Abstract: Dynamic light scattering is a well established technique currently used to determine the average hydrodynamic diameter of nanometer to micrometer particles in suspension. A simple, modified experimental setup and the software to process experimental data are presented in this paper. Results on monitoring the time variation of the average diameter of the particles in suspension are presented and discussed.

Key-Words: Dynamic Light Scattering, Sedimentation, Suspensions.

1 Introduction
Turbidity is the opacity of water caused by particles of extraneous matter [1]. Suspended material can be particles of clay, sand, silt, algae, plankton, microorganisms and other substances. Suspended particles absorb visible light and consequently have their temperature increased. Heat is transferred to water, therefore water temperature rises faster in turbid water than it does in clear water under the same incident light intensity. Warm water contains less dissolved oxygen than cold water, thus the concentration of dissolved oxygen decreases in turbid water.

Turbidity is often used as an indicator of the total amount of material suspended in the water, but is not a measure of the concentration or size of particles in water. Nevertheless, knowing the size and type of the suspended particles is important. Fine particles suspended in water can carry bacteria, excess nutrients and toxic materials, which might be a hazard for drinking water.

In this work a simple physical experimental procedure derived from the Dynamic Light Scattering (DLS) technique, assisted by a set of computer codes, that can be used to assess the average size of the particles suspended in water, in the range of tens of nanometers to µm, is presented in detail. A simple but time consuming experiment that uses the DLS procedure was carried on aiming to establish the type of sediments in river water. The technique and the results are presented in the next sections.

2 The modified DLS technique
The suspended particles have a continuous, irregular motion in fluids, which is the effect of several factors such as Brownian force, buoyant force, friction force between fluid and the particles and gravity, which becomes significant for micron sized particles but can be neglected for nanometer sized particles [2], [3], [4]. The method is called Dynamic Light Scattering (DLS) or Photon Correlation Spectroscopy (PCS) and the physical principles of the method are explained in [3], [4], [5], to name just a few. A coherent light source (a laser) is used to illuminate a cuvette containing particles in suspension.

As previously explained, the scattering centers (SC) undergo a continuous motion. The image that appears on a screen is called speckled image and it appears as a result of the interference of the wavelets scattered by the scattering centers (SC hereafter), each wavelet having a different phase and amplitude in each location of the interference field. The image changes in time as a consequence of the scattering centers complex movement giving the aspect of boiling speckles [3], [4]. A time series can be recorded at a certain angle using a detector and a data acquisition system. References [6] and [7] state that the width of the autocorrelation function of the time series is proportional to the diffusion coefficient, which, on its turn, depends of the particle diameter. These basic facts suggested that the DLS technique can be used to measure the particles diameter in suspension. An modified DLS version is described in this subchapter.
The experimental works [8], [9] and the theoretical works [10 - 12] proved that the power spectrum of the scattered light intensity can be linked to the probability density function (hereafter PDF). The spatial correlations are therefore translated into phase correlations. According to the Wiener-Khintchine-Theorem, this translation relates the power spectrum to the autocorrelation function of a process.

A typical DLS experimental setup is presented in Fig. 1. The power time series is obtained by subtracting the average intensity from the recorded time series and afterwards by squaring the output. The Fourier transform of the power time series is the power spectrum. The spectrum calculated from the experimental data can be compared with the theoretically expected spectrum, which is the functional form of the Lorentzian line \( S(f) \) in Eq. (2). The Lorentzian \( S(f) \) has two free parameters \( a_0 \) and \( a_1 \). The line can be fit to the power spectrum using a least square minimization procedure and the two parameters that provide the best fit can be found.

\[
S(f) = a_0 \cdot \frac{a_1}{(2\pi f)^2 + a_1^2}
\]

The \( a_0 \) parameter performs a scaling of the function to the magnitude of the PSD. The \( a_1 \) parameter enters in a non-linear way, shifting the Lorentzian \( S(f) \) along the frequency axis.

Fitting the whole function is advantageous compared to the alternative method described in [4], [8], [9], where the frequency where half-maximal height is reached was measured, because this alternative takes more data points into account, thus increasing the quality of the fit. This is the first change in the method apart from the conventional DLS where more detectors at different angles are used and the above mentioned measuring of the frequency of the 0.5 point of the normalized autocorrelation function is used, as well. Further details on the modified DLS technique can be found in [13 – 16].

After finding the \( a_0 \) and \( a_1 \) parameters by fitting the Lorentzian line as described above, the diameter of the SCs can be assessed as the double of the radius \( R \) using (3).

\[
R = \frac{2k_BTK^2}{6\pi\eta a_1} \quad \text{where} \quad K = \frac{4m}{\lambda} \cdot \sin \left( \frac{\theta}{2} \right)
\]

In Eq. (3) \( T \) is the absolute temperature of the sample, \( k_B \) is Boltzman’s constant, \( \eta \) is the dynamic viscosity of the solvent, \( \theta \) is the scattering angle, \( n \) is the refractive index of the scattering particles and \( \lambda \) is the wavelength of the laser radiation in vacuum.

The light source was a laser diode operating continuously and the power was 18 mW. The wavelength of the laser beam was 635 nm. The experiment was conducted at 20 °C. The cuvette-detector distance \( D \) was 0.375 m and \( x \) was 0.025 m, thus the scattering angle \( \theta \) was equal to 3° 48' 51". This \( \theta \) angle value is atypical for DLS where a 90° value is currently chosen. The reason for choosing a much smaller angle is to shift the rollover point of the Lorentzian line towards smaller \( a_1 \) values, hence towards smaller frequencies, where the noise is considerably smaller. This is the second modification in the method apart from the conventional DLS where a 90° value is typical.

### 3 Results and discussion

The modified DLS technique previously described was used to investigate the suspension from the Trinkbach river. The water sample was taken in a 250 ml flask, after rinsing the clean flask three times with river water. Special care was taken not to touch the bottom of the river, which might increase the amount of particles in suspension. The flask was rolled upside down several times, slowly, to have the precipitate back in suspension right before aspiring 4 ml and placing it in a glass cuvette, 10 mm thick. A data acquisition system was used having a data acquisition rate of 12 KHz. A time series lasting for 30 seconds was recorded right after the sample was poured in the cuvette. A sequence of the time series is presented in Fig. 2. We notice an overlap of signals with different frequencies. The power spectrum was calculated for the whole time series and the parameters of the Lorentzian line were found using a non linear least square minimization algorithm. The average diameter was found to be 0.385 μm. According to the U.S. Department of Agriculture Soil Texture Classification system,
the sand-silt distinction is made at the 0.05 mm particle size [17], which makes the sediment to be primarily silt.

![Figure 1](image1.png)

*Fig. 1 – A sequence of the time series recorded for the water sample after filling the cuvette*

The cuvette was kept in the sample holder for six days, allowing the suspension to slowly, naturally sediment and the time series recording and data analysis procedure was repeated each day. The results of the average diameter monitoring during the six days is presented in Fig. 4, with upward pointing triangles. Examining Fig. 4 we notice that the average diameter of the particles that remain in suspension increases as time passes. Actually, after 24 hours the average diameter increased and passed 0.6 µm. This fact is surprising apparently, as we expect that the particles that wave a density bigger than water density to sediment.

If a particle having a density bigger that water is allowed to move freely in water it will undergo a sedimentation motion, as the gravity force \( G \) is bigger than the buoyant force \( F_A \). The sedimentation motion will undergo with a constant velocity.

\[
F_s + F_A - G = 0
\]  

which means, considering a spherical particle of radius \( r \):

\[
6 \pi \eta rv + \frac{4 \pi}{3} r^3 \rho_0 g - \frac{4 \pi}{3} r^3 \rho g = 0
\]

Where \( \eta \) is the water viscosity, \( v \) is the particle sedimentation velocity, \( \rho \) and \( \rho_0 \) are the particle and water densities. Solving equation (4) we find that the velocity is given by equation (5):

\[
v = \frac{2g}{9\eta} (\rho - \rho_0) r^2
\]

Reverting equation (5) we can find the radius of a particle that has the velocity \( v \):

\[
r = \sqrt{\frac{9\eta v}{2g(\rho - \rho_0)}}
\]

The distance from the top of the cuvette that was completely filled with the water sample and the laser beam was 38 mm. As the sedimentation carries on, if we assume that the particles in suspension have a continuous distribution, all the particles having a sedimentation velocity bigger that \( v_1 \), hence a diameter bigger than twice the radius computed with equation (6) for \( v_1 \) will be below the laser beam level. For a sedimentation time of 24 h \( v_1 \) is:
\[ v_1 = \frac{0.038 m}{24 \cdot 3600 s} = 4.398 \cdot 10^{-7} \text{ m/s} \]  

and the diameter of the particles that still remain in suspension at the level of the laser beam is smaller than \( d_t = 2.25 \mu m \). This is actually the first data point, corresponding to time 24 h in Figure 4, which presents the diameters of the particles that still remained in suspension assuming that they have a continuous distribution and a density \( \rho = 2600 \text{ kg/m}^3 \), a generic value for quartz and clay.

The DLS measured diameter increased quickly. Comparing the measured diameter evolution with the expected diameter evolution, in the assumption that the particles have a continuous distribution, we note that the assumption we made is not correct. The silt particles have a narrow size distribution rather than a wide distribution and the average diameter is bigger than the average diameter measured at \( t=0 \), that is bigger than 0.385 \( \mu m \). As time passed all the silt particles went below the laser beam level and bigger particles, having a diameter around 0.64 \( \mu m \) remained in suspension. As the average diameter remained constant (within the systematic error level of the method) we can conclude that the remaining particles are organic particles having a density close to water density.

4 Conclusion

A physical procedure using a laser beam that is scattered by particles in suspension, a detector, a data acquisition system and a computer, assisted by a set of computer codes, actually a modified version of the dynamic light scattering technique, is presented. The technique was used to monitor the average suspension particle diameter evolution in a time interval of several days. The time variation of the diameter indicates that the suspension is made of silt, with a narrow size diameter distribution, bigger than 0.385 \( \mu m \) and organic particles, with a diameter of 0.64 \( \mu m \). The article proves that the procedure can be used in investigating the nature and the size of the complex suspension of particles in natural water.

References: