of measurement. Provided a rigorous method of sample preparation was employed, laser diffraction analysis produced results indistinguishable from the primary sizing methods.

Laser diffraction particle size analysis now not only produced impressive graphics, but also gave highly accurate results.



Figure 3. Glass microspheres for Sieve Calibration

The next challenge was for the users to match the performance of the manufacturers.

It cannot be emphasised enough, but the single biggest problem in particle size analysis is in obtaining a representative sample. A close second is running the instrument in a systematic and rigorous way.

One of the problems with the BCR quartz samples was that they were sold in bottles containing up to 10g. During transit, large particles could settle to the bottom of the bottle, so taking a sample from the top not only gave an erroneous result because a smaller size fraction was being analysed, but the remaining particles in the bottle were no longer representative of the original size distribution supplied by BCR. This problem was never seen with the monodisperse latex standards because all the particles were more or less the same size.

Today most particle size instrument manufacturers will supply polydisperse standards in single shot bottles produced from a spinning riffler; the most accurate method of producing identical distributions in polydisperse standards. Using single shot bottles minimises sub-sampling errors from larger weight bottles.

Malvern for example has commissioned a reference standard programme capable of producing up to 2.5 million bottles in weights from 0.1 – 2.5g. The stock is expected to last at least 15 years, thereby giving excellent continuity in critical industries such as pharmaceuticals.

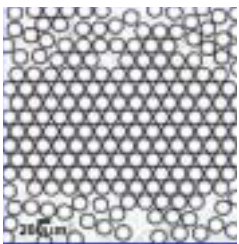


Figure 4. Monodisperse Particle Standards

Whatever the method of size analysis used, the provider of the results must be able to prove traceability to an international unit of length such as the National Institute of Standards and Technology (USA) or the National Physical Laboratory (UK).

It is interesting that the rigours developed in proving the accuracy of the laser diffraction method have spread, not just to traditional methods of size analysis such as microscopy and sieve analysis, but to some of the latest methods that can measure shape as well as size.

NIST and NPL traceable particle size standards, both monodisperse and polydisperse, are now available for most methods of particle size analysis including sieve analysis, microscopy, sedimentation, Coulter Counting, laser diffraction and the most recent method, image analysis.

Image analysis has been accelerated by the advent of high speed computers and video cameras. One of the problems with most method of particle size analysis is that particle size is reduced to a single parameter, the equivalent spherical diameter.

Powder properties, in particular flow rates, can be very dependent on the shape of the particles. For example, glass beads will flow much faster than needle-like particles.

The major advantage of the microscope is that it is the only method where actual particles can be seen. The disadvantage is that only milligram quantities are required for an analysis. In order to obtain accurate results therefore, a representative sample must be taken and sufficient particles counted to give a statistically robust analysis. For a 10:1 ratio of particle sizes, BCR recommends that at least 6,000 particles are counted.

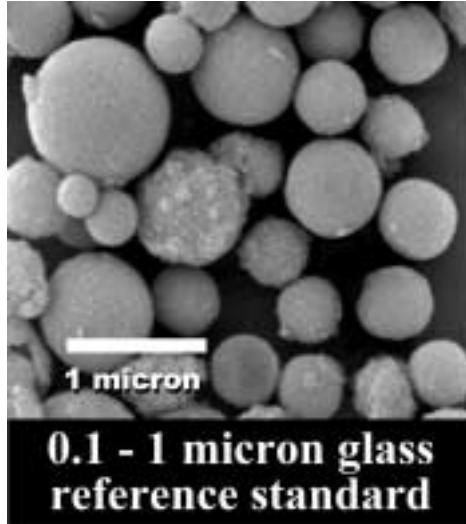


Figure 5. Sub Micron Polydisperse Standards

It is now possible with the latest image analysers to count millions of particles in flight or in a passing suspension, and provide fine detail on shape at a very high resolution.

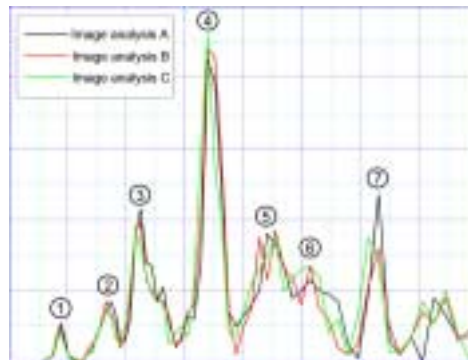


Figure 6. A 'Finger Print' Reference Standard for Image Analysis

Consequently, some image analysis manufacturers are asking for standards to be produced with fine 'finger print' distributions comprising of a cocktail of monodisperse peaks over a wide particle size distribution.

The days are now long gone when a well designed print out was all that was required in support of particle size data. As the quality control in all industries is being improved every year and with every new instrument being introduced, all data must be traceable to international units of length. All particle size analyses whatever method, from sieves to lasers, must therefore be backed up by performance measurements against an independent particle size reference standard.