HORIBA Scientific

Application Note

Refractive Index Selection
AN157

Refractive Index Selection for Powder Mixtures

Laser diffraction is one of the most widely used methods for particle size analysis of micron and submicron size powders and dispersions. It is quick and easy and provides very consistent, repeatable information. Since these instruments use scattered light intensity to determine particle size, knowledge of the optical properties, specifically the complex refractive index of the material being analyzed is required. While the optical properties of the individual components of a mixture are readily available, what happens when we want to determine the size distribution of a mixture? This note briefly describes an approach that allows determination of a suitable index of a typical ceramic mixture using knowledge of the materials and statistical goodness-of-fit parameters provided by the analyzer software.

Background

Determining an accurate particle size distribution of a mixture of materials using laser diffraction particle size analysis can be a challenging task. Each individual material has a unique particle size distribution, as well as different particle shapes, densities and optical properties. Although many industries face this issue, it is particularly common in the ceramics industry. A typical ceramic application contains multiple oxides and carbonates of various metals. Particle size distributions and morphologies can vary widely in these materials, and there are typically grinding processes involved that further alter the particle shapes and sizes.

Laser diffraction particle size instrumentation is based on the measurement of the intensity of radiation scattered from the particles as a function of scattering angle. Scattered intensity and scattering angle are both related to particle size. Smaller particle sizes scatter at higher angles and with lower intensity than larger particles. Detectors at various angles measure the radiation intensity and a light flux pattern is generated. This pattern is the raw scattered intensity data as a function of detector, as shown in Figure 1.

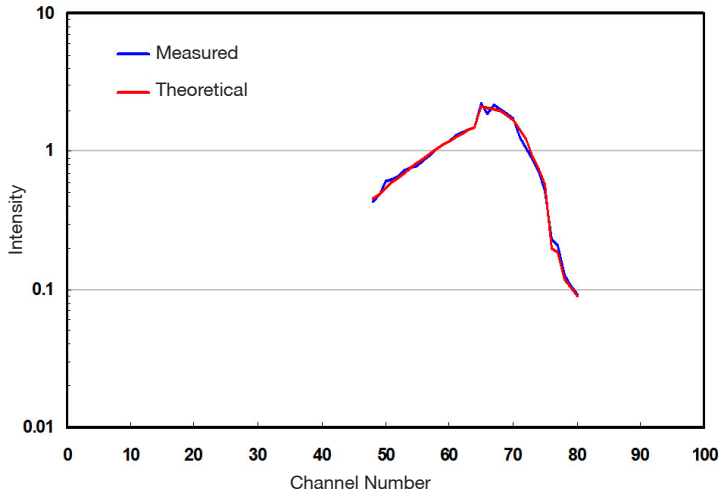

Figure 1

The mathematical theory, developed by Gustave Mie [1] allows very precise calculation of the flux pattern for a particle size distribution using a given set of optical properties [2]. However, it does not allow a particle size distribution to be directly calculated from the flux pattern. Therefore, an iterative approach is used to produce a scattering pattern that matches the measured data. The number of iterations is usually fixed in the software for the HORIBA LA series instruments at one of two levels – a lower number for wider distributions and a higher number for narrow distributions. More information about the affects of iteration number can be found in Ref. [2].

The LA-960 software also allows selection of any iteration value up to 1000. The theoretical raw data for the reported particle size distribution as determined by Mie theory is also plotted in Figure 1. As shown, there are small differences between measured and theoretical patterns. By changing the optical properties used by the theory to determine the theoretical curve, the match between measured and theoretical can be altered. Ideally, a good match between measured and theoretical curves indicates that the optical properties chosen were appropriate for the measured distribution.

Goodness of Fit

A value of Chi Square is calculated for each data set and provides a quantitative measure of the "goodness-of-fit" (GoF) between the measured and theoretical distributions. Chi square (χ^2) is calculated as follows:

$$\chi^2 = \sum \left\{ \frac{1}{\sigma_i^2} [y_i - y(x_i)]^2 \right\}$$

Where:

y_i = Actual scattering measurement
$y(x_i)$ = Theoretical scattering measurement (based on input optical properties)
σi = Standard deviation of scattering data

Chi Square is a commonly used statistic for comparing distributions of discrete data, such as particle size data [4]. The closer this value is to zero, the more closely the two distributions match. Therefore, we can use this value to help determine if the correct optical properties have been chosen. A relatively new and highly useful feature of the LA-960 software allows users to quickly and easily create new refractive indices and recalculate the distribution. By finding the conditions where Chi Square is at or near a minimum, we can home in on a suitable refractive index.

Real Component Determination

As described in HORIBA TN118 [3], the complex refractive index required by Mie theory is made up of two parts – the real part, which is a physical property of a material, and an imaginary part, which accounts for the absorption of light during it's interaction with the particle. The complex refractive index, n^*, is given by:

$$n^* = n' - \kappa i$$

Here, n' is the real component and κ is the extinction coefficient. The real component of many individual materials is readily available in the literature. However, when confronted with a mixture, which value should be chosen? When the components of a mixture are of similar particle size, it is commonly recommended that the mixture rule or weighted average be used:

$$n_{mix} = \sum_{i=1}^{z} n_i V_i$$

Where n_{mix} is the refractive index of the mixture, n_i is the refractive index of the ith component, V_i is the volume fraction of that component, and z is the total number of components. The real components of many materials are now available for selection and use in the LA-960 software. Note that if any components are small (below ~10 µm) and represent a significant fraction of the mixture, the results will be more sensitive to the refractive index used for analysis.

Another approach to finding the real component of a mixture is that of Gladstone-Dale [5]. Here the refractive index is linearly related to density, ρ, by a constant, k, as follows:

$$n = 1 + \rho k$$

For a mixture, the relation would change to:

$$n_{mix} = 1 + \rho_{mix} \sum_{i=1}^{z} m_i k_i$$

The term m_i is the molar fraction of the component in the mixture and k_i is its Gladstone-Dale constant. These constants have been tabulated for many oxides and carbonates [6]. Note that the density, ρ, is for the mixture. While this method was originally developed for minerals, which are essentially mixtures of oxides, it has applicability in other areas [7].

Using either one of these approaches will give the user a reasonable starting point for the real refractive index.

Imaginary Component

As mentioned earlier, the imaginary component of the refractive index is associated with absorption phenomena. Since tabulations of imaginary values are not usually available, one must use some rules of thumb to find a suitable starting point. Some rules to keep in mind are:

- For opaque materials, a high imaginary is needed.
- The smaller the particles the greater the importance of the imaginary.
- Value of 0.0 only valid for transparent spheres (ISO13320-1)
- Colored materials such as pigments may require higher imaginary values.
- Particles with a rough surface or irregular shape may require higher imaginary values.

These rules only provide general guidelines. To get a more quantitative idea of the suitability of the value, we can minimize the GoF parameter, Chi Square, provided in the software by changing the imaginary component used in the calculations.

An Example

The approach described above was used to find the refractive index for a ZrO_2-Y_2O_3-Al_2O_3 mixture. Applying the mixture rule, the real component is found to be 2.35. The Gladstone-Dale approach gives us a value of 2.05. To determine an appropriate imaginary component, we start with the rules of thumb. These are white powders, with a significant fraction below 1 µm. Since they were milled together, they will have irregular shapes. With these facts in mind, it can be concluded that a non-zero imaginary is required and it may turn out to be fairly high.

Using the two real indices determined above, the imaginary component was varied and changes in Chi Square monitored. Figures 2(a) and (b) show the change in Chi Square and median particle size as a function of imaginary component. Both real components give similar results, indicating that either value could be used in practice. At an imaginary value of 3.0i, Chi Square levels out and does not change significantly after that. Although 3.0i is not the location of the minimum of Chi Square, a look at some tabulated imaginary values shows that, typically, only metals have imaginaries as high as 4.0 or 5.0. Therefore, 3.0i should be used in this case.

Verification

Obviously, minimizing Chi Square is only appropriate if it provides accurate information about the actual particle size distribution. Verification using a scanning electron microscope (SEM) image is the preferred method for particles of this size.

Image analysis, was performed using ImageJ, a freeware application developed by The National Institute of Health. An example of the images at various stages of processing is shown in Figure 3. The software calculated the area of each identified particle and both number and volume statistics were determined. To minimize the error of these calculations, at least 1000 particles should be analyzed. For the purposes of this example, only ~400 were included in the analysis of a total of six SEM images.

Table 1 summarizes and compares the image analysis results to the data from the LA-960. The histogram in Figure 4 compares the volume based distributions from the LA-960 using both the mixture rule index and the Gladstone-Dale approach to the SEM data. As shown, there is relatively good agreement between the LA-960 distributions and the SEM data. With this level of correlation between the image based technique and the laser scattering method, it is fair to conclude that the optical model that was chosen based on minimization of Chi Square is suitable and should give accurate particle size distribution information.

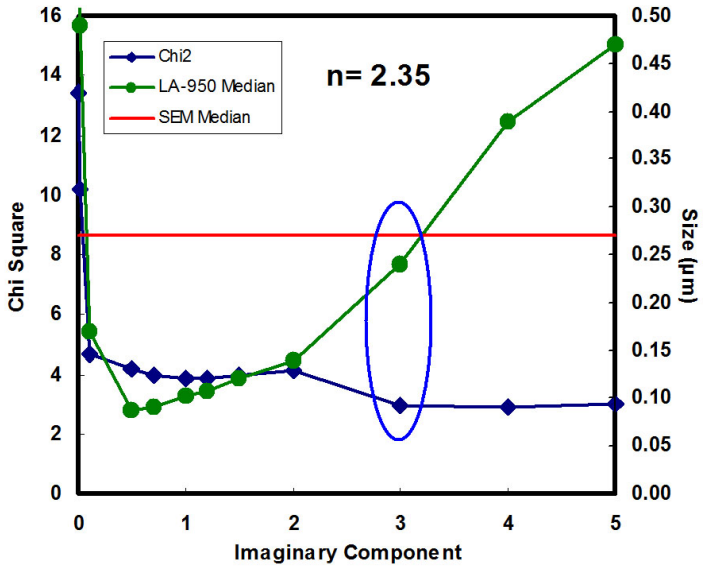

Figure 2 (a)

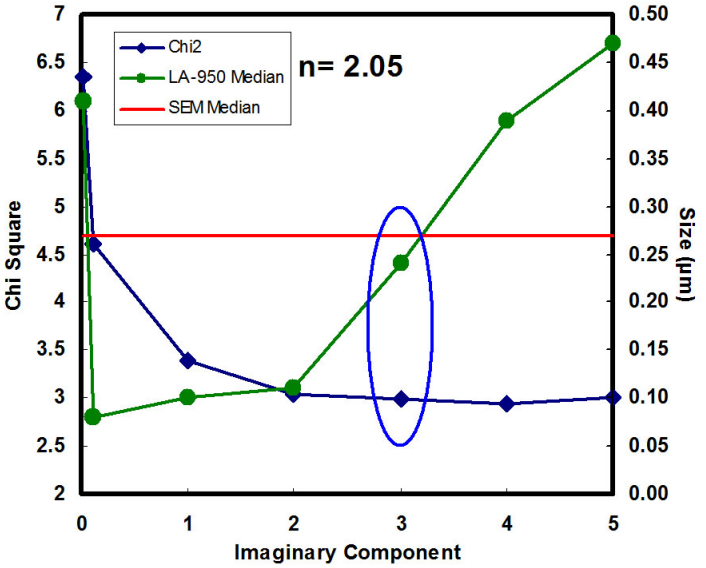

Figure 2 (b)

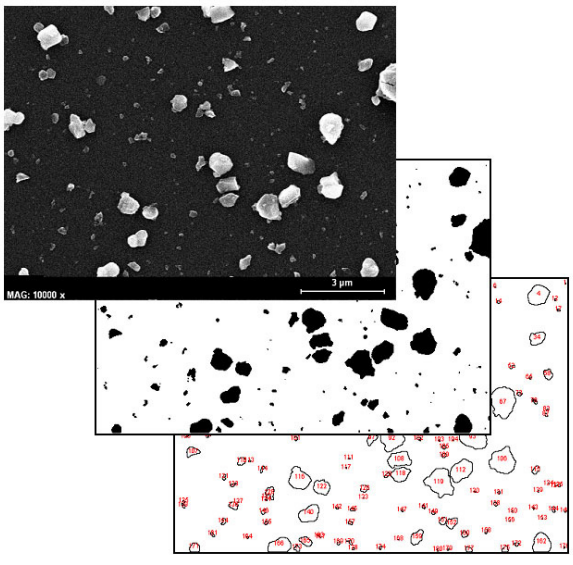

Figure 3

Table 1

	Median Size (µm)	Volume Number
SEM	0.75	0.27
2.05-3.0i	0.64	0.24
2.35-3.0i	0.65	0.24

Conclusion

Although particle size distributions of mixtures can be a challenge to measure accurately, use of the statistical information provided by the LA-960 analyzer can be of great help. Using a systematic approach to home in on suitable optical properties can provide data that is consistent, repeatable, and accurate.

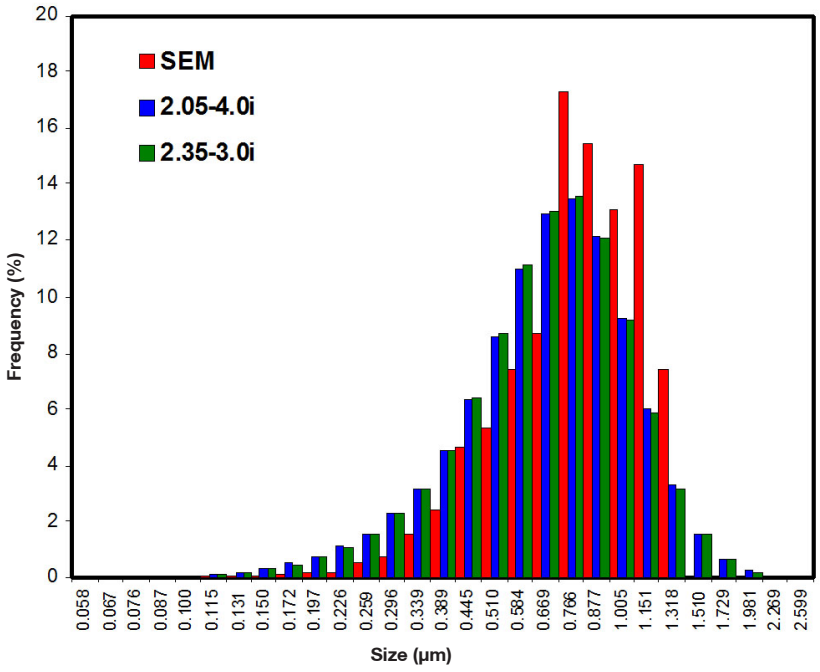

Figure 4

References

[1] Mie, Gustave, Beitrage zur Optik truberModien, speciel Kollaidaler Metallosungen, Annalen der Physik, Vol. 25, No. 3,pp. 377-445, 1908

[2] Algorithm Iterations, TN149, HORIBA Instruments Technical Note

[3] Guide to Selecting Refractive Index, TN118, HORIBA Instruments Technical Note

[4] NIST/SEMATECH e-Handbook of Statistical Methods, http://www.itl.nist.gov/div898/handbook/, November, 2007.

[5] http://www.webmineral.com/help/Gladstone-Dale.shtml

[6] Larsen, E.S., Berman, H., The Microscopic Determination of the Non-Opaque Minerals, Second Edition, United States Department of the Interior, Geological Survey Bulletin 848, 1934, US Government Printing Office, Washington, DC.

[7] Mandarino, J. A., The Gladstone-Dale Relationship: Part III: Some General Applications, Dept. Mineral. Geol., Royal Ontario Mus., Toronto, ON, Can. Canadian Mineralogist (1979), 17[1], 71-6.