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Part 2: The New Customizable Correlator Layout - Last Delay

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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 **Part 1**, we discussed the *First Delay* feature of the advanced correlator layout found in the SOP section of Particle Solutions v4. In this article, **Part 2**, we will investigate and discuss the use of the *Last Delay* feature when optimizing the correlator layout.

What is the Last Delay?

The last delay is the established upper limit in τ (µs) of the ACF. Increasing the last delay allows for the measurement of samples containing larger and slower moving particles. Additionally, increasing the last channels is useful for samples with higher viscosities or lower temperatures. It is also beneficial to increase run time when increasing the last delay in order to obtain results that are statistically significant.

Effect of Last Delay on Correlation Function

Experimental Methods

To explore the impact of changing the last delay of the advanced correlator layout found in the SOP editor of Particle Solutions v4, the *first delay* and *channels* were kept at their default values of 5 µs and 200, respectively as seen in **Figure 1**.

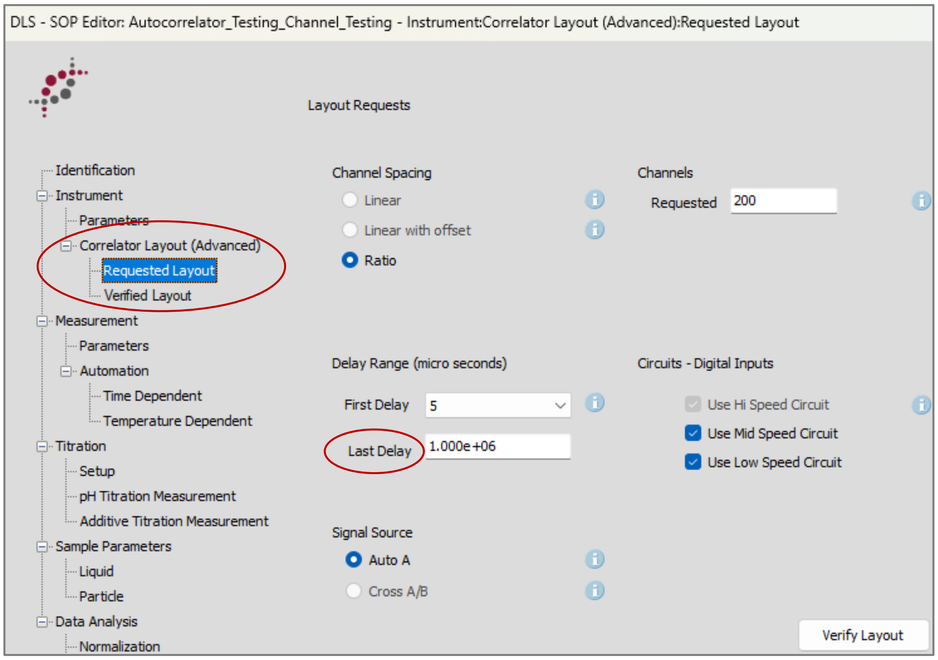

Figure 1: *Particle Solutions SOP window containing the Correlator Layout (Advanced) feature. In the Requested Layout section, users can choose various Last Delay values.*

An 88 nm Polystyrene Latex (PSL) monodispersed standard diluted in 10 mM KNO_3 was used to test changes in the last delay. A short last delay of 1.0×10^3 µs and the default last delay of 1.0×10^6 µs were used for this study. Note: The following measurements were performed using the 90° scattering angle, which has a default last delay of 1.0×10^6 µs.

Importance of the Baseline Index

To better understand the results in this study, it is important to define the baseline index and why it is important. The baseline index is a measurement used to quantify the effects of dust contamination, aggregates, or any particle that defies the laws of Brownian motion, which is the basis of all DLS measurements. Accurately determining an effective particle size relies on correctly normalizing the autocorrelation function. A necessary component of this normalization process is establishing an accurate baseline. Once correctly normalized all correlation coefficients, C(τ), will ideally fall between 0 and 1.

In this case, a correlation function with a last delay greater than 1.0×10^4 µs allows for the correlation function to plateau and for the establishment of a proper baseline, as seen in **Figure 2** as the black line at the bottom of the curve. **Figure 3** demonstrates an autocorrelation function with a short last delay, in this case 1.0×10^3 µs, where the baseline has shifted to the right and resulted in a correlation function that did not level off and plateau. This further results in an inaccurate baseline assignment, and thus an incorrectly normalized ACF.

Since correlation functions are fit by a model to obtain a proper particle size, having an incorrect autocorrelation function due to several factors, including a short last delay, will result in inaccurate hydrodynamic particle sizes.

This article provides more information regarding the baseline index, DLS FAQ: The Baseline Index

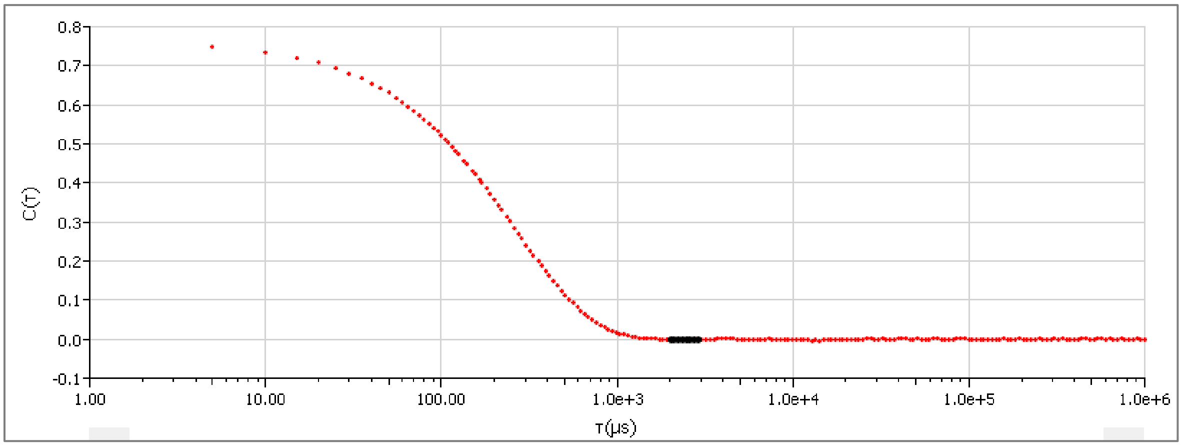

Figure 2: *Correct ACF where the curve plateaus and where a baseline can be established.*

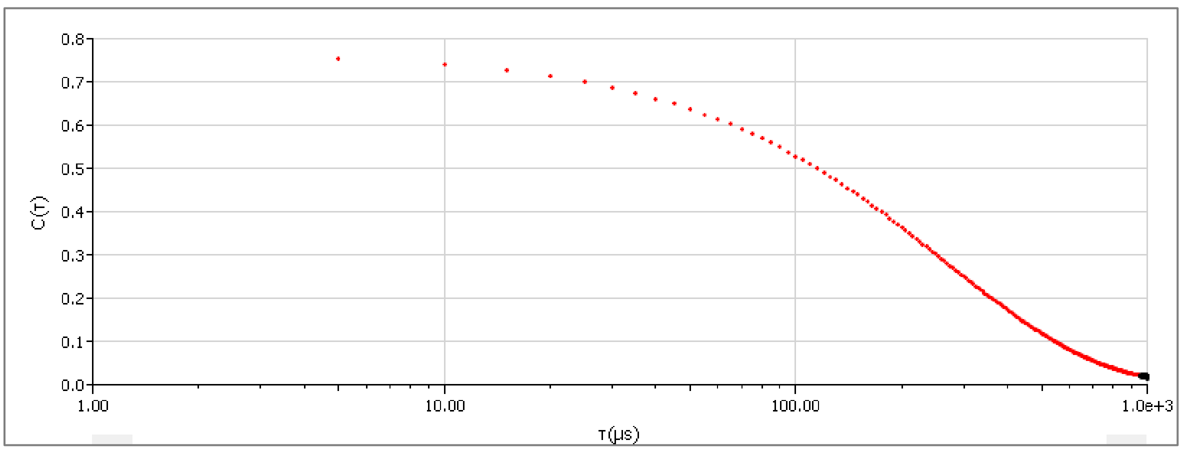

Figure 3: *Incorrect ACF where curve is abruptly cutoff, and baseline is not properly established. There is no plateau.*

Results

Impact of the 1.0x10^3 µs Last Delay

The mean effective diameter and PDI of the 88 nm PSL monodispersed sample, measured using a 1.0x10^3 µs last delay, were 91.88 nm ± 0.62 nm and 0.255 ± 0.018. respectively as seen in **Figure 4**. The 1.0x10^3 µs last delay is too short to allow for a proper baseline measurement since the ACF abruptly stops and there is no plateau, as seen in **Figure 5**. As a result, the mean effective diameter of the sample is reported 4 nm higher than the expected measurement of 88 nm. The PDI value of 0.255 is high and represents a polydisperse sample, but from **Figure 6** it is found from the MSD that there is a single peak, which is indicative of a monodisperse sample.

	DLS							
Sample ID	Eff. Diam. (nm)	Polydispersity	Baseline Index	Count Rate (kcps)	Data Retained (%)	Diffusion Coeff. (cm²/s)	Rel. Variance By Surface	Peak 1 Diam. by Num (nm)
Mean:	91.88	0.255	0.0	449.3	98.64	5.342e-08	0.04	57.25
Std Err:	0.28	0.008	0.0	1.2	0.34	1.596e-10	0.00	1.09
Std Dev:	0.62	0.018	0.0	2.7	0.77	3.568e-10	0.00	2.44

Figure 4: *Results of 88 nm PSL monodispersed sample measured with 1.0x10³ µs last delay.*

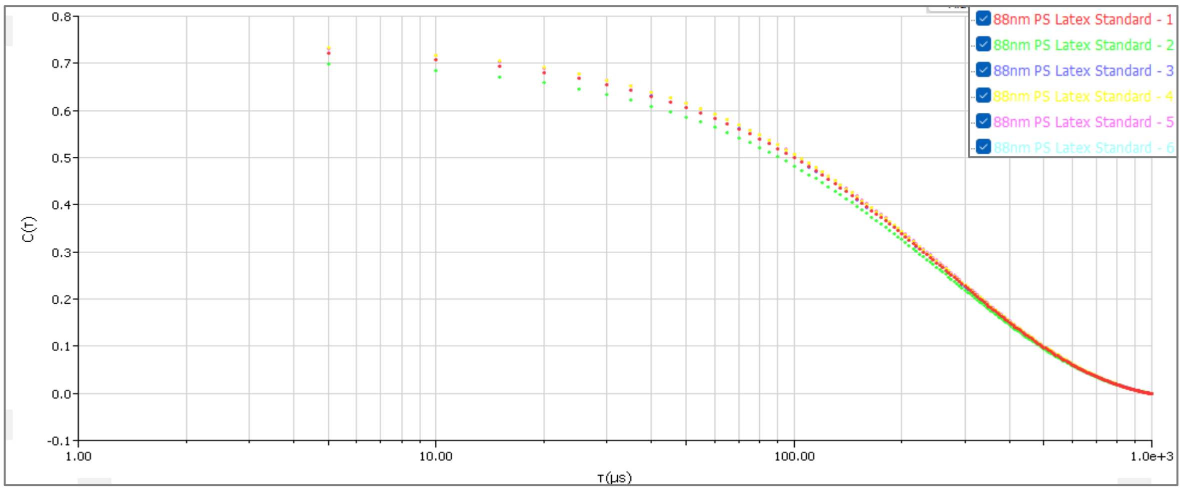

Figure 5*: ACF of the 88 nm PSL monodispersed sample measured using a last delay of 1.0x10³ µs.*

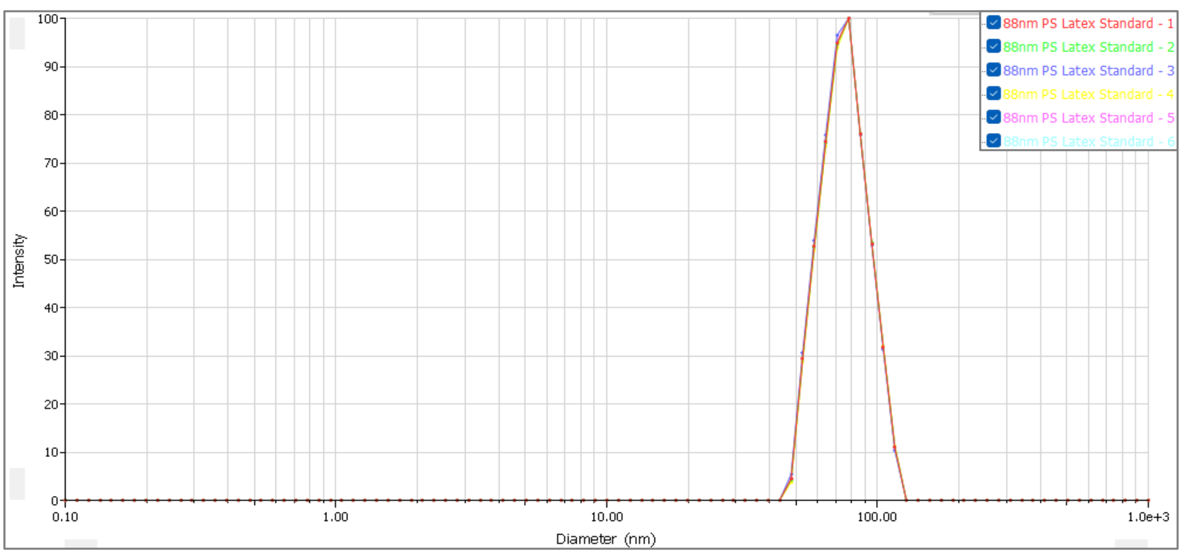

Figure 6*: MSD of the 88 nm PSL monodispersed sample measured using a last delay of 1.0x10³ µs.*

300 Innovative Way, Suite 222, Nashua NH 03062 USA
www.brookhaveninstruments.com
+1 (631) 758-3200

Impact of Using a Last Delay of 1.0x10^6 µs (Default)

The mean effective diameter and PDI of the 88 nm PSL monodispersed sample, measured using a 1.0x10^6 µs last delay, were 89.18 nm ± 0.46 nm and 0.027 ± 0.019, respectively, as seen in **Figure 7**. The default last delay resulted in a proper ACF from which a baseline could be established, **Figure 8**. An accurate ACF further resulted in expected effective diameter and PDI values. Additionally, the MSD graph, **Figure 9**, displayed a peak at 89 nm, which falls within the ± 3 nm limit of the expected PSL particle size.

Note: the small purple peak that appeared in measurement 5 indicated the presence of a dust or aggregate particle.

	DLS							
Sample ID	Eff. Diam. (nm)	Polydispersity	Baseline Index	Count Rate (kcps)	Data Retained (%)	Diffusion Coeff. (cm²/s)	Rel. Variance By Surface	Peak 1 Diam. by Num (nm)
Mean:	89.18	0.027	9.2	445.4	99.55	5.503e-08	0.04	65.05
Std Err:	0.21	0.009	0.3	0.5	0.20	1.281e-10	0.00	1.54
Std Dev:	0.46	0.019	0.6	1.1	0.45	2.864e-10	0.01	3.45

***Figure 7**: Results of 88 nm PSL monodispersed sample measured with 1.0x10^6 µs last delay.*

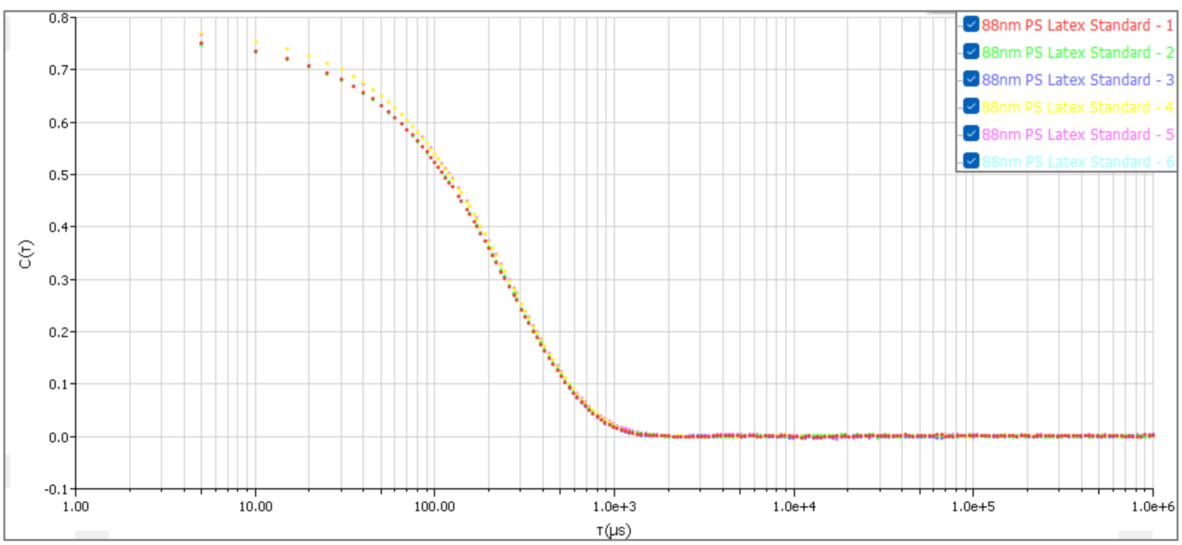

***Figure 8**: MSD of the 88 nm PSL monodispersed sample measured using a last delay of 1.0x10^6 µs.*

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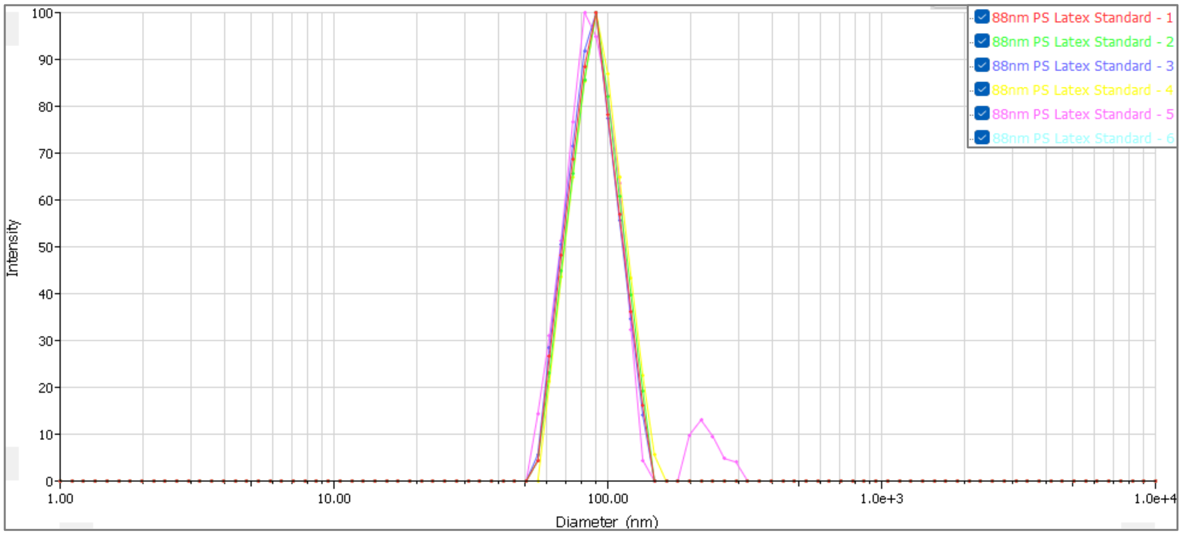

Figure 9*: MSD of the 88 nm PSL monodispersed sample measured using a last delay of 1.0x10^6 µs.*

Conclusion

This study examined the last delay feature of the new customizable correlator layout using an 88 nm polystyrene latex sample diluted in 10 mM KNO_3. DLS measurements were performed using last delays of 1.0x10^6 µs (default last delay) and 1.0x10^3 µs.

Based on the conducted experiments, it is evident that a proper last delay must be established to accurately measure a sample. The default last delay of 1.0x10^6 µs was a better setting since it allowed for the establishment of a proper baseline from the ACF for the 88 nm PSL standard. It is important to note that the default last delay will not necessarily work for other samples, especially non-standards. Samples with larger particles, higher viscosities, and/or lower temperatures that do not display the plateau of the baseline should have the last delay increased. Additionally, to ensure proper statistical analysis of the sample, it is important to increase the sample run time when the last delay is increased.

Part 1: The New Customizable Correlator Layout – First Delay

Part 3: The New Customizable Correlator Layout – Channels