



The Development of New Reference Standards For Particle Size Instrument Calibration

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Laser Techniques are becoming one of the most popular methods of particle size analysis but calibration using existing BCR quartz standards has shown unacceptably high deviations from instrument to instrument. As some of the variations were attributed to the irregular shape and optical properties of the quartz, the BCR decided to develop a new set of spherical reference standards that were to be analysed by the four principle primary sizing methods of Sedimentation, Sieving, Microscopy and the Electrical Sensing Zone (ESZ) method. This paper describes the results of the BCR round-robin exercise using a duplicate set of broad range spherical standards to both develop prescriptive guidelines for each method and to short-list the applicant laboratories for the final analysis of a new set of standards.

Key words: Particle Size Analysis, Reference Standards, Sedimentation, Sieve Analysis, Electrical Sensing Zone.

INTRODUCTION

The European Community Bureau of Reference (BCR) brought out a range of crushed quartz reference standards in 1980 for particle sizing instrument calibration¹. These had maximum to minimum size ratios of approximately 10 to 1 and covered the size range 0.3 to 650 microns. With the exception of the largest size which was measured by sieve analysis, all the other references were certified using the Andreasen Pipette method.

Analysis of the sedimentation data for the 5 participating laboratories showed that the maximum deviation about a mean size was approximately +/- 10% in the middle 80% of the particle size distribution.

The intervening years have seen a proliferation in Laser based particle sizing techniques, however, when compared to the more traditional methods, Laser analyses of the BCR standards have shown excessively large deviations of up to +/- 70%^{2,3}. Such variations were attributed to a combination of factors including:

- (a) calibration problems from complex scattering of the angular quartz particles
- (b) poor sampling of the 10g bottles
- (c) dispersion problems (both surfactant and ultrasonic bath choice)
- (d) unspecified statistical modelling
- (e) non-prescriptive analytical procedure

To overcome these problems the BCR planned to bring out a new set of spherical standards that were to be analysed by as many primary particle sizing methods as possible. (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, Brownian Motion or computer modelling.) Furthermore, prescriptive methodologies were to be developed to reduce the possibility of operator error.

The five primary methods selected were:

1. Gravitational Sedimentation - guidelines developed by Prof. K Leschonski (Clausthal TU)
2. Centrifugal Sedimentation - guidelines developed by Dr G Rideal (Whitehouse Scientific)
3. Electroformed Sieve Analysis - guidelines developed by H G Mercus (Delft TU)
4. Optical Microscopy - guidelines developed by Prof. J A Dodds (CNRS - France)
5. Electrical Sensing Zone (Coulter) - guidelines developed by Dr P J Lloyd (Loughborough)

As nearly 40 European Laboratories expressed an interest in certifying the new BCR references, Whitehouse Scientific was asked to produce a duplicate range of spherical standards in soda-lime glass to short-list the laboratories into five laboratories per method.

This paper describes the subdivision of the Whitehouse bulk samples, reviews the development of the primary analysis guidelines and compares the results from the best four or five laboratories per method. Finally, primary method comparisons are made for several of the duplicate standards.

RESULTS

1. SAMPLE SUBDIVISION

Custom built spinning rifflers developed Clausthal University and Whitehouse Scientific were used to subdivide the duplicate reference standards. Particle sizing data from the rifflers were independently evaluated at Loughborough University to ensure accurate subdivision.

In the case of the Whitehouse riffler, 25 x 1g samples of the 10-100 μ m standard were taken from a 100 stage spinning riffler and analysed by the Electrical Sensing Zone method (Elzone - 280PC). In order to ensure an accurate and representative sub-sample, each 1g sample was placed in a Waring blender containing 60ml of 0.1% sodium hexametaphosphate solution filtered at 0.05 μ m. The suspension was then mixed at approximately 12,000 rpm for 10 seconds. While still running, 2ml of the suspension was withdrawn through a syringe port in the lid and injected directly into the Elzone.

60,000 particles were counted per analysis.

The sizes at fixed percentiles from 5 to 95% were measured for the 25 samples from which a mean size distribution was calculated. The absolute deviation of each of the samples from the mean was then plotted - figure 1.

It can be seen that the maximum deviation was only +/- 2.5% with a Mean Standard Deviation (MSD) of +/- 1.07% confirming that all the samples sent to the participating laboratories were virtually identical.

2. PARTICLE SIZE ANALYSIS RESULTS

(a) Gravitational Sedimentation

The Andreasen Pipette as described in reference 1 was used for the gravitational sedimentation of the standards. The analysis guidelines were developed for the following references: 1-10 μ m, 3-30 μ m and 10-100 μ m although most participants only analysed the first 2 standards. For this method and all others using soda-lime microspheres in suspension, the samples were dispersed in a 0.1% aqueous solution of sodium hexametaphosphate for 5 minutes in an ultrasonic bath.

To measure the 3-30 μ m standard, the sedimentation height in the Andreasen Pipette was set to 20cm and extraction times calculated to give 13 particle size points from 29.3 μ m down to 3.7 μ m (4 minutes to over 2 hours respectively).

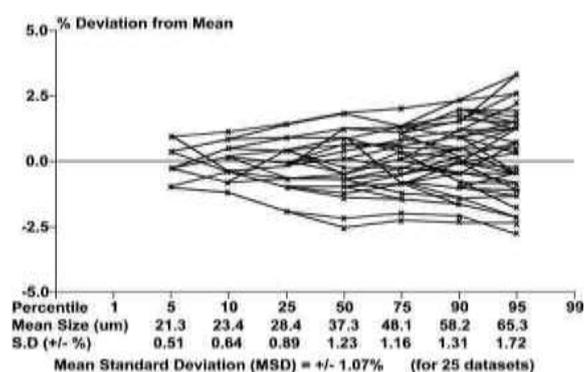


figure 1: Spinning Riffler Reproducibility

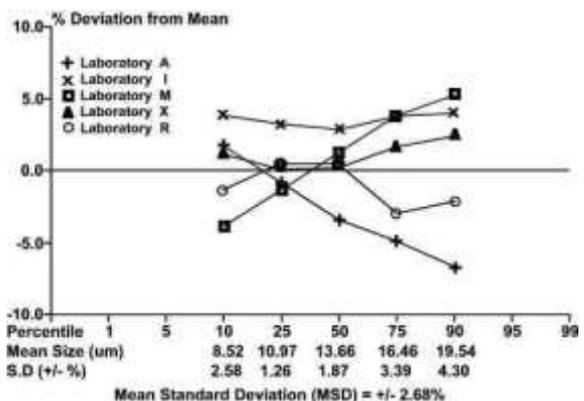


figure 2: 3-30 μ m Andreasen Pipette Review

The entire contents of the 1g vial was used for the analysis.

To minimise turbulence by convection currents, the Andreasen Pipette was submerged at 20°C in a water bath controlled to $\pm 0.10^\circ\text{C}$.

Cumulative percent undersize points were plotted for 5 repeat analyses, from which mean sizes at the selected percentiles were calculated. The results from the five best laboratories for the 3-30 μm standard are shown in figure 2.

The maximum deviation of $\pm 5\%$ and MSD of $\pm 2.68\%$ are significantly better than those seen for the equivalent BCR quartz standards.

In the case of the 1-10 μm standard, a settling height of 10cm was used; 7 extraction times from 14 minutes to approximately 6 hours corresponded to sizes from 10.1 μm to 1.5 μm respectively.

Figure 3 shows a slightly wider spread of points although the results were still in closer agreement than those observed from the equivalent quartz reference standards.

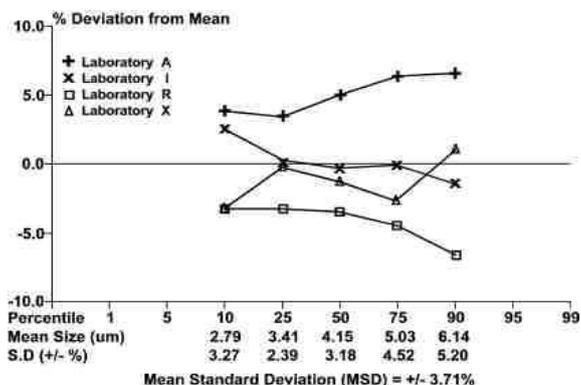


figure 3: 1-10 μm Andreasen Pipette Review

(b) Centrifugal Sedimentation

The small volume (180ml) Pipette Centrifuge as described by Allen⁴ was used for this work. It is essentially a centrifugal analogue of the Andreasen Pipette and so utilises a similar methodology. Centrifugal speed, internal volume and pipette volume were calibrated prior to measurement and extraction times were predetermined for each laboratory. For the 0.1-1 μm standard, the centrifuge was run at 1500rpm, the first sample being extracted after 1 minute, the time thereafter was doubled on each subsequent extraction until the last sample was withdrawn after 64 minutes. The seven extractions corresponded to a size range from 2.06 μm down to 0.15 μm . 5 analyses were performed from which a mean particle size distribution was calculated. The results are summarised in figure 4.

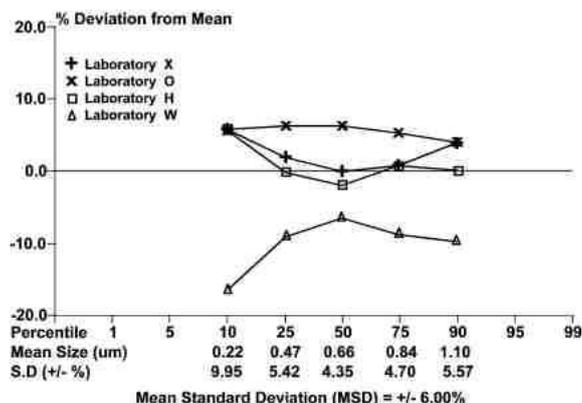


figure 4: 0.1-1 μm Pipette Centrifuge Review

The accurate analysis of the sub-micron powder was found to be very dependent on the energy of the ultrasonic bath used for dispersion. The deviations seen by some laboratories were therefore a function of sample preparation in relation particle agglomeration rather than poor analytical procedures. Although the results were not as good as the Gravitational Sedimentation they are nevertheless quite acceptable for the comparatively more difficult centrifugal analysis.

(c) Electroformed Sieve Analysis

Electroformed nickel sieves having square apertures accurate to ± 2 microns were specified for this method which was based on ISO 3310-3 (1990). The sieves were calibrated by microscope using the National Physical Laboratory (NPL) graticule⁵ as the traceable unit of length. Each sieve was calibrated by measuring the height and width of six apertures in 9 measurement fields across the sieve.

Sieve frame dimensions could vary from 70 - 200 μm . For the 150-650 μm standard the following sieves were specified: 180, 212, 250, 300, 355, 425, 500 and 600 μm . Any method of mechanical shaking could be used, but the end point was determined by hand shaking when less than 5mg per minute of the initial 10g sample should pass each sieve. The sample loss at the end of the analysis should be less than 0.5% of

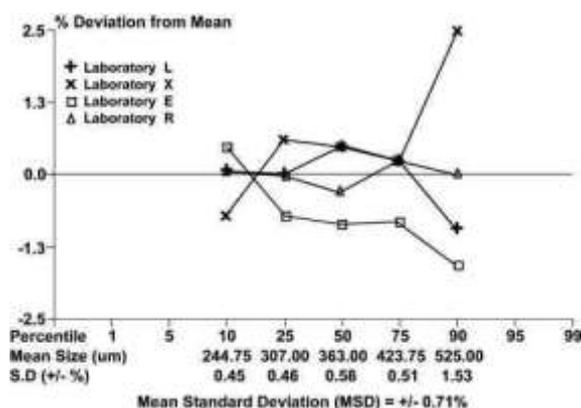


figure 5: 150-650 μm Electroformed Sieve Analysis Review

the charge (ie. 50mg). Five analyses were performed from which the sizes at the prescribed percentiles were calculated.

The results in figure 5 show excellent agreement between the laboratories; the MSD of +/-0.71% being the closest agreement of all the primary particle sizing methods. These results mirror similar high reproducibilities seen in the earlier equivalent quartz standard.

Electroformed sieve analysis was also applied to the 10-100µm reference standard. For this sample, the analysis could be performed in suspension using an ultrasonic bath (40W, 40kHz) or as a dry powder using sonic energy (eg. Gilsonic Autosiever) to effect particle separation. The following Electroformed sieves were specified: 20, 25, 32, 36, 45, 63 and 90µm. The end point for dry sieving was when less than 1mg per minute of the initial 1g passed the finest sieve.

The sample loss should be less than 2% of the charge. Only three laboratories had the required equipment for this work.

Figure 6 shows the average of five analyses per laboratory and confirms the excellent reproducibility of this method.

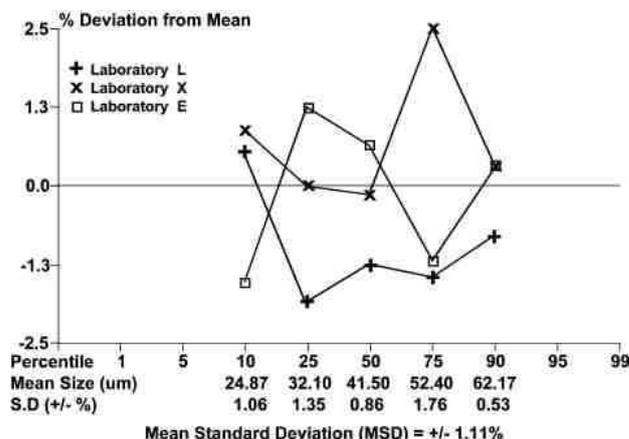


figure 6: 10-100µm Electroformed Sieve Analysis Review

(d) Microscopy And Image Analysis

Microscopy and Image Analysis were specified for the 3-30µm, 10-100µm and 150-650µm powders. Although microscopy was one of the most oversubscribed methods, in practice, few laboratories had the equipment necessary or the considerable time required for an accurate analysis.

The 3-30µm and 10-100µm powders were supplied as 1g samples so accurate sub-division into the milligram quantities required per slide was the first problem. It was recommended that slides should be prepared from single drops of a concentrated glycerol paste of the complete contents of the sample bottle. Space precludes a detailed description but, from a single 1g sample, 35 slides were prepared, 15 fields per slide counted and 10-20 particles per field analysed. This gave an average count per analysis of about 8,000 particles.

Touching particles were noted but no attempt was made at numerical separation. However, if the total number of touching particles exceeded 20%, the data was discarded and a new slide was prepared. Given the amount of work associated with this method, it was recommended that the microscopy should be linked to an image analyser.

Distortions of camera/microscope lenses were measured using the NPL graticule and limited to 5%. Edge detection was determined by setting the grey scale of the particle to black and the background to white so that, when set to two shades of grey, the computer automatically defined the particle perimeter during scanning.

The Miles-Lantuejoul^{6,7,8} correction was implemented for particles cut by the edge of the video frame. Particle Shape Factor (SF) was determined by taking the ratio of the maximum length of the particle to the equivalent circle diameter. The microscope technique was therefore the only method of measuring particle shape as well as size.

The primary data, (number count) from the 10-100µm standard for 5 laboratories, (figure 7) shows a larger than usual scatter of results and was attributed to a combination of lens quality, calibration uncertainties, pixel shape or, in one case, manual calculations.

The sampling procedure was not thought to be a contributory factor as there was good agreement

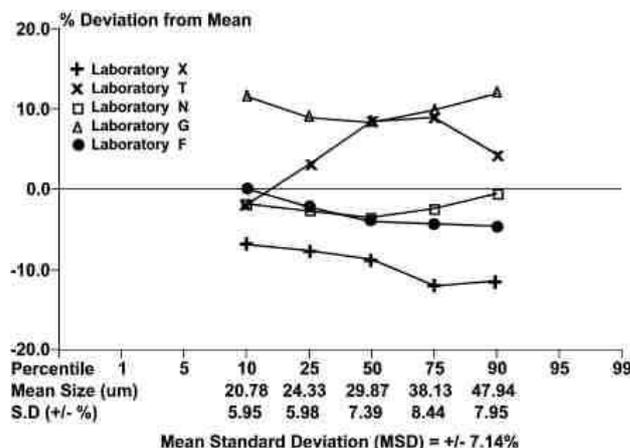


figure 7: 10-100µm Microscope Analysis Review (by number)

between the laboratories with the highest quality equipment - data converted to a volume basis is shown in figure 8.

Only a few laboratories succeeded in measuring the 3-30µm standard, the results of which are compared with other methods of analysis at the end of this report. CNRS - France also measured the 1-10µm standard even though this was outside the scope of the microscope method.

The sphericity of the 3-30µm standard, which was representative of all the reference standards, is illustrated in figure 9 where the Shape Factor (SF) of every particle - 6775 in total - was plotted against its particle size. (Extracted from the Whitehouse ShapeSizer).

The results show that only 7.5% of the particles were out of shape.

(e) The Electrical Sensing Zone Method- (Coulter Principle)

The Electrical Sensing Zone (ESZ) method was employed for the 1-10µm, 3-30µm and 10-100µm samples. Like the optical microscope method, the weight of the powder involved could be as low as 5mg so particular attention was paid to the subdivision. A stock suspension was prepared from the 1g bottle of sample using the dispersant sodium hexametaphosphate as electrolyte (1g sample in 400ml of a 5% solution).

In the case of the 10-100µm sample, 40% glycerol / 60% distilled water was used to reduce sedimentation during analysis. By careful weighing, the stock suspension concentration was accurately calculated.

A sub-sample (5 or 10ml) was then taken from the rapidly stirred suspension and injected into a known volume of electrolyte in the instrument sample beaker. Thus the sample concentration, and so volume of particles in the measuring syphon of the mercury manometer could be calculated. This predetermined particle volume should not vary by more than 5% from that calculated internally by the instrument. 100,000 particles were analysed and the experiment repeated 5 times for the same beaker of suspension.

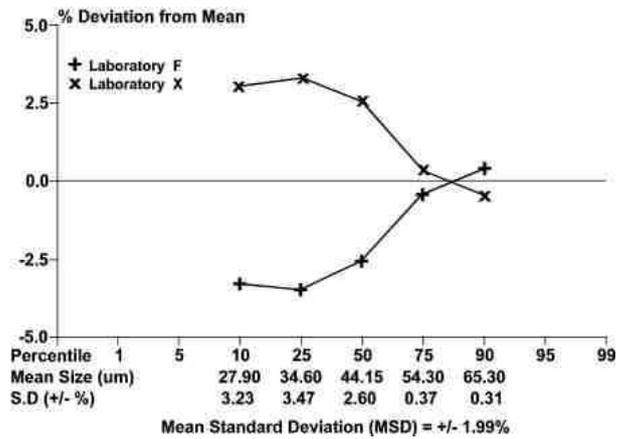


figure 8: 10-100µm Microscope Analysis Review (by volume)

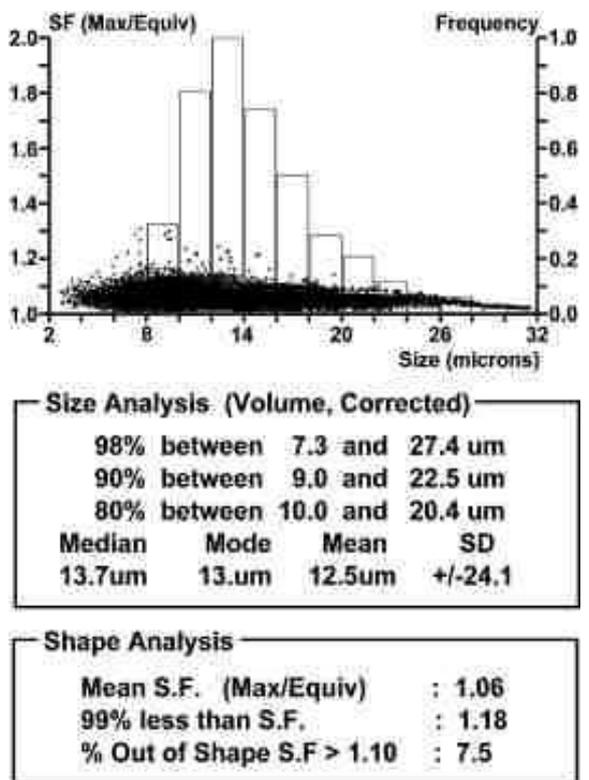


figure 9: 3-30µm Size and Shape Distribution

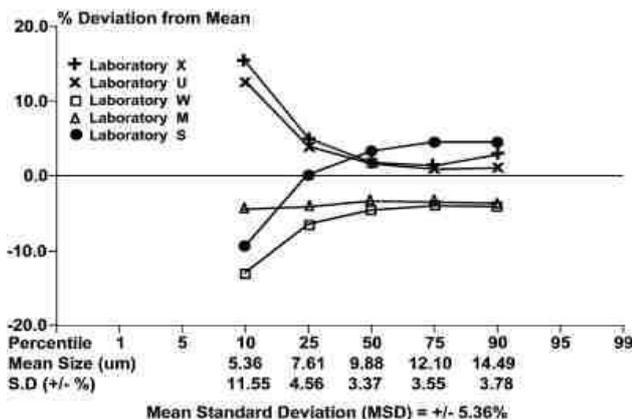


figure 10: 3-30µm Coulter Review (by number)

Data was accumulated for a further 4 dispersions giving a particle count of 2.5 million per sample. The instruments were calibrated using traceable reference standards.

The primary (number based) data for the 3-30µm sample showed larger deviations than expected at the lower end of the particle size distribution (figure 10) and suggests that some participants may have had problems with background noise. Other possible sources of error were calibration, dispersion, high particle coincidence levels and mass balance inconsistencies.

(Errors of up to 20% were reported). When converted to weight however, the variations were suppressed and closer agreement was observed between the laboratories - figure 11.

The weight based results for the other two reference standards is shown in figures 12 and 13.

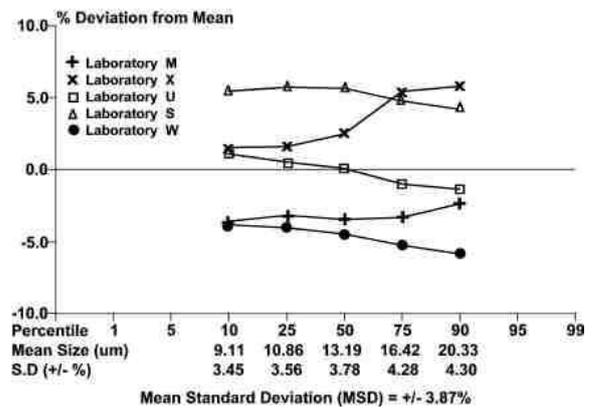


figure 11: 3-30µm Coulter Review (by weight)

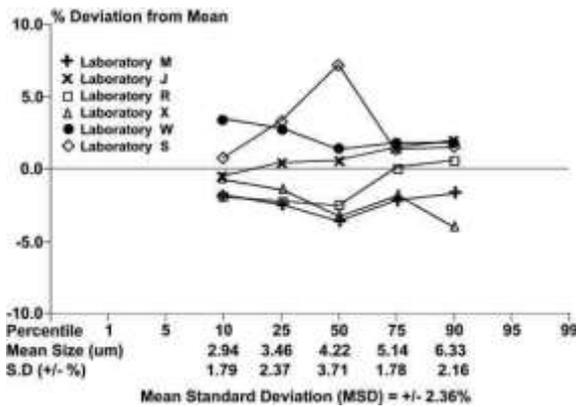


figure 12: 1-10µm Coulter Review (by weight)

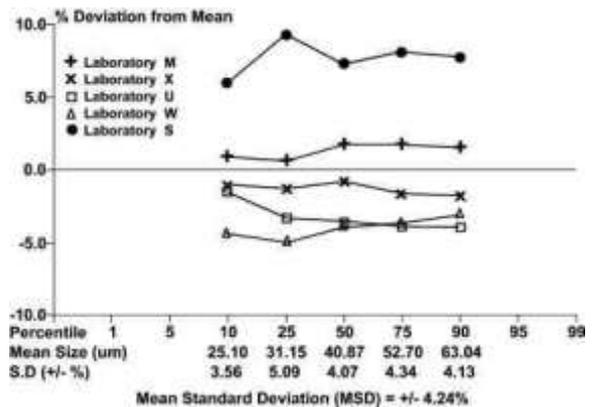


figure 13: 10-100µm Coulter Review (by weight)

3. PRIMARY METHOD COMPARISONS

Most particle size analysers measure a dimension close to the equivalent spherical diameter however, when measured by sieve analysis, elongated particles are sized according to their width. Hence the same irregular particles can give different sizes depending on the method of measurement. The advantage of using spherical reference standards is that the size is independent of the analytical technique used. Three standards were sufficiently well analysed to make comparisons - figures 14, 15 and 16. NB. Only one set of results from the French laboratory CNRS was used in the 1-10µm comparison.

The results show excellent agreement between the primary methods of analysis with deviations above the median size of about +/-3%. Below 50% there tends to be an increasingly larger deviation but never more than +/-6%.

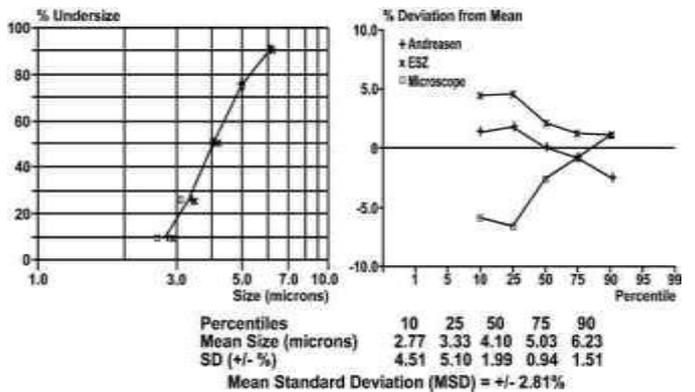


figure 14: Summary of 1-10µm Standard (by weight)

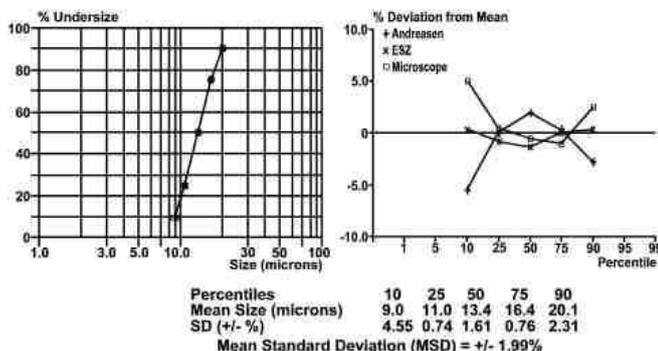


figure 15: Summary of 3-30µm Standard (by weight)

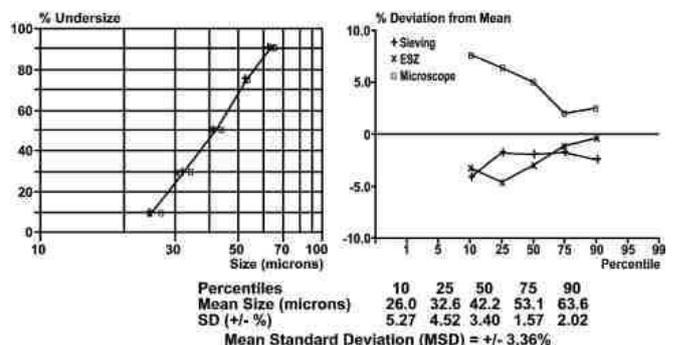


figure 16: Summary of 10-100µm Standard (by weight)

CONCLUSION

The BCR round robin has shown that, by using spherical materials, smaller 1g samples and prescriptive analytical guidelines, it has been possible to obtain better agreement from four primary particle sizing methods than was previously achieved with just one method for the BCR quartz standards.

The surprising observation was that the comparatively sophisticated methods of Microscopy with Image Analysis and the Electrical Sensing Zone method gave larger laboratory to laboratory variations than the other methods, particularly when the data was number based. (By applying the experience gained, it is expected that the results will be even closer at the next stage.) The work confirms the excellent performance previously seen for the Electroformed Sieve Analysis where absolute deviations half those of the other methods were recorded. The sub-micron analysis highlighted the agglomeration problems that could occur and emphasised the need for a tighter specification of both dispersant and ultrasonic bath. The finalists will now go on to analyse a new set of spherical BCR standards. In the meantime the duplicate set of reference standards described herein (also referred to as 'Mirror Standards') are available as supporting secondary standards and will now be characterised by the leading suppliers of Laser Diffraction analysers.

ACKNOWLEDGEMENTS

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Organisation	Country	Primary Sizing Method
AEA Technology	UK	Gravitational and Centrifugal Sedimentation
Bologna University	Italy	Optical Microscopy
Bradford University	UK	Gravitational and Centrifugal Sedimentation & ESZ
Clausthal - TU	Germany	Gravitational Sedimentation, ESZ & Sieve Analysis
CNRS	France	Optical Microscopy & Centrifugal Sedimentation
Coulter Electronics	UK	ESZ
Delft - TU	Holland	Sieve Analysis, ESZ & Gravitational Sedimentation
Health & Safety Executive	UK	ESZ
IFTS, Foulyronnes - Agen	France	ESZ, Optical Microscopy & Sieve Analysis
INRS, Vandoeuvre	France	ESZ
Kodak, Chalons sur Soane	France	Optical Microscopy
LERMAT, Caen	France	Optical Microscopy
Loughborough University	UK	ESZ, Gravitational & Centrifugal Sedimentation
Nissan Flour Mills	Japan	Sieve Analysis
Pavia University	Italy	ESZ & Gravitational Sedimentation
Salerno University	Italy	Sieve Analysis
Solvay et Cie, Brussels	Belgium	Optical Microscopy
Whitehouse Scientific	UK	Gravitational Sedimentation, Centrifugal Sedimentation, Sieve Analysis, ESZ & Optical Microscopy

Laboratories indicated were the working group leaders responsible for specifying the prescriptive methodologies for each primary method of analysis.

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