

The Development of Particle Size Reference Standards

G Rideal and J Storey, Whitehouse Scientific, Chester, UK

Abstract

This paper reviews the production and certification of the first polydisperse glass microsphere standards spanning the size range 1 – 650 microns, initially conceived 20 years ago, which were designed primarily for laser diffraction instruments. Particular emphasis is placed on the primary particle size methods used for certification and the packaging into 'single shot' bottles to minimise sampling errors during analysis. The good agreement obtained between the various primary methods of certification was not always the case for laser diffraction instruments as the results depended on the diffraction theory used, especially for small transparent particles.

One way of eliminating diffraction theory dependent results is to use opaque spherical reference standards. A new 19 – 190 micron standard has shown excellent agreement between particle sizing instruments including lasers, the Coulter Counter and image analysers. Two new 'multimodal' standards have been developed to test the performance of high resolution instruments at either end of the size spectrum: an 8 peak standard between 500 and 2000 microns for Image analysers and a 10 peak standard from 0.1 and 1.5 microns for centrifugal size analysis. Finally, a unique set of sieve calibration standards with a resolution down to 1 micron will be discussed.

1. Background

The Coulter Counter, introduced in the 1950's revolutionised particle size analysis in that it was the first automatic method available. Up to that point, sieving and the Andreason sedimentation pipette were the only routinely used particle sizing methods.

Unfortunately, along with professionally produced charts and graphs came the belief that the results were infallible. Such a view was reinforced in the late 1970's, with the development of the laser diffraction method of particle sizing, which produced much faster results with even more impressive graphics.

It was therefore of paramount importance that new particle size reference standards were available that could differentiate between good and bad results.

Although polymer latex standards provided an excellent method of calibrating the narrow size bands of a Coulter Counter, they were not so suitable for challenging the dynamic range of some of the latest particle sizing instruments and standards with a wider distribution were demanded.

NIST introduced a 5 – 30 micron polydisperse glass microspheres standard in 1965¹ then, in 1980, the Bureau Communautaire de Référence, in Brussels, more commonly known as the Bureau of Certified Reference - (BCR), released a series of broader distribution crushed quartz reference standards with a maximum to minimum ratio of approximately 10:1. These standards were certified mainly by the Andreasen Pipette, although sieve analysis was used for the larger sizes².

As far as they went, these standards were a brave attempt to provide the polydisperse standards demanded by the industry but suffered from a number of disadvantages; the two major ones being, firstly, the pioneering laser diffraction

instruments of the time had varying degrees of success in analysing the irregular shaped, semi-transparent particles and secondly, the 10g bottles were far too large for a single analysis and poor subdivision by the operators often led to a wide scatter in the results³.

Realising that they were being overtaken by events, the BCR responded by embarking on a new programme to produce a duplicate set of spherical reference standards both in clear and opaque glassy materials. Bottle sizes were reduced to 1g but these were still too large for some instruments, notably the Coulter Counter and image analysis, which only require a few milligrams for a measurement.

As part of the BCR programme, a duplicate set of clear glass microsphere standards, initially known as 'mirror' standards, was produced to shortlist the laboratories competing to certify the new standards⁴. These evolved into the current set of polydisperse standards available from Whitehouse Scientific and bottled into single shot bottles down to 25mg.

2. Results

2.1 BCR 'Mirror' standards

2.2.1 Subdivision

The initial set of clear glass, polydisperse standards comprised of the following sizes:

1 – 10, 3 – 30, 10 – 100 and 150 - 650 microns

The master batches were subdivided into 1g bottles, which were then sent to the 40 applicant laboratories competing to certify the standards.

In order to minimise the processing operations and therefore maximise the accuracy of subdivision, 100 stage spinning rifflers were built, figure 1. It was then possible to subdivide a 10kg master batch into 1g sub-samples in just two steps.

Excellent repeatability was found when all 100 bottles of 10 - 100 micron glass microsphere powder was analysed by Electrozone sensing, figure 2. Furthermore, there was no bias dependent on the sample position on the riffler.



Fig 1. A 100 stage spinning riffler

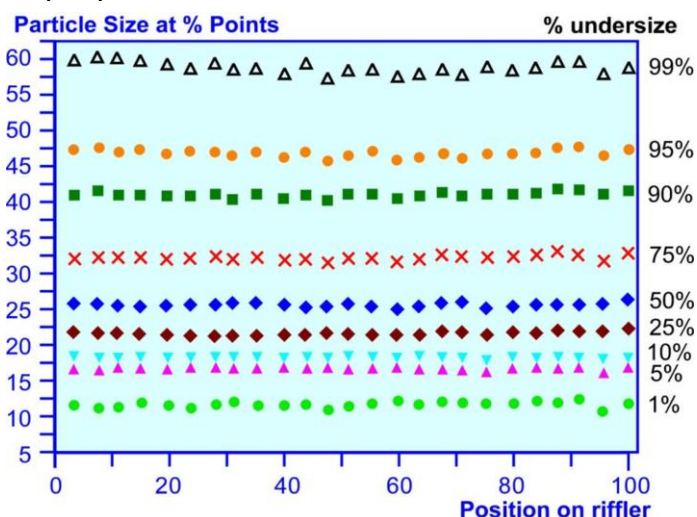


Fig 2. Results repeatable and independent of position: 10 – 100 micron Mirror standard (bv number)

2.2.2 Certification of the BCR Mirror standards

Certification methods were restricted to 'primary' particle sizing methods, that is, those which have a direct link to the International metre and do not have a 'black box' for data manipulation⁴. These included sedimentation by the Andreasen Pipette, Microscopy and Image Analysis, Electroformed sieving and the Coulter Counter.

Because of the spherical nature of the particles, all the results were very similar, figures 3 and 4.

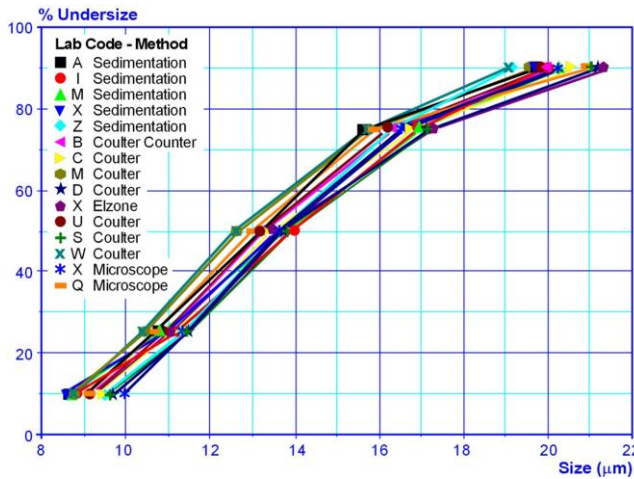


Fig 3. Certification results for a 3 – 30 micron polydisperse standard

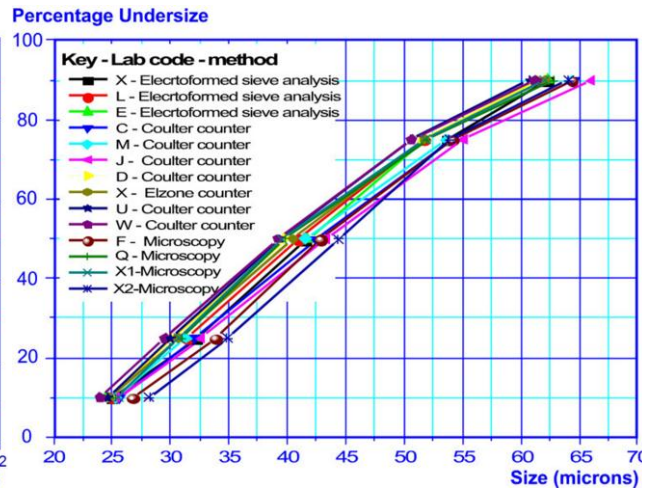


Fig 4. Certification results for a 10 – 100 micron polydisperse standard

2.2.3 Initial laser diffraction results

By 1994 the polydisperse Mirror standards had been analysed by the lasers of the day and, although good agreement was seen for most of the particle size range, deviations were observed, particularly at low particle sizes, figure 5.

These differences were attributed to the laser diffraction theory applied in the analysis. Of the two scattering theories, Mie and Fraunhofer, the latter could overestimate the fines in a sample, especially when clear microspheres are analysed.

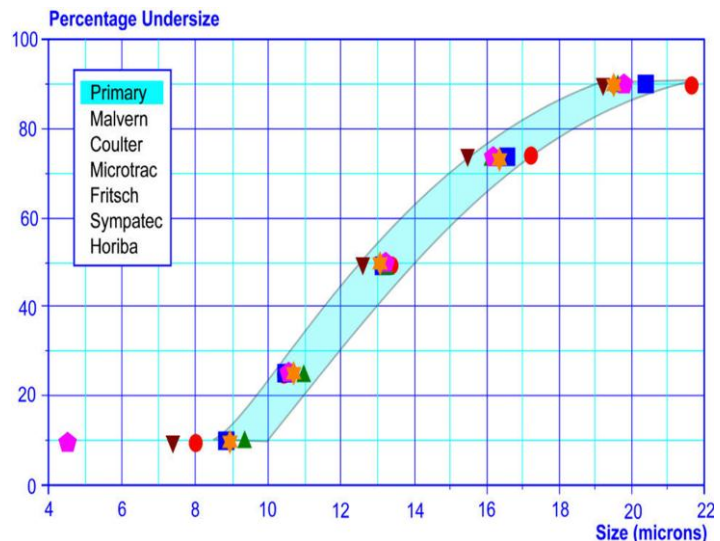


Fig 5. 1994 laser diffraction analysis of a 3 – 30 micron clear spherical glass standard

In order to minimise the effect of transparency during laser diffraction analysis, an opaque spherical material is to be preferred. The results would then be independent of the diffraction theory used.

2.2.4 Characterisation of the BCR Mirror standards

Unlike certification, where a number of laboratories using a range of traceable primary sizing methods determine 'absolute' results, characterisation is where an analysis is performed using a generic class of instrument, eg. Coulter Counter, Image Analyser or laser diffraction.

5g bottles of the 3 – 30 micron and 10 – 100 micron standards were analysed by up to 65 laboratories under a Quality Audit scheme (PACQS) currently run by LGC⁵. The results, reported at 10, 50 and 90 percentiles, figures 6 and 7 show wide variations, especially at the smaller sizes.

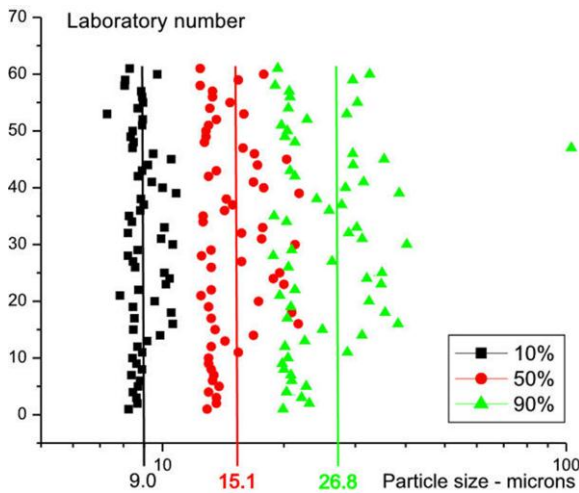


Fig 6. Laser analysis of a 3 – 30µm glass microsphere standard (5g bottles)

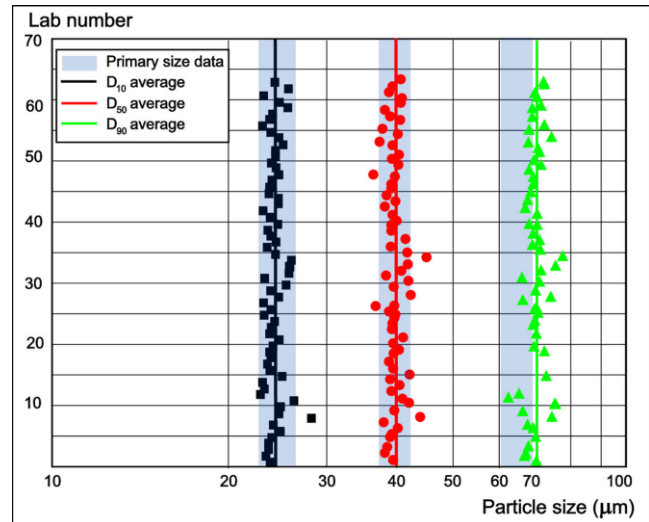


Fig 7. Laser analysis of a 10 – 100µm glass microsphere standard (5g bottles)

The interesting observation from these results is that, although the 10 – 100 micron standard is more problematic to sub-sample compared to the 3 – 30 micron standard, because the powder is not so cohesive, there was an unexpected larger scatter for the latter, one laboratory reporting a d90 of 100 microns! This suggests that the 3 – 30 micron standard was inadequately dispersed before analysis.

All the laboratories used Mie scattering theory so any discrepancies were not due to anomalies resulting from the application of Fraunhofer scattering theory.

2.3 A new 19 – 190 micron opaque standard

As indicated above, the advantage of opaque reference standards is that results are not affected by the diffraction theory used.

In this new 19 – 190 micron standard, some fine definition has been introduced so that the standard can be used for image analysis techniques as well as laser diffraction, figure 8.

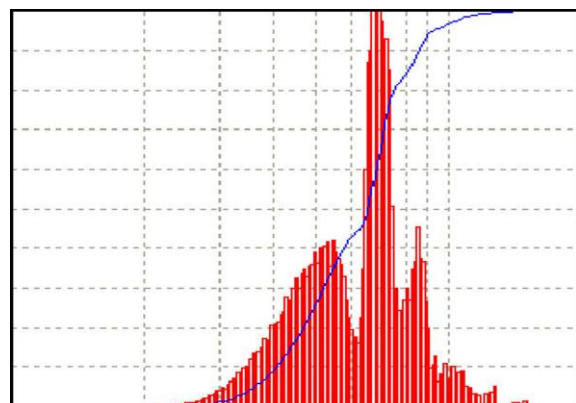


Fig 8. Image analysis of 19 – 190 micron opaque standard showing fine detail

By reducing the bin size in the Image Analysis, the fine detail can be smoothed out so that the distribution more closely resembles that of a typical laser diffraction measurement, figure 9.

2.3.1 Subdivision

In order to provide a long term supply of reference standards, a master batch of 550 kg was prepared and sub-divided into single shot bottles of the following weights: 0.1, 0.25, 1 and 2.5g

54 x 1g bottles were sampled from various positions on the carousel during the subdivision. The results in table 1 show excellent repeatability with uncertainties of 1% or less.

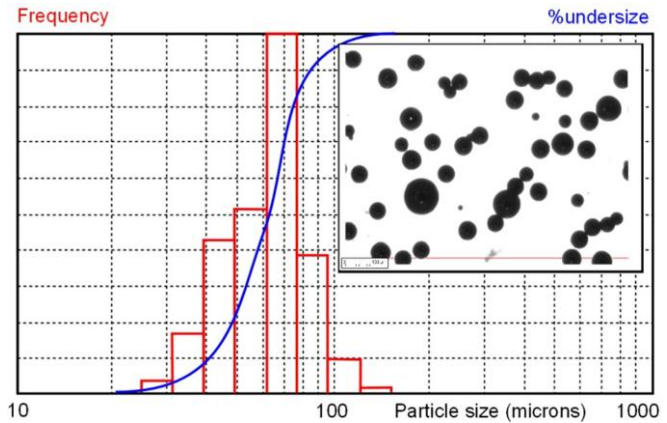


Fig 9. Effect of reducing the resolution on Image analysis of 19 – 190 micron opaque standard

Percentile	10	25	50	75	90
Size (microns)	37.4	46.9	61.0	74.7	87.8
Uncertainty (+/-%)	1.0	0.9	0.8	0.7	0.8
54 tests					

2.3.2 Primary particle size data

The initial results from Image Analysis and Coulter Counter were very close, table 2.

Percentile	5	10	25	50	75	90	95
ShapeSizer Size (µm)¹	36.02	40.51	49.31	65.80	72.91	85.75	92.65
Uncertainty (+/-%)	10.55	8.49	5.64	6.47	3.20	4.66	8.27
Coulter² (av. 50 tests)	34.3	39.3	49.1	64.5	74.7	85.6	92.4
Uncertainty (+/-%)	4.52	4.78	7.66	6.98	6.93	9.14	9.59
Malvern Morphologi³	33.9	38.1	47.3	64.6	73.2	87.4	100.4
Uncertainty (+/%)	1.3	0.84	1.10	0.67	1.69	1.40	2.28
1. 5 x 10,000 particles 2. 5 x 60,000 counts 3. 5 x 80,000 particles							

It is interesting to note that the uncertainty values are much higher than seen for the Sympatec laser diffraction method, especially for the ShapeSizer and the Coulter. In the former case, this is probably due to the fact that relatively few particles were counted while in the latter case only milligrams were required per analysis so the statistics of sub-sampling was poor.

2.3.3 Laser diffraction results

The laser diffraction results gave very comparable results, table 3.

Table 3. Laser diffraction analysis of a 19 – 190 micron opaque standard							
Percentile	5	10	25	50	75	90	95
Sympatec (Dry)	32.2	37.4	46.9	61.0	74.7	87.8	97.0
Beckman (wet)	34.5	38.8	49.3	63.0	75.7	88.3	97.6
Horiba (wet)	38.1	42.2	50.5	61.3	74.7	88.6	100.1
Horiba (dry)	40.8	44.8	51.9	61.6	73.8	87.2	97.7
Fritsch (wet)	34.1	38.8	48.1	61.1	76.3	91.4	100.6
Malvern (wet)	33.3	38.2	48.6	61.7	75.6	88.2	95.7
PACQS ¹ (15 labs)		37.9		62.2		89.2	
1. A quality audit scheme run by LGC							

Space precludes the inclusion of all the results, but the excellent overlays from Sympatec were typical of all the laser instruments, figure 10.

Also included in table 3 are the results from 15 end user laboratories who analysed the standard as part of a quality audit scheme (PAQCS) run by LGC (UK).

2.4 Multimodal image analysis Standards

In the past, several monodisperse spherical standards have been used to check the linearity of the calibration across the dynamic range of an Image Analyser. In this new multimodal standard having eight clearly defined peaks, the Image Analyser can confirm not only the percentile values across the distribution but the position of each individual peak, figure 11. Single shot bottles of 20g ensure minimal sampling errors and thus maximum accuracy.

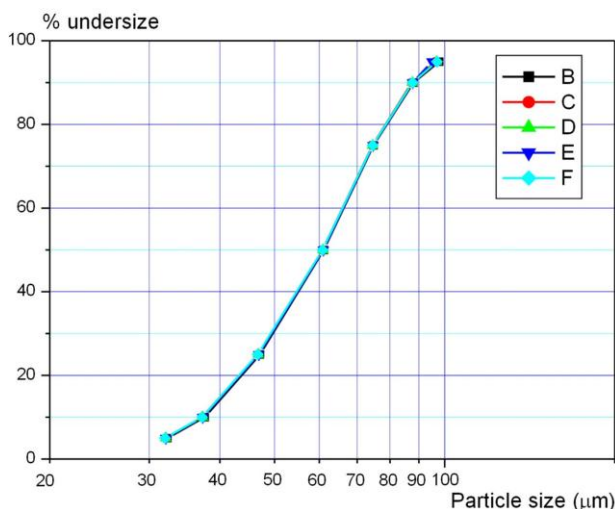


Fig 10. Sympatec laser diffraction results for 1g samples of a 19 – 190 micron opaque standard

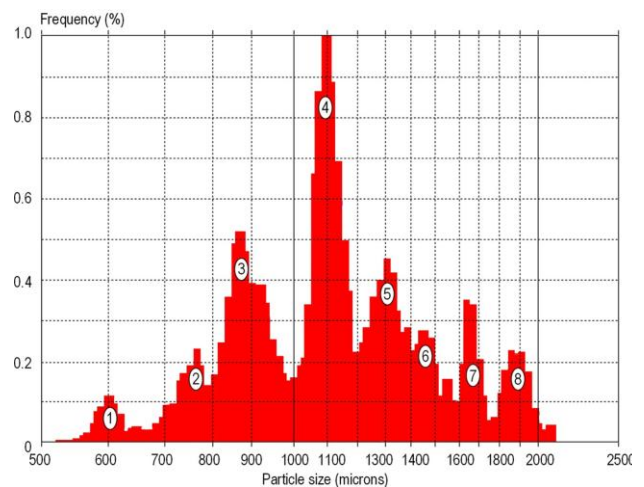


Fig 11. A 500 – 2000 micron multimodal image analysis standard (glass microsphere)

2.5 Submicron multimodal standard

This standard is in the early stages of development and comprises of 10 non-overlapping peaks from 0.1 – 1.5 microns, figure 12. It is a highly challenging reference standard for this particular size range and is aimed especially for the disc centrifuge, and other high resolution instruments^{6,7}.

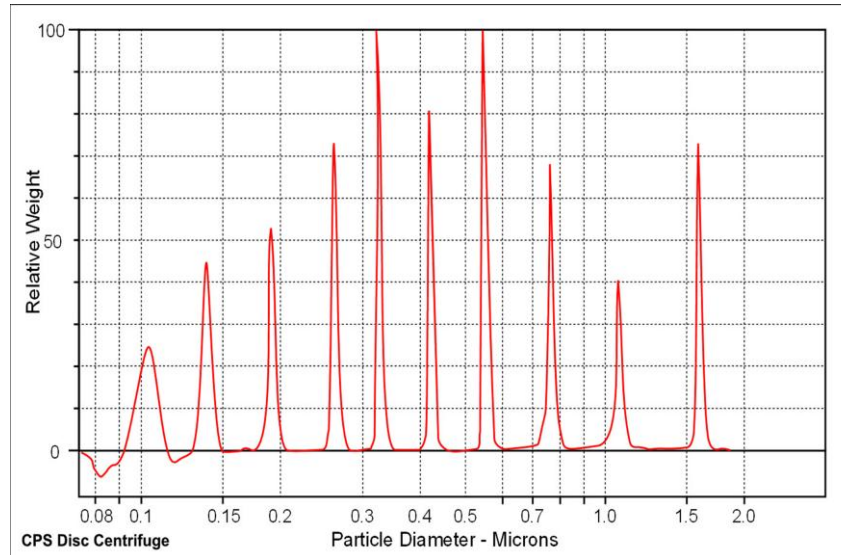


Figure 12. A high resolution multimodal reference standard

2.6 Sieve calibration microspheres

At the other end of the size/technology spectrum, sieving is one of the oldest methods of particle size analysis and is still used extensively throughout the world. Its main advantage is that it is one of the least expensive methods. However, its major disadvantage is that it is perceived (erroneously) as one of the least accurate methods of particle size analysis.

Hitherto, sieves have had to be returned to the manufacturer to recalibrate, but with the latest sieve calibration standards, this can now be performed by the analyst in their own laboratories.

The principle of the method is to prepare narrow size distribution calibration standards for individual sieves from 20 – 3350 microns and then analyse them by high precision, NIST traceable sieves, usually electroformed sieves⁸. Once a calibration graph has been set up, it can be used to determine the aperture size of an unknown sieve, figures 13.

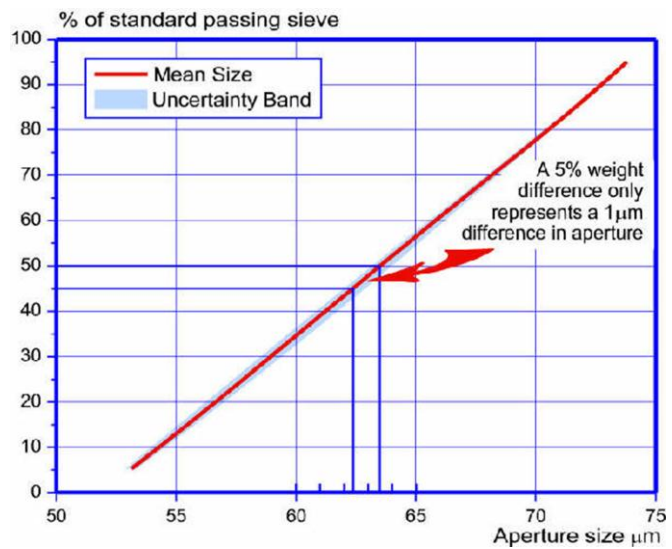


Fig 13. Interpolation of a sieve calibration graph can resolve down to 1 micron

3. Conclusion

Particle size reference standards have seen a continuous development over the last 30 years as they respond to the latest advances in particle sizing instruments. Without question, the most significant development has been in the field of laser diffraction.

Although initial results on both the BCR quartz irregular particles and the clear glass microspheres were quite variable, all the latest instrument manufacturers are achieving remarkably consistent results, especially in the latest opaque reference standards.

The accuracy seen from the laser instrument manufactures has been replicated by the end users. The reason for such consistent results has been a combination of a standard, which gives results independent of the diffraction theory used, supplying the standards in single shot bottles and taking great care in sample preparation.

In addition to laser diffraction, on the springboard of revolutions in camera and computer developments, image analysis has more recently taken an equally significant technological leap. Because of their very high resolution powers, multimodal standards can be used where NIST traceability can be conferred across a 10:1 dynamic range in one test.

The use of multimodal standards can be extended into the sub-micron region but here the resolving power of the instruments available is quite variable, so it is not possible to produce a 'one size fits all' multimodal standard.

Finally, the use of calibration standards has led to a resurgence in the oldest particle sizing method of them all, sieve analysis. This is without doubt the most ubiquitous method with literally millions of sieves being used on a daily basis. Through the use of sieve calibration standards, it is now also possible to confer NIST traceability to the father of all particle sizing instruments.

4. Acknowledgements

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