Physics of Particle Size Spectrophotometry

Technical Note

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Abstract

Particle size is often determined by measuring light that is scattered by the particles. Laser diffraction instruments measure light scattering as a function of the angle of detection. In contrast, the Agilent 7010 Particle Size Spectrophotometer measures light scattering at a fixed angle as a function of the wavelength of the incident light. The instrument uses a wide range of wavelengths, from 190 to 1100 nm. The advantages of this extended wavelength range include the ability to measure smaller particles and the capability to correctly measure particle sizes for mixtures of large and small particles.

This Technical Note explains the physics and mathematics behind the measurement of particle size distribution and concentration by UV/visible spectrophotometry. The note also describes the implications for the operating range of the 7010 Particle Size Spectrophotometer.
The relationship between light scattering and particle size

The Agilent 7010 Particle Size Spectrophotometer calculates the particle size distribution of a colloidal dispersion from the measured optical scattering spectrum. The size dependence of light scattering by particles is well-understood, and many common techniques for measuring particle size, such as laser diffraction, are based on light scattering. Indeed, Maxwell’s equations for scattering of electromagnetic waves by a dielectric sphere were originally solved by Gustav Mie in 1908.\(^1\) The theory has been expanded in detail in a number of texts, for example those by van de Hulst\(^2\) and Bohren and Huffman.\(^3\)

The Mie solution to Maxwell’s equations computes two quantities – the absorption efficiency \(Q_{abs}\) and the scattering efficiency \(Q_{sca}\). These add together to produce a third quantity, \(Q_{ext}\), the extinction efficiency. All three are unitless and represent the effective cross-sectional area of a scattering or absorbing particle divided by its physical cross-section. Light that is lost to scattering is lost by radiation in other angles. Light that is absorbed is captured by the particle and ultimately is turned into heat. Transparent particles like silica have zero absorption efficiency. In the particle size spectrophotometer, it is \(Q_{ext}\) that is important, since we do not care how the light is lost.

It is straightforward to show that as long as the particles are dilute (so that we do not have to consider multiple scattering) then the transmission \(T\) of a cell (power out divided by the power in) that contains \(N\) particles per unit volume is

\[
T = e^{-aL} \quad (1)
\]

where \(a = NQ_{ext}\) and \(L\) is the cell length.

The particle size spectrophotometer measures attenuation, which is the negative logarithm of the transmission or

\[
AU = aL \times \log_{10} e = NQ_{ext} \log_{10} e \times L \quad (2)
\]

\(AU\) stands for absorbance units, the numbers computed by the spectrophotometer. The particle density \(N\) can be expressed in terms of the volume fraction \(C_v\) in the following way:

\[
C_v = \frac{4}{3} na^3 N \quad (3)
\]

where \(a\) is the particle radius. In other words, the number of particles per unit volume times the volume of a single particle is the fraction of the volume occupied by particles \((C_v)\).

By combining equations 2 and 3, we get an expression for the attenuation per unit length:

\[
\frac{AU}{L} = \frac{3 \log_{10} e}{4a} C_vQ_{ext} = \frac{3 \log_{10} e}{4a} C_v(Q_{sca} + Q_{abs}) \quad (4)
\]

This result gives the expected attenuation as measured by the particle size spectrophotometer for a dispersion of known particle size, volume concentration, and refractive indices of the fluid and particle phases.

The inverse problem

While the calculation of \(Q_{ext}\) is a relatively complicated mathematical formula involving spherical Bessel functions (which was challenging for Mie in 1908), the mathematics is easily and quickly solved by computers. The much more difficult solution is the inverse problem, that is, to calculate particle size from the observation of light scattered from a particle. In fact, this problem is “ill-posed” – there may be more than one set of different particle sizes in different concentrations that could add together to create an observed measurement of light scattering. This ill-posedness is true for all measurements of scattering of an ensemble of particles, including, but not limited to particle size spectrophotometry, laser diffraction, dynamic light scattering, and acoustic spectroscopy. The challenge therefore is to use the technique with the most “information-rich” data as possible, so that there are fewer sets of different particle size distributions that can produce the same observed scattering distribution.
**Scattering as a function of angle or wavelength?**

A particle that is exposed to optical light can be thought of as an optical antenna, and depending on the wavelength of light in the material ($\lambda/n$, where $n$ is the index of refraction) and the size of the particle, the particle will scatter the light into different directions. The well-known technique of laser diffraction (LD) measures the scattering of a fixed frequency of light over a range of angles.

Often, the measurement is performed by fixed detectors at discrete wavelengths, but sometimes (as in classical static light scattering measurements) the detector is mounted on a goniometer and scanned over wavelengths. The observed measurement of intensity versus angle is then deconvolved into sets of particle sizes that could have produced the result – an ill-posed problem as mentioned above. Figure 1 shows the scattering of 632.8 nm wavelength light versus angle of 1.5 μm polystyrene particles dispersed in water.

![Figure 1](image1.png)

**Figure 1.** Intensity of 632.8 nm laser light as a function of scattering angle for a dispersion of 1.5 μm polystyrene particles in water.

An entirely analogous technique is to measure the scattering of particles, but instead of varying the angle of detection, to measure at a fixed angle and vary the wavelength of the incident light. Figure 2 shows the exact same calculation of scattering by 1.5 μm polystyrene particles, but this time shown at a fixed angle of 0 degrees (transmitted light), with the wavelength varied from 190 to 1100 nm.

![Figure 2](image2.png)

**Figure 2.** Intensity of white light as a function of wavelength at a fixed scattering angle for a dispersion of 1.5 μm polystyrene particles in water.

This second technique has two clear advantages. First, if the wavelengths that are measured extend into the ultraviolet (UV) range, smaller particles may be measured. (This would not be true if one created a laser diffraction instrument with a laser wavelength of 200 nm, but typically, LD instruments contain visible lasers.) Figure 3 shows the calculated Mie scattering spectrum from silica particles over a diameter range from 100 nm to 1 μm. Figure 3 clearly shows significant scattering of light at visible wavelengths for 1 μm particles, but the amount of scattering drops off precipitously as the particle size shrinks towards 100 nm. (Note the logarithmic spacing of the z-axis). By including UV wavelengths in the measurement, the technique of particle size spectrophotometry allows measurement of smaller particles.
In addition, measurement over a wide range of wavelengths allows correct particle sizing for mixtures of large and small particles. As an example, Figure 4 shows the attenuation spectrum and associated particle size distribution of a mixture of 9% by volume 92 nm polystyrene latex and 91% 3 μm polystyrene latex. If the UV wavelengths are excluded from consideration, as shown in Figure 5, it is apparent that the scattering in the visible wavelengths is due to the 3 μm particles alone. If the visible wavelengths are excluded from consideration, as shown in Figure 6, the fit to the UV wavelengths shows that this part of the spectrum is contributed by the 92 nm particles. Only by fitting the entire spectrum of 190 to 1100 nm can the correct particle size distribution be measured.
The case of metal particles

As Maxwell’s equations can be solved regardless of whether materials are metals or dielectrics, the Mie scattering equations apply to all particles regardless of the type of material. In fact, the title of Gustav Mie’s original 1908 paper translates from German to English as “Contributions to optics, opaque media, especially metal colloidal solutions.” The Mie scattering calculation for colloidal metal nanoparticles determines their characteristic plasmon resonances.

The only input parameter that specifies whether a material is a dielectric or a metal is the complex index of refraction. As an example, the index of refraction of gold and polystyrene are shown in Figure 7. The strong difference between the metallic properties of gold and the dielectric properties of polystyrene are clearly seen. For the dielectric particle, the real part of the refractive index is everywhere greater than the imaginary part of the refractive index. For the metal, the situation is reversed.

Previously we have talked about the interaction of light with the particles acting as optical antennas. In the case of metals, the real part of the dielectric constant $e_r$ is negative. The relationship between the index of refraction shown in Figure 7 and the dielectric constant is given by

$$ e_r = n^2 - k^2 \quad (5) $$

where $n$ is the real part of the refractive index and $k$ is the imaginary part.

Maxwell’s equations show that this means that electric fields are excluded from a metal. The result is that at the surface of a metal nanoparticle in a dielectric medium, an optical field results in a collective excitation of conduction electrons, called a localized surface plasmon resonance (LSPR). Solving Maxwell’s equations for a metal-dielectric interface and applying electromagnetic boundary conditions, we find the wavelength of the surface plasmon is:

$$ \frac{2n}{\lambda} = \frac{\omega}{c} \sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}} \quad (6) $$

where $\varepsilon_m$ is the dielectric constant of the metal, $\varepsilon_d$ is the dielectric constant of the dielectric medium, $\omega$ is the angular frequency, and $c$ is the speed of light.

From this equation, it is clearly seen that the wavelength is imaginary, since the numerator of the fraction inside the square root is negative. This is realized in the surface plasmon resonance being an evanescent wave at the metal-dielectric interface. Quite importantly, the wavelength can be quite small. As discussed previously, particles in solution can be thought of as optical antennas, and resonances occur when particles are approximately the size of the wavelength of light. As a result, the particle sizes where Mie scattering spectra are pronounced are smaller for metals than for dielectrics. The result is that the 7010 Particle Size Spectrophotometer works best for metal particles in the range of 10 to 500 nm in diameter, and for dielectric particles in the range of 100 nm to 15 μm in diameter. The rough guidelines for the limits of size and concentration range of the 7010 Particle Size Spectrophotometer are given in Figure 8; in practice, the absolute limit for every material is different.

![Figure 7](image-url)
Figure 9. Scattering spectra for silver particles of varying diameter.

Figure 10. Scattering spectra for polystyrene particles of varying diameter.

A note on non-spherical particles

For the most part, Mie scattering calculations reduce Maxwell’s equations to spherical coordinates and the solution is calculated assuming a perfect sphere. While the Mie scattering problem has been solved for core-shell and elongated nanoparticles, adding these additional degrees of freedom would add even more ill-posedness to the inversion problem, reducing the ability of the algorithms to produce a correct answer. It is for this reason that the 7010 Particle Size Spectrophotometer, along with all commercial laser diffraction instruments, assumes a spherical particle for its algorithms for particle size measurement.

Limits of particle size and distribution for particle size determination

As shown in Figure 8, there are limits to the range of particle sizes that may be measured by the spectrophotometric technique. This can be seen more readily in Figure 9 for the case of silver nanoparticles and Figure 10 for the case of polystyrene particles. At the small-particle end, particles undergo Rayleigh scattering. The spectral shape is not dependent on particle size and the spectra all look self-similar. As a result, the particle size spectrum cannot independently determine both the particle size and particle concentration. At the large particle end, again the spectra all look fairly flat and self-similar, and no size may be determined. Essentially, the particle casts a shadow on the detector over all wavelengths.
In addition, as a particle size distribution gets broader, the corresponding Mie scattering spectrum appears smoother – closer to a flat line. In these cases, the solution again becomes “more ill-posed” and in the extreme of very broad distributions, a unique solution for particle size cannot be found. This limit is hard to quantify and is material-dependent. In general, if the attenuation spectrum measured by the 7010 is fairly flat and the calculated particle size distribution varies widely with different wavelengths chosen as the input, it is very difficult for the spectrophotometer to produce an accurate result. Again, this limitation is not unique to the particle size spectrophotometer and is present for any technique that measures an ensemble of particles simultaneously.

**Additional capabilities of particle size spectrophotometry**

The Agilent 7010 Particle Size Spectrophotometer is a fast, easy-to-use instrument for particle size analysis. Because of the fast detection with a photodiode array detector in the UV-visible range, particle size measurements are performed in seconds, opening up new applications – for example in samples that rapidly settle or in monitoring unstable systems. Cuvettes are available in a wide range of path lengths, from 10 cm to 10 μm, enabling the wide range of particle concentrations shown in Figure 8 to be measured with no dilution. In addition, Agilent supplies a number of accessories, including flow cells and magnetically stirred cuvettes. In summary, the 7010 Particle Size Spectrophotometer provides fast, accurate results over a large particle concentration range and in a size range of practical interest to many researchers.

**References**


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