

# THE PRODUCTION AND APPLICATION OF PARTICLE SIZE REFERENCE STANDARDS

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## Summary

This paper reviews the background of calibration standards for particle size analysis and describes in detail the preparation and subdivision of the world's largest production run of single-shot reference standards for Malvern Instruments - a total of over 120,000 bottles from a 250kg master-batch. A comprehensive analysis of the subdivision strategy using a reference Mastersizer showed a sample-to-sample variation of less than 1% across the entire width of the particle size distribution.

Key words. Standards, reference, quality audit, transfer, subdivision, laser diffraction

## Background

In 1980, the Community Bureau of Reference (BCR) introduced a series of crushed quartz particle size reference standards<sup>1</sup>. The primary method of analysis was sedimentation using the Andreasen Pipette method. 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 sedimentation and the random shape and optical properties which could affect the diffraction behaviour of the quartz particles.

It was not until the early 1990's when Laser Diffraction was becoming a predominant method of size analysis that the BCR decided to introduce a series of spherical references designed to overcome the ambiguities associated with the crushed quartz standards. 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 laboratories, it was predicted by Maurice Wedd of Malvern Instruments that the entire supply would be used up by his company alone in just 18 months. Whitehouse Scientific was therefore asked to develop a duplicate set of standards which became known as 'Mirror' standards<sup>2</sup>. The purpose was not only to dilute the demand for the new standards but to short-list over 40 laboratories who applied to certify the standards. In the event, although most of the official BCR standards were prepared and sub-divided, they were never sent to the short-listed laboratories for analysis because administration problems caused the programme to over-run and funding was withdrawn.

Even if the project were eventually to receive funding, two major problems still exist. First, key personnel in the selected laboratories would have moved on so a new selection programme would need to be undertaken, causing additional delays. Second, and perhaps more importantly, the number of samples required is now estimated to be at least ten times the 1993 figure because of the increased number of manufacturers now offering Laser Diffraction particle size analysers, and the increasing desire for the highest calibre quality assurance. There would simply now be an insufficient number BCR samples; for example, only 7,200 bottles of the equivalent 10 - 100µm grade were produced. Furthermore, at an estimated price of \$200 a bottle, the samples would be too expensive for daily use.

To compound the problem, NIST (Gaithersburg, MD), the only other supplier of certified reference materials, have withdrawn their glass bead standards because fusion problems have been encountered in long-term storage.

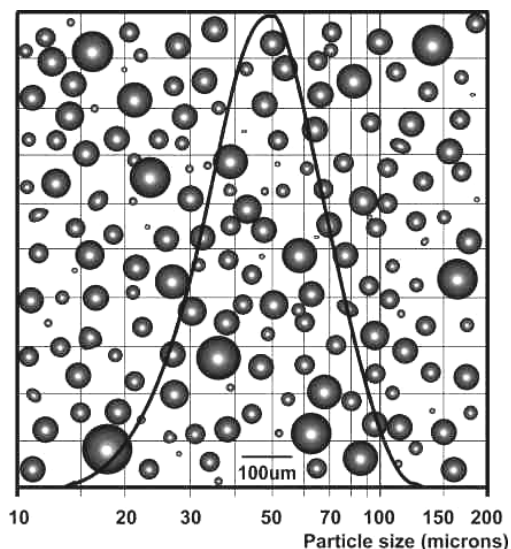
The manufacturers have therefore been seeking an alternative source of standards, this time imposing their own criteria to meet their specific requirements.

## Specification

Although narrow distribution latices have been available for many years and are routinely used for checking the optics of particle size analysers, the narrowness of their distributions does not challenge the overall sample handling capability of the complete instrument. To meet this requirement the ideal

distribution should be at least 10:1, maximum to minimum diameter and this has been specified in the new ISO Standard on Laser Diffraction Particle Size Analysers, ISO 13320. The use of polydisperse sample material poses its own particular problem for the user however, since polydisperse samples in bulk can easily be incorrectly sampled unless scrupulous care is taken to mix and split them.

Consequently, the most important attribute of any polydisperse reference standard is that it is available as an instrument-specific single shot specimen so that the biggest uncertainty - operator sampling - can be removed. There should also be sufficient quantity produced to last at least 5 years so that any validation methods do not have to be changed as the specification changes from batch to batch. Finally, the standards should be inexpensive so that operators can check the instrument on a daily basis.



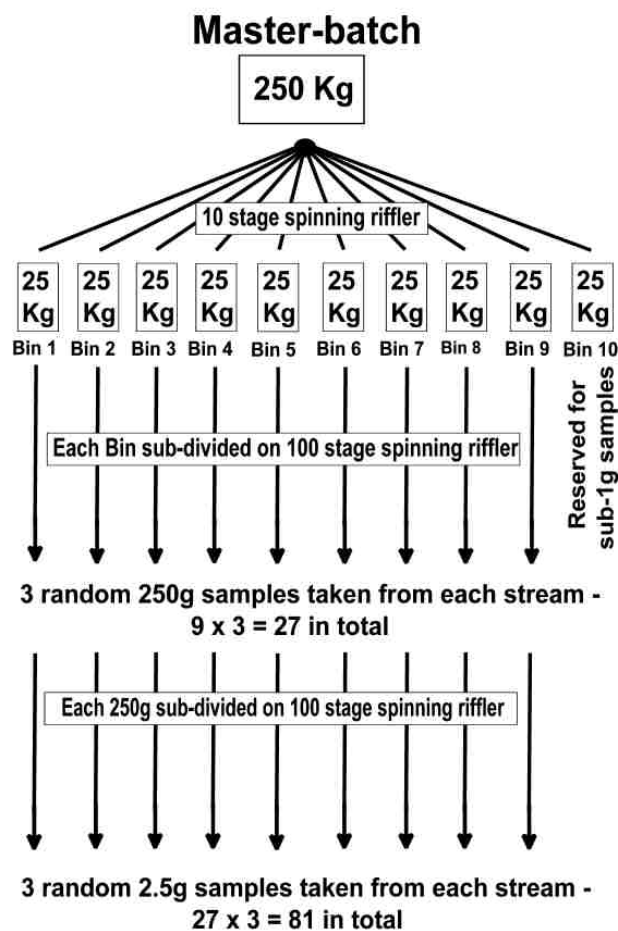
**figure 1:** Optical micrograph and superimposed size analysis of Quality Audit Standards

Proprietary 100-stage spinning rifflers were then used to minimise the handling to 3 generations (4 for the 0.25g samples) and the master-batch was sub-divided to produce approximately 120,000 samples - the largest sub-division programme ever undertaken. Although the Whitehouse rifflers had been independently evaluated and used for most of the BCR standards, it was nevertheless important to check that all the samples produced for Malvern were sub-divided to a similar level of high precision; all the samples had to be identical irrespective of their position in the riffling strategy. The repeatability experiment was based on randomly selected 2.5g samples produced at the third generation (figure 2).

The 81 samples extracted were analysed using the reference Mastersizer S at Malvern Instruments. From the sizes at fixed percentiles, the mean values and the sample standard deviations (SD) were calculated and the data was used to determine the measurement uncertainty at each percentile point. The calculated uncertainty means that there is better than a 95% chance of any sample from the series falling within an error bar twice the width of the sample standard deviation. In simple terms, uncertainty is the figure after the +/- of the mean value.

## Production and analysis

Given the above specification, Malvern Instruments approached Whitehouse Scientific to produce a range of Quality Audit or Transfer standards suitable for all combinations of their Laser Diffraction size analysers, both for the Mastersizer S and the new Mastersizer 2000 series. Soda-lime glass microspheres were selected as the most stable and robust material and were graded into fractions from 15 to 150 $\mu$ m using a Gilson Production Sonic Sifter (Gilson Company, Lewis Center, OH). After thorough mixing, the fractions were recombined to produce a 250kg master-batch of a near Gaussian distribution about a mean size of 50 $\mu$ m (figure 1). The final weights selected for the single shot samples were 5g, 2.5g and 0.25g. Using such a large feed-stock, the projected life span of the batch was at least 10 years.



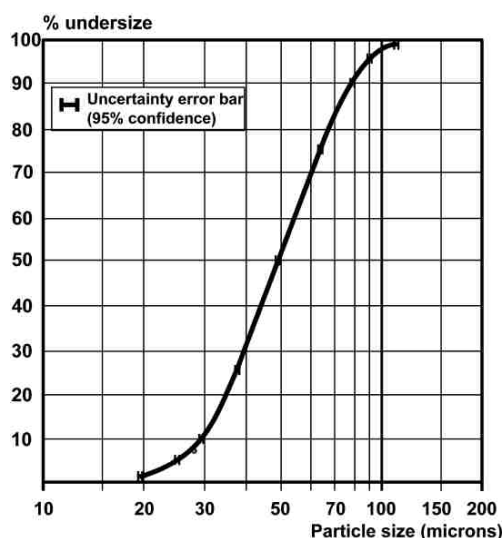
**figure 2:** Subdivision strategy and sampling procedure for a 250kg master batch of the Quality Audit Samples

The results in table 1 were quite remarkable in that the sample-to-sample variation at the median (D50) was only  $0.36\mu\text{m}$ . In most percentiles across the distribution the uncertainty was below 1%.

Table 1: Tabular results from repeatability analysis of 81 samples using Mastersizer reference instrument

Percentile	Mean ( $\mu\text{m}$ )	SD ( $\mu\text{m}$ )	Uncertainty ( $\mu\text{m}$ )
1	18.47	0.10	0.20
5	24.94	0.13	0.26
10	29.12	0.13	0.26
25	37.21	0.15	0.30
50	48.28	0.18	0.36
75	62.44	0.27	0.54
90	79.06	0.35	0.70
95	90.00	0.40	0.80
99	108.04	0.28	0.48

**Median Size (D50) =  $48.28 \pm 0.36\mu\text{m}$**



**figure 3:** Quality Audit Standards:  
Repeatability experiments on 81 samples  
extracted by spin riffler

When plotted on a cumulative basis, the error bars were so narrow that the data points did not exceed the thickness of the graph line (figure 3). The analysis therefore confirms that every bottle of the reference standard is virtually identical.

Having proved that the standards are identical, any significant variation in repeatability experienced by an operator, whatever the machine configuration and wherever it is used in the world, can only be due to either a fault on the machine or the analytical technique of the operator. By writing a prescriptive methodology for the latter and determining the expected instrument to instrument variation, it is possible to isolate the performance of the entire analytical system and thus monitor stability on a daily basis. Any drift in performance can therefore be readily detected so minimising the costs associated with producing off-spec product. If the instrument should fail to meet the pass/fail criteria detailed on the Certificate supplied with the standard, it is a simple procedure to determine whether the problem lies with the sample dispersion unit or the optical bench by

measuring a monodisperse latex. Measurements obtained by using monodisperse latices are largely unaffected by variations in sample dispersion units so that if the latex measurement is correct, this would clearly indicate that the problem lay with the sample dispersion unit. If the latex test was to fail then the optical bench would be the source of the problem. If, as is increasingly the case, the user has a remote diagnostics package (Malvern Instruments), it is then a simple matter to trouble-shoot the problem on-line.

One of the key drivers for the use of the Quality Audit Standards is the perennial question which users of any scientific equipment are faced with when that equipment is subject to a formal annual re-qualification process: "If the instrument fails its OQ, when did it drift out of specification? Was it the day before this annual check or was it the day after the last annual check?"

Clearly most users have procedures designed to pick up inconsistencies and trap the out-of specification situation as soon as it occurs. The availability of the Malvern Quality Audit Standards and the consistency of the shot-to-shot measurements which they offer ensures that users now have a powerful and universally applicable tool to ensure that systems are maintained within specification. The very large quantity produced by Whitehouse Scientific for Malvern Instruments will ensure continuity of supply so that users' protocols can remain unchanged for a number of years without revision.

## Bibliography:

1. BCR Quartz Reference Standards: R Wilson, K Leschonski, W Alex, T Allen, B Koglin, B Scarlett, Certification Report on Reference Materials of Defined Particle Size, Commission of the European Communities, Document EUR 6825 EN (1980).
2. BCR 'Mirror' Standards: G R Rideal, J A Dodds, M-N Pons, K Leschonski, P J Lloyd, H G Mercus, The Development of New Reference Standards for Particle Size Instrument Calibration, World Congress on Particle Technology 3 (I Chem E), July 1998, Brighton, UK.