EVALUATION OF NUMBER BASED PARTICLE SIZE ANALYSERS

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Abstract

Alcan recently evaluated particle size analysers reporting number distributions based on counts rather than derived from volume distributions. Several new analytical techniques have been developed and have matured over the last decade. This work identified those that are close to being viable alternatives to techniques presently in use.

Electrical Sensing Zone instruments are the most commonly used technique for counting particles with Bayer process samples. Their main disadvantages (slow, labour intensive, high operator skill requirement) prompted examination of available alternatives. Of the new instruments investigated, the Single Particle Optical Sensing (SPOS) instrument accurately reported number distributions in a single operation for a significant saving of time in measurement and data handling. Both instrument types show similar resolution, as demonstrated by analysis of a sample mixture with a bimodal distribution.

Direct comparison of Bayer samples analysed by both SPOS and Elzone further demonstrated the applicability of SPOS for Bayer application.

1 Introduction

The current standard in the Bayer industry for particle counting is the Coulter (or Elzone) Counter. Wallace Coulter developed this technology in the 1940s and patented it in 1953 (Wallace H Coulter Biography, 1998). The Coulter range of instruments has 12 orifice tubes (20 to 2000 µm diameter), with the working size range of each orifice tube being from 2% up to 60% of its diameter. The limited dynamic range of each orifice tube inhibits routine application across wide size ranges. Combinations of orifice tubes make the instrument capable of analysing wide particle size ranges, with a practical lower limit of detection of ~2 µm (theoretically 0.4 µm). However, the additional sample and data handling required (e.g. sample screening, swapping tubes, and matching distributions) to overlay data into one distribution make this a slow process even for experienced operators.

For these reasons, particle counting with electrical sensing zone instruments requires a skilled operator and remains slow, labour intensive and operator dependent. Several new analytical techniques have been developed over the last decade which are now maturing, and appear close to being viable alternatives to the techniques presently in use. Five of the particle size analysers presently available were evaluated for their number distribution accuracy.

2 Instrument Principles, Advantages and Weaknesses

2.1 *Coulter Counter (Multisizer)*

The 'Coulter Counter' is the longest serving particle counter used in the Bayer industry, having been used for more than 20 years. The 'Elzone', a competitor of the Coulter using the same principle is favoured by some alumina producers.

The principle of the instrument (Lines, 1992) is to draw a very dilute suspension of the solid to be measured through a small orifice. The instrument measures the resulting change in conductivity of the electrolyte, between immersed electrodes, caused by the suspended particles. The reduction in conductivity caused by each particle passing through the electric field is proportional to the volume of the particle. Particle size and numbers are collected as a sequence of electrical pulses of various sizes.

A significant weakness of this instrument is that the orifice has to be large enough to prevent blockage by any of the coarser particles in transit. This inevitably reduces the measurement sensitivity for the smaller particles to a point where quite often the use of at least 2 orifices is required to cover the whole distribution.

Moreover, because the suspension has to be dilute (to avoid coincidental particle transit) the measurement is slow to produce statiscally significant counts. The accurate reduction of the sample down to the very small mass required by the instrument also consumes considerable time and introduces potential errors.

Notwithstanding these issues, and because of the high number of channels (up to 300) (Coulter Counter – Multisizer™ 3, 2001) used to count particles, its accuracy has so far been unsurpassed. Multimodal distributions can be characterized with great accuracy.

2.2 *Coulter Laser (LS 230)*

This instrument was introduced by Coulter over 10 years ago to compete with the Malvern Mastersizer laser diffraction instrument. While it is based on the same principle, the Coulter LS230 has additional capabilities with associated advantages (Sizing small particles with light scattering instruments, 1997; LS™ 100Q/200/230 Series Laser Diffraction Particle Size Analyzers, 1998.).

The number of detectors (132 in total) and the way they are positioned in an X pattern enhance both accuracy and repeatability by making the laser beam easier to align to the center of the detector array. One of the key features of the instrument is the use of an independent technique to refine the resolution in the submicron range. This technique, called PIDS (Polarization Intensity Differential Scanning) (Row, 1993; Laser Diffraction Particle Size Analysis: Issues and Answers LS Series, nd.) uses three wavelengths of light, filtered for polarization in the vertical and the horizontal planes. Six detectors (in addition to the 126 detectors used for measuring scattered light) are positioned at around 90 degrees to the direction of the light path to measure the differential intensity between scattered light of vertical and horizontal polarizations.

Although PIDS uses a second light source split into 'flavours', the scattering of these light beams by particles is described by the same Mie theory as laser scattering, so all scattering information is converted to particle size using the same algorithm in a single operation (PIDS – Polarization Intensity Differential Scattering, 1998).

Conversion from a volume to number based distribution is application of classical theory. However, particularly for fine particles, particles that occur in the largest number do not necessarily reflect the largest crystal volume. For this reason, these derived number based distributions are considered to incorporate large errors.

2.3 *RapidVue*

The RapidVue (RapidVUE® Particle Shape and Size Analyzer, 2000; RapidVue Image Analyzer – Launch Package, 2001) is a particle shape and size analyser offering a wide dynamic range (20 to 2500 µm). As particles pass in front of a camera, a picture is taken and converted to size and number information. The RapidVue takes an image in continuous-tone format (gray-scale) and converts it to a digital form through the processes termed sampling and quantization.

'Sampling' is the term for the measurement of the intensity of the continuous-tone at specific points. Quantization is where these points or samples are converted to a 'brightness' value or greyscale value, 0 representing black and 255 white.

A simple algorithm identifies and measures particles in an image. A threshold is chosen between '0' and '256'. All pixels lower in value (darker) than the threshold are considered to belong to a particle. The image is scanned from top to bottom, identifying dark segments on each line, and associating them with the segments on the previous line.

2.4 *Aerosizer*

The Aerosizer (Aerosizer® DSP high resolution particle size analyser, 2001) measures particles one at a time in the range of 0.20 to 700 µm. The particles may be sprayed as an aerosol from a liquid suspension, but the preferred sample presentation is as a dry powder. The particles are blown through the system and dispersed in air to a preset count rate.

The Aerosizer operates on the principle of aerodynamic time of flight. The particles are accelerated by a known (and constant) force due to airflow, and are forced through a nozzle at nearly sonic velocity. Smaller particles are accelerated more than large particles due to a greater force-to-mass ratio. Two laser beams measure the time of flight through the measurement region by detecting the light scattered by the particles. Statistical methods are used to correlate the start and stop times of each particle in a particular size range (channel) through the measurement zone. This instrument has been mostly used to date in the pharmaceutical industry.

2.5 *Accusizer (780AD)*

The AccuSizer uses Single Particle Optical Sensing (SPOS) (White, 2002) to size and count large numbers of particles, one at a time. The Accusizer (780AD) has a dynamic range of 0.5 to 400 µm, recording the distribution in a number of channels (from 8 up to 512) depending on desired resolution (AccuSizer AD user manual, 2003; AccuSizer Specifications, 2005). Counting and sizing is achieved by a combination of light extinction (1.5 to 400 µm) and light scattering (below 1.5 µm).

According to the manufacturer, the introduction of an auto dilutor to automatically find the optimum suspension density improves the instrument precision markedly, while making the instrument easier to operate.

3 Comparison of all Five Instruments

Micro-riffled samples of plant fine seed 'hydrate (A)' and an artificial bi-modal hydrate were sent to each of the instrument manufacturers (3g each) for analysis.

3.1 *Plant Fine Seed 'Hydrate (A)' Analysis with all Instruments*

To enable direct comparison, all results were converted to weight density distribution. The standard output for all instruments is a histogram representing the weight percent or number percent in various size intervals, where the size intervals are normally increasing from small to large. The weight or number density is the derivative of the cumulative distribution (S shape curve) which is often used to report size distributions. To convert the histogram to a size or number density, the weight percent or number percent (in the size interval) is divided by the difference in diameter.

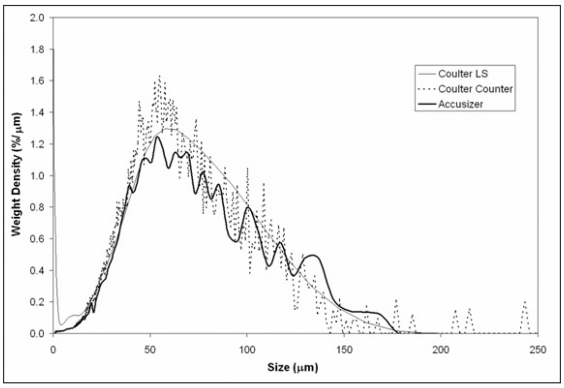

Figure 1: Weight density size distribution of a hydrate (A).

Figure 1 is a chart comparing the weight density results of hydrate (A) from 3 of the 5 instruments evaluated. The RapidVue and Aerosizer were not included, as the values were off-scale. The graph demonstrates that these instruments compare quite well for this sample. The biggest difference is at the larger end of the distribution, where the Coulter Counter apparently sees coarse particles that are not seen on the other instruments.

Comparing the same analyses in terms of number density (Figure 2), confirms that the three instruments agree well over the whole range, except that the Coulter Counter shows no particle counts below ~10 µm. It is interesting to note that the Coulter Laser Sizer (LS) calculates the counts in this region very well, remembering that this number distribution is interpreted from diffraction data, and is not a 'real' count. This is undoubtedly due to the PIDS feature, which compensates for this usual deficiency of laser diffraction instruments.

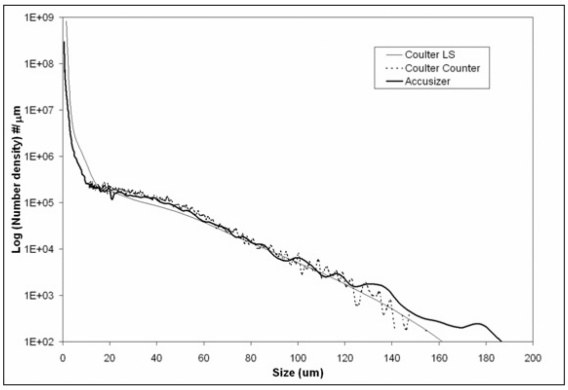

Figure 2: Number density of hydrate (A).

3.2 *Bi-modal Hydrate Sample Analysis with all Instruments*

To examine the instruments resolution a bi-modal hydrate sample was prepared. Equal masses of two sieved fractions, +45 – 75 µm and +90 – 125 µm, were blended and the bulk sample micro riffled. Figure 3 compares the results from the five instruments evaluated. Apart from the Aerosizer, it appears that all instruments give similar results. The main differences are the separation of the two peaks and their absolute positions.

The Coulter Counter clearly gives the best peak separation, and the Coulter Laser gives the worst. The Accusizer however, was the instrument that gave the most realistic proportion of the two peaks (50:50 by weight).

The results of the Rapidvue and the Aerosizer differed significantly from the other instruments. The Rapidvue detected that the sample was bi-modal, but resolution at the finer end was too poor to give a good proportion of the two modes. The Aerosizer gave an analysis disparate to the sample. This result could be related to a property of our samples that makes them difficult to analyse with this instrument.

Comparing the same analysis now as a number distribution (Figure 4), the Coulter Counter and Accusizer both detect a large number of superfine particles not seen on the weight distribution, as is expected. The Accusizer is again able to go to a much smaller size than the Coulter Counter. The Coulter Laser was unable to see any fines with this relatively coarse distribution.

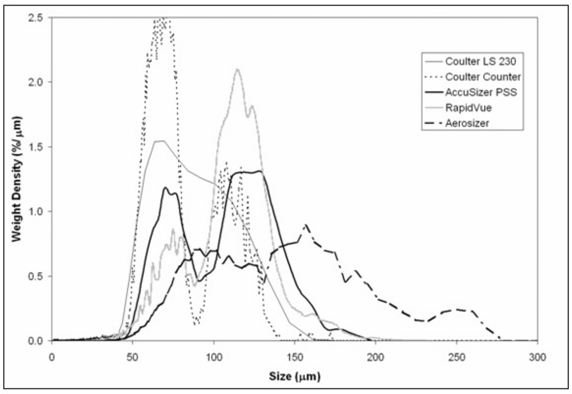

Figure 3: Weight density of the bi-modal hydrate sample.

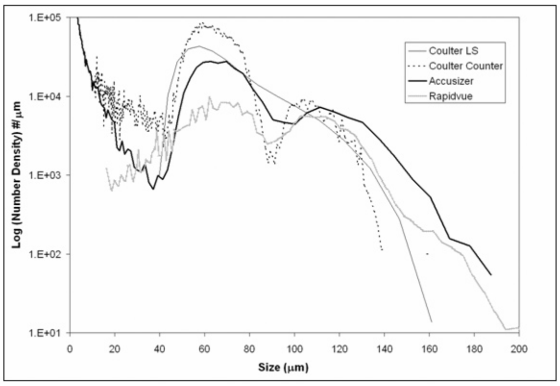

Figure 4: Number density of the bi-modal hydrate sample.

4 Direct comparison of the Accusizer and Elzone

From the results of the above instrument comparison, it is clear that the Accusizer and Coulter Counter (electrical sensing zone instrument) compare well. Subsequently the Accusizer and an Elzone instrument were tested with a number of coarse and fine plant hydrate samples. Note that the Elzone was used from this point, instead of a Coulter Counter, as this had an established Alcan procedure and had already been used to analyse the samples.

4.1 *Full Size/Number Distributions*

The Accusizer measures from 0.5 to 400 μm in a single pass, while the Elzone distribution (1 to 180 μm) is the combination of separate measurements from two orifice tubes (48 μm and 300 μm). Figures 5 and 6 compare the two sizing methods and the measured number densities for samples of coarse and fine hydrate.

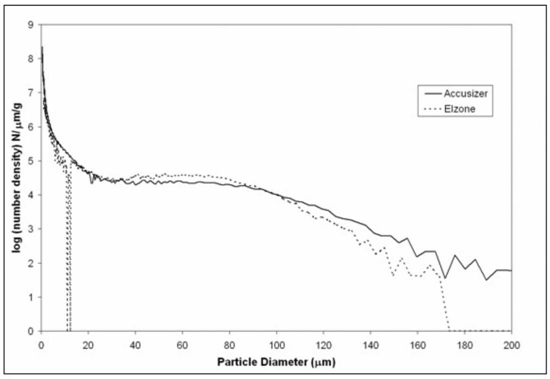

Figure 5: Coarse hydrate seed sample – number density determined by both Accusizer and Elzone measurement.

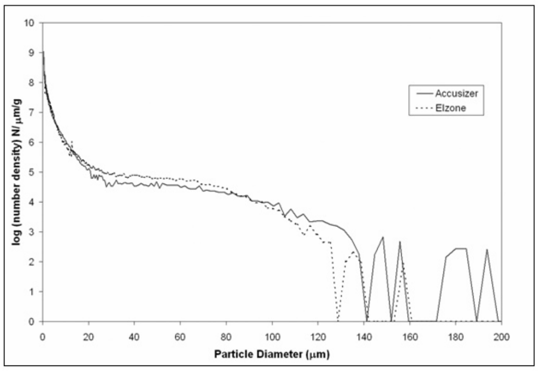

Figure 6: Fine hydrate sample – number density determined by both Accusizer and Elzone measurement.

When measuring samples with reduced fines content (Figure 5), the Elzone showed significant noise around 9.5 to 12 μm, inherent with matching data sets from two orifice tubes. Fine seed hydrate (Figure 6) matched better as a consequence of increased particle numbers in this size range. Aside from the noise where the two data sets are matched, the overall size distributions for each method compare well.

Increased noise visible at the coarser end (>120 μm), of both the Accusizer and Elzone size distributions, is directly related to the lower fraction of coarse material. As the number of particles in the upper size range reduces, single particles in these size 'bins' have a significant effect on the number density; this is seen as a noisy signal especially in samples like fine hydrate where the amount of coarse material is low.

It is also noted that the Elzone is somewhat insensitive above 160 μm. This is a known limitation of this sizing method, and a direct consequence of the orifice size.

Not having to match distributions measured from two orifice tubes gives the Accusizer a clear advantage, particularly when measuring coarser samples. Measurement of fine hydrate appears equivalent but the time taken for data handling still favours the Accusizer.

4.2 *Nominated Size Densities*

Figure 7 compares Accusizer and Elzone analyses of coarse and fine hydrate samples, at a nominated particle size (3.4 μm). Fine hydrate samples are plotted against the right hand y-axis to allow a summary of the data in one figure, using relevant scales and without masking detail.

For the Accusizer, all samples were analysed in duplicate, with repeat sample analysis performed for all coarse hydrate samples and one of the fine hydrate samples. The precision and subsequent repeatability of the Accusizer for both sample types is within the precision demonstrated by the Elzone coarse hydrate sample analyses.

For this particle size both instruments would indicate the same trend in number density, with less instrument variation from the Accusizer.

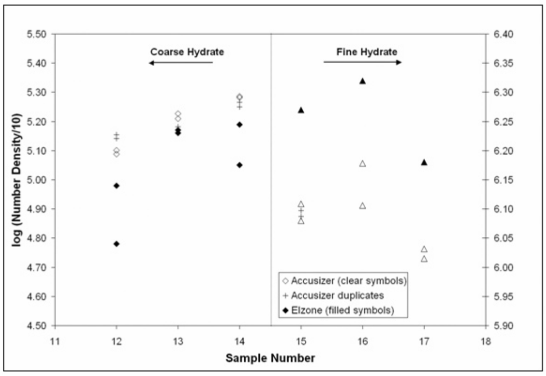

Figure 7: Number density data for hydrate samples measured at 3.44μm (Accusizer) and 3.40μm (Elzone).

4.3 Direct Comparison of Results from each Method

The results from both particle counting instruments (Accusizer and Elzone) across a number of number densities for fine hydrate samples are shown in the following 'X-Y Plot' (Figure 8). There is good agreement across all four size densities. As was concluded from Figure 7, both counting techniques would indicate the same trends.

As was noted with the earlier analysis of the bimodal sample, there is still some underestimation of number density by the electrical sensing zone method for the larger number density. This is consistent with its expected preferential analysis of the finer material.

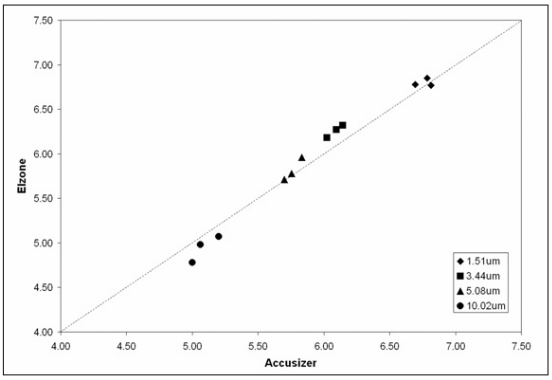

Figure 8: Elzone and Accusizer number densities for fine hydrate samples at four number densities.

5 Conclusions

Of the five instruments examined, the Coulter Counter or Elzone are still better than most sizing methods for number size distributions. However, the Accusizer demonstrated some distinct advantages relative to a Coulter Counter or Elzone:

- Equivalent if not better resolution and quality of the measured distribution, with no tendency to preferentially analyse fine particles;
- Wider range of particle sizes (0.5 to 400 μm) measured in a single pass, increasing the speed of analysis;
- Improvement of the practical lower detection limit from 2 μm to 0.5 μm;
- An 'auto dilution' feature with the potential to dilute over-concentrated samples to within the working concentration (obscuration) range of the instrument;
- Increased sample throughput with a lower operator skill requirement.

Direct comparison of the results from the Accusizer and Elzone shows both methods would characterise fine hydrate samples in a very similar way.

From this study, it appears the Accusizer is capable of measuring particle numbers in a single pass, over a wide size range, to give reproducible measurements at lower size intervals than the Elzone.

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