

Particle size and stability analysis in turbid suspensions and emulsions with Photon Cross Correlation Spectroscopy, PCCS

Particle sizing and stability measurement with table top PCCS!

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Abstract

Modern materials very often derive their properties from nano-particles. This implements a fast growing demand for control of particle size in this field. The most popular technique to do so is PCS, photon correlation spectroscopy. PCS is known for about 30 years but is limited to highly diluted samples all the time. The new instrument of Sympatec called NANOPHOX is able to measure reliably even in suspension of high concentration using recent PCCS.

The physical principle

Photon correlation spectroscopy (PCS) evaluates the intensity fluctuation of scattered light reflected from nano-particles in suspension. This fluctuation is resulting from the “Brownian motion” that keeps the particles in steady movement.

According to temperature and viscosity liquid molecules are moving at a defined speed.

Whenever they run into a particle suspended in the liquid an elastic pulse is resulting. This impact moves the particle in accordance to its size. Small particles will react in a rather fast movement while coarser particles will move much slower as they also may be impacted by more than one molecule from different directions at the same time because of their bigger volume.

This effect can be described as diffusion by the “Stokes-Einstein” equation:

$$D(x) = k_B T / 3\pi\eta x$$

Consisting of:

- D diffusion constant
- k_B Boltzmann-constant
- T absolute temperature
- η liquids dynamic viscosity
- x particle diameter

The frequency of fluctuation in the scattered light intensity there by corresponds directly to the particle size.

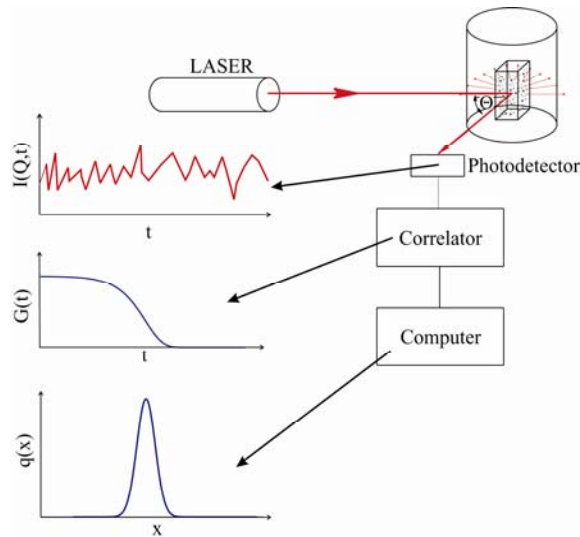


Figure 1. PCS, physical principle

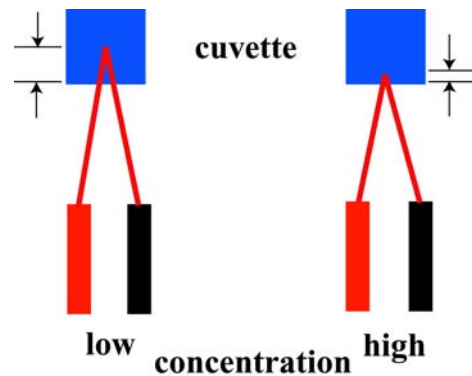


Figure 2. Back scatter set-up

This simple context presupposes that the scattered light reaches the detector without further influence by other particles.

Conditions to avoid such multiple scattering could only be achieved by highest possible dilution. But this meant at the same time very low signal and bad signal-to-noise- ratio.

Many efforts have been taken over the years to cope with this multiple scattering weakness of PCS.

A first approach to higher resolution in results leads to multiple angle set-ups. This enabled more sophisticated evaluation modes as described later but did not help to avoid multiple scattering.

Some years ago back-scatter-set-ups became available. (Figure 2)

This technology tries to reduce the multiple scattering by invading the laser beam only into a thin surface layer of the sample to avoid as much multiple scattering as possible.

PCS is based on the “Brownian motion” enabled by elastic pulses between liquid molecules and particles. Reducing the depth of invasion in high concentrations close to the wall of the cuvette exceeds the principle as wall effects are non-elastic.

Further the influence of multiple scattering is only reduced not avoided and together with its reduction also the scattered light signal is reduced.

The influence of multiple scattering respectively the depth of invasion is able to pretend a 104 nm particle to be of a size down to some 20 nm only.

This uncertainty is more and more taken out of focus by adding further abilities to instruments, as e.g.

- zeta-potential measurement
- molecular weight determination

Such add-ons may be interesting to have, but they don't increase the accuracy and reliability of PCS.

PCCS with NANOPHOX

A new set-up using Photon-Cross-Correlation-Spectroscopy (PCCS) was thought of by : Schätzel (Uni Kiel + Mainz), Overbeck et al. (Uni Mainz), Urban et. al. (ETH Zürich) and Aberle et. al. (Uni/FhG Bremen)

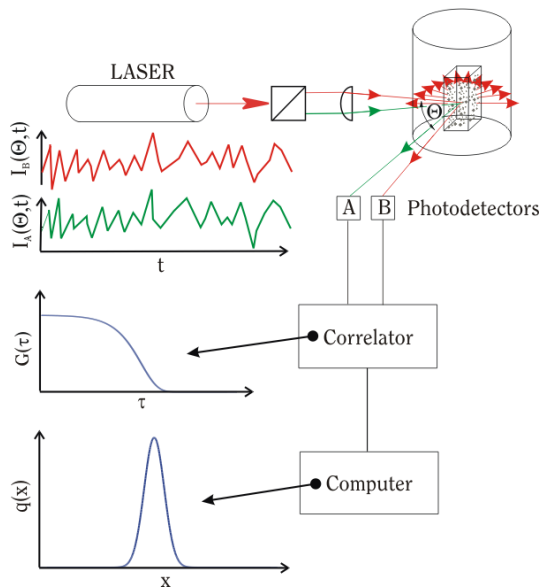


Figure 4. Innovative PCCS set-up

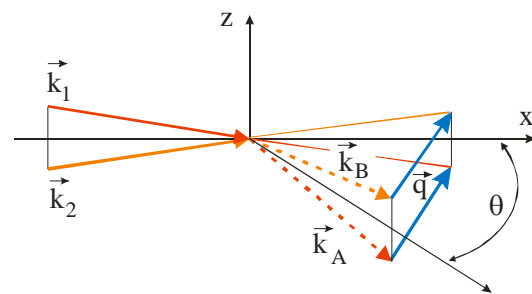


Figure 5. Set-up theorie

The challenge in such a set-up is that:

the scattering vectors q have to be identical as well as the scattering volume does.

Such a set-up enables to receive two results that are identical with respect to the single scattered light but differ in noise as well as in multiple-scattered-information collected along its different ways through the sample.

A cross correlation of the two results is able to act as a filter that extracts the single scattered light only. This for the first time guaranties that at what concentration ever the influence of noise and multiple scattering can be avoided reliably and completely.

Sympatec owns exclusive rights on several patents for this set-up and developed a robust table-top instrument and integrated it into its WINDOX software, proven for laser diffraction particle sizers since many years.

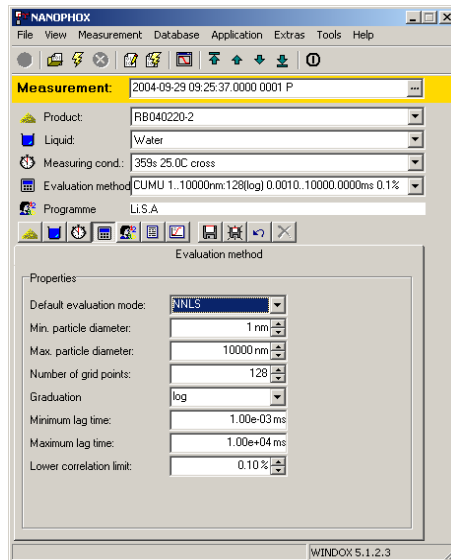


Figure 6. Operational window

This software incorporates:

2nd Cumulant evaluation mode, as defined in ISO 13321, that results in a mean diameter and a width value.

NNLS (Non-Negative-Least-Square), that provides a full size distribution resolving multiple modes as long as their ratio of diameters are above 1:4.

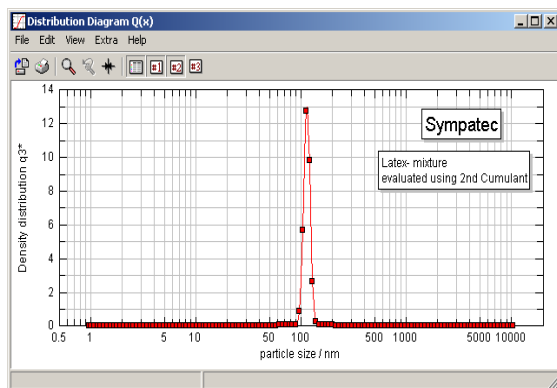


Figure 7. 2nd Cumulant evaluation

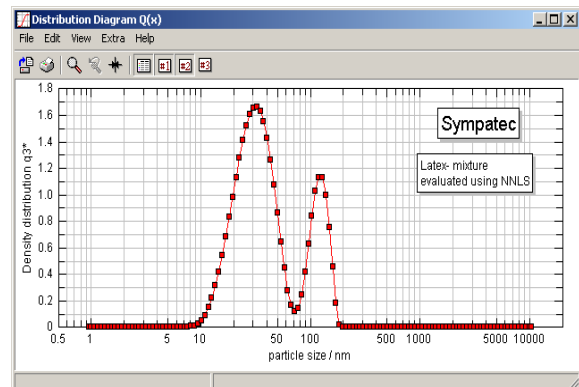


Figure 8. NNLS evaluation

Sympatec GmbH has released a major re-design of its unique Dynamic Light Scattering based NANOPHOX PCCS instrument.

The Sympatec specific NNLS evaluation algorithm, allowing for secure determination of size distributions even with multimodal structures has now been enhanced with the “auto-NNLS” mode. The outstanding performance provides very reliable and realistic information about the

particle size distributions, which are at the same time highly reproducible. The auto-NNLS mode requires no operator input for optimum determination of evaluation parameters and thus is applicable in validated environments and for FDA conform SOPs as well. However, for special tasks manual operation and optimisation if requested is still available.

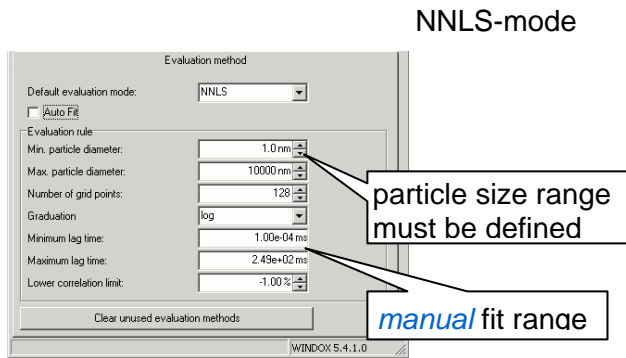


Figure 9. NNLS evaluation fit-range set up

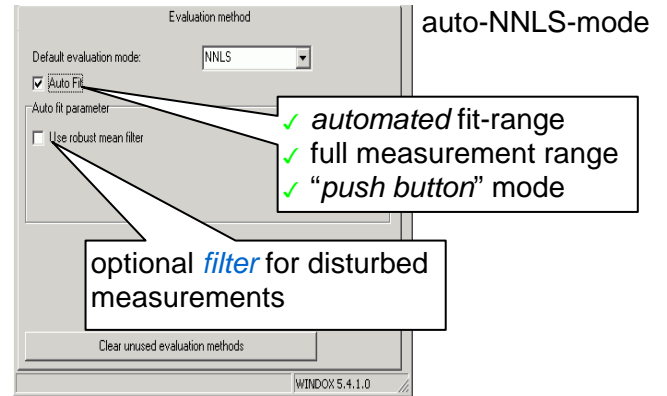


Figure 10. auto-NNLS evaluation

Precise recording and evaluation of the progression of the cross correlation function during the measurement and the application of robust statistics result in reliable particle size distributions. The new quality of results is a consequence of the direct calculation of the Q_3 distribution and hence no need for primary calculation of an intensity distribution (Q_{int} distribution) as is common for the 2nd Cumulant PCS method and the secondary conversion into a Q_3 distribution, which inevitably leads to unrealistic Q_3 results and cannot be compared to other methods such as TEM and Ultracentrifuge.

auto-NNLS is the missing link to availability of an operator independent push-button-instrument maintaining the ambition to use appropriate raw signals only and evaluate according to scientifically sound and correct methods without any assumptions regarding the final results.

auto-NNLS also features an optional filter that can be applied whenever the measurement is disturbed by extraordinary peaks. The filter does only affect the data evaluation and not the measured and data-base stored raw data. Thus the filter can be applied even after a measurement has been made and evaluated and results from different evaluation modes can be compared and be subject to further investigations, e.g. to other particle size measurement methods.

Depending on the dispersing liquid the instrument can be used with glas cuvettes or disposable plastic cuvettes. The position of the cuvette can be adjusted and the laser lamp

dimmed to gain optimal signal intensities. All these adjustments are done either via software control or even fixed in application procedures (SOPs).

All raw data as well as evaluated data are stored in a powerful database. The data handling is prepared to work compliant to CFR21part11.

Stability measurement in addition

With PCCS a never reached quality in particle size analysis of suspended nano-particles has become available with NANOPHOX.

To make this instrument even more valuable there is a side effect that enables stability measurement of emulsions and suspensions in a much more reliable way than zeta-potential can do.

As in NANOPHOX it is possible to extract the single scattered information only, the amplitude of this scattered light intensity is available for further evaluation.

In the “Rayleigh”-area the context between particle size and scattered light intensity describes that a growth of size by times 10 results in an intensity increase by 10^6 . This means that even slightest changes in size during a sequence of measurements will directly lead to remarkable changes in the amplitude of the scattered light intensity.

Aside of a precise particle size measurement also a stability test is performed with every series of measurements.

On the other hand all influences to a suspension that influence coagulation, dispersion or aggregation are open for quantification via the change in particle size measured with NANOPHOX realising the new PCCS-technology in the most compact and reliable way.

This capability of stability analysis even for non ionic samples has been scientifically confirmed by publications of the University of Dresden.

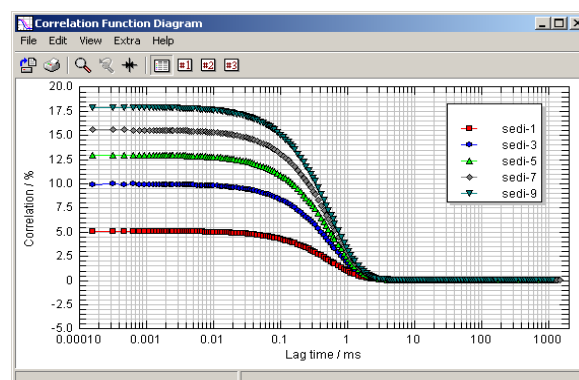


Figure 11. Amplitude changed by instability

Future perspectives

Already today it seems to be magic what detail information from the nano-range can be achieved by using PCCS. The securely extracted single scattered information is the backbone to multiple evaluations. Those used today, 2nd Cumulant and NNLS, have been taken over from earlier PCS technology but with the new quality of raw data even more accurate methods could be applied. To increase the statistical reliability it is possible now to do averaging based on single results as well as synthesising results from averaged raw data of multiple measurements.

The ability to focus on certain areas of the correlation function by restricting the evaluation range can reveal detail information that up to now could only be estimated from much more complicated and expensive research.

Using NANOPHOX with its singular accuracy will be enable to unfold any users magic power to draw back the curtain of the former nebulous but highly important and interesting nano-cosmos.

Literature

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Hands on

NANOPHOX will be shown & demonstrated at:

- Permanently in the **NANO- truck**, an initiative of
- Sympatec's PITTCON-booth
- Sympatec's ANALYTICA-booth
- Sympatec's POWTECH-booth



and many more, visible on Sympatec's homepage: www.sympatec.com