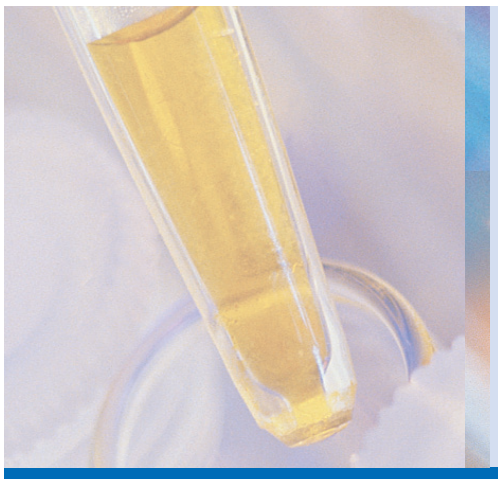


Spotlight: Particle Characterisation

PARTICLE SIZE CALIBRATION STANDARDS - KEEPING UP WITH TECHNOLOGY

Dr G R Rideal

Quartz reference standards for particle size analysis were produced by the European Community over 20 years ago and coincided with the development of laser diffraction methods of particle size analysis.

However, for a number of reasons, some of the early instruments produced equivocal results. These included poor sampling from the large pots, the inhomogeneous optical properties of the quartz and incorrect application of diffraction theory.

Existing monodisperse microspheres used in calibrating Coulter Counters produced better results but were not a challenging reference standard because they had such a narrow size distribution.This short review follows the development of particle size reference standards in line with the latest automated particle sizing instruments.

"10,000 PARTICLES WERE MEASURED BY MICROSCOPE, WHICH PROVIDED DATA MOST SUITABLE FOR THE COULTER COUNTER"

Author Details:
Dr G R Rideal
Whitehouse Scientific Ltd
Chester, UK

MONODISPERSE MICROSPHERES

One of the earliest methods of particle size analysis, which combined both high speed and a degree of automation, was based on the Electrical Sensing Zone method, more commonly called the Coulter Counter.

This high-resolution method, still available today, uses electrical pulses produced as particles flow through an orifice to determine particle size, *Figure 1*. The area under each pulse is directly proportional to the particle volume and is assigned to a number of channels. To convert the area of the pulse to a particle size, the channels are calibrated using monosized microspheres, usually a polymer latex. At least two and sometimes three polymer standards are required to calibrate a useable dynamic range of the instrument.

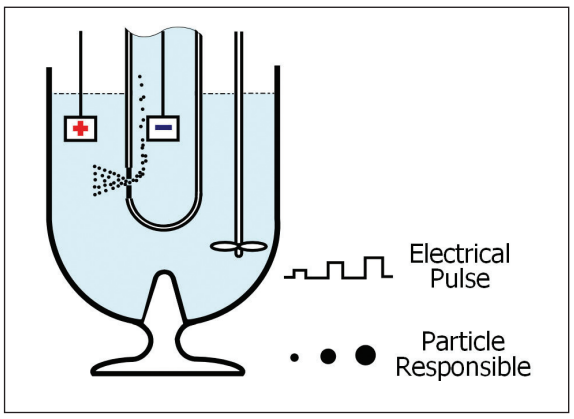


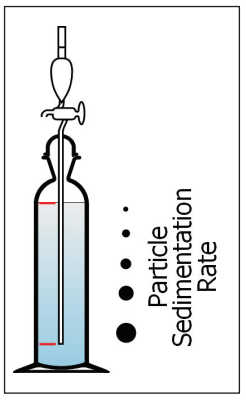
Figure 1. The principle of the Coulter Counter

One criticism levelled against the mono-disperse standards for non ESZ instruments however was that they were too idealistic and did not represent real materials encountered in particle metrology. Most powders found in industry are polydisperse ie. have broad particle size distributions.

POLYDISPERSE MICROSPHERES

In response to this criticism, in 1965 the National Bureau of Standards of America, (now known as NIST – the National Institute of Standards and Technology) brought out a series of polydisperse glass microspheres.

These were mainly for calibrating sieves, although the smallest size, 5–30µm, was also aimed at the rapidly developing automated sedimentation techniques as well as the Coulter method.



10,000 particles were measured by microscope, which provided data most suitable for the Coulter counter.

To support the automated sedimentation techniques, the standard was also certified by sedimentation using the Andeasen Pipette, *Figure 2*.

In the event, because the particles were spherical, both sets of data were very similar.

Figure 2. The Andreasen Pipette

The success of the Coulter Counter unveiled a hitherto unforeseen difficulty: obtaining a representative sample from a polydisperse reference standard.

Early methods of size analysis such as sieving required 10's if not 100's of grams of sample. Even the Andreasen Pipette could use up to 10 grams.

By contrast, the Coulter only required about 30 milligrams of the 5–30µm standard for an analysis, microscopy required even less, so very careful procedures had to be adopted to ensure that the sample taken for analysis was representative of the bulk sample.

The standards were used very successfully for a number of years, but a request went out to the standards producers to develop an irregularly shaped polydisperse standard as well as its spherical counterpart.

POLYDISPERSE QUARTZ

The European Community Bureau of Reference (BCR) responded in 1980 by producing a range of standards based on crushed quartz.

The primary method of analysis was sedimentation using the Andreasen Pipette method, although sieving was also used for the largest size. Five standards were produced from 0.3 to 650 microns, *Table 1*.

Table 1: BCR Reference Standards

Size Distribution (µm)	BCR Number's	Weight (g)
0.35 – 3.5	BCR66	10
1.20 – 20	BCR70	10
2.40 – 32	BCR67	10
14 – 90	BCR69	10
160 – 630	BCR68	100

Unfortunately, the standards were only available in weights of 10g and above so the accuracy of the results on instruments requiring much smaller weights depended very much on the ability of the operator to take a representative sub-sample.

Concurrent with the production of these standards was the emergence of Low Angle Laser Light Scattering (LALLS - more commonly referred to as Laser Diffraction) as a powerful method of particle size analysis.

Discrepancies observed when analysing these irregular quartz standards with some of the early Laser instruments were attributed to a combination of the poor resolution of the sedimentation method and the random shape and optical properties, which could affect the diffraction behaviour of the quartz particles.

In addition, there still remained the uncertainty associated with taking a representative sample - the new Laser instruments only required about a gram of sample.

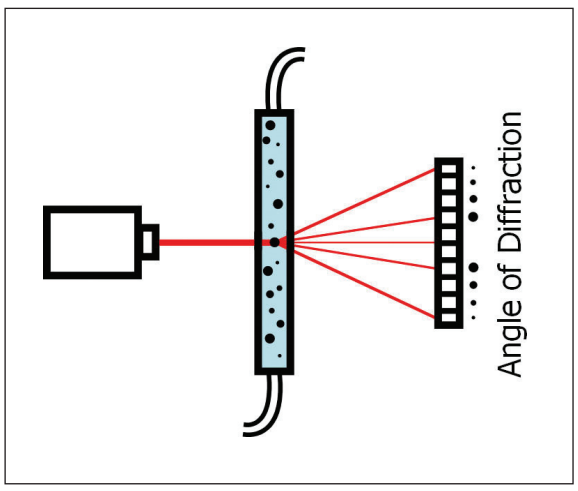


Figure 3. Laser Low Angle Laser Diffraction analysis

THE RETURN OF POLYDISPERSE MICROSPHERES

By the early 1990's Laser Diffraction was becoming a predominant method of size analysis and the quartz standards were seen as increasingly unsuitable for the technique.

The BCR then decided to introduce a parallel series of spherical references designed to overcome the ambiguities associated with the crushed quartz standards.

The standards were to be certified by primary or absolute methods only i.e. methods where size could be linked directly to International standards and did nor rely on secondary effects of the particles such as diffraction patterns, turbidity, Brownian motion, elutriation or computer modelling. The methods specified were: sedimentation (both gravimetric and centrifugal), microscopy and image analysis, precision sieve analysis and the Coulter method.

However, the rapid development of the Laser technique and the consequential requirement for improved quality assurance meant that, by the time the new spherical references were commissioned and made, the demand far exceeded all expectations.

Indeed, at the inaugural meeting at the Commission headquarters in Belgium in May 1993 attended by the leading European particle sizing laboratories, it was predicted by one Laser manufacturer that the entire supply would be used up by his company alone in just 18 months. Unfortunately it was too late to increase the sizes of the master batches.

A duplicate set of standards in much larger weights, which became known as 'Mirror' standards was therefore commissioned. The purpose was not only to dilute the demand for the new standards but also to short-list over 40 particle sizing laboratories who applied to certify the official BCR standards.

Five leading laboratories were selected as consultants to develop prescriptive methods of analysis for each of the five primary methods:

1. Professor K Leschonski (Clausthal TU, Germany) – Andreasen Pippete method,
2. Dr J Lloyd (Loughborough University, UK) Coulter Counter method,
3. H Mercus (Delft TU, Holland) – Electroformed sieve analysis,
4. Professor J Dodds (CNRS, Nancy, France) – optical microscopy and image analysis,
5. Dr G Rideal (Whitehouse Scientific, UK) - Pipette Centrifuge method

Because the samples were spherical and strict sampling guidelines were issued, much improved reproducibilities were observed compared to the quartz analysis, both within a given primary method, and when the results of several methods were compared, see *Figure 4*.

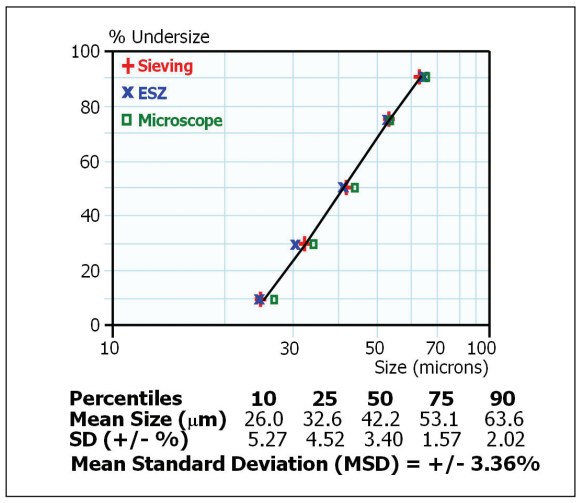


Figure 4. Primary size analysis methods show excellent agreement

MINIMISING SAMPLING ERRORS

Just as many people start assembling flat pack furniture without reference to the instructions, so particle metrologists sometimes take a spatula of powder from a bottle for analysis and are surprised when they cannot achieve the certificated results (Particle segregation in transit is quite common in dry powders, especially as the size increases).

Not only can the extracted sample be non-representative, but that remaining in the bottle may also no longer be representative.

The best way of minimising the sampling errors is to supply the standards in 'single-shot' weights designed specifically for the particle sizing instrument being used. The most efficient subdivision method is the spinning riffler. One of the biggest spinning rifflers used today has 100 stages capable of producing sub-samples as low as 10mg. *Figure 5* shows that the sub samples have virtually identical particle size distributions.

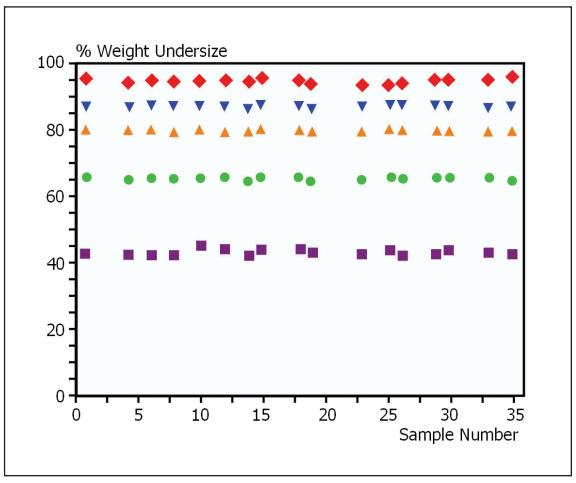


Figure 5. Coulter Counter results from a 100 stage spinning riffler

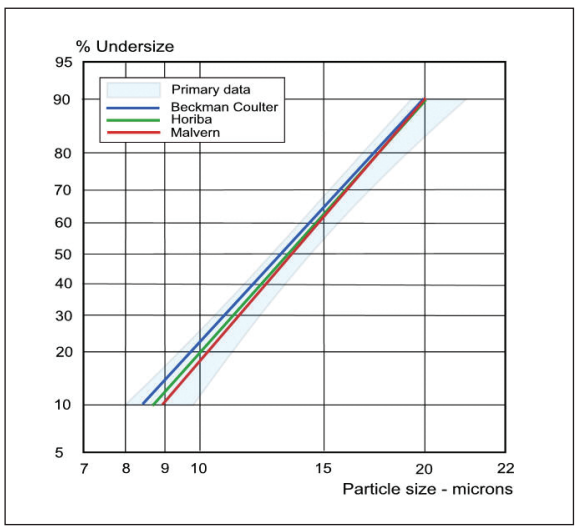


Figure 6. Laser Diffraction results now agree well with certificated results

CONCLUSION

Particle size analysis has come a long way in the last 40 years, but it is no longer sufficient just to get an answer. The answer must be proved to be correct by using traceable particle size reference standards. It is comparatively easy to calibrate with idealised monodisperse spherical standards but the real challenge is to calibrate instruments with polydisperse standards, where the competence of both the instrument and the analyst is tested.

The leading manufacturers of all particle sizing instruments now supply single shot reference standards usually produced by an independent laboratory and very good agreement with the primary methods of analysis is regularly achieved, *Figure 6*. In some cases batches as large as 1000kg, capable of generating over 2 million bottles have been produced to guarantee a consistence of supply for up to 20 years