LIMITATIONS IN THE LASER PARTICLE SIZING OF SOILS

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INTRODUCTION

Many studies, such as Loizeau *et al.* (1994), Buurman *et al.* (1997) and Beuselinck *et al.* (1998), have focused on the comparison of laser diffraction and pipette or sieve methods of particle sizing. The main focus of these studies has been to establish a correlation between the two techniques so as to allow interchangeability and direct comparison of these methods. The consensus of these studies was that laser particle sizing gave consistent repeatable results, with some limitations. Notable of these limitations was the under-reporting of the percentage clay content and the dependence on well-described optical properties of refractive index and absorption.

Tests on laser diffraction devices for accuracy and precision have indicated that the method works well for test particles such as glass spheres (Stuut 2001, Xu & Di Guida 2003). This is to be expected as test particles used to certify laser diffraction instruments are spherical glass beads. Also the conversion from light scattering data to particle size distribution uses Mie theory, in which a tacit assumption is that the particles are perfect spheres.

Performance on natural sediments such as soil materials is poorly documented, except by comparison with pipette or sieve results. Buurman *et al.* (1997) point out that non-spherical particles should become averaged as spheres during a measurement due to random orientation as the sample is pumped through the machine. More advanced work of Xu & Di Guida (2003) stated that progressively larger particle size means and broader sample distributions were measured on a laser diffraction device when compared to a Coulter-type unit. This was the result of particle non-sphericity when using a range of particle shapes such as cubes, rectangles and rod-like particles. Specifically, they reported that the measured particle size is heavily skewed towards the length of a particles longest axis by the random orientations of a particle passing the laser during measurement.

This study seeks to demonstrate the effects of soil particles on laser diffraction derived particle size distributions, and suggest measurements that must be supplied with any laser diffraction derived particle distribution to assess the accuracy of the analysis.

METHODS

The laser particle analyzer used in this study is the Malvern Mastersizer 2000 from Malvern Instruments. This unit utilizes Mie theory in making the conversion from light scattering data to particle size distribution data. Some authors have used the Fraunhofer method for data conversion (Beuselinck *et al.* 1998, Loizeau *et al.* 1994), but as stated by Wedd (2003) this technique is only valid for large particles greater than 100 µm diameter and will seriously compromise results below 10 µm. The unit has been tested with Malvern quality audit standard QAS2002 glass beads and correctly reported the 10th, 50th (median) and 90th percentile of the size distribution to within a two percent tolerance of diameter (analysis available from author upon request).

All analyses were conducted using a Malvern Mastersizer 2000 with a HydroG large sample dispersion unit. Samples were processed using Elix filtered water in measured quantities; this was to allow later checking of the concentration indicated by the sample analysis with the concentration expected for a given mass of sample and known volume of dispersant. The samples were run at 900 rpm and 2000 rpm on the sample stirrer and cell pump respectively. Background signals were measured prior to each test run and were close to baseline. This, together with two minute sampling times means that air bubbles are unlikely to have had a significant effect on the analysis.

The Mastersizer uses two lasers, meaning that two sets of optical properties are required. Identical settings of refractive index and absorption were used for both laser wavelengths. The refractive index was set to 1.544, that of Quartz (Beuselinck *et al.* 1998), whilst the absorption was set to 0.008. It was found that this absorption value gave a good fit to the light scattering data as described by Wedd (2003), with the residual error reported by the Malvern being less than 1%. The issue of optical parameters will be addressed further in the discussion.

The soil material used was classed as a Petroferric Red Kandosol by the Isbell (1996) classification (Geoff

Humphreys *pers. comm.* 2003). It comprises an aeolian derived accretionary mantle, with a sizable contribution of locally sourced granitic sands. This soil was separated into three size classes, the fine fraction comprising material less than 100µm sieve diameter, a coarse fraction greater then 180 µm sieve diameter, and a fraction between the two sieve diameters that was discarded. Another comparison was undertaken using the QAS2003 glass beads and a sieve fraction between 250 µm and 500 µm from the same soil as described above.

Real concentration values were calculated from the mass of sample added divided by the density and volume of dispersant. This figure was then multiplied by one hundred to become a unit-less volume percentage (volume sample / volume dispersant). The measured concentration was supplied with the Mastersizer analysis result file and is in the form of a volume percentage.

RESULTS

### 1. Testing the influence of concentration
Both the fine and coarse fraction concentrations were measured with the Mastersizer at four known concentrations. Table 1 shows the result for the two sample types. Both materials had a linear relationship between the real concentration and the measured concentration, indicated by r-squared values in excess of 0.99. The slope of the relationship was different for the two samples however, with the fine fraction concentration over-reported by 1.15 times, the coarse fraction by 3.56 times.

Table 1: real versus calculated concentration relationships.

Sample	Slope of linear relationship	R^2
< 100 µm fraction (fine fraction)	1.15	0.997
> 180 µm fraction (coarse fraction)	3.56	1.000

2. Testing a mixture of samples
Known masses of both the fine (0.5981 g) and coarse fractions (0.2466 g) were added to the Mastersizer. Sample runs were conducted to confirm that they were separate distributions with no overlap. Assuming the density is identical between these samples, the result should show that the sample is 70.8% fine and 29.2% coarse fraction, Figure 1 shows the measured result, the Mastersizer reports that 52% of the sample is composed of the coarse fraction. It also shows the predicted result of how the distribution should appear assuming the Mastersizer is correctly reporting the particle size. As the volumes in any particle size distribution add up to 100%, the predicted result has been rescaled to allow visual comparison with the measured result.
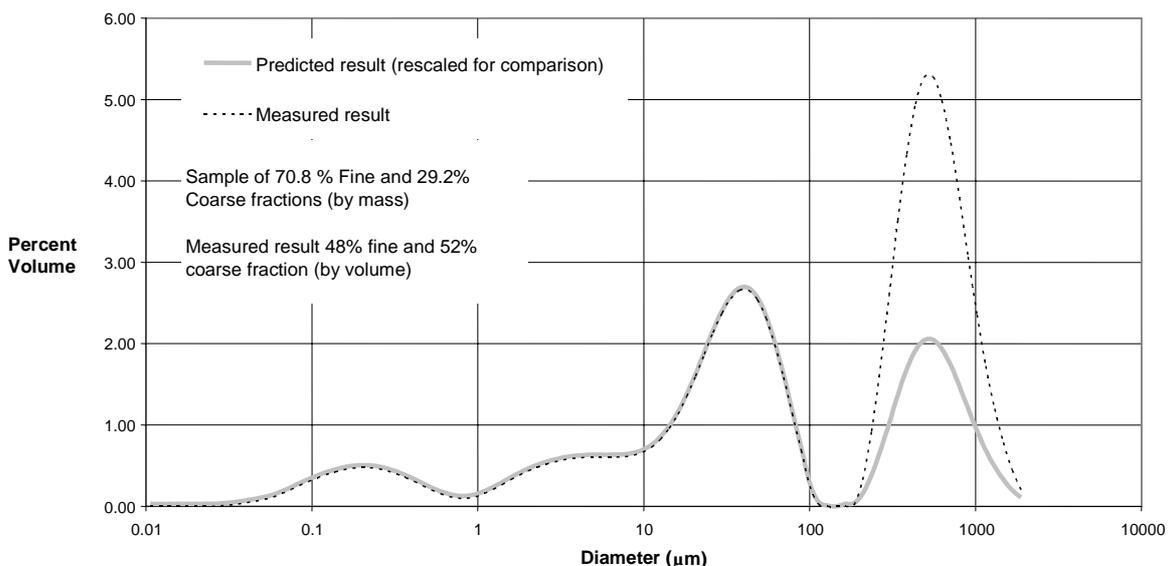

Figure 1: laser diffraction analysis of a known mixture of fine and coarse materials

The measured concentration for the fine material was 1.15 times greater then the real concentration, and 3.46

times for the coarse fraction (similar to values shown in Table 1). The measured concentration of the mixed sample shown in Figure 1 was 1.62 times greater then the real concentration.

3. Testing a known mixture of spherical glass beads and coarse sample

Using the Malvern Quality audit standard glass spheres together with a fraction of coarse material should show whether the overestimation is sample specific or machine specific. A sample comprising 0.1951 g of glass spheres and 0.2006 g of coarse soil fraction (sieve fraction between 250 and 500um) gave the result shown in Figure 2. On a volume basis the glass beads are over-represented by 5.6% (using a density of 2.6 gcm^{-2}) while the coarse fraction over-represents by 234%, leading to size distribution considerably different to that predicted. The optical properties of the two materials tested here are different, setting these properties to that of the glass beads or the coarse fraction as discussed in the methods had little effect on the volume overestimation shown.
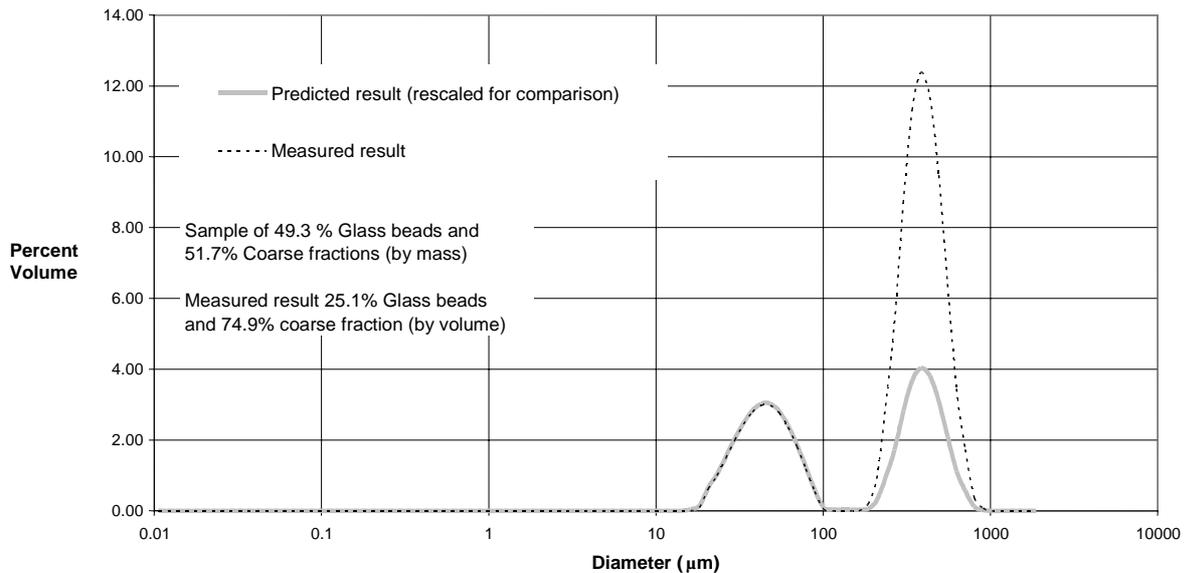
Figure 2: analysis of a mixture of glass beads and coarse soil material.

DISCUSSION

The results shown in Table 1, Figure 1 & Figure 2 consistently show a distinct departure from the expected size distribution. Any causal explanation of these departures, excepting operator error, should therefore explain why other studies have failed to show this effect.

The optical properties of the soil materials tested are always estimates, as the sample optical properties are controlled by the effective refractive index and absorption, a unique average value of the properties of all the particles used in a particular analysis. The optical properties were adjusted to minimize residual errors for these samples, but a potential exists for creation of misleading results. Changing the optical properties could account for the overestimation of the fine fraction by 15% (see Table 1), but the validity of doing so is uncertain. No combination of optical properties will correct the overestimation of the coarse fraction; the size range of the coarse fraction is well into the region where the Fraunhofer approximation of scattering by spherical particles operates. In this size range (greater then 100um), the effect of optical properties on a particle size distribution is negligible (Wedd 2003).

A further possibility is that the density of 2.65 gcm^{-2} used to calculate the real concentration is incorrect. The density of the fine material was measured and found to be 2.5 ± 0.2 gcm^{-2} by the Archimedean displacement method. The density of the coarse fraction (sands) was not measured, however to correct the overestimation of the volume (as shown in Figure 1) a density of 0.74 gcm^{-2} would be required. Therefore a density difference between the fractions is unlikely to be the cause of these results.

The consensus from the literature of Loizeau *et al.* (1994), Buurman *et al.* (1997), Konert & Vandenberghe (1997) and Beuselinck *et al.* (1998) is that laser particle analysers consistently underestimate the clay fraction. This was first reported by Loizeau *et al.* (1994) who stated that laser particle sizing underestimates clay content in an inverse proportion to the clay content measured by the pipette method. The results shown (Table 1, Figure 1) support this statement as an observation, but not as an explanation.

An alternate explanation, supported by the overestimation of the volume of the sand fraction, but possibly correct measurement of the clay fraction, is based on the constant sum effect. Table 2 shows a series of theoretical mixtures of the materials tested here. It shows how the Mastersizer will under-report the fine fraction in inverse proportion to the amount of fine fraction present, an identical effect to that listed by Loizeau *et al.* (1994), but in this case it is caused by the overestimation of the volume of coarse material present, as supported by Table 1 and Figure 1.

Table 2: mixtures of fine and coarse fractions and the theoretical Laser diffraction result.

Known fine fraction %	Known coarse fraction %	Measured fine fraction %[a]	Measured coarse fraction %[a]	Percentage of fine fraction measured[b]
10.0	90.0	3.5	96.5	34.6
20.0	80.0	7.5	85.8	37.4
30.0	70.0	12.2	75.1	40.5
40.0	60.0	17.7	64.4	44.3
50.0	50.0	24.4	53.6	48.8
60.0	40.0	32.6	42.9	54.4
70.0	30.0	43.0	32.2	61.4
80.0	20.0	56.4	21.5	70.5
90.0	10.0	74.4	10.7	82.7
95.0	5.0	86.0	5.4	90.5

[a]calculations based on Table 1: volume of fine fraction multiplied by 1.15 times, volume of coarse materials multiplied by 3.56 times, then recalculated as percentages.
[b]percentage of original value of fine fraction that laser diffraction will measure.

The result shown in Figure 2 demonstrates a coarse fraction volumetric overrepresentation in comparison with spherical beads. A difference in the sphericity of the particles is the most likely explanation of this result. The photograph in Figure 3 gives some indication of the non-sphericity of the coarse fraction. As discussed in the introduction, Xu & Di Guida (2003) believe that for non-spherical particles both the mean particle size and standard deviation is overstated by laser diffraction results and this amount depends on the degree of non-sphericity. Figure 2 demonstrates clearly a volume overestimation, but does not explain whether it is caused by overestimation of particle size, or overestimation of the number of particles present. As described by Wedd (2003) the volume in each size class is determined by the number of particles in each size class. As volume is proportional to the diameter cubed, any over-sizing of particles will cause large changes in the volume distribution. It is also likely that the effect of non-sphericity is different in the diameters below 20μm (Xu & Di Guida 2003), this is also supported by Table 1, where the clay silt mixture comprising the fine fraction shows much closer agreement with the real concentration used. For particles of consistent shape, greater than 20μm, such as sugar crystals, this over-sizing will be constant across the size range and will result only in a shift in diameters, rather than a large change to the particle size distribution (Xu & Di Guida 2003). For soil samples this scenario of consistent shape across the entire size range is unlikely. Representative particle sizing by the laser method is therefore also unlikely.
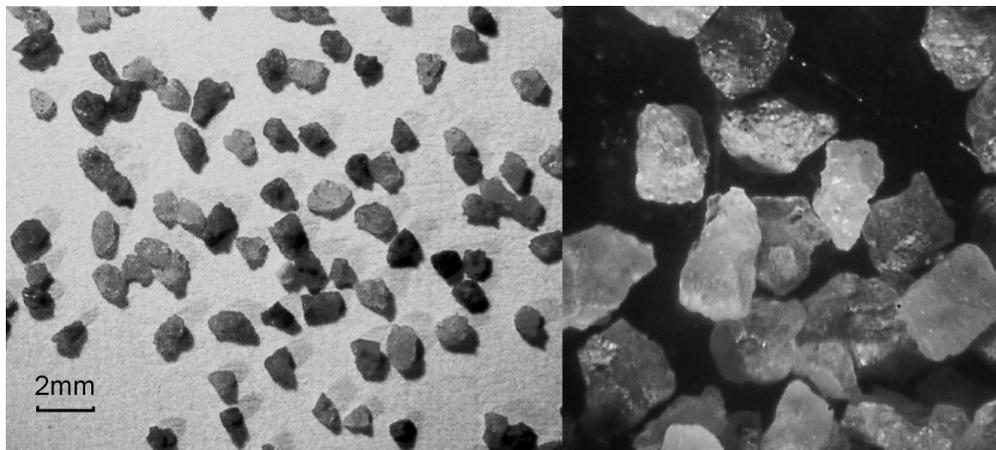
Figure 3: coarse fraction sands shown on left with scale: close up view on right.

CONCLUSION

The effect of particle non-sphericity on mean particle size and standard deviation have been shown by Xu & Di Guida (2003); extension of the consequences of this for soil analysis has not previously been demonstrated. The possibility of an analysis showing a sand to clay ratio of 3 to 1, misrepresenting a true ratio of 1 to 1, points to serious limitations in the laser diffraction technology. Soil studies require the analysis of complex mixtures of particle shape and size, as any soil containing a mixture of particle non-sphericities will be prone to the volume overestimation effects shown. It should be possible to create conversion factors to normalize laser diffraction results for soils. Such an approach could involve correcting the result of a laser diffraction device with a Coulter-type instrument, then testing the efficacy of the correction on other samples. Such an approach would require that the samples were all of similar non-sphericity, or that the changes in sphericity with size were constant across all samples.

To allow a measure of confidence in laser diffraction results, all analyses should be made from a known mass of sample material and a known volume of dispersant. Calculation of the real volume concentration can then be compared with the measured concentration, highlighting when the non-sphericity effect is operating and giving an indication of the volume overestimation for a sample. Without this figure the accuracy of any soil based laser diffraction particle size analysis is unknown and unquantifiable.

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