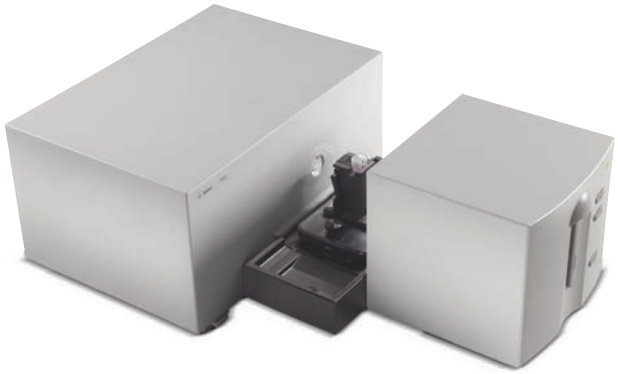
Accurate Measurement of Particle Sizes of Polymers with the Agilent 7010 Particle Size Analyzer

Application Note



Abstract

Many properties of polymeric particles depend on particle size distribution (PSD), so it is important to be able to measure particle sizes in the nanometer to low micrometer range without error. When the PSD contains particles of more than one size population, traditional light scattering techniques are often unable to resolve them, and these instruments typically fail to detect a population of small particles in the presence of a population of large particles. The Agilent 7010 Particle Size Analyzer overcomes these limitations to quickly and accurately measure both particle sizes and concentrations in complex mixtures of fine polymeric particles.

Agilent Technologies

Introduction

Applications of fine polymeric particles are diverse. Coatings, paints, adhesives, drug delivery systems, and medical diagnostics are just a few examples. Unerring characterization of particle sizes is critical because many properties of these materials depend on their particle size distributions (PSDs). For example, the final attributes of a latex product include stability, film-forming ability, covering capacity, viscosity, opacity, texture, mechanical resistance, and processability. All of these properties are affected by its PSD. And in polymerization processes, controlling the PSD allows the synthesis of high-solids-content latexes with improved rheological properties and viscosity.

By correctly manipulating the PSD of the final product, concentrated polymer dispersions (over 65% on a volume basis) can be produced without overly increasing the viscosity of the dispersion. Small latex particle size (< 200 nm) gives best gloss, binding, and adhesion. Large particle size (> 500 nm) gives useful rheological properties (thixotropy, film build, etc), but less efficient binding and low gloss.

Agilent has developed an accurate particle size analyzer that is built on its robust UV-Visible (UV-Vis) spectrometric instrument platform. The Agilent 7010 Particle Size Analyzer is simple to use and maintain, and excels at characterizing the particle size distribution in polymer dispersions.

Measurement of reference monodisperse materials

Reference particles from several suppliers (Duke Scientific Corporation, Polymer Laboratories, Bangs Laboratories, Corpuscular Inc., Spherotech, Seragen Diagnostics) and ranging in size from 74 nm through 15 µm were extensively tested and measured with the Agilent 7010 Particle Size Analyzer. The particle sizes determined by the Agilent 7010 consistently agreed within 5% of the manufacturer-specified values and typically within 2%. The relative standard deviation for all these samples after five consecutive measurements was better than 1.5%. Figure 1 displays size analyses by the Agilent 7010 for a few of the many polystyrene reference sizes that were measured to check accuracy and precision in the range of 240 nm to 800 nm.

The Agilent 7010 accurately measures the particle size distribution of a variety of polymers, as shown in Figures 2 through 5. Fluorescent and dyed polystyrene particles commonly used for tagging applications in biotechnology are also measured easily; the absorptions of the dyes and fluorophores have a negligible effect on the scattering spectrum and do not alter the calculated particle size distribution, as shown in Figure 2. Figure 3 depicts the PSD for polymethylmethacrylate (PMMA) particles from Seragen Diagnostics. Various sizes of polybutadiene particles have also been tested. Figure 4 shows the particle size distribution for 160 nm, 400 nm and 590 nm polybutadiene particles dispersed in water. Melamine formaldehyde particles have been successfully measured, as shown in Figure 5 for 1.7 µm and 2.54 µm standards. Accurate measurement of polymer dispersions are not limited to dispersions in water, as is shown by measurement of polystyrene in 2-propanol in Figure 6.

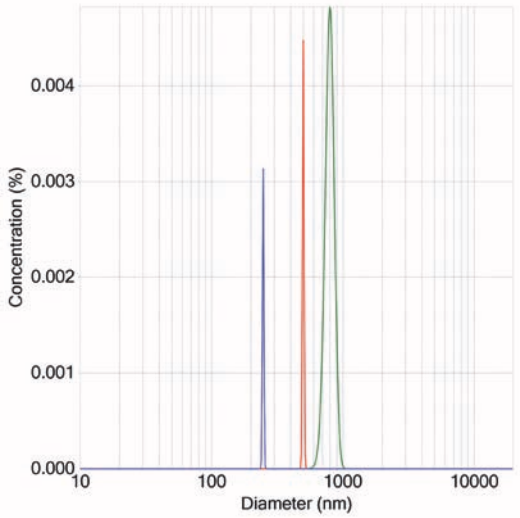


Figure 1. *Duke polystyrene 240 nm (blue), 500 nm (red), and 800 nm (green)*

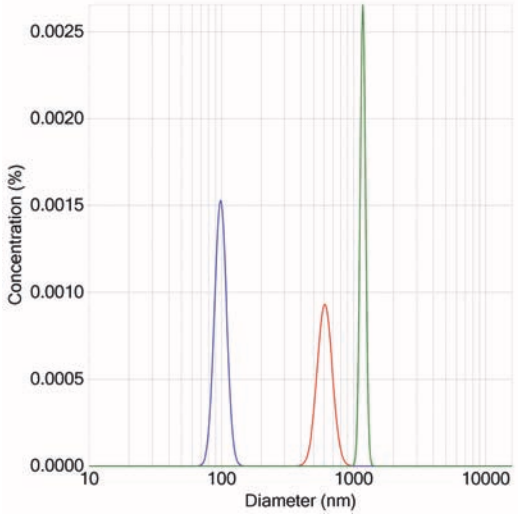


Figure 2. *Particle size distribution of blue-, red-, and green-dyed polystyrene.*

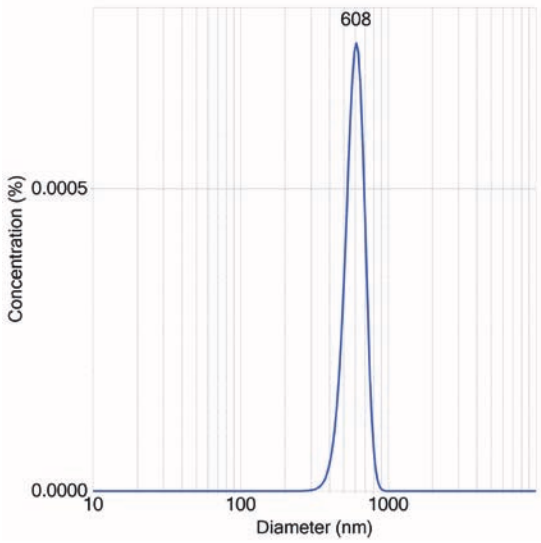


Figure 3. *Seragen polymethylmethacrylate (PMMA) at 586 nm*

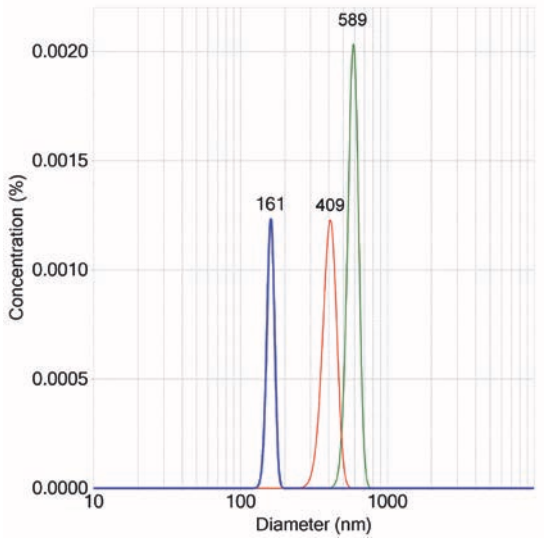


Figure 4. *Dow polybutadiene at 160 nm (blue), 400 nm (red), and 590 nm (green).*

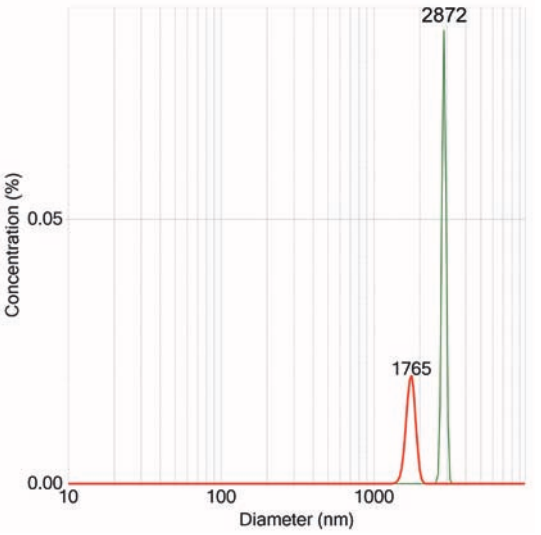


Figure 5. *Melamine formaldehyde at 1.7 µm (red) and 2.54 µm (green).*

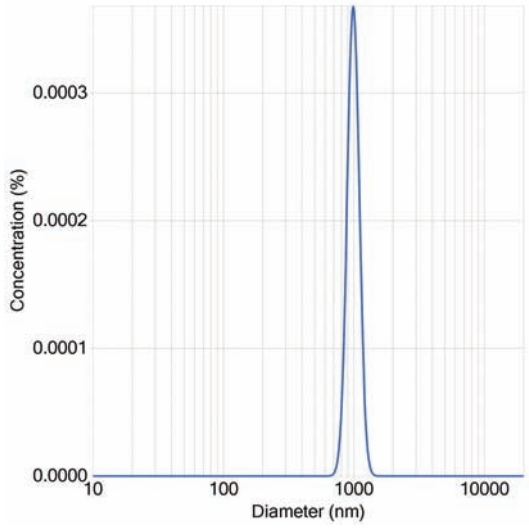


Figure 6. *1.2 µm polystyrene dispersed in 2-propanol.*

Coarse and fine populations mixed in different proportions

Figure 7 depicts a mixture of two polystyrene reference particles (Duke Scientific Corporation) of sizes 92 nm and 3000 nm. These images were obtained with the Hitachi S-4500 Field Emission Scanning Electron Microscope (FE-SEM). Samples were prepared with varying proportions of the fine 92 nm and coarse 3000 nm particles from a ratio of 2%/98% to 98%/2%, respectively.

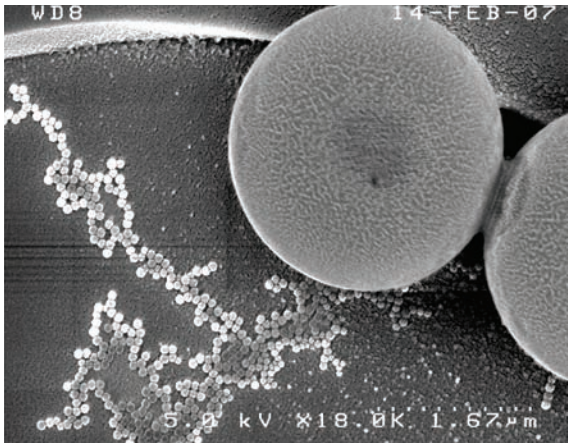


Figure 7. *Mixture of 92 nm and 3000 nm polystyrene particles (Hitachi S-4500 FE-SEM).*

Resolution of multimodal distributions is generally difficult for traditional light scattering techniques. Furthermore, the detection of fine particles in the presence of a large population of coarse particles is even more challenging since a few large particles can scatter too much light, masking the presence of the small particles. Figure 8 shows that the 7010 Particle Size Analyzer is able to detect even 9% of fine 92 nm particles in the presence of 91% of 3 µm particles.

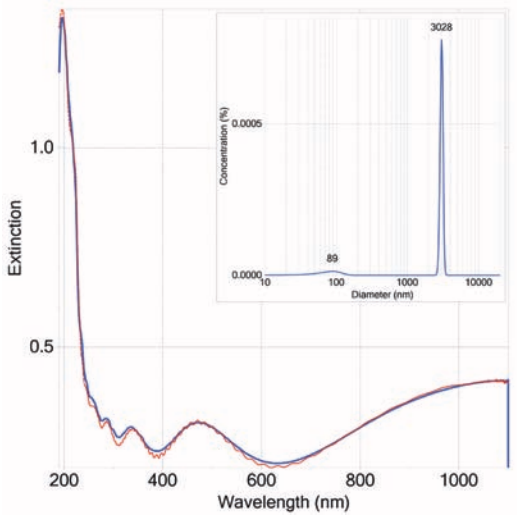


Figure 8. *Detection of 9% by volume of the fine 92 nm particles in a background of 91% of 3 µm particles.*

To understand how this UV-Vis spectroscopic technique is able to detect and resolve these complex dispersions, Figures 9 and 10 dissect the measurement. If the entire measured UV-near infrared (NIR) spectrum is to agree with theory within experimental accuracy, the instrument's size analysis must include the two populations. Static light scattering and dynamic light scattering instruments have difficulty detecting fine particles in the presence of a population of coarse particles because in visible wavelengths, the coarse particles scatter much more strongly than the fine particles. The Agilent 7010 does not have this difficulty because the respective signatures of the fine and coarse populations do not overlap throughout the wavelength range of the instrument.

Figures 9 and 10 assist in understanding why this instrument can discriminate two particle populations that are different in both size and concentration. In Figure 9, the 7010 Particle Size Analyzer was set to analyze the spectrum without considering the information in the wavelength range of 190 nm to 400 nm. The analysis delivered a peak at 3.028 µm. By analyzing the spectrum again and using only the wavelength range of 190 nm to 230 nm, Figure 10 shows a peak at 97 nm. Because those two peaks are very close to the actual sizes of the two populations, these measurements show that in the original spectrum, the signature associated with the fine population is predominantly in the UV region, while the signature associated with the coarse population is primarily in the visible region.

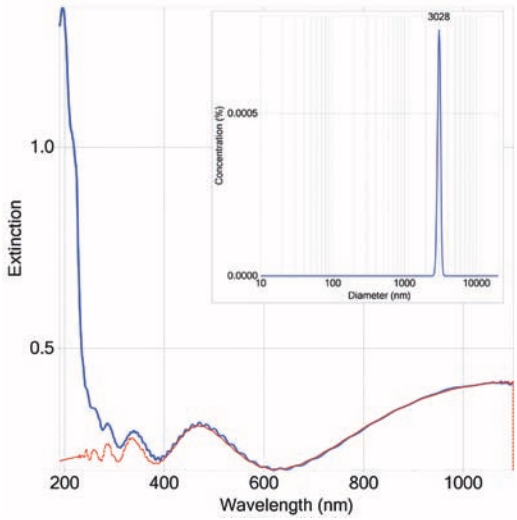


Figure 9. *Same measurement as in Figure 8, with elimination of information in the 190 nm to 400 nm range.*

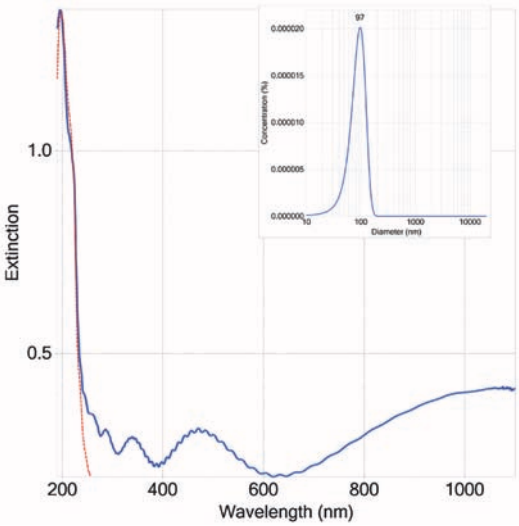


Figure 10. *Same measurement as in Figure 8, with elimination of information in the 230 nm to 1100 nm range.*

Figure 11 compares the size analysis for samples in which the volume percentage for the fine population was 4.8%, 9%, and 17%. From inspection of the spectra, it is apparent that as the proportion of fine particles increases, the spectral signature of the coarse particles becomes more and more insignificant in amplitude as the attenuation in the short wavelengths increases. The sharp decrease in extinction as a function of increasing wavelength in the UV range due to Rayleigh scattering of the fine particles is clearly observed. As the feature due to Rayleigh scattering of fine particles grows, the relative size of the signature for the coarse population decreases.

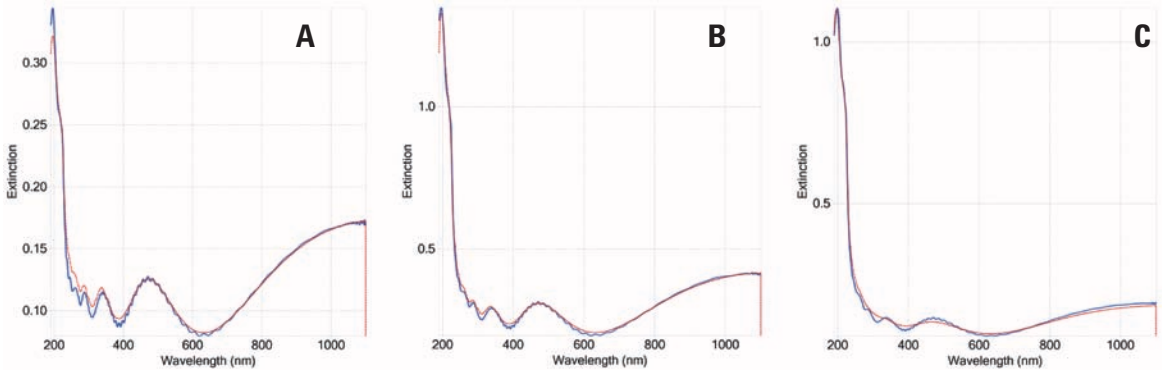


Figure 11. *A) 4.8% 92 nm and 95.2% 3 µm polystyrene. B) 9% 92 nm mixed with 91% 3 µm polystyrene. C) 17% 92 nm mixed with 83% 3 µm polystyrene.*

Resolution test

The results shown up to this point demonstrate that the 7010 Particle Size Analyzer can resolve populations that differ greatly in particle size, as well as in their volume proportions. The following examples demonstrate how close in size two populations can be while still being resolved by the Agilent 7010. Polystyrene at 200 nm was mixed first with 1 µm polystyrene, and then with incrementally smaller polystyrene particles to determine the population size limits that the Agilent 7010 can resolve. Figure 12 illustrates the size resolution of 50%/50% polystyrene mixtures: 200 nm/1000 nm (blue); 200 nm/800 nm (red); 200 nm/600 nm (green); and 200 nm/500 nm (black). In fact, the Agilent 7010 has resolved two different size populations that are as close as a ratio of 1:1.5. This is demonstrated in Figure 13 for 1 µm and 2 µm (blue), 2 µm and 3 µm (red) and 3 µm and 5 µm (green) polystyrene particles. Comparing these distributions, it appears that the broadening of the 1 µm peak in the mixture is an artifact of the fitting algorithm. There appears to be a trend in close bimodal samples of the smaller peak becoming artificially broadened.

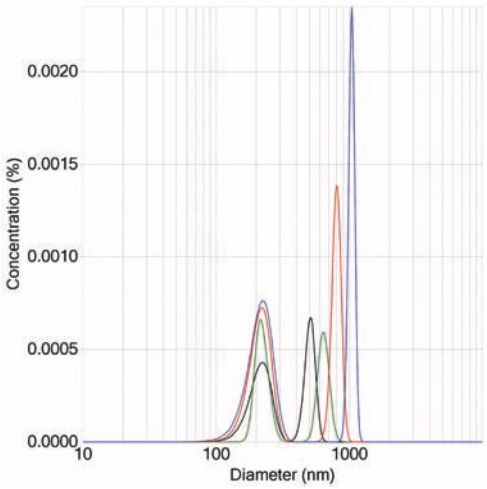


Figure 12. *Size resolution of 50% 200 nm polystyrene mixed with 50% 1 µm polystyrene (blue), 50% 800 nm polystyrene (red), 50% 600 nm polystyrene (green), and 50% 500 nm polystyrene (black).*

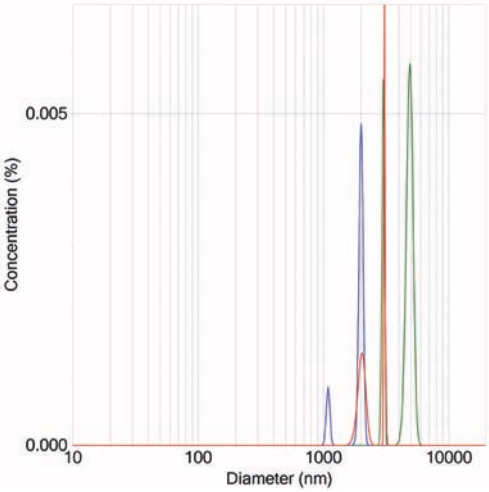


Figure 13. *Demonstration of 1:1.5 size resolution capability with polystyrene mixtures: 15% 1 µm mixed with 85% 2 µm (blue), 50% 2 µm mixed with 50% 3 µm (red), and 50% 3 µm mixed with 50% 5 µm (green).*

Polymer dispersions with UV-absorbing additives

Very often, dispersions of polymer particles in water contain additives that absorb in the UV range. For example, biocides may be added to reduce bacterial growth, surfactants may be added to promote colloidal stability, or ligands with specific chemical functionality may be attached. These UV-absorbing features must be either subtracted or ignored in order to produce the best particle size results. If the software tries to fit the UV-absorbing features to particle scattering, phantom small-particle peaks may be created in the PSD.

One method to produce results that are more accurate is to measure a blank using the exact suspending medium of the dispersion. This may be accomplished by separately preparing a solution with the correct concentration of additive, or if the particles are sufficiently large and not buoyant, by centrifuging the particles and using the supernatant as a blank. Note that if the centrifugation is not complete and some particles are present in the blank, it is still possible to get a very good measurement of particle size, but the particle concentration will be underestimated and the dynamic range for the sample will be drastically reduced.

A simpler procedure to reduce artifacts caused by UV-absorbing additives is to use pure water as a blank and to remove the UV wavelengths from the calculation of particle size. This is especially advisable if the particles are in the micron size range and the spectral scattering features are not in the UV range. To disregard the UV wavelengths in the calculation, the Agilent 7010 software has a feature called "UV Autocorrect."

Figures 14A and 14B give an example of a commercial latex emulsion with a broad distribution that maximizes around 7 µm. The correct particle size distribution, verified by comparison with SEM image analysis, is found with UV Autocorrect selected (Figure 14A). With UV Autocorrect off, a poor spectral fit (red and blue lines not corresponding) is found and the wrong particle size distribution is produced (Figure 14B).

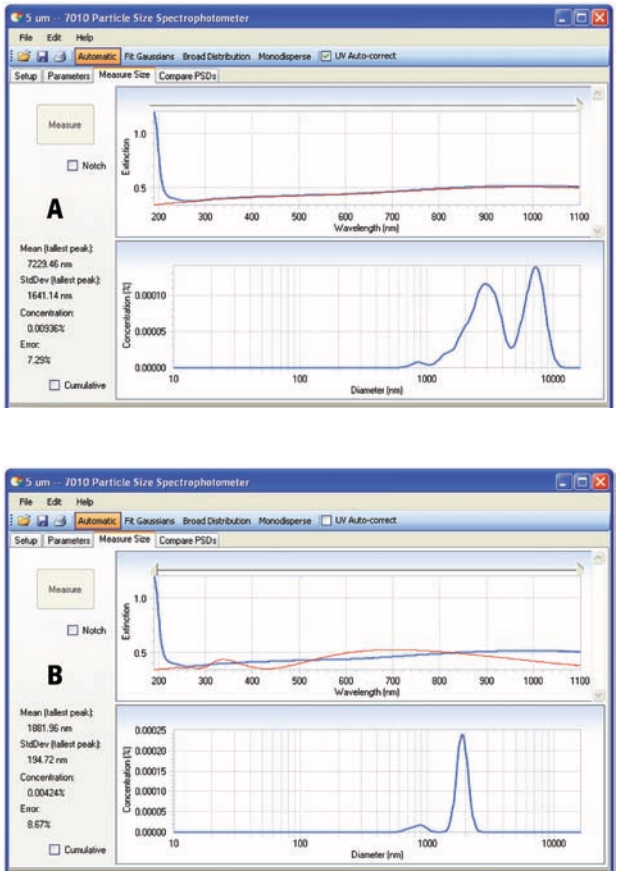


Figure 14. *Automatic mode measurement of commercial latex emulsion. A) Correct PSD found with UV Autocorrect on. B) Incorrect PSD found with UV Autocorrect off.*

The particle size distributions for several polystyrene reference standards in the range of 1 µm to 15 µm were also measured. Two of these are shown in Figures 15 and 16. Despite this, even if UV Autocorrect is off and pure water is used as the blank fluid, the size analysis in many cases will be accurate due to the high information content for monodisperse particles in this size range. However, the error will be higher than the advised range of 0 to 3% due to the discrepancy between measurement and theory in the UV wavelengths.

When *not* to use UV Autocorrect

Although the default setting of UV Autocorrect is on, it may be advisable to deselect this feature when measuring small particles (< 200 nm) of nonmetals. These particles scatter strongly in the UV range and may be entirely ignored by UV Autocorrect.

The screen shots in Figure 17 show a mixture of 100 nm and 400 nm polystyrene latex in a 1:3 mixture. With UV Autocorrect on (Figure 17A), the particle size distribution algorithms completely ignore the 100 nm particles. With UV Autocorrect deselected, as shown in Figures 17B and 17C, the software correctly finds both the 100 and 400 nm polystyrene peaks, and correctly determines their relative concentrations as well.

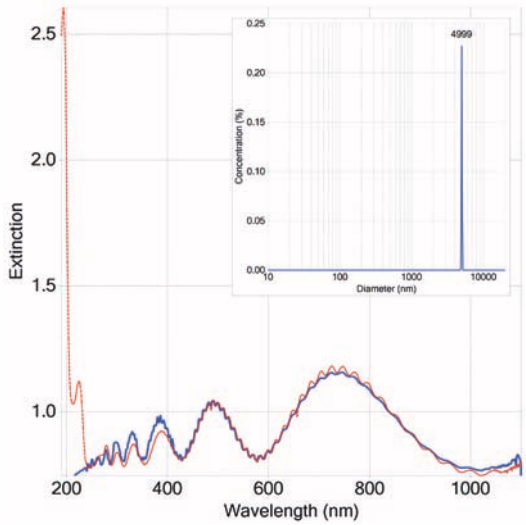


Figure 15. *5 µm polystyrene (Duke Scientific Corporation).*

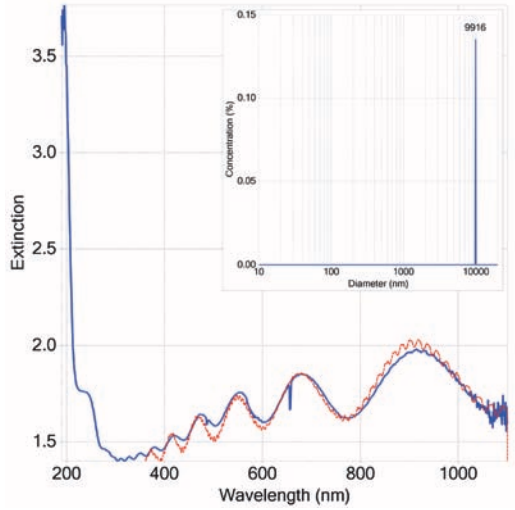


Figure 16. *10 µm polystyrene (Duke Scientific Corporation).*

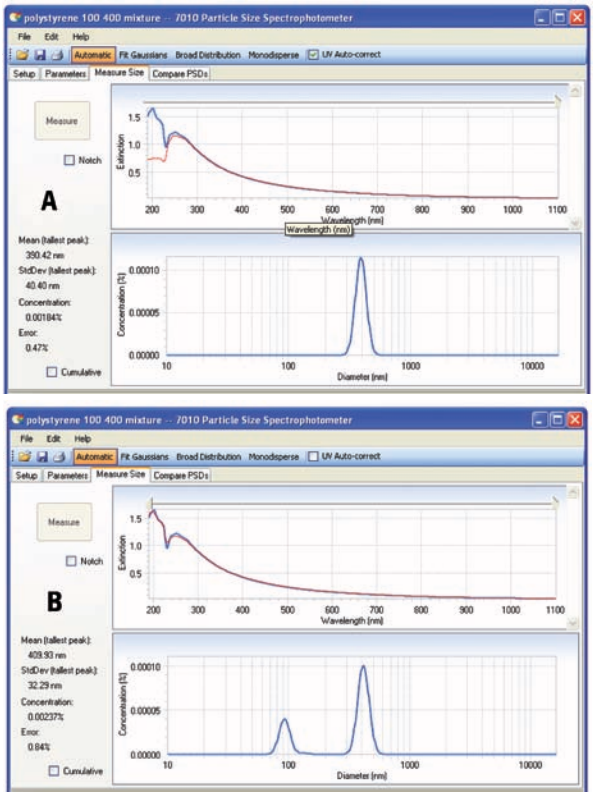


Figure 17. *Particle size distributions from mixture of 100 and 400 nm polystyrene size standards. A) Incorrect PSD with UV Autocorrect selected. B) Correct PSD with UV Autocorrect deselected. C) Same as B, except cumulative PSD is displayed.*

Conclusion

The Agilent 7010 Particle Size Analyzer provides accurate results for complex particle size distributions of polymer dispersions. The UV-Vis technology in the Agilent 7010 allows one to measure multimodal dispersions or mixtures of very small particles in the presence of very large particles, which are typically challenging for light scattering techniques (dynamic light scattering or laser diffraction). With its ease of use, ability to give concentration information as well as particle size, and fast measurement time (less than 10 seconds), the Agilent 7010 Particle Size Analyzer is an indispensable technology for characterizing polymer particles ranging in size from 50 nm to 15 µm.

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