Nanometre particle sizing and stability measurement with table top PCCS

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Properties of advanced materials very often are related to nano-particles. A continuously growing demand for control of particle size in the nano metre range is resulting in innovative new instruments. The most popular technique to date based on the Dynamic Light Scattering (DLS) principle is photon correlation spectroscopy (PCS). PCS has been accepted for the last 30 years, but its application is limited to highly diluted samples. The new instrument from Sympatec, called NANOPHOX overcomes this drawback as it measures reliably even in suspensions of high concentration using an advanced PCCS principle.

The physical principle

Photon correlation spectroscopy (PCS) evaluates the intensity fluctuation of scattered light reflected from nano-particles in suspension. This fluctuation is a result of the "Brownian motion", which keeps the particles in steady movement.
Based on temperature and viscosity, liquid molecules are moving at a defined speed. Whenever they run into a particle suspended in the liquid an elastic pulse results.

This impact accelerates the particle in accordance to its size. Small particles react with a rather fast movement while coarser particles, because of their bigger volume, move much slower as they also may be impacted by more than one molecule from different directions at the same time. The frequency of fluctuation in the scattered light intensity thereby corresponds directly with the particle size.

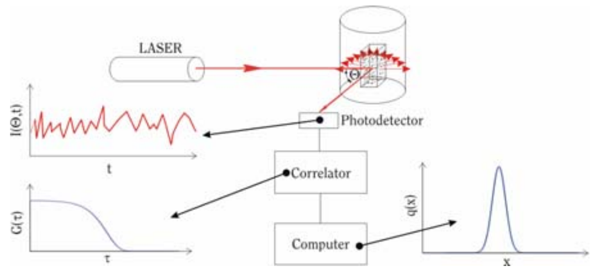

Figure 1: Conventional PCS, principle set-up

This simple context presupposes that the scattered light reaches the detector without further influence from other particles.
Conditions to avoid such multiple scattering can only be achieved via extreme dilution. But such extremely low concentrations of particles in suspension at the same time generate very low scattering signals and consequently poor signal-to-noise ratios.

Many efforts have been undertaken to overcome the multiple scattering disadvantage of the PCS technique. An initial approach to achieving better resolution in higher concentrations led to multi-angle set-ups. These allow for a more sophisticated evaluation modes, but cannot help to overcome the influence of multiple scattering.

Some years ago back-scatter set-ups became available. With this technology the multiple scattering in higher concentrations is reduced by having the illuminating laser beam crossing with the back-scatter detector beam in a thin surface layer of the sample:

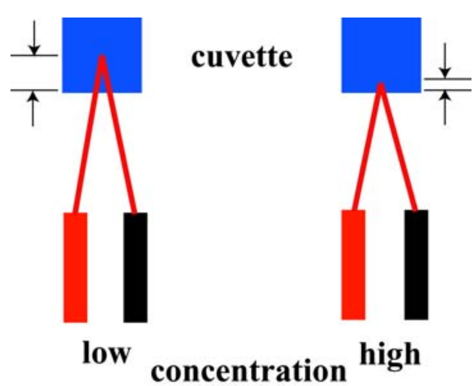

Figure 2: Back scatter set-up

Bringing the depth of laser intrusion in high concentrations close to the wall of the cuvette negatively affects the principle, as wall influences are non-elastic.

Furthermore the influence of multiple scattering is only reduced, not avoided, and in conjunction with its reduction the scattered light signal is reduced. The influence of multiple scattering, respectively the depth of invasion, results in a 104 nm particle to be measured as only 20 nm.

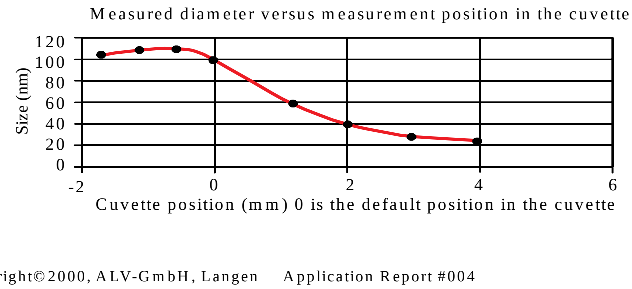

Figure 3: Uncertainty caused by cell position

It seems that some instrument makers try to mask this principle source of error related to their instrument's design when expanding basic function of size analysis, with additional functions such as:

- zeta-potential measurement
- molecular weight determination

The determination of these additional characteristics may be interesting to have, but certainly does not improve the accuracy and reliability of PCS.

PCCS with NANOPHOX

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

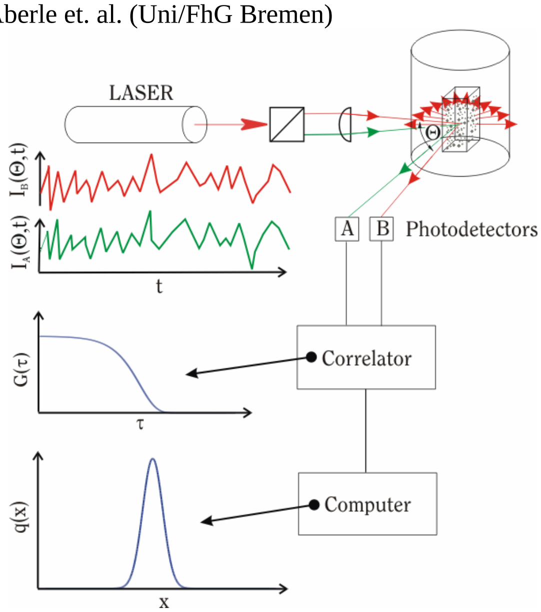

Figure 4: Innovative PCCS set-up

The challenge of such a set-up is that the scattering vectors q have to be identical, as well as the scattering volume.

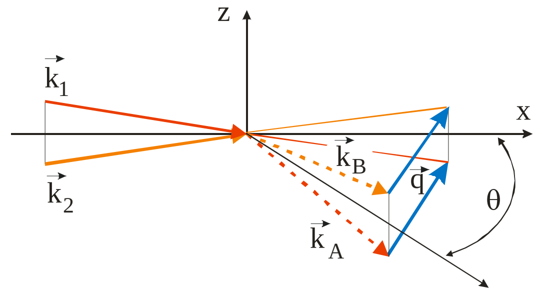

Figure 5: Set-up of measuring volume

This set-up collects two scattering outputs, identical with respect to the single scattered light but different in noise as well as in multiple-scattered information along their different pathways through the sample cell.

A cross correlation evaluation on the two intensities acts as a filter and extracts only the single scattered light. Cross correlation for the first time guarantees that even for high concentrations, as can be found in turbid suspensions and emulsions, the influence of noise and multiple scattering on the particle size determination is reliably and completely eliminated.

Sympatec owns exclusive rights on several patents for this concept and developed a robust table-top instrument.
It is operated with the WINDOX software package, which has many years of user acceptance in conjunction with the Sympatec HELOS laser diffraction particle size analysers.

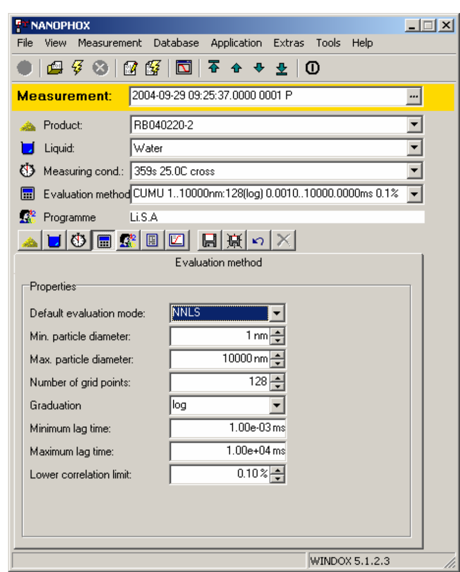

Figure 6: WINDOX User Interface

WINDOX for NANOPHOX controls the operation of the instrument and it provides two evaluation modes for the particle size distribution:

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

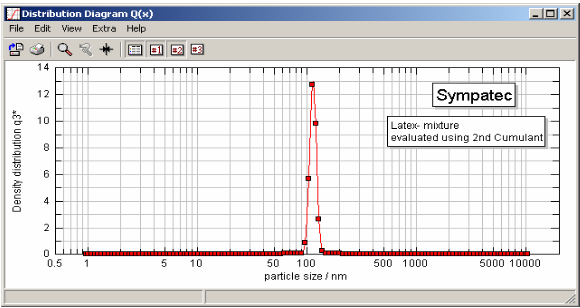

Figure 7: 2nd Cumulant evaluation

- NNLS (Non-Negative-Least-Square), provides an in-depth information on the product subject to analysis with a complete size distribution, which reliably also resolves multiple modes as long as their ratio of diameters is above 1:4

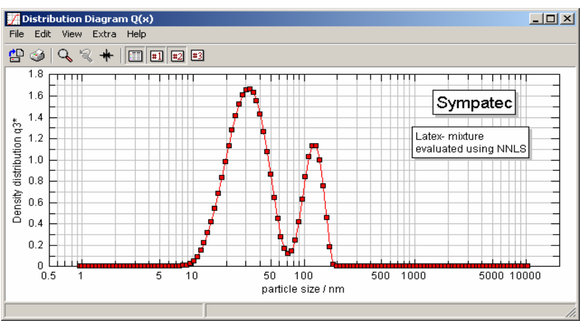

Figure 8: NNLS evaluation

Depending on the dispersing liquid the instrument can be used with compact disposable plastic cuvettes or glass cuvettes. The position of the cuvette can be adjusted and the laser lamp intensity varied to gain optimal signal intensities. All of these adjustments are obtained either via software control or with easy to set-up product specific application procedures (SOPs).
All raw data as well as evaluated reports and graphic presentations are stored in a powerful multi-user, multi-tasking data base. WINDOX completely fulfils the requirement or compliance with CFR 21part 11.

Stability measurement is also possible

With NANOPHOX, pioneering the PCCS technology, a never before achievable level of nano particle data quality is now easy to obtain. To make this instrument even more valuable it provides supplementary stability information of emulsions and suspensions in a much more reliable way than obtained from zeta-potential.

As described above, only the single scattered information is extracted from the basic signals, 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 a factor of 10 results in an intensity increase by 10^6. Thus even slightest changes in size during a sequence of measurements will lead to remarkable changes in the amplitude of the scattered light intensity.

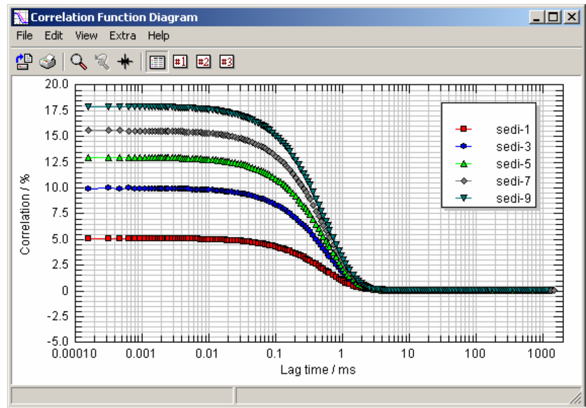

Figure 9: Amplitude changed by instability

Not only is a particle size measurement made, but also a stability test is performed with every series of measurements.
On the other hand all influences on 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.

Future perspectives

Already today the detailed information generated from the nano-metric particle size range with the PCCS principle outperforms standard PCS instruments in an unexpected way. The reliably extracted single scattered light information is the key to a number of advanced evaluation modes. The modes used today, 2nd Cumulant and NNLS, have been inherited from previous PCS technologies. However, due to the enhanced quality of raw data, more accurate methods can 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 when restricting the evaluation range can reveal details of information on the structure of particle size distributions, which up to now were only available from much more complex, time consuming and expensive research equipment.

ITRI (Industrial Technology Research Institute) of Taiwan has thoroughly evaluated NANOPHOX and has been awarded a Certificate from the Taiwanese government, appointing NANOPHOX as the “Standard Instrument for Nanometric Particle Size Analysis”.

Technical data

Measuring range:	1 nm – 10.000 nm
Principle:	Dynamic light scattering
Scattering angle:	90°
Evaluation:	Cross-correlation
Measuring volume:	ca. 0.3 ml
Sample container:	Cuvette 10 x 10 mm^2
Cuvette position:	automatic or manual
Light source:	HeNe-Laser, Intensity software adjustable, 10 mW max.
wavelength:	632.8 nm
Laser class of light source:	3B
Laser class of instrument:	1
Optics:	no adjustment necessary
Temperature range:	15 – 40° C , typ. 22 – 25°C recommended, software adjustable
Temperature stability:	0.05°C (≅ 0.1 % accuracy in particle size calculation)
Accuracy in temperature adjustment:	0.1°C ≅ 0.2 % with respect to accuracy in particle size

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