Brookhaven Instruments Corporation

White Papers • Application Notes • Theory Guides

Part 1: The New Customizable Correlator Layout - First Delay

Contents

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Correlator

The correlator is the key technology that makes dynamic light scattering (DLS) possible, facilitating accurate measurement of particle sizes. Brookhaven Instruments has introduced an upgraded correlator to provide researchers with enhanced DLS measurement capabilities.

The autocorrelation function (ACF) is a mathematical algorithm employed to measure the self-similarity between a signal and a version of itself shifted in time. The ACF is used to quantify the rapid intensity fluctuations resulting from the Brownian motion of dispersed particles. In DLS, changes in the intensity of scattered laser light are transformed into an ACF to produce a particle size distribution. The ACF transforms the raw data in DLS to calculate the effective diameter and polydispersity index (PDI) through Cumulants analysis. More complex regression techniques, such as Non-Negative Least Squares (NNLS or CONTIN) can be used to produce multimodal size distributions (MSDs).

A New Customizable Correlator Layout

A unique feature found in Particle Solutions v4 that is not found in other DLS instrumentation is the ability to customize the correlator layout for samples measured using 15° forward scatter, 90° side scatter, or 173° back scatter configurations. The ability to modify the number of channels as well as the first and last delay times is especially useful with samples that have a very slow decay rate due to low mobility, resulting from either large particle sizes or a high viscosity of the diluent used in sample preparation.

In the following study, we demonstrate uses for the *first delay* parameter in the advanced correlator layout.

What is the first delay?

The first delay is the fastest sampling time and the established lower limit τ (μs) of the ACF. Typically, the default first delay for the 15° (forward scatter) and 90° scattering angles is 5 μs, while that of the 173° (back scatter) scattering angle is 2 μs. The new adjustable first delay allows the user to set first delays ranging from 0.1 to 40,000 μs (40 ms). Decreasing the first delay is useful for measuring smaller and faster moving particles; however, too low of a first delay can negatively affect results due to a phenomenon known as afterpulsing. Information regarding afterpulsing will be provided below. This article will help to determine methods for finding the optimal first delay setting. **Figure 1** displays the SOP window where the first delay can be set.

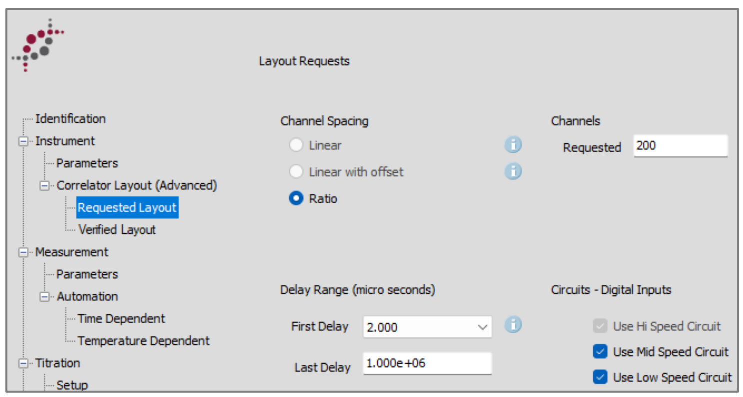

Figure 1: *Particle Solutions SOP window containing the Correlator Layout (Advanced) feature. In the Requested Layout section, users can select a First Delay value ranging from 0.1 μs to 40,000 μs.*

Experimental Methods

To explore the impact of changing the first delay of the advanced correlator layout feature of Particle Solutions, the *last delay* and number of *channels* were kept constant at the default values of 1.0×10^6 μs and 200, respectively, as seen in **Figure 1**. A 20 nm Polystyrene Latex (PSL) Standard diluted in 10 mM KNO_3 was used to test changes in the first delay. Three different first delays were measured: 2 μs (default setting), 1 μs, and 0.100 μs.

Note: Due to the small size of the PSL, the samples were measured using 173° backscatter angle, which has a default first delay of 2 µs.

Results

Default first delay of 2 µs

The mean effective diameter and PDI of the 20 nm PSL sample measured using the 2 µs first delay setting were 23.65 nm ± 0.20 nm and 0.166 ± 0.012. respectively, as seen in **Figure 2**. The MSD graph of the 20 nm PSL sample measured with a 2 µs (default) first delay can be seen in **Figure 3**. This graph displays a large peak at approximately 23 nm. Any additional peaks or variations of peaks indicate the presence of dust or aggregates. The ACF in **Figure 4** is a representative of an accurate correlation function, where there is no afterpulsing effect. Afterpulsing will be discussed later in this article.

Sample ID	Eff. Diam. (nm)	Polydispersity	Baseline Index	Count Rate (kcps)	Data Retained (%)	Diffusion Coeff. (cm²/s)	Rel. Variance By Surface
Mean:	23.65	0.166	9.0	500.6	90.64	2.075e-07	0.08
Std Err:	0.08	0.005	0.2	3.5	0.68	7.038e-10	0.01
Std Dev:	0.20	0.012	0.5	8.5	1.67	1.724e-09	0.02

Figure 2: *Results of 20 nm PSL measured with 2 µs (default) first delay.*

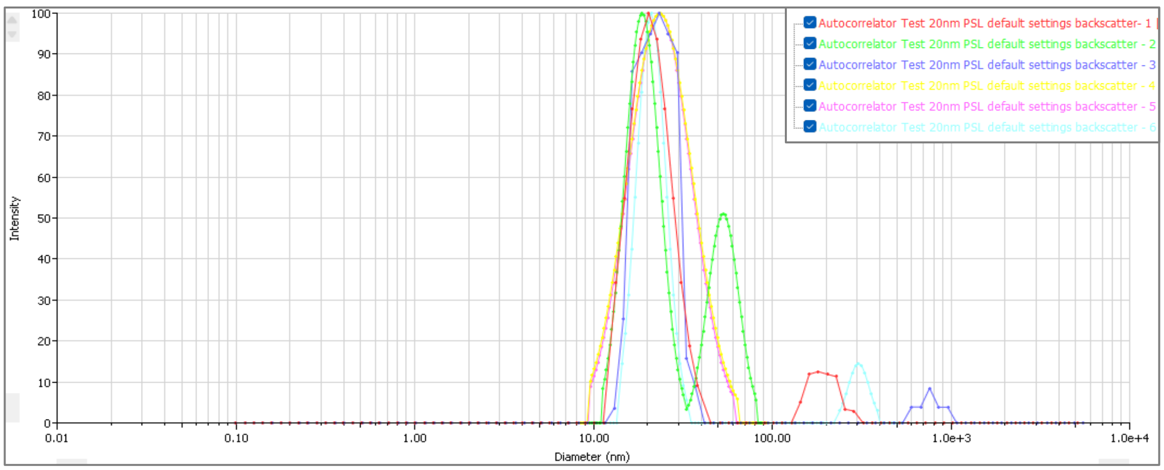

Figure 3: *MSD of 20 nm PSL measured with a 2 µs (default) first delay.*

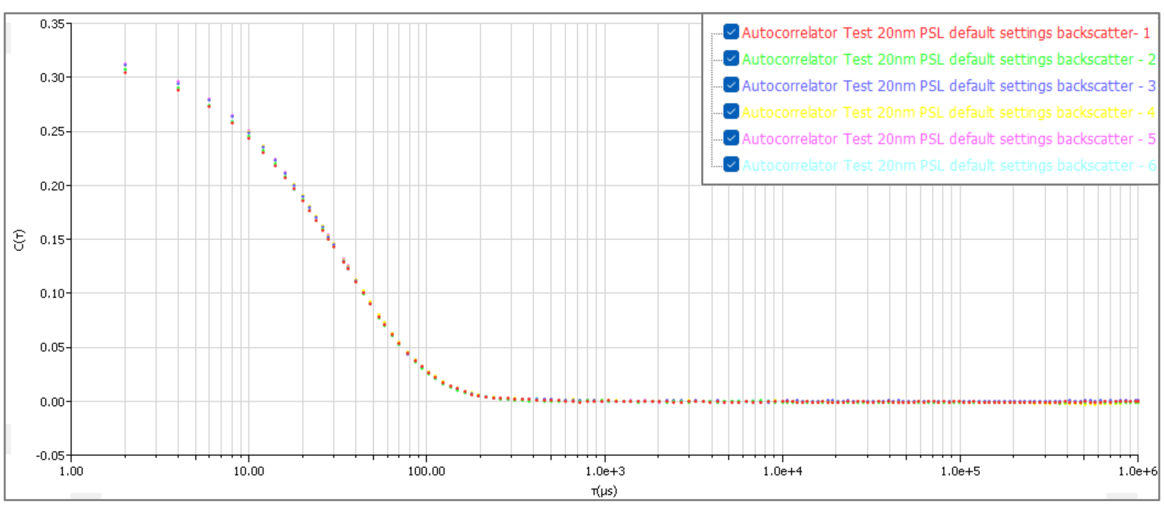

Figure 4: *ACF of the 20 nm PSL using a first delay of Tau (τ) = 2 µs.*

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Impact of Changing the First Delay to 1 µs

The mean effective diameter and PDI of the 20 nm PSL sample measured using a first delay of τ = **1** µs were 24.30 nm ± 1.84 nm and 0.152 ± 0.036. respectively as seen in **Figure 5**. **Figure 6** displays the MSD for the 20 nm. A large peak is observed at around 24 nm. The presence of other peaks is indicative of aggregates or dust particles in the sample. **Figure 7** displays the ACF of the 20 nm PSL using the 1 µs first delay. Several more points appear between 1 µs and 2 µs (the circled region) due to the decrease in the first delay time.

Sample ID	Eff. Diam. (nm)	Polydispersity	Baseline Index	Count Rate (kcps)	Data Retained (%)	Diffusion Coeff. (cm²/s)	Rel. Variance By Surface
Mean:	24.30	0.152	6.0	487.6	92.56	2.028e-07	0.13
Std Err:	0.75	0.015	1.8	5.2	1.23	5.807e-09	0.03
Std Dev:	1.84	0.036	4.4	12.7	3.01	1.422e-08	0.07

Figure 5: *Results of 20 nm PSL measured with 1 µs first delay.*

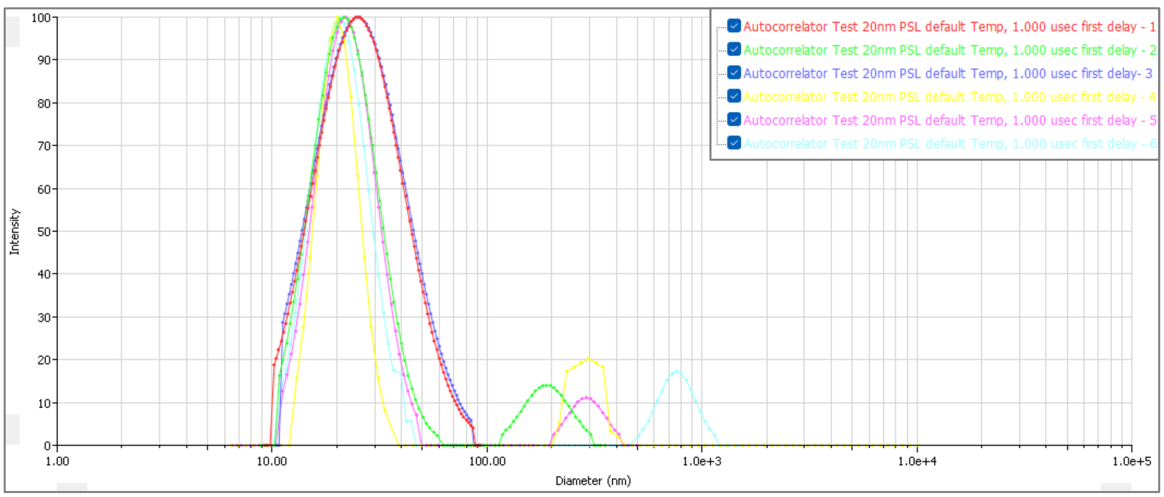

Figure 6: *MSD of 20 nm PSL measured with a 1 µs first delay.*

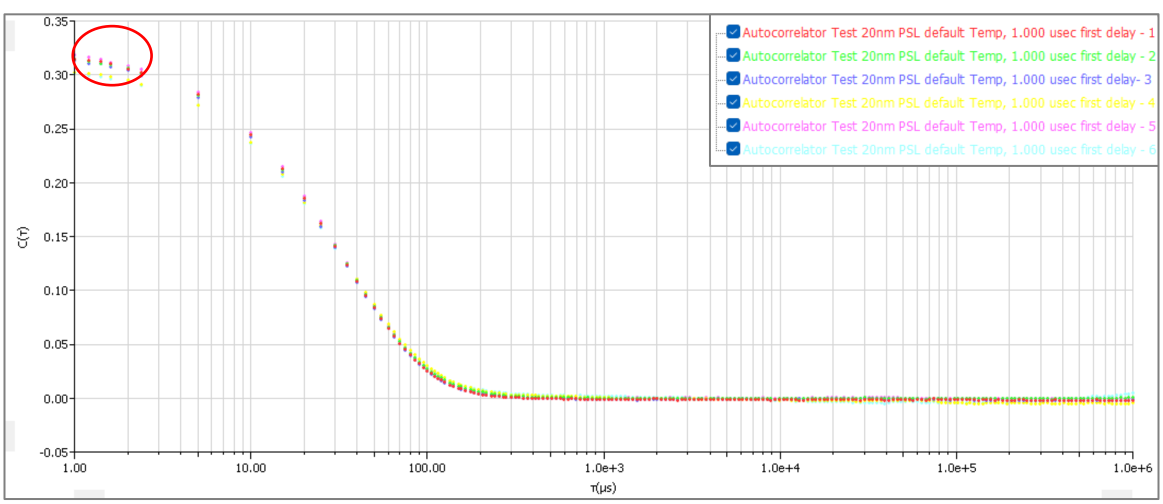

Figure 7: *ACF of the 20 nm PSL using a first delay of τ = 1 µs.*

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Impact of Changing the First Delay to 0.100 µs

Using a first delay of 0.100 µs, the mean effective diameter is measured as 12.06 nm ± 0.97 nm as seen in **Figure 8**. Furthermore, the MSD displays the presence of two peaks, the first being at 0.65 nm and the second being around 24 nm, as seen in **Figure 9**. The ACF, shown in **Figure 10** indicates that the 20 nm PSL particles should not be measured using a first delay of 0.100 µs because of an effect known as *afterpulsing*. As seen in **Figure 10**, afterpulsing appears as false peaks below 1-2 µs. This occurs due to processes in the detector that results in pulses being correlated. More information regarding afterpulsing can be found in this article: The Measurement of Very Small Particles by Cross Correlation or Avalanche Photodiode Detectors

Sample ID	Eff. Diam. (nm)	Peak 1 Diam. by Int (nm)	Peak 2 Diam. by Int (nm)	Polydispersity	Baseline Index	Count Rate (kcps)	Data Retained (%)	Diffusion Coeff. (cm²/s)	Rel. Variance By Surface
Mean:	12.06	0.64	25.14	0.296	8.5	449.9	89.63	4.091e-07	0.06
Std Err:	0.40	0.00	0.40	0.016	0.1	1.8	2.18	1.304e-08	0.01
Std Dev:	0.97	0.00	0.99	0.039	0.3	4.3	5.35	3.193e-08	0.01

Figure 8: *Results of 20 nm PSL measured with 0.100 µs first delay.*

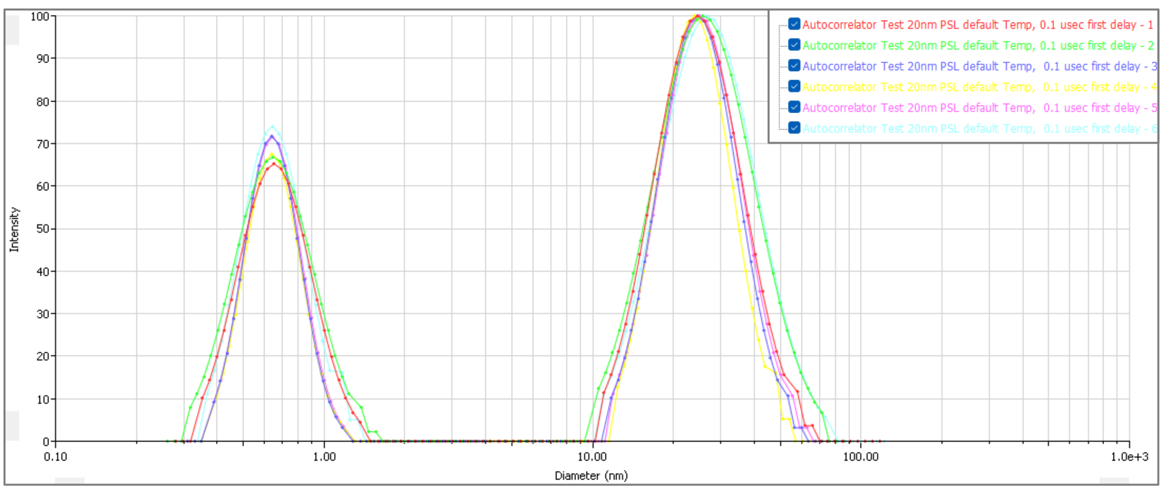

Figure 9: *MSD of 20 nm PSL measured with a 0.100 µs first delay.*

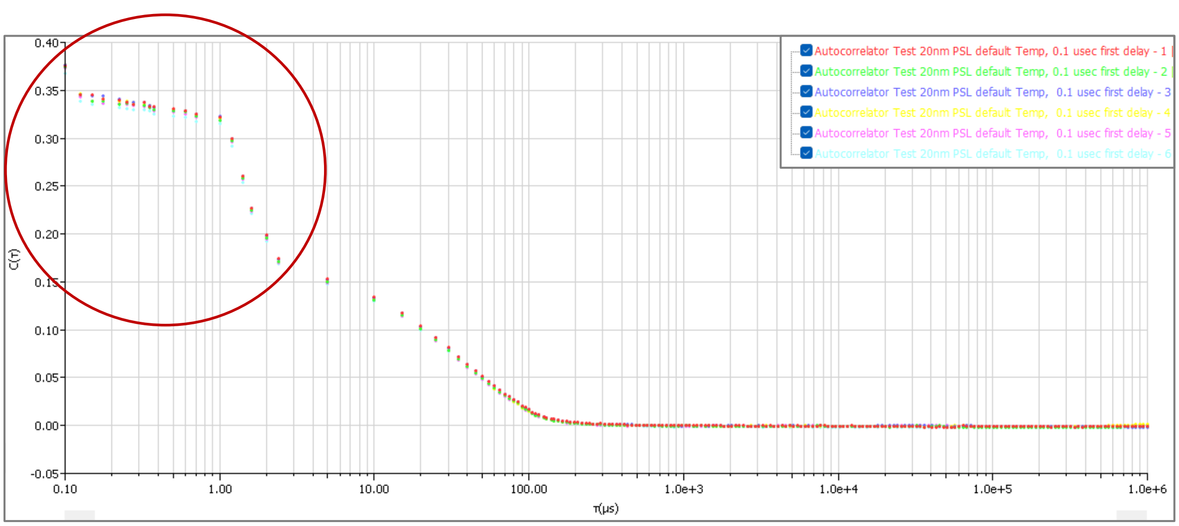

Figure 10: *ACF of the 20 nm PSL using a first delay of τ = 0.100 µs.*

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Conclusion

This study examined the first delay feature of the new customizable correlator layout using a 20 nm polystyrene latex sample diluted in 10 mM KNO_3. DLS measurements were performed using various first delays including: 2 µs (default first delay), 1 µs, and 0.100 µs. The other adjustable features of the new customizable correlator layout, including the last delay (click here to read more) and number of channels (click here to read more) were kept constant and at their default values of 1.0×10^6 µs and 200, respectively.

Results indicate that decreasing the first delay can be useful for measuring the sizes of smaller and faster moving particles. It is important to determine the lowest value that the first delay can be set to, without resulting in afterpulsing, although this will depend on the exact type of detector used (PMT, APD, etc). Afterpulsing can appear as false peaks in the correlation function below 1-2 µs, that further results in incorrect particle sizes. Additionally, increasing the first delay can be useful for measuring larger and slower moving particles. It is important to note that a 20 nm PSL standard was used for this study, which has been evaluated to work optimally at the default conditions. For other samples, it is essential that various first delays are measured to determine the optimal value without seeing the effects of afterpulsing, which are very clear to observe.

Part 2: The New Customizable Correlator Layout – Last Delay

Part 3: The New Customizable Correlator Layout – Channels

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