



EFFECT OF CONCENTRATION ON LASER DIFFRACTION MEASUREMENTS

Proper method development when using laser diffraction requires investigating the effect of changing system or measurement parameters on calculated results. One of the measurement parameters that should be examined is sample concentration. A concentration that is too low can lead to erratic results due to poor signal-to-noise ratio. Concentrations that are too high lead to multiple scattering errors. This technical note explains how concentration affects results and makes recommendations for proper method development.

Introduction

The operator can typically control the sample concentration during a particle size analysis measurement when using laser diffraction. When measuring suspensions the operator adds sample to the recirculating diluent until a desired concentration is achieved. When measuring powders the sampler must be prepared and operated in such a way that a desired concentration is achieved during the measurement. In both cases concentration is displayed and reported either as a percent transmission or obscuration. All HORIBA instruments display percent transmission (%T), which is the average percent of the initial laser intensity detected during the measurement. The initial laser intensity is detected and stored after alignment and the background reading. This is the laser intensity with no particles present, or 100 T%. This value decreases as particles are added to the system. A 90 T% indicates that 10 % of the initial intensity has been blocked by the presence of particles. Obscuration is the inverse of transmission, so 90 T% equals 10% obscuration.

Results vary with concentration on all instruments for all samples and the variation is sample dependent. Factors influencing the variation include particle size, width, and optical design of the instrument. During method development it is important to investigate the effect of concentration on results generated. According to the ISO standard for laser diffraction¹: "The particle concentration in the measurement zone should

be high enough to produce an adequate signal (or in other words to reach an acceptable signal-to-noise ratio with respect to precision), yet low enough to ensure multiple scattering to be insignificant to the particle size result". Enough sample material must be added so that the signal-to-noise ratio is high enough so that the results are reproducible and accurate. But this must be balanced with the effect of multiple scattering, causing a decrease in reported size if the concentration is too high (%T too low).

Multiple Scattering

The algorithm used for converting scattered light to particle size distribution assumes that light interacts with a particle and then scatters onto the detectors. Multiple scattering occurs when light scatters off one particle and then interacts again with one or more particles before reaching the detectors. As light scatters off additional particles the angle of scatter increases – light is bent toward the wider angle detectors. Since small particles scatter at wider angles than large particles, the effect of multiple scattering is to reduce the calculated particle size distribution. The concentration at which this multiple scattering significantly changes the calculated particle size distribution denotes the maximum allowable T% for any given sample. Smaller particle size distributions experience multiple scattering effects at lower concentrations (higher %T) than larger particle size distributions. Ascertaining the initiation of multiple scattering effects is best determined experimentally, but basic guidelines are also



useful. For most samples keeping the %T above 80% should minimize effects from multiple scattering. But, as previously noted, this value is sample dependent. For particles < 1 μm the operator should attempt to keep the concentration above ~85-90 %T. If all particles are > 100 μm, it may be possible to measure at up to 70 %T before experiencing significant changes from multiple scattering. A proprietary algorithm is written into all LA-950 software versions after version 5.0 which reduces the effect of multiple scattering.

Experimental

Several samples were investigated for this study to determine optimum concentration ranges and when multiple scattering produces unacceptable changes to the results.

The first sample investigated was a mixed sulfide dispersed in DI water with a D50 near 83 μm. The %T was varied from 98-31%, and the d10, d50, and d90 were recorded, see Table and Figure 1.

| %T | D10 | d50 | d90 |
|----|------|------|-------|
| 98 | 51.1 | 83.4 | 131.8 |
| 96 | 51.7 | 83.9 | 132.7 |
| 89 | 52 | 83.5 | 132.3 |
| 75 | 49.4 | 82.9 | 139.9 |
| 59 | 47 | 80.7 | 137.6 |
| 42 | 41 | 75.7 | 132.4 |
| 31 | 37.4 | 74.4 | 129.9 |

Table 1: %T vs. size for mixed sulfide

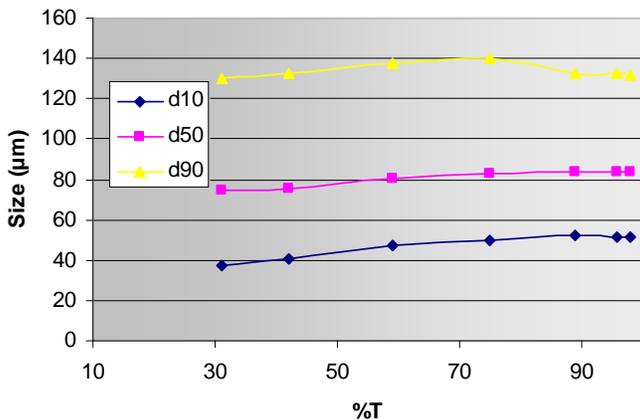


Figure 1: %T vs. size for mixed sulfide

If we accept 83.5 as the best d50 value, the d50 only changes by 4 % at %T up to 59%. For this sample a %T from 98 to 75% appears acceptable.

The second sample investigated was a glass bead standard PS202 dispersed in DI water. The %T was varied from 85-19%, and the d10, d50, and d90 were recorded, see Table and Figure 2.

| %T | d10 | d50 | d90 |
|------|-------|--------|--------|
| 85.4 | 8.046 | 13.367 | 19.77 |
| 70.7 | 7.956 | 13.422 | 20.191 |
| 58.1 | 7.579 | 13.108 | 19.802 |
| 48.1 | 7.278 | 13.022 | 19.87 |
| 39.4 | 6.836 | 12.758 | 19.822 |
| 27.7 | 5.356 | 12.122 | 19.513 |
| 18.9 | 2.771 | 11.604 | 19.475 |

Table 2: %T vs. size for glass beads

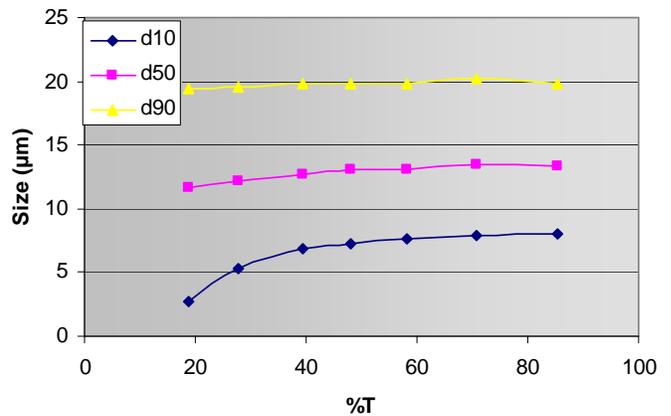


Figure 2: %T vs. size for glass beads

This sample has a known particle size distribution. The reference values for this standard along with upper and lower limits at the d10, d50, and d90 is shown in Table 3.

| PS202 | d10 | d50 | d90 |
|--------------------|-------|--------|--------|
| Stdard value | 9.14 | 13.43 | 20.34 |
| Uncertainty | 0.86 | 0.86 | 1.44 |
| ISO standard error | 5% | 3% | 5% |
| Lower limit | 7.866 | 12.193 | 17.955 |
| Upper limit | 10.5 | 14.719 | 22.869 |



Table 3: Standard values for PS202 glass beads

Referring to the data in table 3 we see that the results lie within the accepted values for %T up to 70.7%. The d50 value lies within acceptable limits up to 39.4 %T, and the d90 value is acceptable all the way to 18.9 %T.

The third sample investigated was an oil-in-water emulsion, where %T was varied from 97.4-92.5%. For this sample the focus was d50 as a function of %T and Chi square error value calculation. Rather than look for the effect of multiple scattering, this test investigated the minimum signal-to-noise ratio required for stable results. Figure 3 plots T% on the x-axis, d50 on the right y-axis and Chi square on the left y-axis.

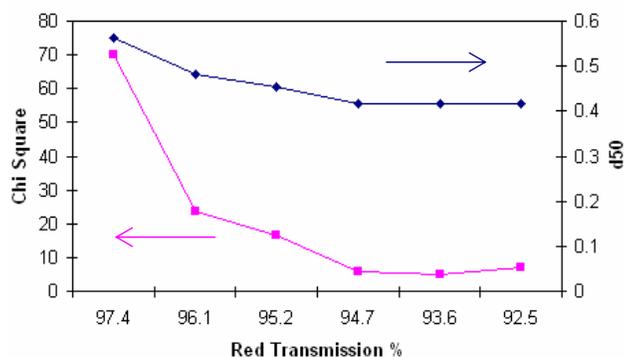


Figure 3: %T vs. d50 and Chi square for an oil in water emulsion

In Figure 3 we see that the d50 initially decreases with decreasing %T, and then stabilizes near 0.41 μm . The reason for this change in d50 can be understood by looking at the effect of concentration on the Chi square value. A Chi square value greater than ~10 indicates that there were significant fluctuations on the detectors during the measurement. At the higher %T values the Chi square values are unacceptably high. The Chi square value drops to below 10 and stabilizes at the same %T values as when the d50 stabilizes. This can be interpreted as showing that at least 94.7 %T is required for the signal-to-noise ratio to improve to the point where stable measurements can be made. Above 94.7 %T there isn't enough

scattering signal to make proper measurements.

Conclusions

Selecting the proper concentration for an unknown sample can be easily determined by performing a study of %T vs. results and/or Chi square values. Most samples can be analyzed in the range of 90-80 %T with little concern for signal-to-noise ratio or multiple scattering. But if the accuracy and reproducibility of the results are important to the user, we suggest investigating at least three %T vs. result measurements in order to understand the effect of concentration on final results.

References

1. ISO 13320, Particle size analysis – Laser diffraction methods, available from <http://webstore.ansi.org/SdoInfo.aspx?sdoid=39>

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