APPLICATION NOTE

MICROTRAC MRB

PARTICLE CHARACTERIZATION

part of VERDER scientific

# Particle size and zeta potential measurement of ink samples with the Nanotrac series at high and low concentration

## Introduction

Microtrac Dynamic Light Scattering (DLS) instruments of the Nanotrac series are perfectly suitable for measuring the particle size of pigment suspensions used in printers. One big advantage is that measurements can be performed at high concentrations to avoid effects of dilution on dispersion.

Printing and writing have involved the use of color or black materials contained in various vehicles since the time of cavemen. The first pigment believed to be used was probably lampblack dating back as long as 4000 -5000 years. Modern printing inks contain many components each having a specific purpose in maintaining color, intensity, dispersion, viscosity, as well as acting as a milling aide.

Approximately 50% of the cost of inkjet ink is due to the coloring agent. The colorant can be of two types: pigment or dye. Dyes are very small molecules below 1 nm in size, which are usually considered to be in complete solution. Pigments are larger particles and in suspension (not solution). These may be either organic or inorganic in chemical composition. The type of black pigment used in the past was spinel, rutile, or iron. These have been substituted mostly by carbon black.

The ink is developed by mixing the components in a primary blender. Milling or grinding is performed after the gentle blending operation and includes addition of one or more components. Adding surfactants reduces surface tension to allows mixing of all the components in water. Along with dispersants, surfactants also assist in maintaining dispersion during the subsequent step of ball or roller milling. Dispersants may also to be used to lower the mechanical energy required for grinding. Polymers such as polyacrylates, polyurethanes and polyesters are used to obtain the best "blocking" characteristics of adherence to a substrate. It is necessary to be careful with balancing the relative quantities of surfactants and polymers since they may interact with each other, which would reduce their effectiveness in maintaining suspension applicability and color strength.

The purpose of all the components is to finally provide a colloidal suspension of crystals or particles which scatter light according to the characteristics of the pigment and other materials present. The resulting light scattering affects light fastness, hue, and intensity of color. Modern advances in electronics and paper coatings allowed the commercial development and availability of color printers in the early 1980s. Of these printers, probably the most popular is inkjet technology. The ink for these printers has the same general composition but small particle size and low viscosity are necessary to pass through the small nozzle of the print head. There are three types of technology used for transfer of the ink: Drop on demand, Continuous Ink Jet and Piezo Ink Jet DOD. These vary depending upon printer manufacture.

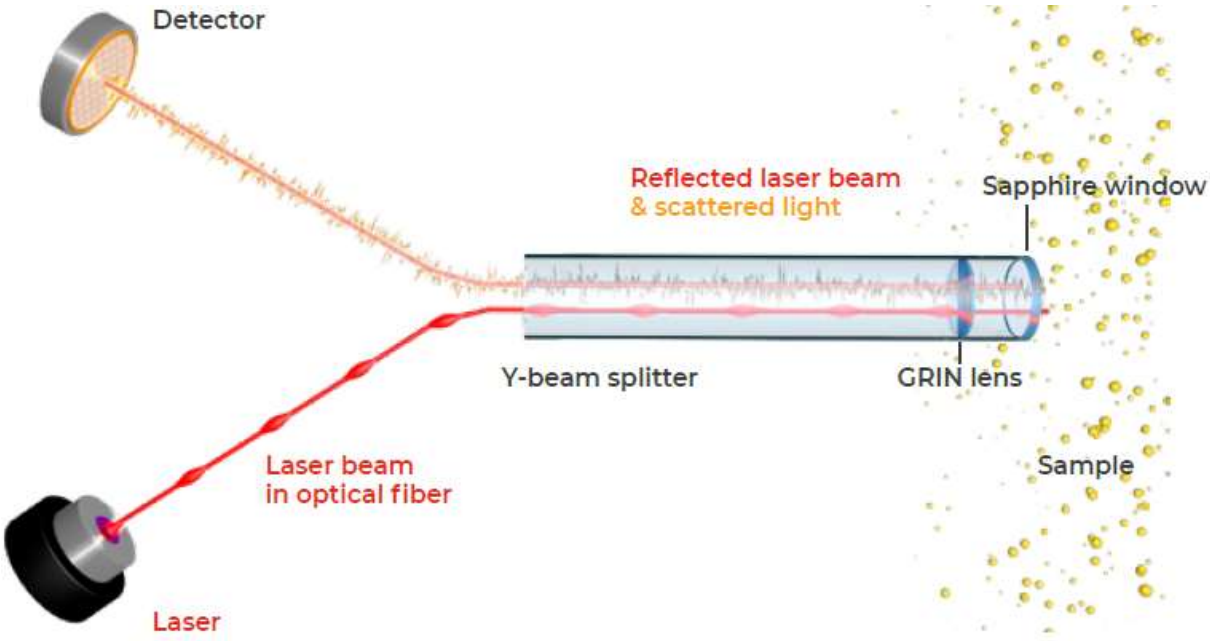
## DYNAMIC LIGHT SCATTERING

Microtrac MRB's NANOTRAC product line consists of highly flexible Dynamic Light Scattering (DLS) analyzers that provide information on particle size, zeta potential, concentration, and molecular weight. The innovative design of the NANOTRAC series allows faster measurements with reliable technology, higher precision, and better accuracy. The unique probe design allows to choose from a wide array of measurement cells to satisfy the needs of any application. It also allows measurement of samples over a wide concentration range, monomodal or multimodal samples, all without prior knowledge of the particle size distribution.

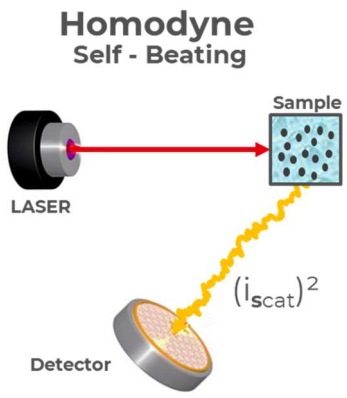


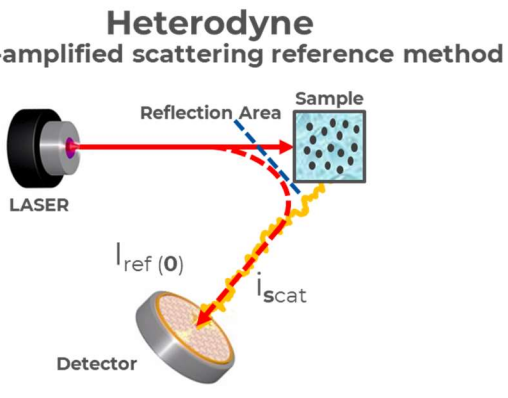
# 180° DYNAMIC LIGHT SCATTERING

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.

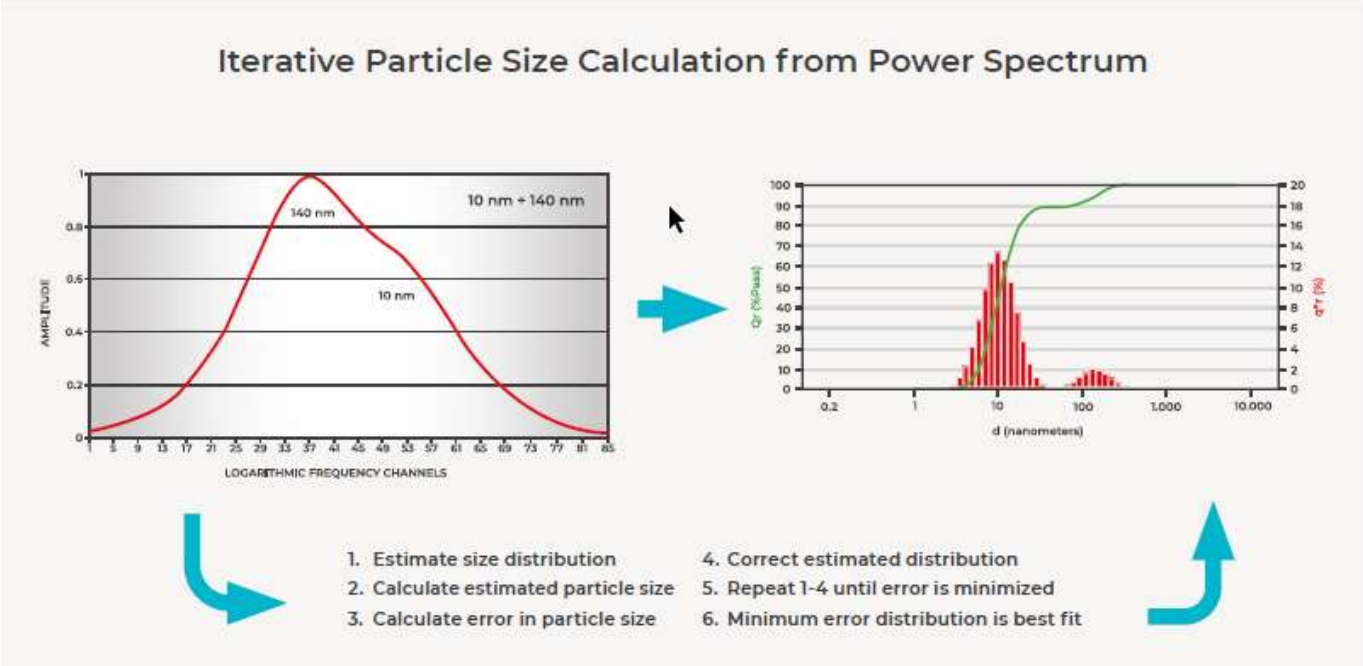



The optical bench of the Nanotrac line is a probe containing an optical fiber coupler with a Y splitter. Laser light is focused on a volume of sample close to the interface of the probe window and the dispersion. The high reflectivity sapphire window reflects a portion of the laser beam back to a photodiode detector. The laser light also penetrates the dispersion and the particles' scattered light reflects at 180 degrees back to 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 Laser Amplified Detection method provides up to $10^6$ of times the signal to noise ratio of other DLS methods like Photon Correlation Spectroscopy (PCS) and Nanoparticle Tracking Analysis (NTA).



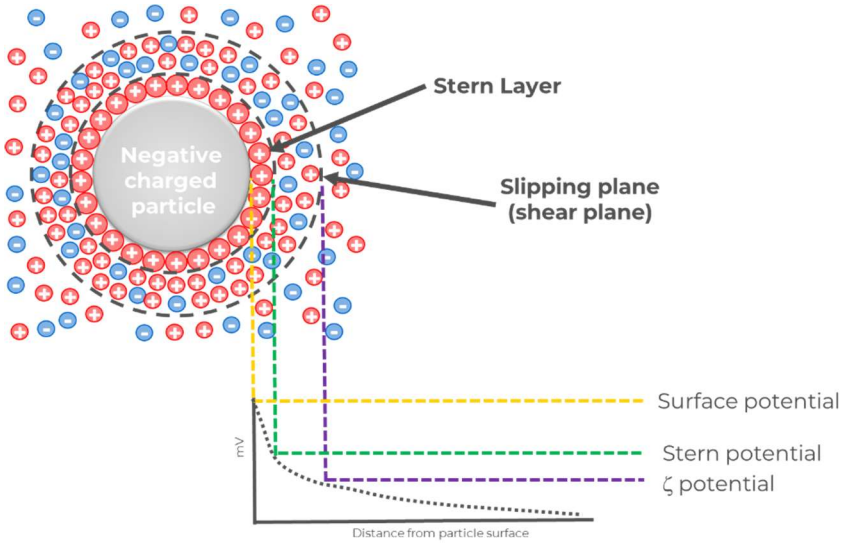



A Fast Fourier Transform (FFT) of the laser amplified detection signal results in a linear frequency power spectrum which is then transformed to a logarithmic scale and deconvoluted to give the resulting particle size distribution. Combined with laser amplified detection, this frequency power spectrum 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.

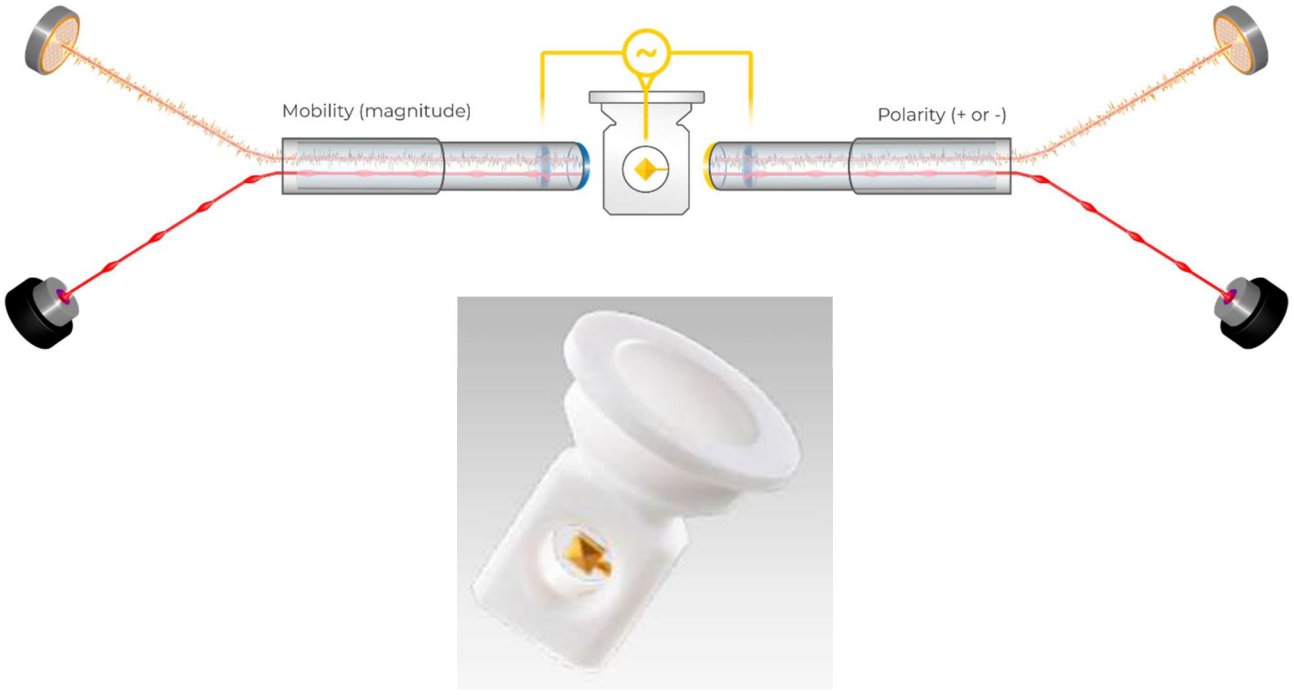



## ZETA POTENTIAL ANALYSIS

The measurement of zeta potential in the Microtrac MRB DLS analyzers takes advantage of the same Power Spectrum methodology used for measuring nanoparticle size distributions. The same stable optics to sample interface means that no adjustments are required. The backscatter and laser amplified detection signals are collected as in the sizem measurement, and the rapid sequencing of applied electric fields prevents electroosmosis.



The optical probe interface surface is coated to provide electrical contact with the sample. Two probes are used, one to determine the polarity of the particle charge at the slipping plane and one to measure the mobility of the particles in an electric field. Polarity is measured in a pulsed electric field, whereas mobility is measured in a high frequency sine wave electric field excitation. The Zeta cell has two detection probes on opposite sides to detect first polarity and then mobility.




From the linear frequency power spectrum distribution (PSD), the Loading Index (LI), which is proportional to particle concentration, can be calculated. Loading Index values provide a single number for total scattering that can be used to determine particle mobility in microns / sec / volt / cm and particle polarity as + / -, positive or negative. Analyzing mobility and zeta potential begins with measuring the PSD and determining the LI with the excitation off. Then the PSD is measured with the high frequency sine wave on, and a ratio is taken. Polarity is determined by measuring the LI before and after pulsed DC excitation. A ratio of LI after the excitation divided by LI before excitation of less than 1 is a positive polarity (concentration decreasing) and a ratio greater than one is negative (concentration increasing) for a positively charged probe surface.

$$Mobility = \frac{C * (ratio\ [PSD(on) - PSD(off)]}{LI(off)}$$

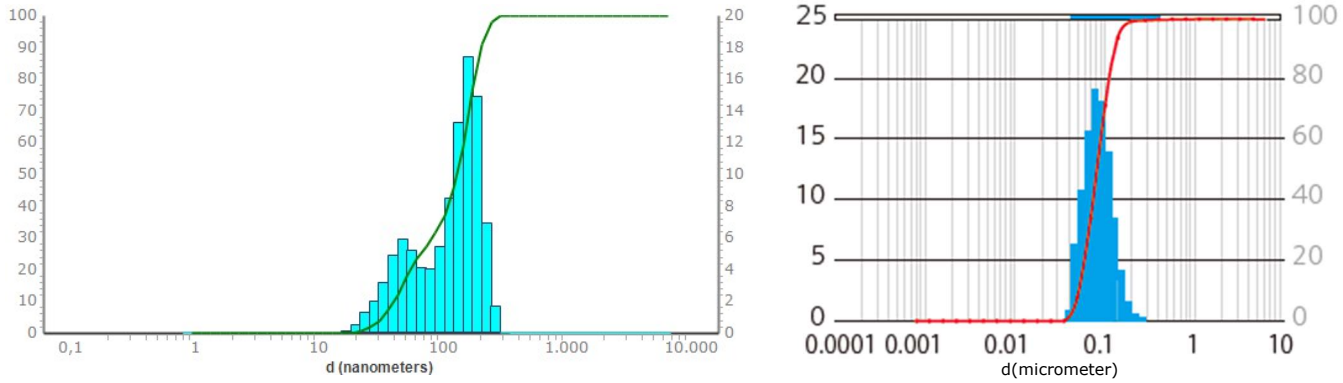
$$Zeta\ Potential\ \propto Mobility$$

# SAMPLES AND SAMPLE PREPARATION

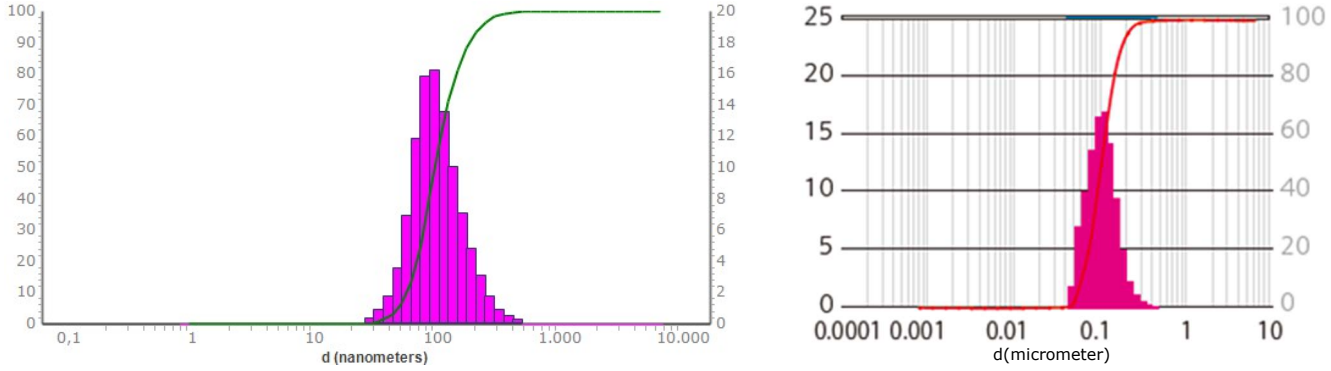
Here we will show different ink samples which were measured with the Nanotrac Flex and Nanotrac Wave II for sizing and also with Nanotrac Flex Wave II for Zeta Potential. For the sample preparation normally the ink samples will be diluted by a factor of 1:1000 in most cases only with DI water. This dilution can affect to the particle size and even more to the results of zeta potential. For the original concentrated samples for the calculation the viscosity of the original samples was used.

# RESULTS

The following graphs show the difference between original concentrated inks and inks which were diluted 1:1000 in DI water.

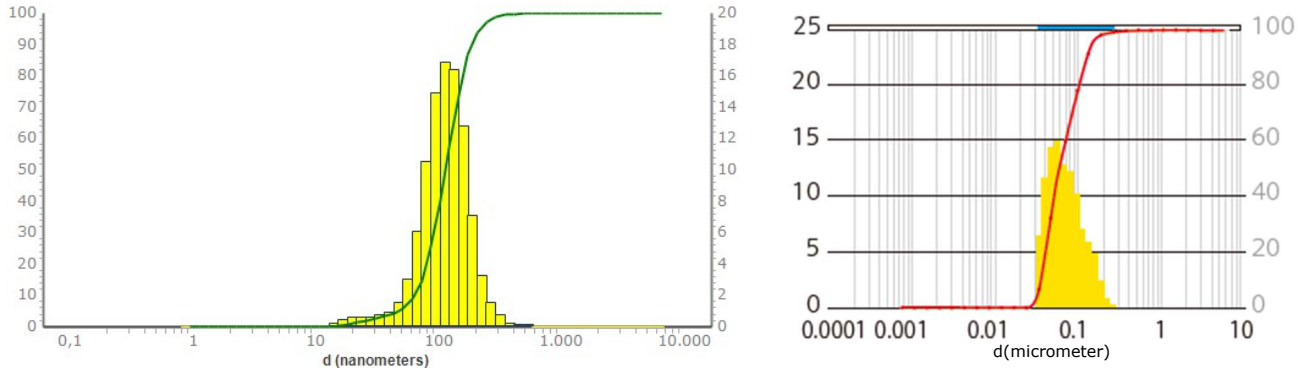



The picture shows the result of Cyan ink in original (5w%) concentration on the left side and in a dilution of 1:1000 on the right side. Here it can be seen that the original concentration is slightly bimodal. This information will be lost in the dilution.

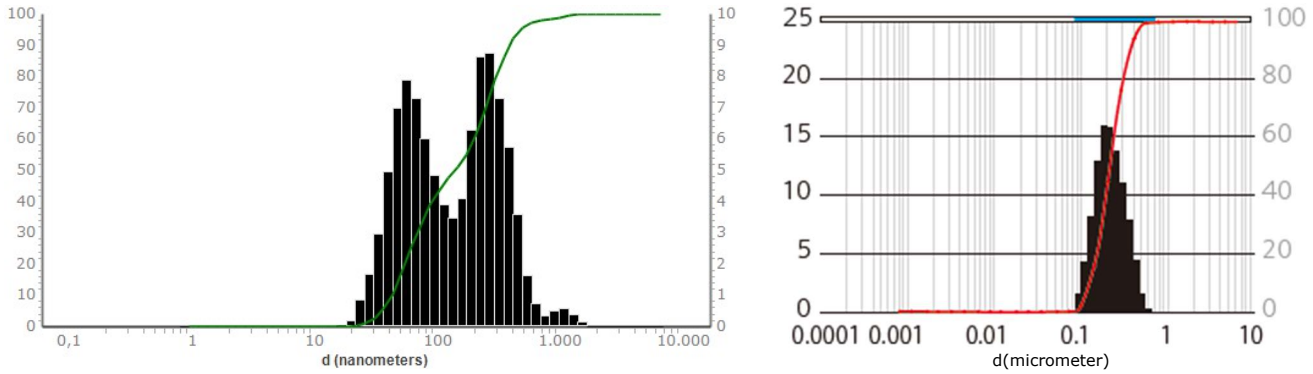



The Magenta ink results in original (5w%) concentration on the left side and in a 1:1000 dilution on the right side shows in this case the same results.

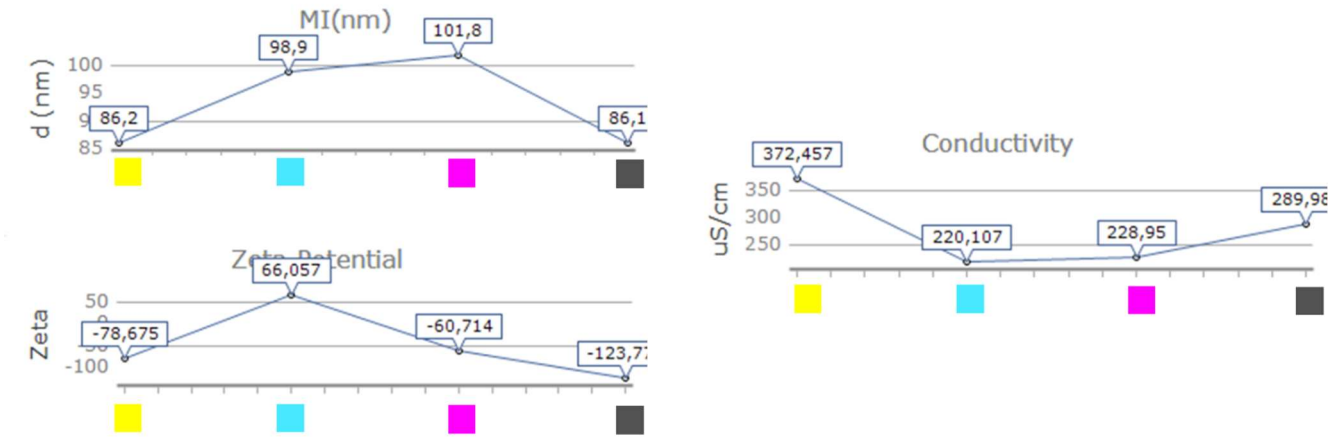
In the case of the Yellow ink the results in original (5w%) concentration on the left side and in a dilution of 1:1000 on the right side the information of the tail in the smaller size range will be lost in the dilution.




The biggest difference between the original (5w%) concentration on the left side and the dilution of 1:1000 on the right side will be seen at the black ink. The diluted shows only a mono modal peak at around 170 nm. The original one shows a bimodality and some agglomerates over 1 µm which can block the nozzles of the printer head.




Form the same sample also the zeta potential in the original concentration was measured. The results compered with the mean particle size in intensity, the zeta potential and the conductivity are shown below.

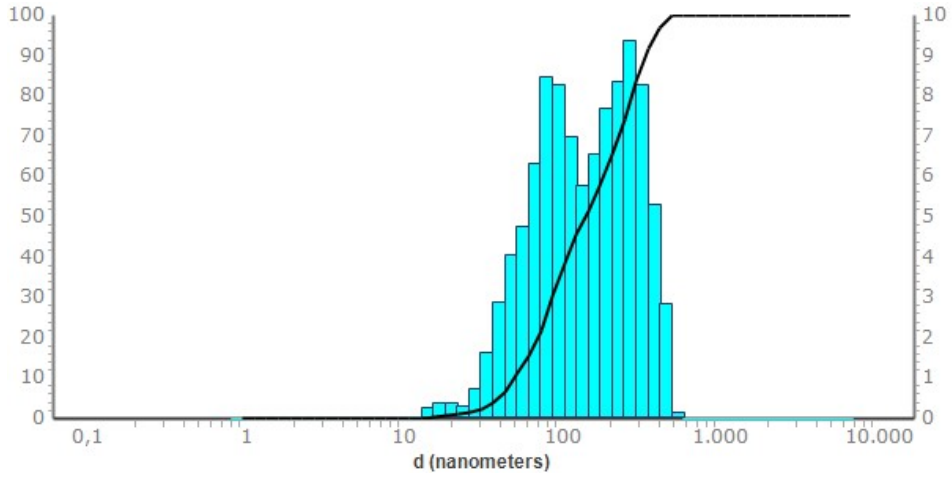



The zeta potentials for the yellow, magenta, and black inks are like expected in the negative range between -60 mV to -125 mV. The cyan ink shows a positive zeta potential with +66 mV. This positive value was unexpected because all inks should be negative charged to be fixed better on the surface of the paper. In the 1:1000 dilution the cyan ink also shows a negative zeta potential.

To get a closer look into the phenomena of switching the sign in dilution some more experiments with even higher concentration was done.

In the first step a Cyan ink with 15 w% of pigments was measured in original concentration and a dilution of 1:1000. The results are shown below.

*Original concentrated cyan ink (15 w%)*

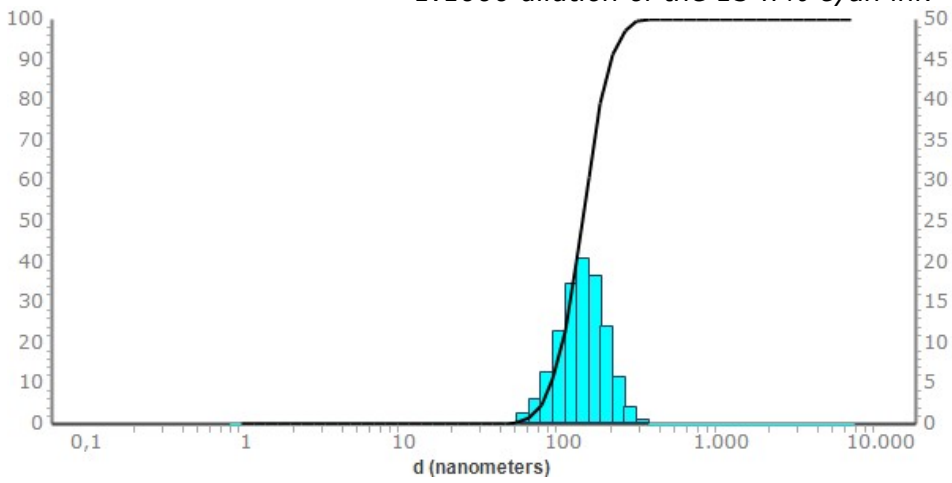



| Summary | |
|---|---|
| Data | Value |
| MI(nm): | 168,4 |
| MN(nm): | 33,40 |
| MA(nm): | 99,80 |
| CS: | 60,12 |
| SD: | 115,4 |
| PDI: | 0,458 |

| Peaks Summary | | |
|---|---|---|
| d(nm) | Vol% | Width |
| 237,3 | 54,4 | 184,2 |
| 73,8 | 45,6 | 57,3 |

| Measured Data | |
|---|---|
| Zeta Potential | 24,4 mV |
| Polarity | Positive |
| Mobility | 1,91 um/s/V/cm |
| Conductivity | 3058 uS/cm |

*1:1000 dilution of the 15 w% cyan ink*




| Summary | |
|---|---|
| Data | Value |
| MI(nm): | 137,9 |
| MN(nm): | 96,90 |
| MA(nm): | 123,0 |
| CS: | 48,77 |
| SD: | 44,70 |
| PDI: | 0,1048 |

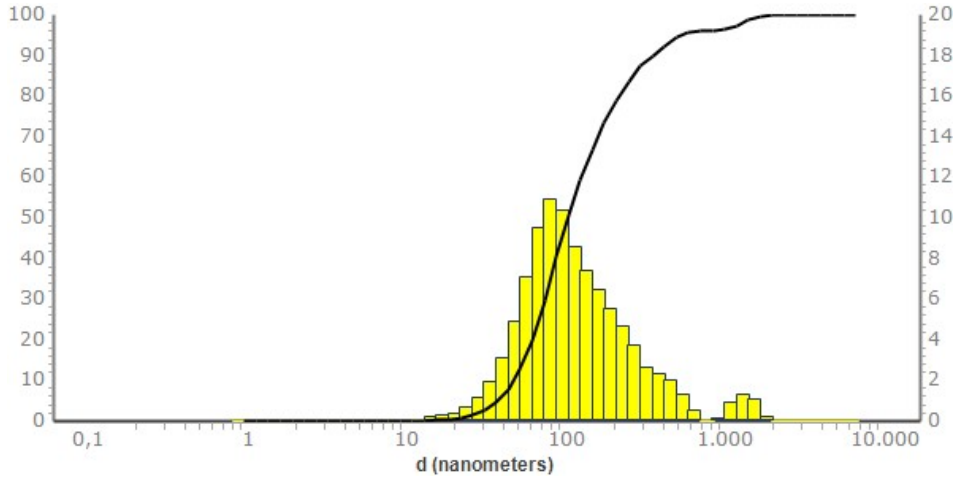
| Peaks Summary | | |
|---|---|---|
| d(nm) | Vol% | Width |
| 131,9 | 100 | 89,3 |

| Measured Data | |
|---|---|
| Zeta Potential | 48,5 mV |
| Polarity | Negative |
| Mobility | 3,79 um/s/V/cm |
| Conductivity | 42 uS/cm |

The difference between the measurement results of both samples is obvious. The diluted one shows a monomodal distribution and a zeta potential of -48 mV. The conductivity is also very low at 42 µS $cm^{-1}$. The original concentrated shows also a bimodality and even a zeta potential of +24 mV like it was obtained also in the measurement before at original concentration. Also, the conductivity is much higher with 3058 µS $cm^{-1}$. So, dilution of 1:1000 will dramatically affect to the behavior of the measured sample. The diluted sample has nothing to do with original concentrated one.

To check this effect and to find out if it is the same with other colored inks, the same experiment was done for a yellow ink with 15 w% of pigments. The results of the yellow ink show the difference between original concentration and dilution. One important point will be also that the agglomerates which are seen in the original concentration measurement are not seen in the diluted one. The agglomerates can lead the blocking the nozzles of the printer head. The results are shown below.

Original concentrated yellow ink (15 w%)

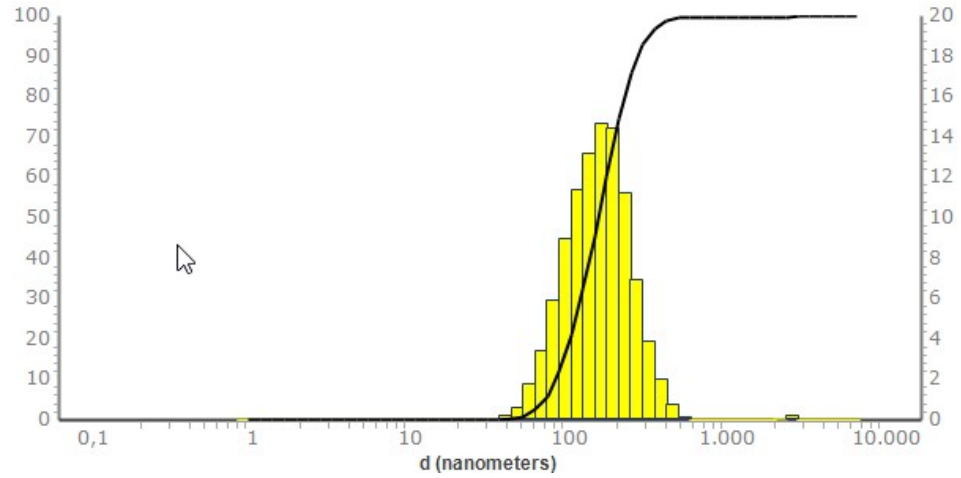



| Summary | |
|---|---|
| Data | Value |
| MI(nm): | 178,9 |
| MN(nm): | 35,60 |
| MA(nm): | 86,30 |
| CS: | 69,52 |
| SD: | 95,90 |
| PDI: | 0,937 |

| Peaks Summary | | |
|---|---|---|
| d(nm) | Vol% | Width |
| 1279 | 3,8 | 466 |
| 97,4 | 96,2 | 164,1 |

| Measured Data | |
|---|---|
| Zeta Potential | 23,4 mV |
| Polarity | Positive |
| Mobility | 1,83 um/s/V/cm |
| Conductivity | 4007 uS/cm |

1:1000 dilution of the 15 w% yellow ink




| Summary | |
|---|---|
| Data | Value |
| MI(nm): | 170,8 |
| MN(nm): | 89,50 |
| MA(nm): | 134,8 |
| CS: | 44,51 |
| SD: | 70,70 |
| PDI: | 0,1802 |

| Peaks Summary | | |
|---|---|---|
| d(nm) | Vol% | Width |
| 152,5 | 100 | 141,4 |

| Measured Data | |
|---|---|
| Zeta Potential | 48,2 mV |
| Polarity | Negative |
| Mobility | 3,76 um/s/V/cm |
| Conductivity | 23 uS/cm |

The zeta potential changes here the sing from -48 mV in dilution to +23 mV in org. concentration. Also, the conductivity is decreasing from 4000 µS $cm^{-1}$ to 3,8 µS $cm^{-1}$.

# SUMMARY

All Microtrac MRB DLS analyzers have the capability to measure samples up to a very high concentration as shown in the results. Also, it is shown that strong dilution can lead to misinterpretation of the results of size and especially of the zeta potential. This will be caused by changing the composition of the dispersion by dilution in terms of pH and conductivity. These two properties have direct influence on the zeta potential value.

This dilution effects are not only happening for ink samples it can be obtained in different application fields.

The best way to characterize a dispersion will be as close to the reality as possible, which DLS can do.