

Characterisation of reference standards by low-angle laser light scattering (laser diffraction) particle size analysis

G R Rideal*, Whitehouse Scientific, UK
J P Mitchell, Trudell Medical International, Canada
R Bunker, Beckman Coulter, UK
B Brookman, LGC, UK

Summary

Polydisperse glass microsphere standards were analysed by 25 international teams of particle metrology specialists using unambiguous methods such as microscopy, sedimentation, electroformed sieving and Coulter counting. The nominal size distributions were: 1 – 10, 3 – 30, 10 – 100 and 50 – 350 microns (μm). The Laser Diffraction Proficiency Testing Scheme¹ (LDPTS) then sent the samples to about 65 participant laboratories for analysis using a wide range of laser diffraction particle sizing instruments. The standards were spin riffled to minimise sampling error. Excellent accuracy and repeatability was achieved in the homogeneity testing by Beckman, Coulter and Malvern laser diffractometers. Although some laboratories produced seriously flawed data, when the average sizes were calculated corresponding to the values of the sizes corresponding to the 10th percentile (D_{10}), median (D_{50}) and 90th percentile (D_{90}) of the cumulative volume-weighted size distributions, there was good agreement with the primary particle size data.

1. Introduction

The European Institute for Reference Materials and Measurements (IRMM), formerly the Community Bureau of Reference (BCR) brought out a range of crushed quartz reference standards in 1980 for particle sizing instrument calibration². These had maximum to minimum size ratios of approximately 10 to 1 and covered the size range 0.3 to 650 μm . With the exception of the largest size, which was measured by sieve analysis, all the other references were certified by gravitational sedimentation using the Andreasen Pipette method.

The intervening years have seen a proliferation of particle sizing techniques based on the principle of low-angle laser light scattering, more commonly known as laser diffraction (LD). However, when compared to the more traditional methods, LD analyses of the BCR standards have shown excessively large deviations of up to +/- 70%^{3,4}. Such variations were attributed to a combination of factors including:

- (a) complex scattering of the angular quartz particles,
- (b) unrepresentative sampling from the 10g mass of standard supplied per bottle,
- (c) dispersion problems arising from both surfactant and choice of ultrasonic bath operating conditions,
- (d) unspecified statistical modelling,
- (e) the use of the Fraunhofer approximation for sizes finer than 25 μm ,
- (f) non-prescriptive analytical procedure,
- (g) the non-spherical nature of the particles leading to bias by both Andreasen Pipette and LD methods,
- (h) potential for bias arising from the sieve method reporting mass-weighted and laser diffraction reporting volume-weighted distributions for irregular-shaped particles

In the early 1990s, 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 in order to overcome these problems⁵. 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, elutriation or computer modelling. Furthermore, prescriptive methodologies were to be developed to reduce the possibility of operator error. The four primary methods selected were:

1. Gravitational sedimentation
2. Electroformed sieve analysis
3. Optical microscopy and image analysis
4. Electrical sensing zone (ESZ) analysis (Coulter Counting)

Strictly speaking it is almost impossible to have an absolute or primary method of particle size analysis. Thus, size determined by gravitational sedimentation is derived from particle velocity under gravity in a fluid (Stokes' Law). Similarly, size obtained using electroformed sieves and ESZ instruments is determined after calibration, and even in microscopy, if an image analysis system is used, the pixel dimensions have to be calibrated. Nevertheless, these techniques are as close as one can currently get to a 'primary' method of particle size analysis.

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 so-called 'mirror' standards in soda-lime glass both to short-list the laboratories and to provide a large quantity of single-shot bottles to back up the official range of standards. These standards were used test the performance of the LD particle size analysers in the study reported here.

2. Glass microspheres

(a) Size distributions

The glass microspheres selected for this programme were each polydisperse, comprising a unimodal size distribution having nominal maximum to minimum size ratios of approximately 10:1 (with the exception of the largest grade where the corresponding ratio was 7:1):

- 1 – 10 μm
- 3 – 30 μm
- 10 – 100 μm
- 50 – 350 μm

Each grade was initially blended in master batches before subdivision into samples of equivalent mass and size distribution for subsequent analysis.

(b) Subdivision

Single shot bottles of the samples were provided for the laboratories participating in the primary particle sizing analysis in order to eliminate sampling errors. Spinning riffles were used as they are the most precise method of producing representative sub-samples⁶. 2000 bottles of each grade were prepared in various weights to enable at least 5 tests per method to be performed by the 25 selected laboratories.

Key to the success of the subdivision was a specially designed 100 stage spinning riffler, which minimised the number of subdivisions from master-batch to final bottle yet produced identical sub-samples (Figures 1 and 2).



Figure 1. A100 stage spinning riffler

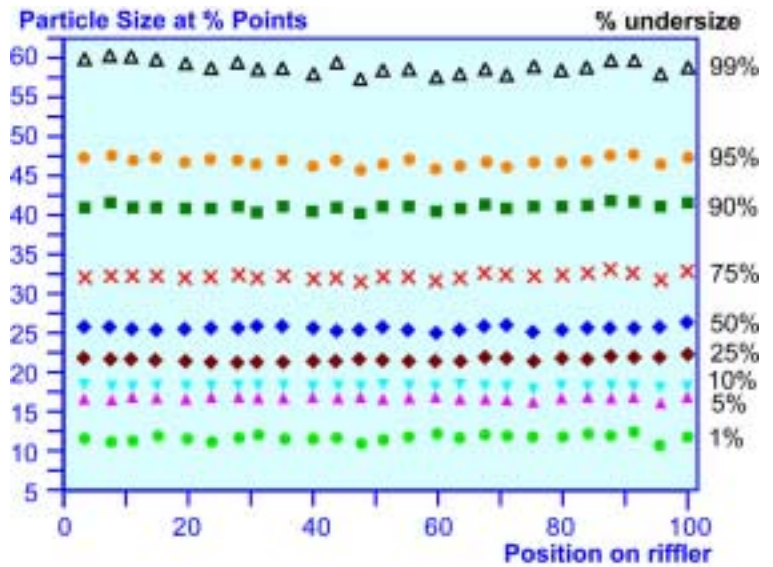


Figure 2. Particle size distribution is independent of the sample position on the riffler

Strict operating procedures were developed to minimise sampling errors for methods requiring milligram quantities, such as microscopy and ESZ analysis⁷.

Laboratories involved in the LDPTS also received riffled sub-samples but in sufficient quantities to make at least 2 analyses per bottle. The total elimination of operator bias by supplying single shot bottles was not considered to be a realistic goal in this characterisation phase of the work because, in most cases, laboratories analysing a new sample will normally receive more than enough for a single analysis. The operating procedure developed therefore assessed the combined impact of the capability of the operator in taking a sample and the intrinsic performance of the LD instrument.

A total of 200 bottles per grade were prepared. This enabled homogeneity testing to be performed by some of the manufacturers prior to dispatch to the laboratories participating in LDPTS.

3. Primary particle sizing methods

Full details of all primary sizing methods can be found in reference 6. A brief description of the methodology employed in these studies follows.

(a) Gravitational Sedimentation

The Andreasen Pipette method² was used to size-analyze the 1-10µm and 3-30µm standards. The pipette was submerged at 20°C in a water bath controlled to +/-0.1°C to minimise turbulence by convection currents.

The entire contents of the 1g vial was used for the analysis of the 3-30µm standard. The sedimentation height in the pipette was set to 20 cm and extraction times calculated to give 13 particle size points from 29.3µm to 3.7µm (corresponding to settling times ranging from 4 minutes to > 2 hours respectively). A settling height of 10cm was used for the 1-10µm standard. In these measurements, 7 particle size points from 10.1µm to 1.5µm corresponded with extraction times ranging from 14 minutes to approximately 6 hours.

Values of cumulative mass-percent undersize were plotted defining the particle size distribution data from 5 repeat analyses. From a polynomial curve fit, the mean sizes

corresponding to 10%, 25%, 50%, 75% and 90% of the cumulative distribution were calculated.

(b) Electroformed sieve analysis

Electroformed nickel sieves having square apertures accurate to $\pm 2\mu\text{m}$ were specified for this method, which was based on ISO 3310-3 (1990). The sieves were calibrated by microscope using NPL and NIST graticules⁷ as the traceable unit of length. Each sieve was calibrated by measuring the height and width of no more than 8 apertures per frame in 9 measurement fields across the sieve. The electroformed sieve method was applied to the 10 - 100 μm and 50 - 350 μm grades.

Sieve frame dimensions could vary from 70 - 200mm. Any mechanical shaking method could be employed for the 50 - 350 μm sample but a dry sonic sieving method was used for the 10 - 100 μm grade (Gilsonic Autosiever). The end points were determined when less than 5mg and 1mg per minute respectively of the initial sample weights passed each sieve. Sample losses were less than 0.5% of the charge for the 50 - 350 μm sample and less than 2% for the 10 - 100 μm grade.

Five replicate analyses were performed in each test from which the sizes at the prescribed percentiles were calculated in the same way as described for the measurements made by gravitational sedimentation.

(c) Optical microscopy and image analysis

Optical microscopy combined with image analysis was specified to analyze the 1 - 10 μm , 3 - 30 μm , 10 - 100 μm and 50 - 350 μm grades.

Since, the three smallest samples were supplied in 1g bottles, accurate sub-division into the milligram quantities required for a single slide was important. It was therefore recommended that slides should be prepared from single drops of a concentrated glycerol paste of the complete contents of the sample bottle. 35 slides were prepared from a single 1g sample. 15 fields per slide were counted, and 10 - 20 particles per field analysed. This gave an average count per analysis of about 8,000 particles.

In the case of the 50 - 350 μm sample, the 5g bottles were subdivided initially into 10 x 0.5g samples and then into 100 x 5mg sub-samples. A single 5mg bottle provided just enough particles for a slide and 10 complete bottles/slides were then prepared and analysed as described above.

Distortion arising from camera/microscope lenses was measured using the NPL graticule⁸ and was limited to 5%, and X/Y pixel correction was applied where possible. 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^{9,10,11} correction was implemented for particles cut by the edge of the video frame. The raw count-based data were subsequently converted to a volume average so that the results could be compared directly with the other mass-based size distribution data.

(d) ESZ analysis

The ESZ method was employed for the 1 – 10 μ m, 3 – 30 μ m and 10 – 100 μ m samples. Particular attention had to be paid to the subdivision process, since the weight of the powder involved per sample was as small as 5mg.

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 – 100 μ m sample, 40% glycerol / 60% distilled water was used to reduce sedimentation during analysis. The stock suspension concentration was accurately calculated by careful weighing. 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 siphon of the mercury manometer could be calculated.

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

4. LD particle sizing

(a) Homogeneity testing

In order to ensure homogeneity, random samples were extracted from the 200 bottles of each grade and analysed by the most technically advanced LD instruments available to the LDPTS committee. These included the Beckman Coulter¹² LS230 with the VSM 1.2 litre dispersion unit, the Malvern¹³ Mastersizer S with the DIF 2012 1 litre dispersion unit and the Mastersizer 2000 (reverse Fourier optics) with the Hydro 2000G dispersion unit.

The homogeneity testing procedure was based upon that recommended by the International Harmonised Protocol for the Proficiency Testing of (Chemical) Analytical Laboratories¹³.

Up to 15 sample vials of each grade were compared at the 10th, 50th and 90th percentiles of the volume-weighted size distributions. These were 'target values' for the participant laboratories and did not exceed +/-5%. +/-3% and +/-5% respectively, in accordance with ISO 13320-1. Although the tolerances recommended in this standard can be doubled for sub 10 μ m samples, the increased latitude was not adopted because of the prescriptive analysis methodologies used by the LDPTS and the quality of riffled sub-samples.

Samples were not sent to the participating laboratories until approved by the homogeneity testing teams.

(b) Analysis by the LDPTS laboratories

Upon receipt, participants in the LDPTS programme were instructed to initially shake the bottles to re-blend in case segregation occurred in transit. The bottle could then be sampled directly using a small spatula or emptied onto a clean sheet of paper and subdivided into weights suitable for an analysis.

The powder was dispersed as a suspension in a 0.1% w/v aqueous solution of sodium hexametaphosphate and dispersed by sonication for 5 minutes, preferably in the instrument sample chamber or if not available, in an external ultrasonic bath. If a stirrer was used, care was taken to prevent the entrainment of air bubbles, which would compromise the results. Similarly, circulating pump speeds were carefully controlled to avoid air entrainment.

Sufficient sample was added to achieve the optimum obscuration recommended by the LD instrument manufacturer, typically 8% to 10%. The repeatability of at least 3 consecutive runs was compared, as any significant differences would indicate poor dispersion. Once stable analysis conditions had been determined, the experiment was repeated on a fresh sample. Refractive index values were supplied. The unimodal (single mode) model was chosen in the case of instruments offering statistical modelling of the size distribution,

A prescriptive analytical methodology was performed by the group members, in accordance with an externally validated test procedure¹⁴.

The particle size analyses were each reported as sizes corresponding to the 10th percentile, median, and 90th percentile of the volume-weighted cumulative distribution.

5. Results

(a) Primary particle sizing methods

The results from all the primary particle sizing methods are shown in Figures 3, 4, 5 and 6. Each line on the graphs represents the average of 5 tests per method. It can be seen that a combination of spherical particles analysed by highly prescriptive methods produce very comparative results. Note. The 50 – 350 μm sample was not available to all the laboratories in the initial round and so was only analysed by Whitehouse Scientific. Nevertheless there was excellent agreement between sieving and microscopy both between laboratory for a given method, and between methods.

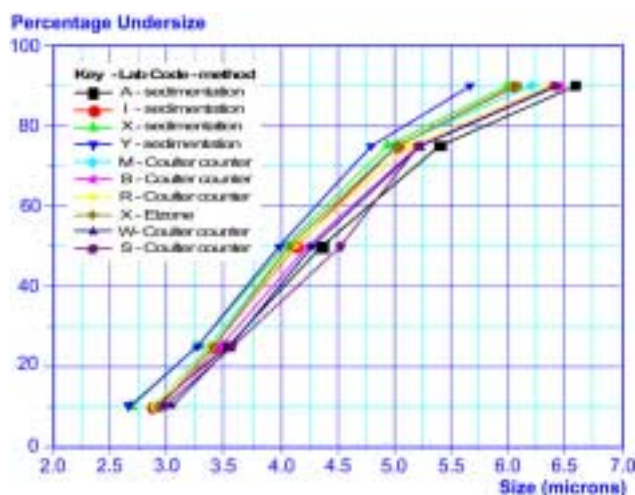


Figure 3. Primary particle size analysis results for a 1 – 10 μm polydisperse standard

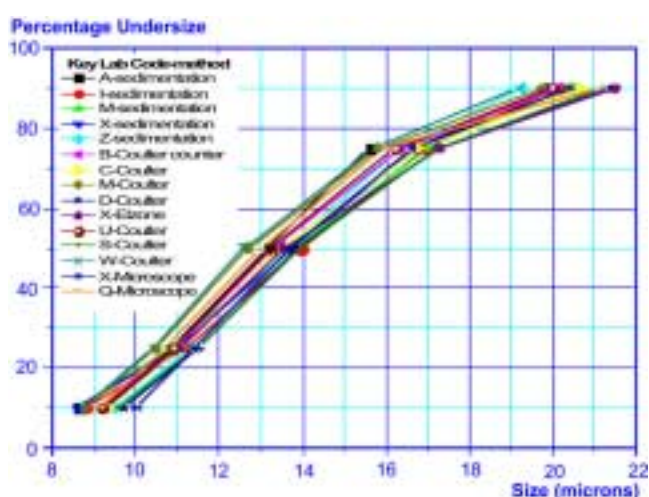


Figure 4. Primary particle size analysis results for a 3 – 30 μm polydisperse standard

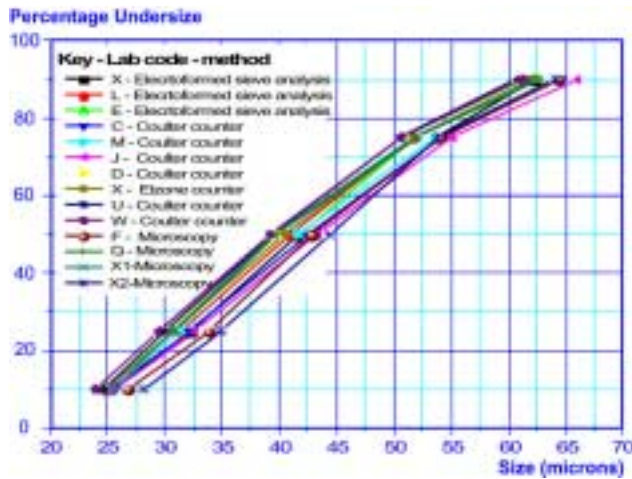


Figure 5. Primary particle size analysis results for a 10 – 100µm polydisperse standard

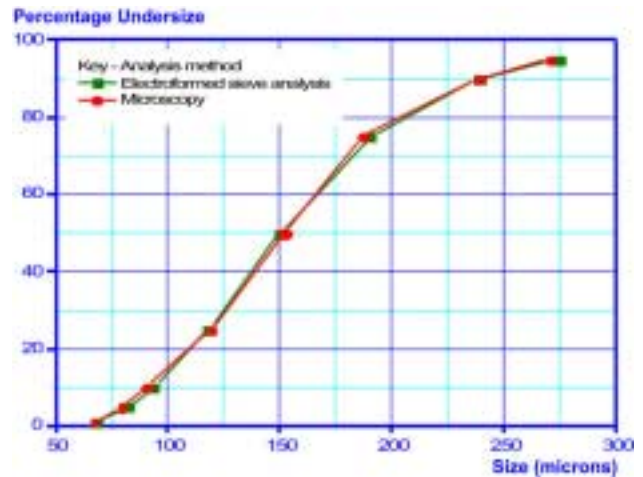


Figure 6. Primary particle size analysis results for a 50 – 350µm polydisperse standard

(b) LD results

(i) 1 – 10µm standard

The particle size analysis was simplified by expressing the uncertainty bands at D_{10} , D_{50} and D_{90} . The results from the LD analysis were then superimposed on the primary data uncertainty bands (Figure 7).

Although the average values for the median size and D_{10} were within the corresponding uncertainty bands, some laboratories reported lower than expected sizes. The average value for D_{90} was noticeably larger than the corresponding value from primary particle size analyses, indicating that some of the laboratories had not satisfactorily dispersed the sample. Two laboratories reported a maximum size of over 200µm, which may have been transcription errors. These outliers were eliminated from statistical calculations.

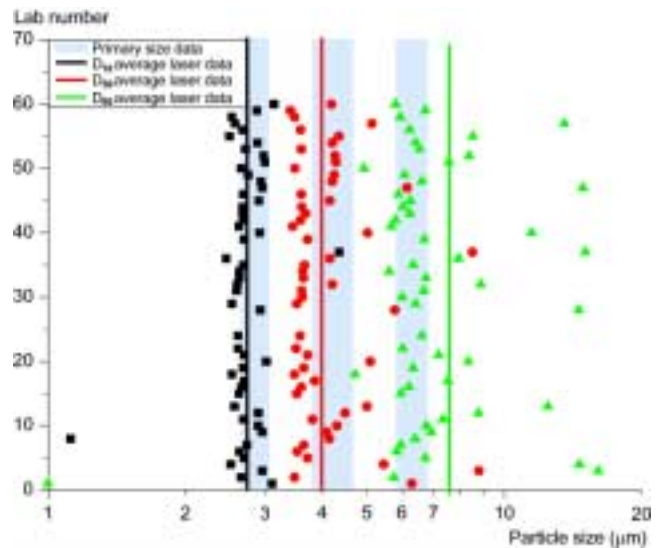


Figure 7. LD-results for the 1 – 10µm standard

Percentile	Band width (µm)		
	D_{10}	D_{50}	D_{90}
Primary methods	2.6 – 3.1	3.8 – 4.4	5.7 – 6.8
Laser method *	2.4 – 3.2	3.4 – 4.3	5.4 – 7.7

* Manufacturers values – at least 10 repeats on 3 different instruments

Table 1. LD manufacturer results for the 1 – 10µm standard glass microsphere standard

Good agreement with the primary data was obtained by the homogeneity testing laboratories (Table 1), showing that following a prescribed method of testing is essential for reproducible results in an inter-laboratory comparison.

(ii) 3 – 30µm standard

Good agreement between the primary particle size data and corresponding measurements by LD analysis was seen at D_{10} and D_{50} (Figure 8). However, as in the case of the 1 –

10 μ m standard, the D₉₀ values were larger than expected, indicating poor dispersion or presentation to the measurement cell of the LD instrument. The homogeneity testing laboratories once again produced excellent agreement across the whole particle size distribution (Figure 9).

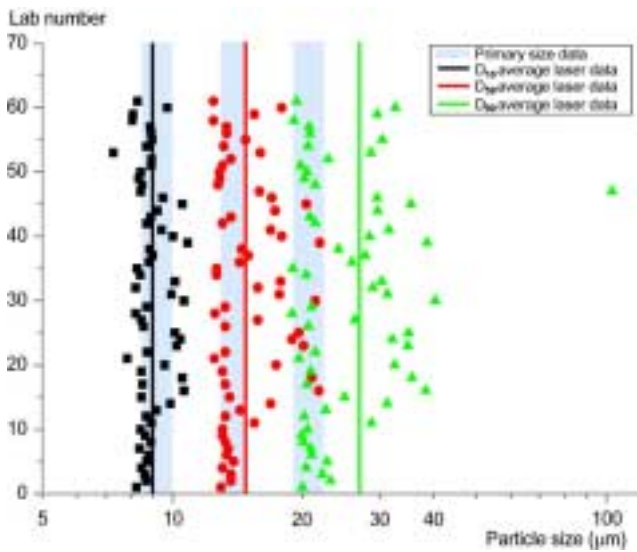


Figure 8. LD-results for the 3 – 30 μ m standard

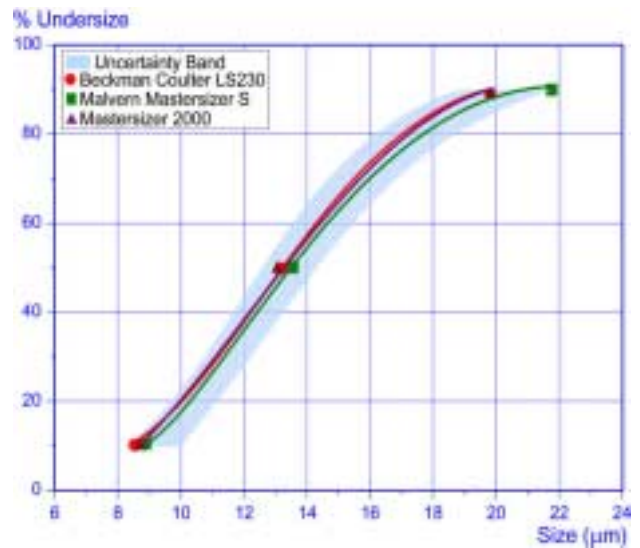


Figure 9. LD manufacturer analysis of the 3 – 30 μ m glass microspheres reference standard

(iii) 10 – 100 μ m and 50 – 350 μ m standards

The 10 – 100 μ m standards proved to be the easiest samples to analyse by LD with very little inter-laboratory variation, however the average of the D₉₀ values was a little higher than expected, based on the values obtained by the primary methods.

Inter-laboratory variation associated with the 50 – 350 μ m standard was larger, but the average at all three chosen volume-weighted percentile values was very close to the corresponding data obtained using the primary sizing methods (Figure 11).

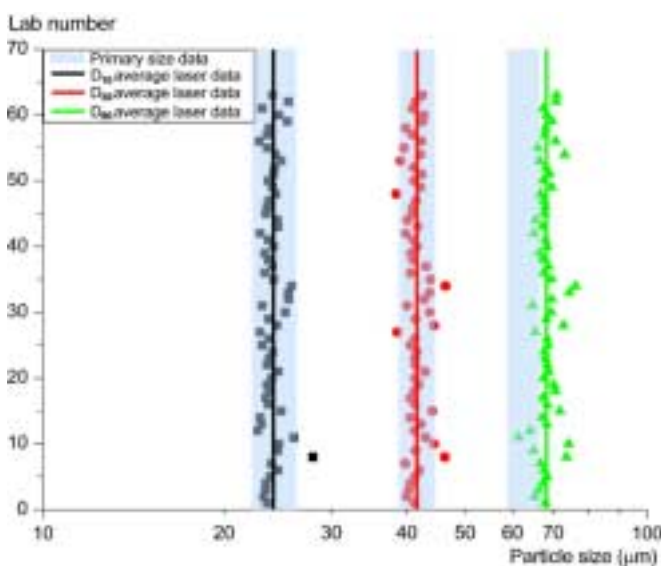


Figure 10. LD-results for the 10 – 100 μ m standard

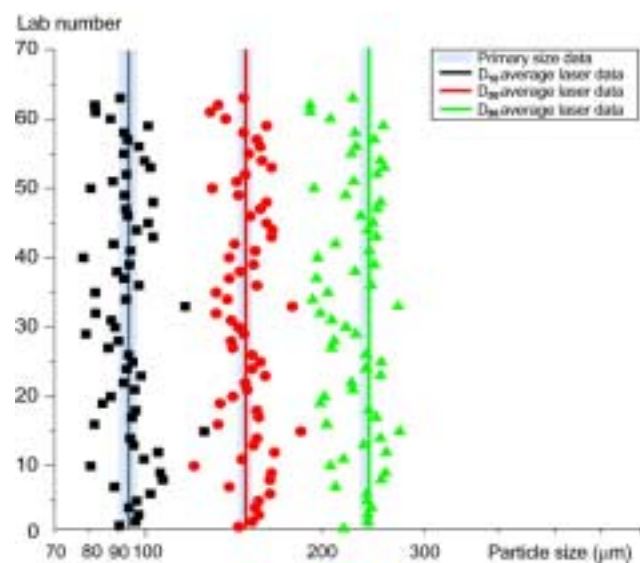


Figure 11. LD-results for the 50 – 350 μ m standard

Conclusions

Compared with reported inter-laboratory variation associated with the earlier BCR quartz reference materials, improved inter-laboratory reproducibility has been achieved by the use of spherical glass particles in single shot bottles, based on the outcomes from the primary particle size analyses. This improvement has been obtained, even though the reference materials were analysed by many more laboratories using a wide range of different analytical methods. The standards certified were: 1 – 10 μm , 3 – 30 μm , 10 – 100 μm and 50 – 350 μm .

When analysed by different LD instruments to a standardized protocol, the group of instrument manufacturers also found excellent inter-laboratory agreement between different LD instruments and also with the reference data obtained by primary methods.

When sent for characterisation by LDPTS to over 60 laboratories employing a wide range of laser diffraction instruments, the overall average particle size values corresponding to the 10th percentile, median and 90th percentile weighted by volume were also very good, although some laboratories reported individual data that were well outside the expected size bands. The samples supplied were very representative as they were produced on a spinning riffler, so such poor results are believed to be most likely the consequence of unrepresentative presentation to the measurement zone of the LD instrument. Common errors are inadequate dispersion of fine materials, for example insufficient time in the ultrasonic bath resulting in the measurement of clusters of powder or, in the case of large particles, sedimentation in the sample chamber or tubes leading to the measuring zone.

Remarkably, some laboratories recorded values of the 90th percentile size to be >200 μm for the 1 – 10 μm standard. These anomalous findings probably resulted from the introduction of a number of artefacts to the measurement process, including air entrainment, electronic noise, poor optical alignment or could possibly have arisen as a transcription error. Whatever the reason for the very few anomalies that were observed, this programme by LDPTS has highlighted the potential for size-analyzing reproducibly spherical-shaped polydisperse reference standards by some of the most sophisticated instruments currently available for particle sizing.

The results supplied from a particle size laboratory can therefore only be treated with confidence provided the instrument is calibrated with a polydisperse reference standard and operated under a proven and reproducible Standard Operating Procedure for the material in question.

Acknowledgements

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