

# Nanoparticle Measurement by Spectroscopic Mie Scattering

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## ABSTRACT

In this paper we present a spectroscopic technique for measuring particle size. The technique utilizes a UV-Visible spectrophotometer (in the range from 190 to 1100nm) to measure the attenuation spectrum of a particle dispersion due to scattering. Using the Mie scattering theory, we compute the particle size distribution and particle concentration that best matches the measured scattering spectrum. While the operating range is material dependent, we have found that the instrument can measure particles sizes from 10 nm to 15 microns. The technique involves minimal sample preparation and clean up, and is fast (less than 10 seconds). Our results show that the UV-Visible spectroscopic technique can be used to resolve complex multimodal dispersions. Particle size populations can be resolved as close as 1:1.5 size ratio. The technique also allows a sensitive determination of as low as 5% small particles in a large-sized particle dispersion.

**Keywords:** nanoparticle size, UV-Visible, light scattering, dispersions

## 1 INTRODUCTION

The size and shape of nanoparticles are their most important characteristic because they determine many other features of the behavior of nano suspensions. The rate of settling, the ease with which they can be filtered, their flow properties when poured or pumped and their capacity to absorb surface molecules all depend on particle size. The optical properties of latexes (gloss and sheen) depend on particle size, as does drug solubility. Colloidal suspensions often exhibit a wide range of particle sizes. For some purposes it is enough to know the minimum, maximum and average size. But in many cases it is necessary to have a complete knowledge of the details of the distribution, width and the presence of multiple modes. Accurate determination of the particle size and characterization of the distribution of nanoscale objects will improve our understanding of their functioning and behavior. However current techniques capable of nanoscale resolution have many limitations. In this paper we report experimental work on identifying nanosize particle size populations in complex samples with more than one size population.

## 2 EXPERIMENTAL

### 2.1 Materials

Two types of commercial particles were used for the experiments reported in this paper. All polystyrene particles were monodisperse polymer microsphere suspensions in water, NIST traceable size standards supplied by Duke Scientific Corporation. All colloidal gold particles were monodisperse gold nanoparticles dispersed in water manufactured by British BioCell International and available through Ted Pella Inc.

### 2.2 Instrumentation

Based on its expertise in UV-Vis spectrophotometry, Agilent has developed an accurate, simple to use and maintain particle size instrument. The optical system shown in Figure 1 produces high dynamic range, low stray light and a highly collimated beam. It uses two light sources, a deuterium and a tungsten lamp. The shutter consists of 2 parts; one serves simply as an optical on/off switch while the second is a filter used to reduce stray light in the UV range. The 1024 element diode array is a series of silicon photodiodes. The diode array combined with the wide spectrum grating allows multiple wavelengths to be collected simultaneously for fast data collection. The measurement time is on the order of 1 second, and particle size distribution calculation can take up to approximately 5 seconds. This results in a total data acquisition time of less than 10 seconds. This enables measurement of samples where dispersion stability is an issue or where particles are dense and the sedimentation rate makes traditional measurement techniques challenging. Since the technique does not rely on observing the Brownian motion of particles, the samples may be stirred or flowed during the measurement via the use of a stir bar accessory or utilizing flow through cells and a peristaltic pump.

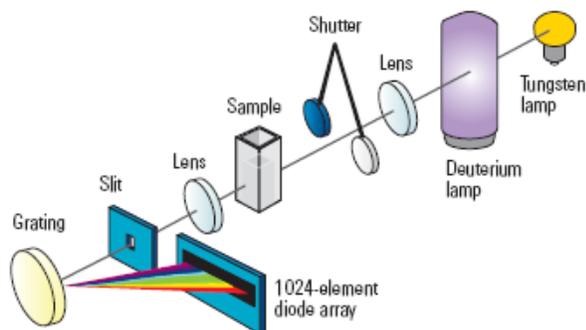


Figure 1: Optical path of particle sizing spectrophotometer

When solutions contain particles, light passing through the solution is attenuated due to scattering. The wavelength dependence was calculated by Gustav Mie in 1908[1]. Mie developed a rigorous method to calculate the intensity of light scattered by uniform spheres. The shapes of light scattering spectra are distinguishable for particles that are much larger than the wavelength of light  $\lambda$  but differ in size by as small as  $\lambda/10$ , and the particle size information can be obtained by analyzing these spectral shapes. Mie theory is an exact solution of Maxwell equations on light scattering by a spherical scatterer of arbitrary size. Mie solution requires only three parameters: the size and the refractive indices of the scatterer and the medium. Using Mie's mathematical theory, the particle size distribution and volume concentration which produce the best agreement with the measured spectra is determined.

### 3 RESULTS AND DISCUSSION

Multimodal distributions are usually thought of and represented as being the sum of two or more normal (or log normal) distributions. In some industrial situations it is important to be able to accurately distinguish the presence of a true bimodal distribution. For example, the presence of a larger population might interfere with the main process. The particle size methods that first separate the different sizes and then measure them are intrinsically better able to detect the presence of a bimodal distribution. The time required to first separate sizes and then measure however can be on the order of hours. The UV-Vis particle sizing spectrophotometer configuration described above is capable of resolving bi- and multi modal particle size distributions. We measured colloidal gold of nominal 80 nm diameter and nominal 150 nm diameter. The SEM micrograph in Figure 3 captures the mix of these two size populations. First, we measured these colloids separately. The 80 nm colloidal gold was measured to be 78 nm in diameter at a concentration of 0.000322% by volume (red line, Figure 2) and the 150 nm diameter colloid was determined to be 156 nm in diameter at a concentration of 0.000344% (blue line, Figure 2). These colloids were then mixed in a 1:1 ratio by

volume. The black line in Figure 2 shows the particle size distribution of the mixture of gold standard dispersions. The spectral fitting algorithm clearly broadens the peaks in the case of the mixture as compared to the monodisperse measurements. However, The particle size measurement correctly shows the nearly 1:1 relationship in concentration of the two peaks. In fact, integration of the peaks reveals that the relative concentration of the two modes is 48% 78nm and 52% 156 nm Au – exactly the expected ratio. The concentration of the mixed sample was measured as 0.000331% - a difference of <1% from the expected value for the mixture. In addition to the detection of these modes, the instrument correctly determines the relative amounts of the two modes and the correct total particle concentration on a %v/v basis.

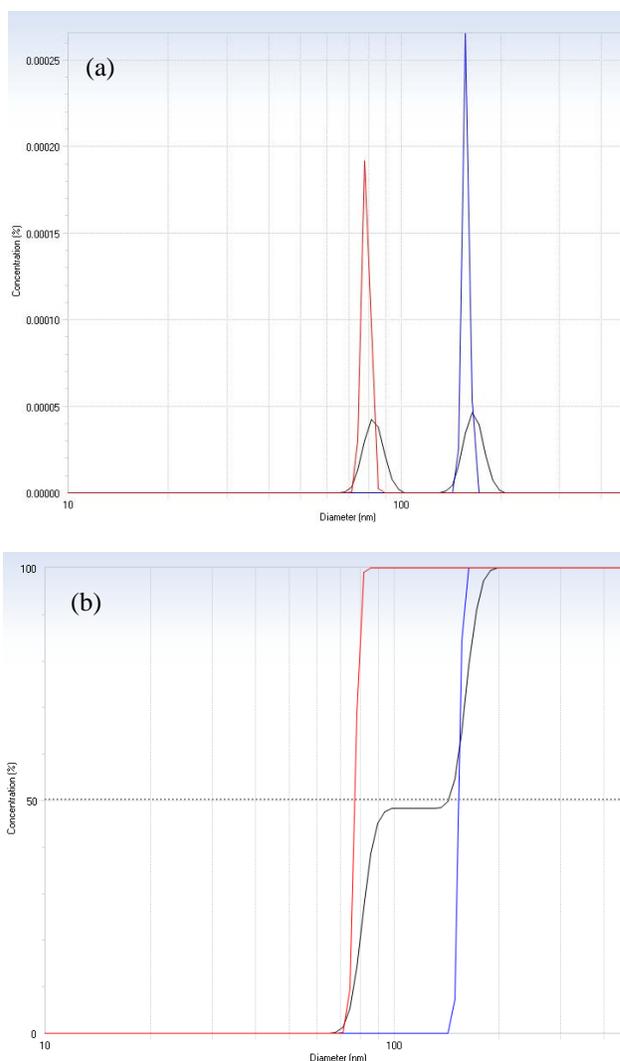


Figure 2: Absolute (a) and cumulative (b) particle size distribution of pure 78 nm Au colloid (red), pure 156 nm Au colloid (blue), and a mix of 50% 78 nm gold and 50% 156 nm gold (black). (Ted Pella Inc.)

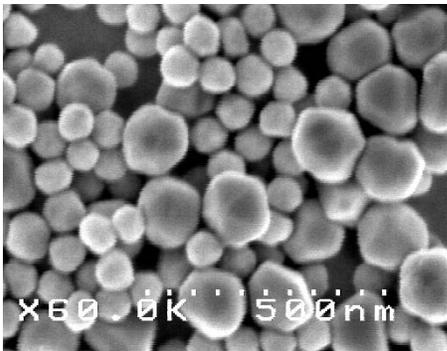


Figure 3: SEM micrograph of 78 nm and 156 nm gold particles (Ted Pella Inc.)

To test the limit of the size resolution capability of this technique, 50/50 mixtures of different size populations of polystyrene particle standards were combined. Particle size measurements were taken as the size ratio was decreased. Figure 4 demonstrates the resolution capability of the UV-Visible particle sizing instrument with a sample of equal concentrations of 2 $\mu$ m and 3 $\mu$ m polystyrene latex (in blue). The UV-Vis spectroscopic technique allows us to resolve bimodal distributions as close as a size ratio of 1:1.5. The particle size distribution of the same 2 $\mu$ m polystyrene sample alone is also shown in figure 4. Comparing these distributions, it appears that the broadening of the 2 $\mu$ m peak in the mixture is an artifact of the fitting algorithm as seen in Figure 2. There appears to be a trend in close bimodal samples of the smaller peak becoming artificially broadened. Figure 4 compares this bimodal sample with a 3 $\mu$ m and 5 $\mu$ m bimodal polystyrene sample (in green). Such 1:1.5 ratio size resolution has also been demonstrated for metal nanoparticles as well.

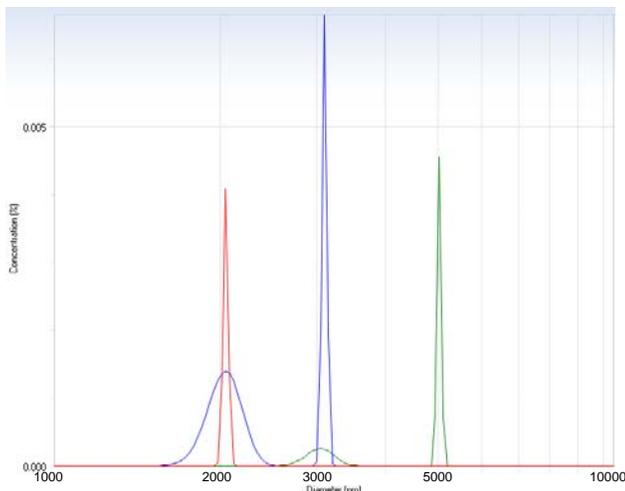


Figure 4: Particle size distribution of a mix of 50% 2 $\mu$ m and 50% 3 $\mu$ m polystyrene standard (Duke Scientific Corp.) (blue) demonstrating 1:1.5 size ratio resolution capability. Red line: monodisperse 2  $\mu$ m polystyrene standard alone;

Green line: mixture of 50% 3  $\mu$ m polystyrene and 5  $\mu$ m polystyrene standards.

A common challenge for light scattering techniques is the measurement of small particles in a population of large particles. Typically the presence of a few large particles can scatter too much light, hiding the presence of small particles. For industrial processes where dispersions are unstable or are designed around 2 or more size populations, the ability to accurately detect the individual populations is critical. The spectral dispersion of the UV-Vis particle sizing spectrophotometer allows accurate measurement of mixtures of small and large particles in suspension. The blue graph in figure 5 demonstrates the ability to detect a mixture of 9% 91nm polystyrene particles in a background of 91% 3 $\mu$ m polystyrene particles. As well the converse situation is also shown by the red graph in figure 5, 9% of 3 $\mu$ m polystyrene in a background of 91% 91nm polystyrene. The limit of the small particle sensitivity has been tested and determined to be 5%. We have been able to detect 5% v/v 91 nm polystyrene latex particles in a background of 95% v/v 3  $\mu$ m particles.

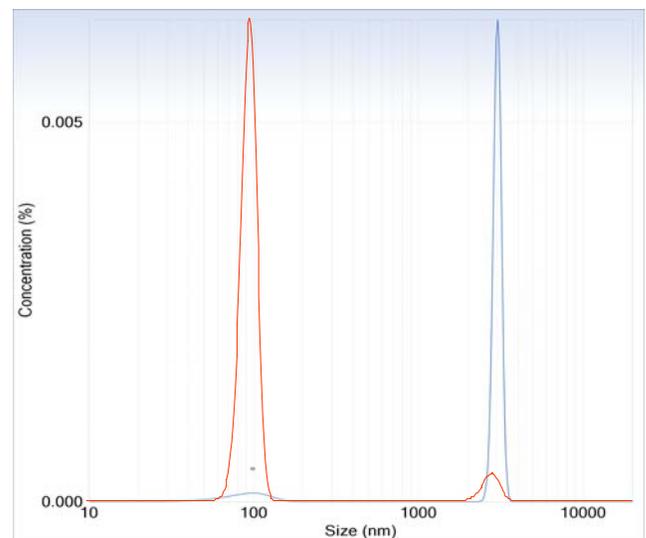


Figure 5: Mixture of 9% 3 $\mu$ m polystyrene (Duke Scientific Inc.) in a background of 91% 91nm polystyrene (in red) and 9% 92nm polystyrene in a background of 91% 3 $\mu$ m polystyrene (in blue).

## 4 CONCLUSION

Agilent has developed an accurate, simple to use and maintain particle size analyzer built around the robust spectrometric hardware provided by the Agilent UV-Vis platform in the wavelength range 190nm to 1100nm. The spectral attenuation of the colloidal particles is accurately

measured in this range and the software calculates the particle size distribution. Bimodal particle size distributions can be measured with size difference as close as 1:1.5 while maintaining accuracy in both the size of the particles *and* the relative concentrations of the modes. Using Mie theory, the particle size distribution and volume concentration which produce the best agreement with the measured spectra is determined. We believe this combination of fast measurement time, high resolution, and ease of sample preparation offers distinct advantages over existing techniques and enables new measurements.

## REFERENCES

- [1] G. Mie, "Beitrage zur Optik truber Modien, speciel Kollaidaler Metallosungen", *Annalen der Physik*, vol 25, no. 3, pp.337-447, 1908.