

Nanometre particle sizing and stability measurement using a table-top PCCS system

by W. Lämmle

The characteristics of many modern materials are often determined by the properties of nano-particles. This fact is responsible for the fast-growing demand for analysis and control of particle size. The most widely-used technique for this is photon correlation spectroscopy (PCS), which has been in use for almost 30 years now. Despite its popularity, PCS however suffers from the disadvantage that it can only be applied to highly diluted samples. A recent development, known as photon cross-correlation spectroscopy or PCCS, has dramatically extended the power of the original technique and enables reliable measurements even in high concentration suspensions. This article describes the theory and applications of PCCS and also the practical embodiment of the technique, namely the new NANOPHOX instrument from the Sympatec company.

The physical principle

Photon correlation spectroscopy (PCS) measures and analyses the fluctuation of the intensity of light scattered from

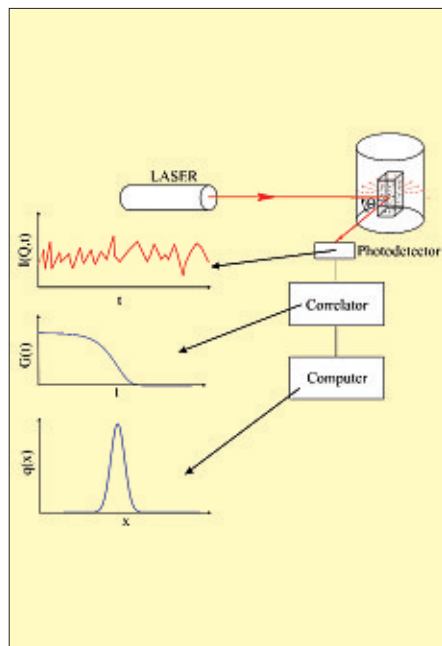


Figure 2. Schematic diagram of the main components of classical PCS.

nano-particles in suspension. This fluctuation is itself a result of the "Brownian motion" that keeps the particles in steady movement. The molecules of a supporting liquid move randomly at a defined speed that is determined by temperature and viscosity. Whenever such molecules collide with a particle suspended in the liquid an elastic impact is produced, which moves the suspended particle. The speed at which the particle moves depends on the size of the particle. Small particles will move quickly whereas coarser particles will move at a much slower rate since, because of their greater volume, such bigger particles have a statistically-increased chance of being impacted from different directions by more than one molecule at the same time.

This diffusion effect can be described by the well-known "Stokes-Einstein" equation:

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

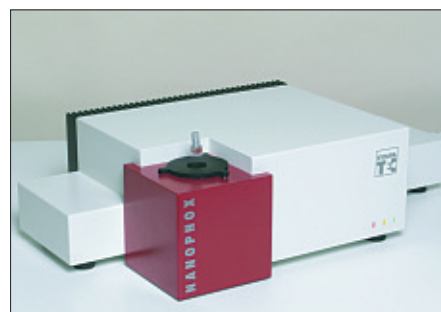


Figure 1. Developed and produced by Sympatec, the NANOPHOX table-top instrument is the first to incorporate PCCS technology.

where:

D is the diffusion constant,
 k_B is Boltzmann's constant,
 T is the absolute temperature,
 η is dynamic viscosity of the liquid,
 x is the particle diameter.

Since the change in the intensity of light scattered by the particle depends on its

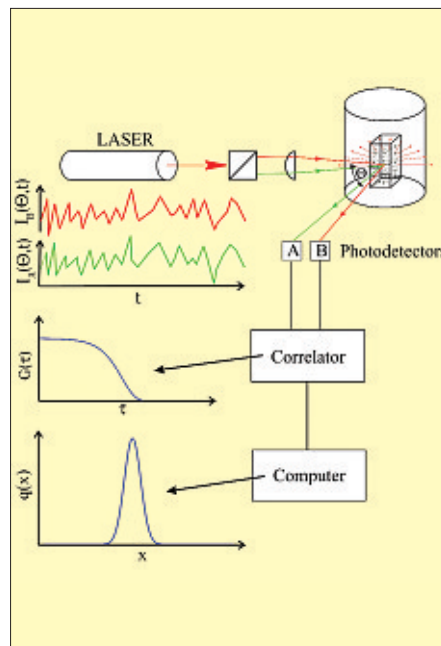


Figure 3. Diagram of the main components of the new PCCS system.

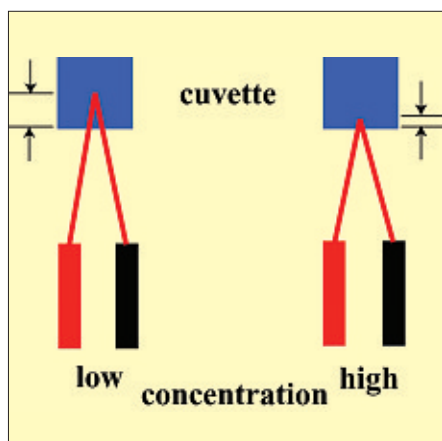


Figure 4. Back scattering.

diffusion, it can be seen that the frequency of fluctuation of the scattered light in turn depends directly on the particle size. This simple description of the light-scattering process presupposes that the scattered light reaches the detector without any further interference by other particles. Such multiple scattering can only be avoided by carrying out the analysis at the highest possible dilution where, unfortunately, signal strength is likely to be very weak and there will be a low signal-to-noise ratio.

Over the years, many approaches have been attempted to overcome this multiple scattering weakness of PCS. One early approach involved the use of experimental set-ups in which the scattering was measured at multiple angles. This did allow more sophisticated and powerful modes of data evaluation (see

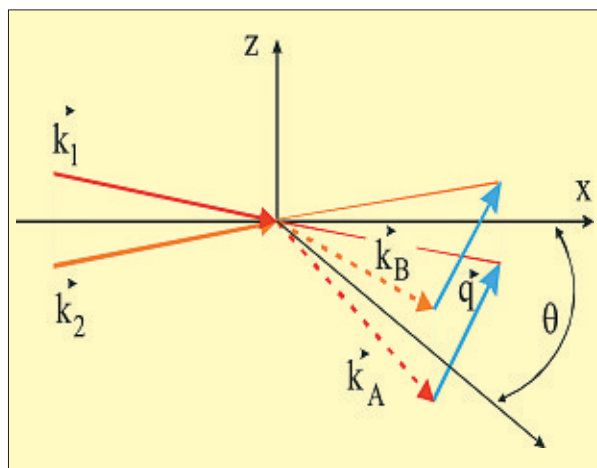


Figure 5. Diagram of the theory behind PCCS.

below) but did not *per se* avoid the multiple scattering problem.

More recently, experimental set-ups have become available that are based on the measurement of back-scattering. The rationale for the back-scattering is that multiple scattering may be reduced by allowing the laser beam only to illuminate a thin surface layer of the sample [Figure 4]. This approach has been implemented in several instruments currently on the market.

As indicated earlier, the theory of PCS is based on the "Brownian motion" that is caused by elastic impacts between molecules in the supporting liquid and particles suspended in it. In back-scattering experiments analysing solutions of high concentrations, the penetration of the incident light is limited to areas very close to the cuvette wall. Under such conditions, however, the theoretical basis underpinning the approach is no longer valid since the so-called wall effects are not elastic.

In addition, even under such conditions, the problem of multiple scattering is only reduced and cannot be eliminated completely. Furthermore, even if the effect of multiple scattering is reduced, the intensity of the scattered light signal is also correspondingly reduced.

The practical effect of increasing multiple scattering with increasing light penetration into the solution results in a particle with a real size of 104 nm being portrayed as having

an apparent dimension of only some 20 nm. Several attempts have been made to compensate for this intrinsic weakness of the back-scattering approach by adding further features to the experimental set-up. For example, modern instruments can also measure zeta-potential and carry out determination of molecular weight. While such additions may provide additional ancillary information, they however still do not

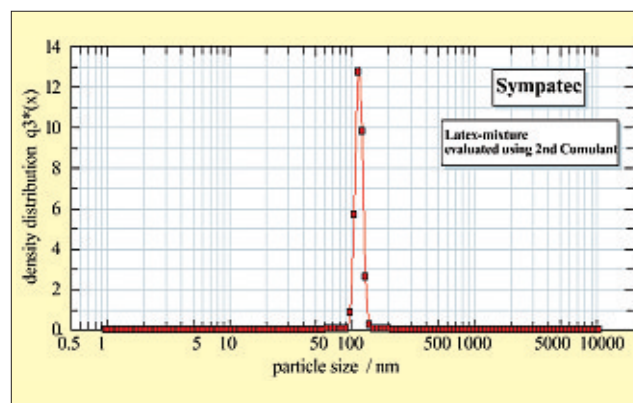


Figure 6. Data generated in standard latex preparations by the second cumulant evaluation algorithm.

solve the fundamental problem nor increase the basic accuracy and reliability of the measurement.

Photon cross correlation spectroscopy.

R&D teams in the German universities of Kiel, Mainz, and Bremen and in the ETH institute in Zurich, Switzerland have developed a new approach known as Photon Cross Correlation Spectroscopy (PCCS) [for references see Further Reading section]. The experimental layout of the PCCS system is illustrated schematically in Figure 3 while Figure 5 illustrates the underlying theory.

As can be seen from Figures 3 and 5 the PCCS system measures two separate scattered light signals. These signals are in theory identical to that of a single scattered light beam but in practice differ from each other due to different noise levels and to the differences in the extent of the multiple-scattering that

affects each beam as it traverses the sample. Key to the success of the approach is that the scattering vectors [q in Figure 5] should be identical as should the scattering volumes. Under these conditions, cross correlation of the two signals is thus able to act as a filter that can cancel out the artefactual effects and enables extraction and quantification of a single scattered light only. For the first time in particle sizing this approach guarantees that at no matter what concentration, the influence of noise and multiple scattering can be completely and reliably eliminated.

Sympatec owns exclusive rights on several patents on the PCCS approach and has been responsible for the practical development of a robust table-top instrument, the NANOPHOX [Figure 1]. The PCCS principles have been incorporated into the company's well-established and user-friendly WINDOX software, familiar to laser diffraction particle sizers for many years. The software includes a second cumulant evaluation mode, as defined in ISO 13321, which generates data on mean diameter and width values [Figure 6]. The software also includes a NNLS routine (Non-Negative-Least-Squares), that provides a full size distribution resolving multiple modes as long as the ratio of their diameters is above 1:4 [Figure 7].

Depending on the nature of the dispersing liquid the instrument can be used with either glass 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 can be carried out entirely by software control or can be fixed at a pre-selected position as defined in application procedures (SOPs). All raw data as well as evaluated data are stored in a powerful database. Data processing complies with the US CFR 21part11 regulations.

Stability measurement in addition

Using the PCCS-based NANOPHOX instrument the quality and reliability of particle size analyses of suspended nano-particles has reached new heights. In addition, the practical value of the system is even further enhanced by an ancillary feature that enables the meas-

urement of the stability of emulsions and suspensions to be carried out in a much more reliable way than can be achieved with traditional zeta-potential measurements. This feature is a result of the fact that the NANOPHOX system enables the extraction and quantification of an equivalent single scattered signal only. The amplitude of this scattered light intensity is thus available for
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better particles

Particle Size Analysis
off- & in-line
1nm - 10000 μm

HELOS & RODOS
Laser Diffraction
(0.1 - 10000 μm)

QICPIC
Image Analysis
(1 - 10000 μm)

NANOPHOX
Dynamic Light Scattering
(1 - 10000 nm)

SYMPA T-TEC System-Partikel-Technik

Sympatec GmbH
System-Partikel-Technik
Am Pulverhaus 1
D-38678 Clausthal-Zellerfeld
Germany
Phone +49-53 23-717-0
Fax +49-53 23-717-229
eMail sales@sympatec.com
www.sympatec.com

See us at Pittcon
booth Nr.3736

Enter 50752 at www.labplusinternational.com

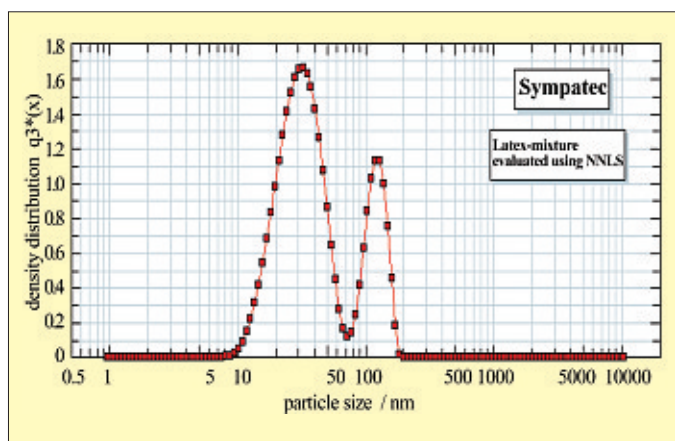


Figure 7. Particle size distribution of a mixture of standard latex preparations measured using NNLS.

further evaluation. Valuable information on the emulsion stability can be generated since the amplitude of the equivalent single scattered signal is directly dependent on the stability.

According to the principles defining Rayleigh-type scattering an increase by a factor of 10 in the size of the scattering particle results in a greater than 1000000-fold increase in the intensity of the scattered signal. This means that even the slightest change in particle size during a measurement sequence will produce remarkable changes in the amplitude of the scattered light intensity. Thus, in addition to precise particle size measurement the system also carries out a stability test with every series of measurements [Figure 8]. In this way, all factors that influence coagulation, dispersion or aggregation of a suspension can easily be quantified via the change in particle size that is measured on the NANOPHOX instrument using the new PCCS-technology in the most compact and reliable way.

Future perspectives

The detailed information on nano-range suspensions that

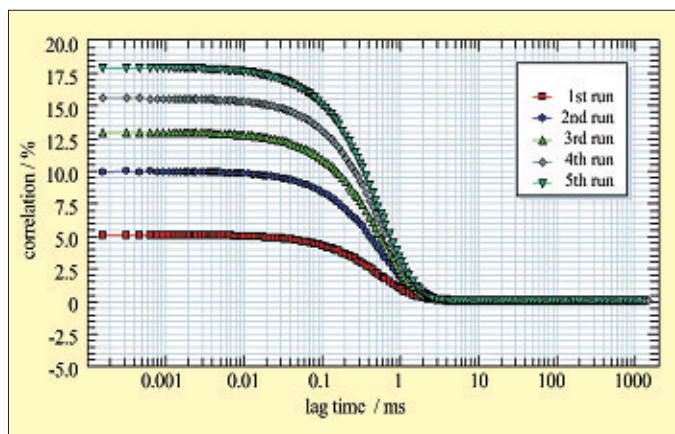


Figure 8. Signal amplitude as a function of instability.

can be obtained through PCCS is astonishing. Central to the approach is the reliability of the extracted equivalent single scattered information. This in turn enables reliable further evaluations of different sorts to be carried out. Examples of data evaluation methods that are currently available, are widely appreciated and are currently superseding earlier PCS technology are the powerful second Cumulant and NNLS analytical methods.

With the new high quality of the raw data, even more powerful and accurate methods could be applied. To increase statistical reliability it is possible now to carry out averaging on single results as well as collating 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 also reveal detailed information that up to now could only be estimated from much more complicated and expensive research.

The astounding accuracy of the NANOPHOX system will enable the previously nebulous but highly important and relevant nanoworld to be unveiled for practical and easy evaluation.

Further reading

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The author

Dipl. Chem. Wolfgang Lämmle
 Sympatec GmbH
 System Partikel Technik
 Am Pulverhaus 1
 D-38678 Clausthal-Zellerfeld
 Germany

Demonstrations of the NANOPHOX in action will be given at the upcoming Pittcon conference on Sympatec's booth 3736

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