Application note
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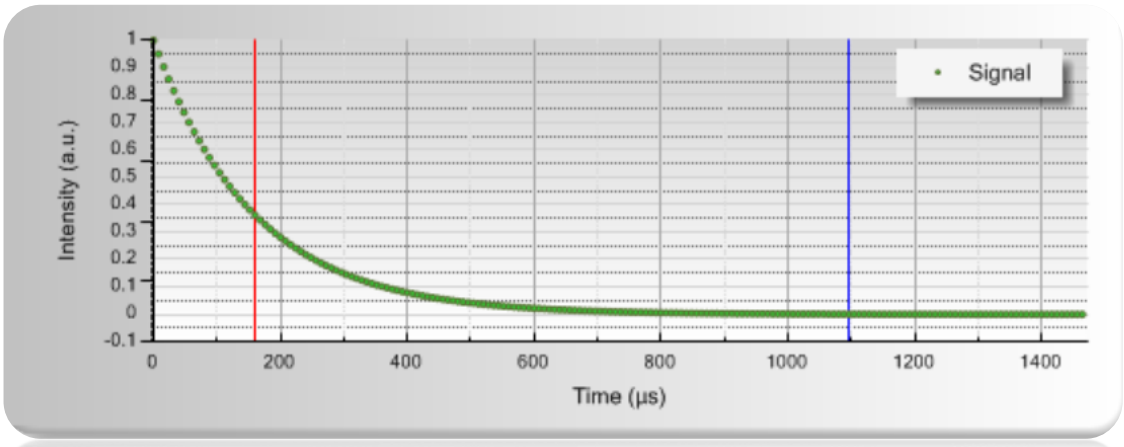
CORDOUAN Technologies

VASCO™ Particle Size Analyzer

Tutorial
"Tune your VASCO™ correlator properly: basic principles, examples and advices to the user"



"Tune your VASCO™ correlator properly: basic principles, examples and advices to the user"

Keywords: *Dynamic Light Scattering, colloids, correlator, VASCO™*

Abstract

The present note intends to help VASCO™ users to optimize the setting of their correlator in order to perform their measurements in the best configuration. Starting with a quick reminder of basics about the DLS principle, we then show the effect of particle size and viscosity on the intensity fluctuation self-correlation function. After introducing the correlator settings, we explain how to optimize them through few examples; to conclude this part with a look at the complex case of very polydisperse samples. We finish with some last advices to the VASCO™ users.

Introduction: Few basic considerations about DLS principle

Dynamic Light Scattering (DLS) principle has been known for many decades and extensively described in many books [1,2,3]. What we need to remember before starting with the settings of the correlator is that the DLS measurement is linked to the determination of the studied nanoparticles' diffusion coefficient. In the case of spherical and homogeneous particles in a Brownian motion, the relation between their hydrodynamic radius R_h and the diffusion coefficient D is given by the **Stokes-Einstein law**:

$$D = \frac{K_B T}{6\pi\eta R_h} \qquad (1)$$

Where D is the diffusion coefficient expressed in $m^2.s^{-1}$, K_B the Boltzmann constant, T the temperature, η the liquid phase viscosity, and R_h the hydrodynamic radius of the particle.

In the case of purely monodisperse particles (i.e., only ***one*** D or τ_c describing the particle motion) the self-correlation function calculated by the correlator is a single "decreasing" exponential function, expressed as:

$$G_2(\tau) \propto e^{-2Dq^2\tau} = e^{-\frac{\tau}{\tau_c}} \qquad (3)$$

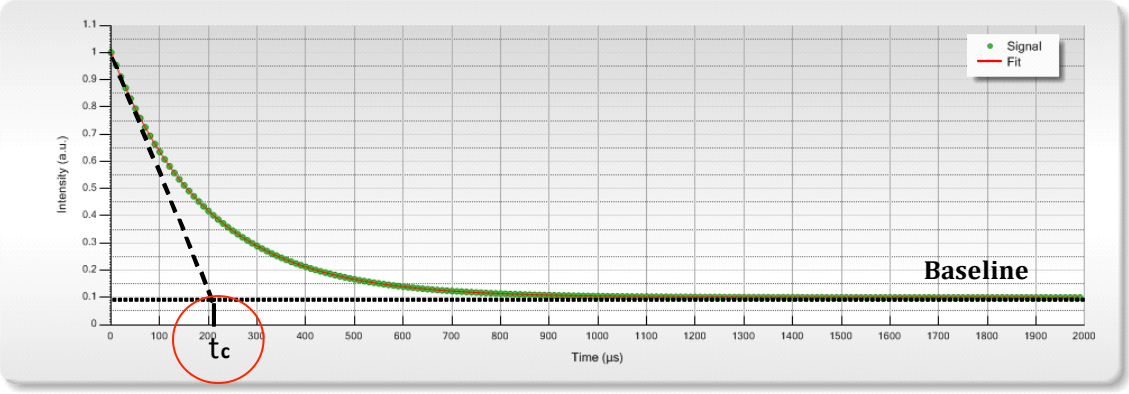


Figure 1: Example of self-correlation function $G_2(\tau)$ for 100 nm particles in water

Also according to this expression, τ_c can be directly measured on the graph since it is given by the intersection of the correlation function's tangent in 0 and the correlation function baseline!

Thus, the slower the particle, the slower decreases the self-correlation function. This phenomenon is illustrated in the next part.

Effect of size and viscosity on the self-correlation function relaxation

As shown by the Stokes-Einstein law, a change in the viscosity or the particles size will affect the motion of the particles in the continuous phase. Intuitively, we expect that the bigger the particle or the higher the viscosity, the slower the particle motion, thus, the longer the relaxation time τ_c.

The effect of particle size and solvent viscosity on the correlation function is illustrated below for the case of monodisperse particles suspended in water at 25°C, with respectively 50 nm, 100 nm, 200 nm and 500 nm of hydrodynamic diameter.

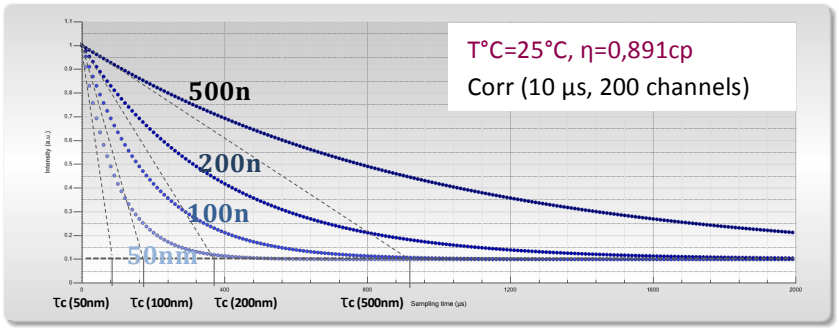


Figure 2: Impact of particle size on correlation function slope for the same correlator settings

Figure 2 below shows simulated correlograms for each of these particle sizes using the same solvent viscosity, the same temperature, and the same correlator settings (10 µs, 200 channels). One can clearly notice that the slope of the corresponding self-correlation function decreases as the particles get bigger.

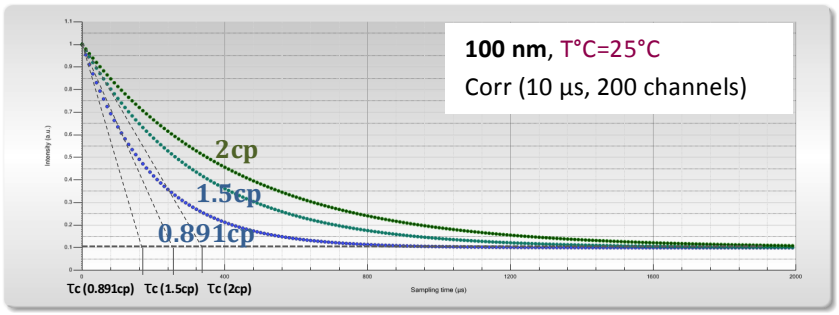
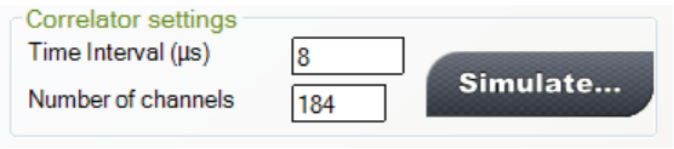


Figure 3: Impact of solvent viscosity on correlation function slope for the same correlator settings

Similarly, a change in the viscosity of the solvent has the same effect on the correlation function. Actually, if the viscosity increases, the mobility of the particle decreases as illustrated in the figure left.

What are the correlator settings and how to optimize them?

The VASCO™ particle size analyzer is equipped with a proprietary **linear time scale correlator**. For such correlator, the settings are usually defined by two major parameters involved in the correlator data processing and calculation: the **time interval** and the **number of channels;** the **time interval** controls the "minimum sampling time" equivalent to the time width of one channel; the **number of channels** is equal to the number of channels or "sampled timeslot" integrated by the correlator (i.e. for 5 µs and 3 channels, the correlator calculates the correlation function at the time 5 µs, 10 µs and 15 µs. for 2 µs and 6 channels, the correlator calculates the function at the time 2 µs, 4 µs, 6 µs, 8 µs, 10 µs and 12 µs).



In practical terms, these two parameters set the scale and binning of the self-correlation function graph: the **number of channels** sets the number of time slot of the function and the **time interval** sets the width of the

binning (i.e., the time resolution of the correlogram). Note that **the total time length of the correlogram is given by the number of channels multiplied by the time interval**.

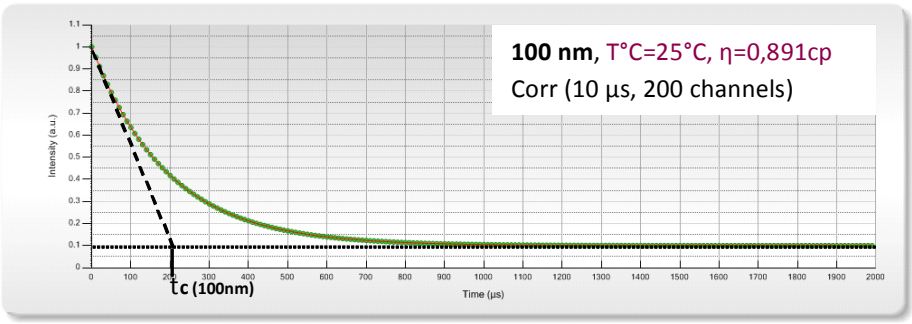


Figure 4: Example of correlogram for 100 nm particles in water with a 10 µs time interval and 200 channels for the correlator settings

For example, if one sets 10 µs and 200 channels, the "gap" between two successive sampled points will be 10 µs and the last point of the correlation function will be at the time 10 µs x 200 = 2000 µs. This is illustrated in the graph left.

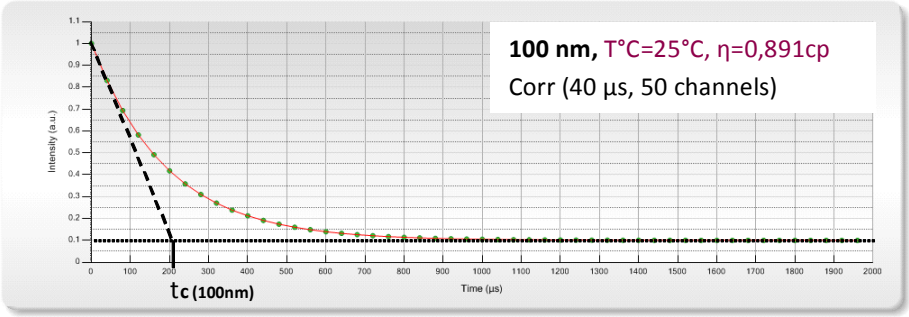


Figure 5: *Example of correlogram for 100 nm particles in water with a 40 µs time interval and 50 channels for the correlator settings*

With the same particle sample, now if one chooses a different correlator setting with time interval of 40 µs and 50 channels, the time resolution is now four time lower than in the previous example but the explored time range is the same (40 µs x 50 = 2000 µs).

In other words, with two different correlator settings, it is possible to measure the same time range but with a different time resolution.

Remark: In both examples (figures 4 and 5), the inversion algorithms find the good result: 100 nm.

Actually, there is not a single good setting for the correlator. Indeed, the correlator settings depend on some tradeoff between the measurement time, Signal to Noise ratio and time resolution. As a general rule of thumb, the algorithms normally find the good solutions for different possible settings as long as the settings satisfy at least **two conditions** (illustrated with some examples below):

Condition 1: The correlogram must have at least 10 points in its "decreasing part" of the function. Actually, this is the main region of interest of the correlation function from which particle size information can be extracted provided that the time resolution is sufficient for the algorithms to be efficient → Decreasing the time interval parameter allows to increase the resolution, if necessary.

Condition 2: The correlogram must have a flat baseline. A useful rule of thumb to remember for a monodisperse system is that the total length of the time scale must be at least six times the characteristic time τ_c. → Increasing the number of channels allows a larger length of the time scale, if necessary.

a) Example of a correct correlator setting

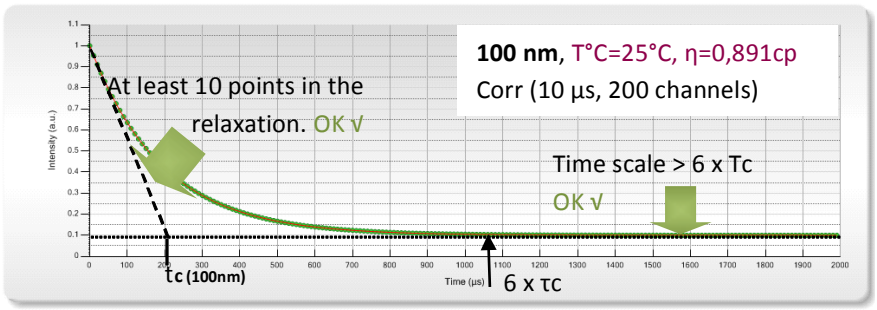


Figure 6: Simulated correlogram for the case of 100 nm particles in water à 25°C; Correlator settings: time interval = 10 µs, number of channels = 200

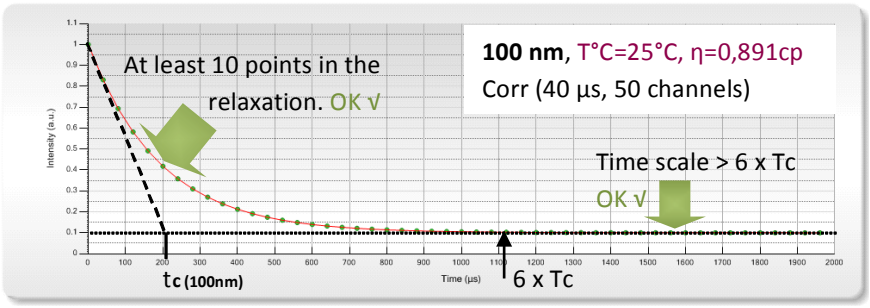


Figure 7: *Same as figure 6 but for time interval = 40 µs, number of channels = 50*

Figures 6 and 7 show that the two different settings are ok according to the two former conditions with a flat baseline and at least 10 sampling points in the relaxation time zone.

b) Example of a bad correlator setting with a too short time interval

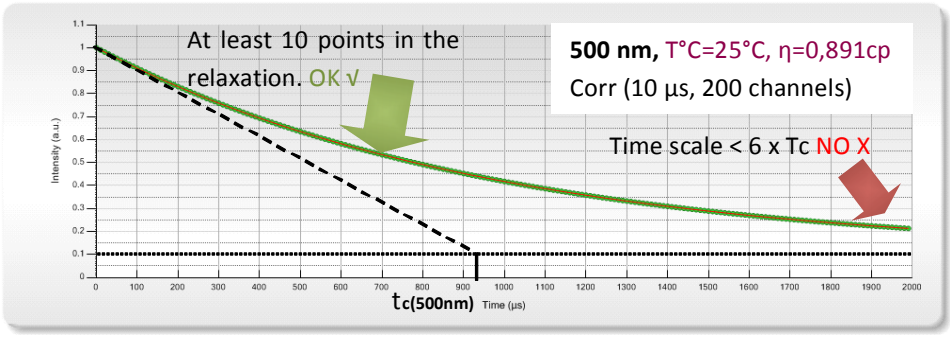


Figure 8: Simulated correlogram for 500 nm particles in water with a 10 µs time interval and 200 channels settings

Figure 8 below shows an example of a bad correlator setting.

One can clearly see that these settings are not optimized since the right end side of the correlogram is not flat, so there is no baseline (see red arrow). To solve this problem one can simply increase the number of channels as shown in figure 9 left.

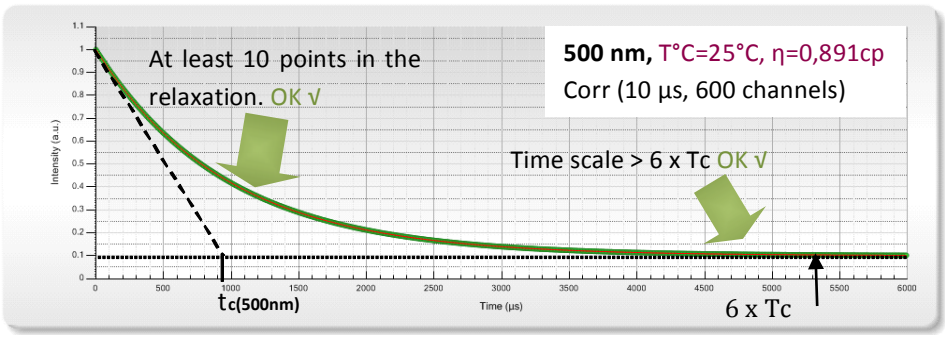


Figure 9: Same as figure 8 with a number of channels sets to 600

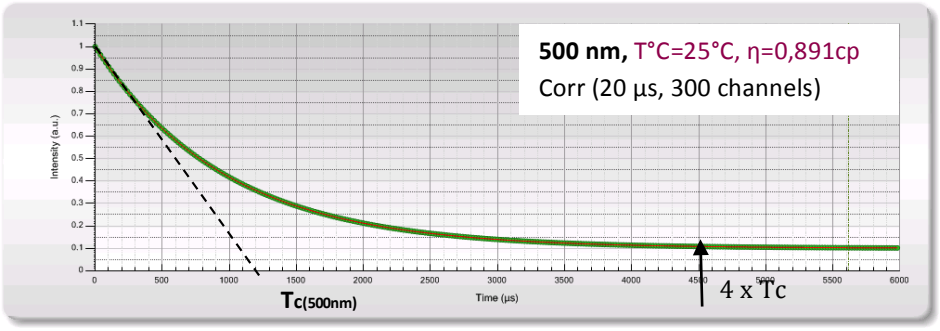


Figure 10: Same as figure 9 with a 20 µs time interval and 300 channels settings

Note that another possibility would be to increase the time interval and reduce the number of channels. For example one can choose 20 µs and 300 channels in order to fulfill both conditions.

c) Example of a correlator setting with a too long time interval

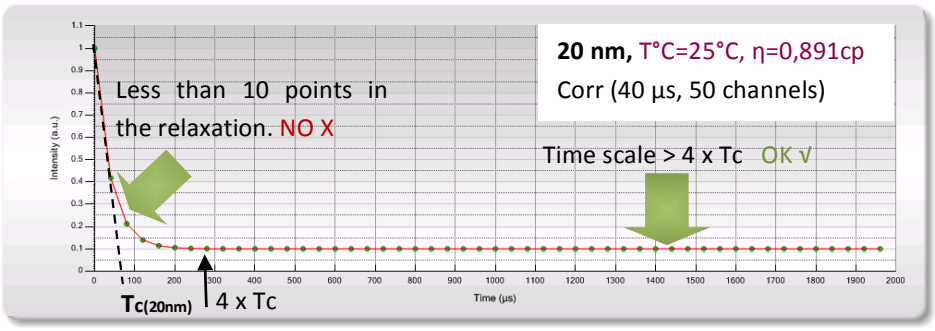


Figure 11: Simulated correlogram for 20 nm particles in water with a 40 µs time interval and 50 channels settings

Figure 11 clearly shows that the settings are not optimized. Indeed, the correlogram exhibits less than 10 points in the relaxation region and does not fulfill condition 1.

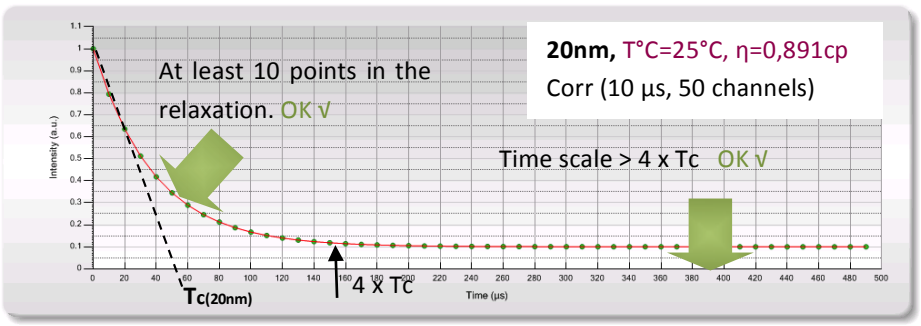


Figure 12: Same as figure 11 with a 10 µs time interval; settings are optimized

This can be corrected by decreasing the time interval to 10 µs which increases the time resolution in the slope region (see figure 12).

The case of multimodal colloidal samples

If a sample is polymodal (i.e. with multiple distinct size populations) and/or very polydisperse (i.e. broad distribution of size), the corresponding self-correlation function can present several relaxation slopes with very different characteristic time τ_{ci}. Figure 13 below shows an example of correlogram for the case of bimodal dispersion containing a population of 10 nm and 200 nm in water at 25°C:

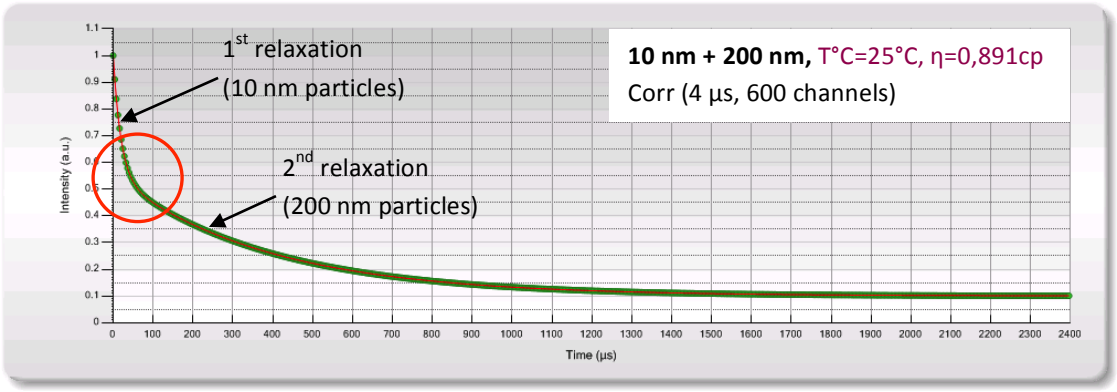


Figure 13: Simulated correlogram of a bimodal colloid with a mixture 10 nm and 200 nm particles in water at 25°C

From figure 13, one can clearly distinguish two relaxation times in the correlogram. Indeed while the 10 nm particles component of the curve decreases quickly on the graph ($\tau_{c(10\ nm)}$ < 100 µs), 200 nm particles component decreases in a significantly longer time ($\tau_{c(200\ nm)}$ > 400 µs). The difference is such that we can see a kink in the correlation function slope at around 80 µs. This is a typical signature on the correlogram when a sample contains two or three distinct populations, each having a narrow size distribution. In such case of polymodal colloid, the correlator settings, and particularly the number of channels, have to be a little bit more "extreme" to see both relaxations and get a nice baseline. However, the rules are exactly the same as in the monodisperse case but the settings are done in two steps:

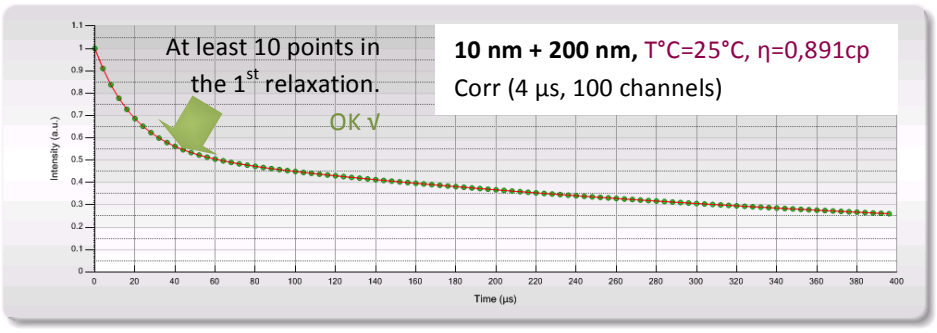


Figure 14: Step 1 - time interval setting for fast relaxation resolution (condition 1)

1. Set the **time interval** to have at least ten points in the quicker relaxation component of the curve.

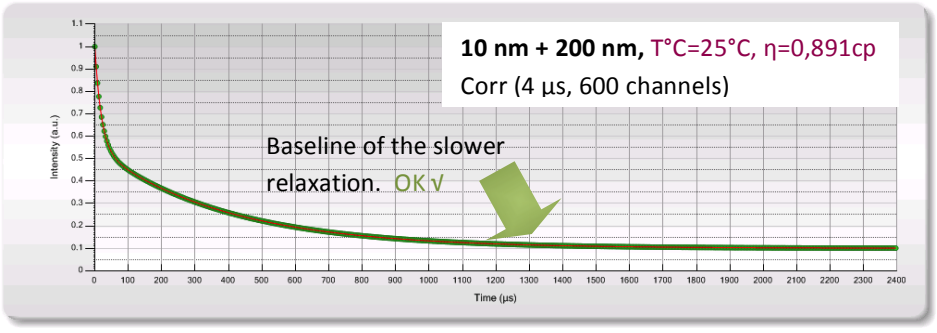


Figure 15: Step 2 – number of channel setting for baseline resolution (condition 2)

2. Then increase the **number of channels** to see the baseline of the slower relaxation component of the curve.

Nota Bene: If one cannot satisfy these two conditions because the size difference between the populations is too important, one should give priority to the first criteria (condition 1), i.e., the time resolution of the first/fast relaxation! Actually, the Padé Laplace algorithm is quite robust, so even if the baseline is not completely flat at the end at the longest time of the correlogram, the inversion algorithm will still able to detect it and give an accurate estimation of the corresponding size. On the other hand, if the fast relaxation has only 3-4 sampled points in a function of 500 points, the algorithm might miss it.