# MEASUREMENT OF GOLD, SILVER & PLATINUM NANOPARTICLES PRODUCED BY A LASER-BASED SYNTHESIS METHOD

## Context

Colloidal dispersions of Gold, Silver and Platinum nanoparticles can be used in a variety of different applications. For example, platinum nanoparticles can be used very effectively as catalysts. Due to their high specific surface, nanoparticles act far more efficiently than the bulk material. Silver nanoparticles can be used as an antibacterial agent in different ways. Colloidal gold is very often used as a diagnostic marker in medical applications or in drug delivery systems. All of these nanoparticles can be produced very easily with the fully automated Nanoparticle Synthesis Machine from the AutoProNANO project, a development initiative at the University of Duisburg-Essen.

## Dynamic Light Scattering

Microtrac NANOTRAC FLEX is a highly versatile Dynamic Light Scattering (DLS) analyser that provides information on particle size, concentration, and molecular weight. The innovative design of the NANOTRAC FLEX allows faster measurements with reliable technology, higher precision, and better accuracy. With the unique probe design, nearly any vessel can be converted into a measurement cell (*Figure 1*). The instrument can handle monomodal and multimodal samples over a wide concentration range, all without prior knowledge of the particle size distribution.

***Fig.1**: The dip-in probe of the NANOTRAC FLEX allows direct measurements in vessel: beaker, bottle, Eppendorf tube, or even a single drop of liquid.*

## 180° Dynamic Light Scattering

Nanoparticles suspended in a liquid dispersion are subject to Brownian motion, which is a result of random collisions of molecules in the liquid medium. The particles' velocity distribution, averaged over time, approaches a known functional form – their size distribution. Dynamic Light Scattering (DLS) is the technology used to calculate that size distribution, based on the particles' measured velocity distribution.

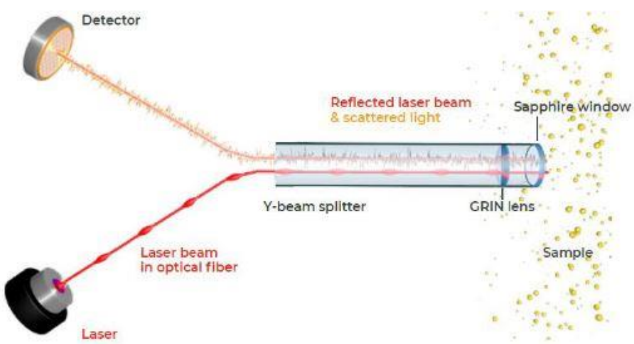



***Fig.2**: Probe design used in Microtrac DLS analysers*

The optical bench of the NANOTRAC FLEX is a probe containing an optical fibre coupler with a Y splitter (Figure 2). Laser light is focused on a volume of sample close to the interface of the probe window and the dispersion. The high reflectivity sapphire window reflects a portion of the laser beam back to a photodiode detector. The laser light also penetrates the dispersion and the 180° backscattered light from the particles reaches the same detector. The scattered light from the sample has a low optical signal relative to the reflected laser beam. The reflected laser beam mixes with the scattered light from the sample, adding the high amplitude of the laser beam to the low amplitude of the raw scatter signal. This heterodyne Laser Amplified Detection method provides up to 106 times the signal to noise ratio of other DLS methods like Photon Correlation Spectroscopy (PCS) and Nanoparticle Tracking Analysis (NTA), Figure 3.

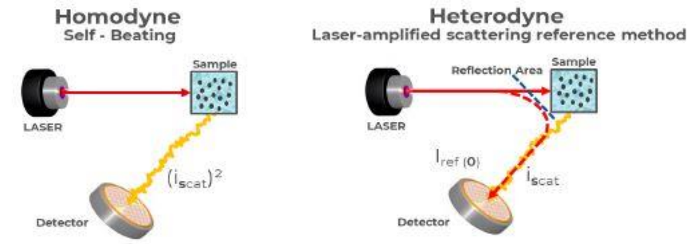



***Fig.3**: Homodyne and heterodyne approach in DLS. The heterodyne setup used provides significantly better signal to noise ratio.*

A Fast Fourier Transform (FFT) of the laser amplified detection signal results in a linear frequency power spectrum which is then transformed to a logarithmic scale and deconvoluted to give the resulting particle size distribution (Figure 4). Combined with laser amplified detection, this frequency power spectrum provides robust calculation of all types of particle size distributions – narrow, broad, mono- or multi-modal – with no need for *a priori* information for algorithm fitting as in PCS.

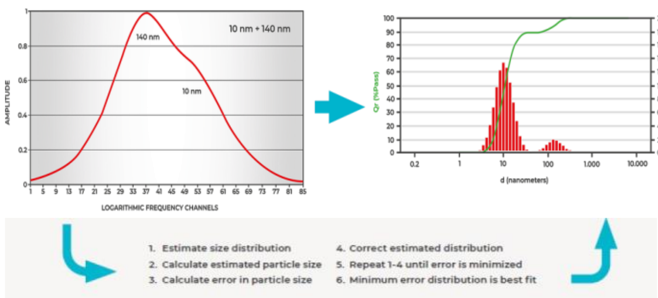



***Fig.4**: Evaluation of DLS measurement with Fast Fourier Transformation and Frequency-Power-Spectrum method*

## Analytical Disc Centrifugation

The Analytical Disc Centrifuge (ADC) is a particle size measurement tool using separation of particles by centrifugal sedimentation in a liquid medium. The sedimentation process is stabilized by a slight density gradient within the liquid. The particles move in an optically clear, rotating disc. As the particles approach the outer edge of the rotating disk, they adsorb or scatter a portion of the light beam passing through the disk. This change in light intensity is continuously measured and converted into a particle size distribution after the density gradient was calibrated with the current rotation speed.[2]

## Production of Nanoparticles

The gold, silver and platinum nanoparticles for these experiments were produced using the compact synthesis machine from AutoProNANO, a development project at the University of Duisburg-Essen (Figure 5). This synthesis method allows various combinations of nanoparticle material and dispersion media. Nanoparticles are produced by laser ablation of a solid metal target, mounted in the target capsule. Chemically produced colloidal nanoparticles usually contain high amounts of ligands, surfactants, and educt residues. This synthesis method guarantees the highest possible nanomaterial purity. The system checks if enough resources are available for the planned synthesis, monitors the process and records a log file of the entire process.[1]

***Fig.5**: Nanoparticle Synthesis Automate, design by Projekter Industrial Design (Duisburg)*

## Samples

Overall, four different samples were produced and were analysed by Dynamic Light Scattering (DLS). Also, three of the samples were analysed by Analytical Disc Centrifugation (ADC).

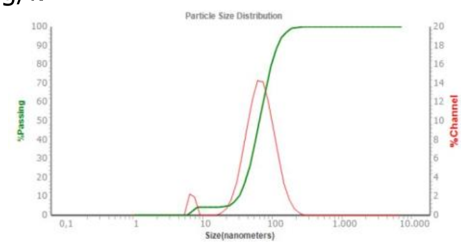
All information about the samples is shown in the following table:

| Sample | concentration | surfactants | DLS | ADC | Sample picture |
|---|---|---|---|---|---|
| Gold (Au) | 200 mg/L | 0,6 mM Sodium Phosphate Buffer | √ | √ |  |
| Silver (Ag) | 120 mg/L | 0,5 mM Trisodium Citrate | √ | √ |  |
| Platinum (Pt) | 150 mg/L | 0,5 mM Sodium Hydroxide | √ | √ |  |

## Results

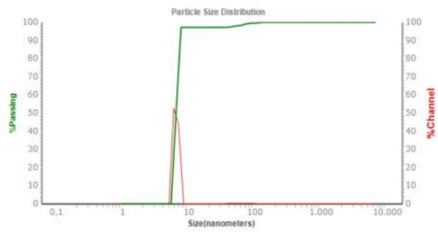
The following graphs show the analyses of the different samples in intensity and volume weighted particle size distribution. Also shown is a comparison of the results of DLS in volume distribution and ADC. Volume and intensity distribution are shown because in intensity distributions the few agglomerated particles have a much higher scattering intensity which is not taken into account in a volume distribution. The volume distribution is needed to compare the results with the ADC data. ADC cannot show intensity distributions.

Figure shows the different results for gold nanoparticles produced with a concentration of 200 mg/l.




Mode Summary

| Dia(nm) | Pct | Width | C(I) | C(V):cc/ml |
|---|---|---|---|---|
| 6,25 | 4,24 | 3,59E-01 | 1,98E-02 | 2,22E-05 |
| 59,35 | 95,76 | 3,18E+01 | 4,47E-01 | 7,6E-07 |




Mode Summary

| Dia(nm) | Pct | Width | C(I) | C(V):cc/ml |
|---|---|---|---|---|
| 6,25 | 96,93 | 3,59E-01 | 1,98E-02 | 2,22E-05 |
| 59,35 | 3,07 | 3,18E+01 | 4,47E-01 | 7,6E-07 |

***Fig.6**: Particle size distribution of 200 mg/l gold nanoparticles based on intensity (top) and volume (bottom). Also shown is the volume concentration of the particles in cm2/ml.*

Figure 7 shows the comparison of the volume weighted size distribution measured with DLS and ADC.

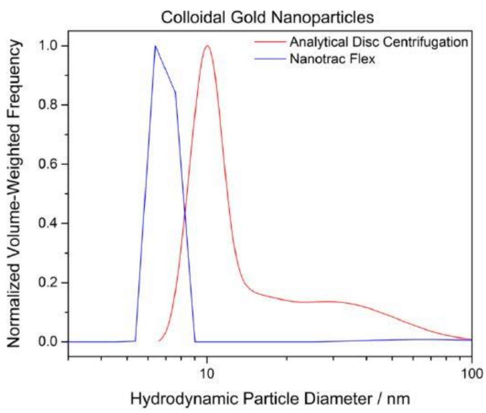
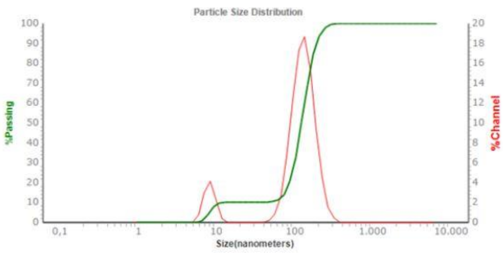


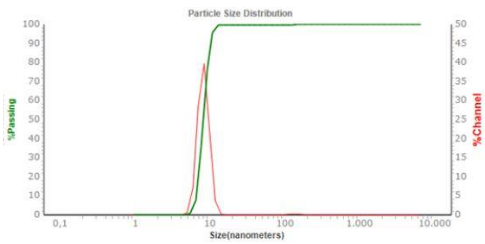

***Fig.7**: Comparison of DLS and ADC for 200 mg/l gold nanoparticles*

The measured particles sizes are in good agreement, considering the fact that these two techniques are fundamentally different.

Figure shows the particle size distribution of silver nanoparticles with a silver concentration of 120 mg/l. This sample was also produced with the Nanoparticle Synthesis Automate.




| Mode Summary | | | | |
|---|---|---|---|---|
| **Dia(nm)** | **Pct** | **Width** | **C(I)** | **C(V):cc/ml** |
| **7,91** | 10,33 | 1,33E+00 | 1,45E-02 | 1,19E-05 |
| **124,8** | 89,67 | 4,43E+01 | 1,26E-01 | 8,26E-08 |




| Mode Summary | | | | |
|---|---|---|---|---|
| **Dia(nm)** | **Pct** | **Width** | **C(I)** | **C(V):cc/ml** |
| **7,91** | 99,35 | 1,33E+00 | 1,45E-02 | 1,19E-05 |
| **124,8** | 0,651 | 4,43E+01 | 1,26E-01 | 8,26E-08 |

***Fig.8**: Particle size distribution of 120 mg/l silver nanoparticles based on intensity (Top) and volume (Bottom). Also shown is the volume concentration of the particles in cm2/ml.*

Figure shows the comparison of the volume weighted size distribution measured with DLS and with ADC.

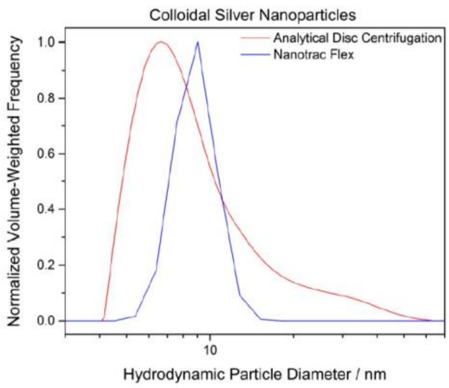
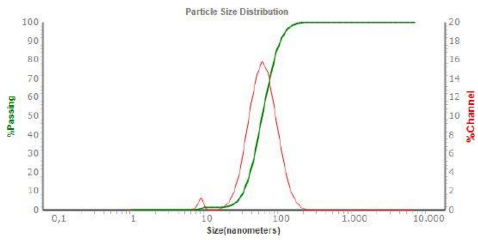


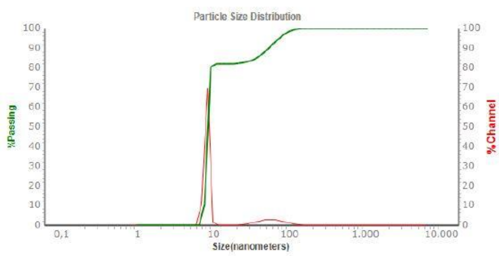

***Fig.9**: Comparison of DLS and ADC for 120 mg/l silver nanoparticles*

The results from ADC and DLS for the silver nanoparticles match very well. Slight differences between the results of both methods are expected.

Also, platinum nanoparticles were produced with a concentration of 150 mg/l. The DLS results of these particles are shown below in Figure 10 as intensity and volume-based distributions.




| Mode Summary | | | | |
|---|---|---|---|---|
| **Dia(nm)** | **Pct** | **Width** | **C(I)** | **C(V):cc/ml** |
| **7,98** | 1,591 | 4,33E-01 | 8,46E-04 | 4,58E-07 |
| **55,12** | 98,41 | 2,72E+01 | 5,23E-02 | 1,06E-07 |




| Mode Summary | | | | |
|---|---|---|---|---|
| **Dia(nm)** | **Pct** | **Width** | **C(I)** | **C(V):cc/ml** |
| **7,98** | 82,00 | 4,33E-01 | 8,46E-04 | 4,58E-07 |
| **55,12** | 18,00 | 2,72E+01 | 5,23E-02 | 1,06E-07 |

***Fig.10**: Particle size distribution of 150 mg/l platinum nanoparticles based on intensity (Top) and volume (Bottom). Also shown is the volume concentration of the particles in cm2/ml.*

Note that the amount of agglomerates at 55 nm is a bit higher than for silver and gold.
Below in Figure are shown the grahps for comperison of ADC and DLS for the Platinum sample.

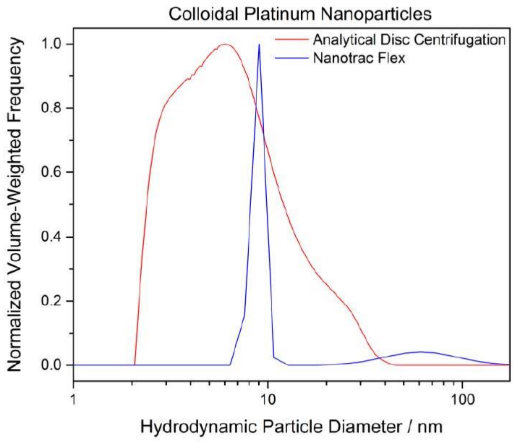



***Fig.11****: Comparison of DLS and ADC results for 150 mg/l platinum nanoparticles.*

In case of the platinum nanoparticles, the results fit not as good as for gold and silver nanoparticles. The DLS results show some more agglomerates, which were not found in the ADC measurement. Here, the ADC measurement was performed two weeks earlier than the DLS measurement and some agglomeration might have occurred in the meantime. Note that only very low amounts of an electrostatic stabilizer were used.

## Summary

Nanoparticles produced with the Nanoparticle Synthesis Automate from the AutoProNano project show mainly particle sizes below 10 nm. The results of Microtrac NANOTRAC FLEX DLS analysers can be very well compared with results from the analytical disc centrifugation. The NANOTRAC FLEX has the capability to measure nanoparticles in a very wide concentration range (up to 40 w%) and in very wide sample volume range (2 µL - ∞). In general, the best way to characterize a nanoparticle dispersion will be as close to the real concentration of sample as possible, which DLS can do.

## Acknowledgment

We thank the team of the AutoProNano project at the University of Duisburg-Essen for sample preparation and ADC measurements. The AutoProNano project is funded by the EU and the state of North Rhine-Westphalia in the START-UP transfer.NRW program.

## Literature

[1]Homepage of the project https://www.autopronano.eu/
[2]https://www.cpsinstruments.eu/centrifuge.html#topic1