Titanium Oxide Using Laser Diffraction

AN204

Titanium Dioxide (TiO_2) is a pigment used in paints and many other applications. The particle size distribution of TiO_2 is critical because it affects many important physical properties that influence final product performance. The particle size analysis is typically performed using the laser diffraction technique. This application note describes suggested methodologies when analyzing TiO_2 on the LA-960 laser diffraction particle size analyzer.

Introduction

Titanium dioxide, also known as titanium (IV) oxide or titania, is the naturally occurring oxide of titanium, chemical formula TiO_2. It typically comes in two different forms, rutile and anatase. It is used as a pigment in a wide range of applications such as paint or food coloring, or for its light scattering and absorption properties in sunscreens. The particle size distribution of TiO_2 influences a range of properties including appearance, gloss, opacity, and absorbance. These properties are also influenced by the state of dispersion, so the TiO_2 surface is often coated to improve ease of dispersion.

Laser Diffraction Technique

Laser diffraction is the most popular particle size analysis technique because it is fast, easy, and flexible. The HORIBA LA-960 can measure powders and suspensions from 0.01 – 3000 µm. The LA-960 has been adopted as the most popular system for TiO_2 analysis due to the high sensitivity abilities for accurate suspension analysis down to 30 nm (median size) and dry analysis down to 300 nm (median size). Method development in the LA-960 is automated and optimized by the Method Expert software wizards (reference), turning every customer into an expert in method development. These features proved extremely useful in the analysis of the samples used in this study.

Experimental

Several commercially available TiO_2 powder samples were sent to the Irvine, CA applications lab for analysis. The samples were analyzed using the LA-960 both as a dry powder and as a dispersed suspension.

Refractive Index

The selection of refractive index is an important parameter when using laser diffraction (1,2). The real refractive index (RI) of this form of TiO_2 is known to be 2.75. The optimum imaginary RI component was selected using the calculation optimization wizard within the Method Expert software (ref). The real component was fixed at 2.75 while the imaginary component was varied from 0, 0.01, 0.1, 1.0, and 10. The wizard then calculated the size distribution results and R parameter, a value that expresses the error in the conversion from raw scattered light data to the final result. A minimum R parameter (3) value indicates the optimum choice for the imaginary RI component. The results from the calculation optimization wizard are shown in Figure 1 (size distribution results) and Figure 2 (R parameter vs. imaginary RI value).

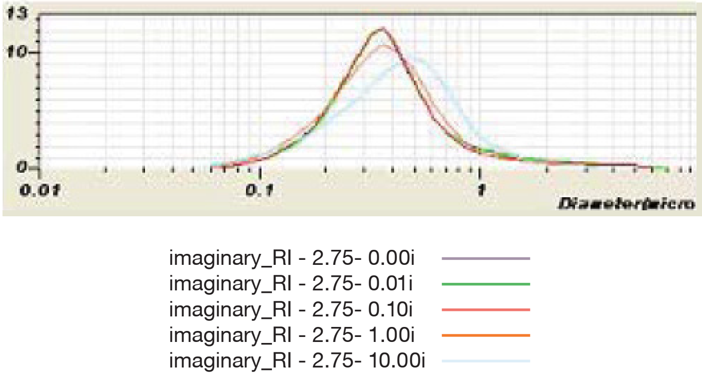

Figure 1: Calculated size distributions for varying imaginary RI component

Figure 2: R parameter (Y axis) vs. RI

The R parameter is at a minimum value of 1.0, therefore, the RI used for all measurements in this study is 2.75, 1.0.

Wet analysis

The TiO_2 powder was dispersed in water following the procedure described below:

- 2g of sodium hexametaphosphate (SHMP) was dissolved into 1L of DI water to use as a dispersant.
- 1 mL of photo-flo was added to 1L DI water to use as a wetting agent .1g (estimated) of TiO_2 powder is placed in a 250 mL beaker 100 mL of photo-flow wetting agent is poured into the beaker.
- The sample is exposed to 60 sec of ultrasonic energy using an external probe.
- The LA-960 is filled with the SHMP dispersant.
- The sample is then pipetted into the LA-960 to the proper concentration (T%) for analysis

LA-960 settings:
Refractive index: 2.75-1.00
Concentration: T% (red laser) between 84-86%
Pump & stirrer speed: 5
Measurement duration: 5 sec

Note: The sample used for this analysis dispersed quite easily and perhaps a less complicated dispersion procedure could have been used but the more rigorous method is documented for reference when working with more difficult samples. The high power ultrasonic probe built into the LA-960 is sufficient for many TiO_2 samples.

Dry Analysis

The TiO_2 powder was also measured as a powder in air using the PowderJet dry powder feeder. Highly repeatable results with excellent dispersion were achieved with use of the unique automatic feed back loop that controls vibration feed rate based on sample concentration (laser transmission, or %T). The LA-960 system setup used for the dry analyses is described below:

- Nozzle: Small Nozzle both top and bottom
- T%: Target T% = 98%
  and Sampling T% Range 97 - 99%
- Stop Trigger at 99.8% (Stop After Waiting)
- Initial Feeder Speed at 60
- Air Pressure 0.40 (4Bar)
- Data Acquisition Time = 50000 (~15sec)

Results

The important calculated results from the wet analysis are shown in Table 1 and the dry results are shown in Table 2. The geometric standard deviation of the distributions is the preferred calculation for describing the width of TiO_2 since this value has proven valuable in predicting dispersion stability.

Mean Size:	**0.42307 (µm)**
Mode Size:	**0.3635 (µm)**
Geo. Std. Dev:	**1.7940 (µm)**
R Parameter:	**6.8993E-2**
D(v,0.1):	**0.16831 (µm)**
D(v,0.5):	**0.35496 (µm)**
D(v,0.9):	**0.71036 (µm)**

Table 1: Wet analysis results

Mean Size:	**0.44614 (µm)**
Mode Size:	**0.3615 (µm)**
Geo. Std. Dev:	**1.8683 (µm)**
R Parameter:	**1.3147E-1**
D(v,0.1):	**0.16820 (µm)**
D(v,0.5):	**0.34653 (µm)**
D(v,0.9):	**0.74838 (µm)**

Table 2: Dry analysis results

The wet (red) and dry (blue) LA-960 results from the measurements reported in Tables 1 and 2 are over plotted in Figure 3. Note the close comparison between the two dispersion methods, adding confidence in the accuracy of the results.

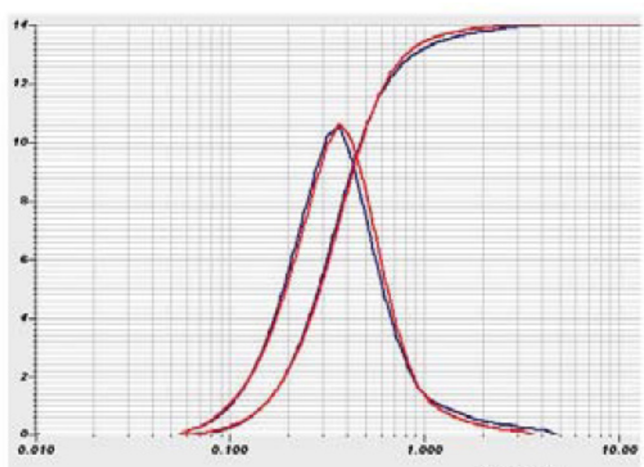

Figure 3: Wet vs. dry TiO_2 results

After the test methods were created and validated by the comparison of wet vs. dry results, two grades of TiO_2 were tested to determine if the LA-960 could discern the difference in particle size. Both samples were analyzed as dry powders using the method previously described in this document. Sample two was expected to be slightly smaller than sample one. The results from these analyses are shown over plotted in Figure 4, and in Tables 3 and 4. Note the ability of the LA-960 to differentiate between these slightly different sample grades; at only a 12 nm difference.

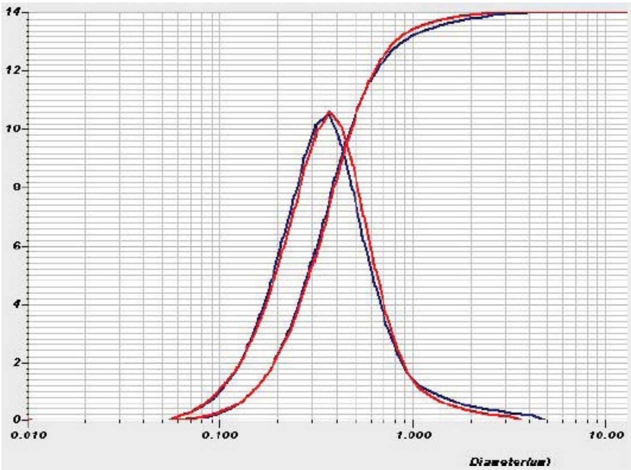

Figure 4: Dry powder TiO_2 results

Mean Size:	**0.44614**	**(µm)**
Mode Size:	**0.3615**	**(µm)**
Geo. Std. Dev:	**1.8683**	**(µm)**
R Parameter:	**1.3147E-1**	
D(v,0.1):	**0.16820**	**(µm)**
D(v,0.5):	**0.34653**	**(µm)**
D(v,0.9):	**0.74838**	**(µm)**

Table 3: Dry result for sample 1

Mean Size:	**0.45286**	**(µm)**
Mode Size:	**0.3183**	**(µm)**
Geo. Std. Dev:	**1.9285**	**(µm)**
R Parameter:	**8.0177E-2**	
D(v,0.1):	**0.16169**	**(µm)**
D(v,0.5):	**0.33394**	**(µm)**
D(v,0.9):	**0.77890**	**(µm)**

Table 4: Dry result for sample 2

Conclusions

The HORIBA LA-960 laser diffraction analyzer proved to be an ideal instrument for measuring the particle size distribution of TiO_2, both as a suspension and in the natural powder state. The wet vs. dry results showed remarkable similarity and the LA-960 proved capable of detecting sample differences on the scale of 12 nm. The methodology described in this document should be useful as a guide to customers using the LA-960 for TiO_2 or other submicron pigment samples.

References

1. ISO 13320, Particle size analysis -- Laser diffraction methods, available at www.iso.ch or www.ansi.org.

2. Webinar on refractive index on horiba.com.

3. TN153 Understanding the Chi Square and R Parameter Calculations in the LA-960 Software, available on www.horiba.com/particle.

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