PROFILING SUSPENSIONS IN NATURAL WATER BY A SIMPLIFIED DYNAMIC LIGHT SCATTERING PROCEDURE AND SEDIMENTATION

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ABSTRACT

A coherent light scattering experiment was carried out. The samples were aqueous natural water suspensions picked from the same river. While sedimentation occurred in the samples, they were subjected to a dynamic light scattering (DLS) experiment and the time series was recorded at certain time intervals. For each recording, a program written for this purpose, performing at least square minimisation, computed the average diameter of the particles in suspension. The variation of the average diameter in time indicates the dominant type of suspensions in water.

ZUSAMMENFASSUNG: Bestimmung der Suspensionenprofile in natürlichem Wasser durch ein vereinfachtes Analyseverfahren der Dynamik des kohärenten gestreuten Lichts und der Sedimentation.

Vorliegende Arbeit befasst sich mit einem Experiment der kohärenten Lichtstreuung. Bei den Proben handelt es sich um natürliche Wassersuspensionen, die zu unterschiedlichen Zeiten alle aus demselben Fluss entnommen wurden. Während der Sedimentierungsphase der Proben wurden sie einem Experiment dynamischer Lichtzerstreuung (DLS) ausgesetzt, während dessen Zeitreihen unterschiedlicher Intervalle aufgezeichnet wurden. Für jede Aufzeichnung wurde ein für diesen Zweck geschriebenes Programm eingesetzt, mit Hilfe dessen der mittlere Durchmesser der Suspensionspartikel bestimmt wurde. Die zeitliche Variation des Durchmessers liefert Informationen zum Typus der Suspensionspartikel.

REZUMAT: Determinarea profilului suspensiilor în apa naturală folosind un procedeu simplificat de analiză a dinamicii luminii coerente împrăștiate și de sedimentare.

A fost efectuat un experiment de împrăştiere a luminii coerente. Probele au fost apă naturală cu suspensii, prelevate din acelaşi râu. În timpul în care suspensiile se sedimentau, acestea au constituit ținta unui fascicul într-un experiment de împrăştiere a luminii coerente, în cadrul căruia s-au înregistrat serii de timp de diferite intervale. Pentru fiecare înregistrare, un program scris în acest scop, a determinat diametrul mediu al particulelor în suspensie. Variația în timp a diametrului oferă informații despre tipul particulelor din suspensie.

INTRODUCTION

Natural water is less than 100% transparent, because light is in part scattered and absorbed by the particles suspended in it. This physical property that describes this partial opacity to water is called turbidity (Waterwatch Australia, 2002). Suspended particles consist of sand, clay, silt, plankton, algae, micro-organisms and other substances in small amounts (National Soil Survey Handbook, 2006). Suspended particles can undergo elastic scattering, which causes changes in water. On the other hand, particles can absorb light and this causes a temperature increase in turbid water. Under the same light exposure turbid water is warmer than less turbid (more transparent) water. Water temperature is a tremendously important parameter in an ecosystem. Gumpinger et al. (2010) stated that "water temperature is considered one of the most essential regulating parameters in aquatic ecosystems". Moreover, because of the intensive interrelations with other physical and chemical parameters, water temperature has a high indicative value when considering the general condition of a river ecosystem (Gumpinger et al., 2010).

This frequently used parameter, turbidity, is related to the total amount of suspended material in water. As previously stated (Chicea, 2013a, b, c) turbidity is not a measure of the concentration or the size of the particles. Moreover, measuring and knowing turbidity does not provide adequate knowledge of the size and the type of particles. As previously stated (Chicea, 2013c), an understanding of the size and the type of the suspended particles is important.

The work presented here is a continuation of previous work (Chicea, 2013a, b, c) aiming to assess the type of suspension in natural water (organic or inorganic) using a combination of two physical procedures, sedimentation and Dynamic Light Scattering, details and results are presented in the next sections.

MATERIALS AND METHODS

Particles sedimentation

When a particle is placed inside a carrier fluid, such as a suspension particle in natural water, it is subject to the action of three forces: gravity, buoyant force and the Stokes drag, if the motion of the particle takes place in laminar regime (Chicea, 2008).

For a particle of radius R the three forces, gravity, buoyant and Stokes drag are expressed as:

$$G = \frac{4\pi}{3} R^3 \rho g \tag{1}$$

$$F_b = \frac{4\pi}{3} R^3 \rho_0 g \tag{2}$$

$$F_s = 6\pi\eta R v \tag{3}$$

where ρ is the density of the particle, ρ_0 is the density of the fluid (water), g is the gravitational acceleration, v is the velocity of the particle in fluid, and μ is the dynamic viscosity.

If the density of the particle, ρ, is bigger than the density of the fluid, ρ_0, the particle will start the sedimentation motion and velocity v will increase. As the velocity increases, so does the Stokes drag, up to the point that makes the sum of the three forces null, as illustrated in figure 1 and equation (4). When the limit velocity of falling is reached and kept constant thereafter. The limit velocity v_l is given by equation (5).

$$\overline{F_b} + \overline{F_S} + \vec{G} = 0 \tag{4}$$

$$v_l = \frac{2(\rho - \rho_0)R^2 g}{9\eta} \tag{5}$$

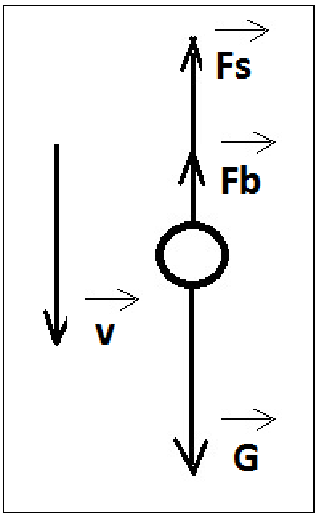

Figure 1: The forces that act upon a particle in a fluid, as water.

The limit velocity can be used in more ways, either to assess the viscosity of the fluid, like in falling sphere viscometers, or to assess the diameter of the particles that are still suspended in the fluid after a certain time from the beginning of the experiment, as presented below. For this purpose we can consider a cuvette with the suspension, as in figure 2.

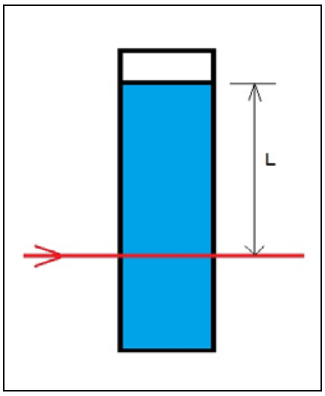

Figure 2: A cuvette with a suspension and a laser beam.

Equation (5) shows that bigger particles have bigger velocity, therefore they fall faster from the part of the cuvette above a certain mark, like the laser beam. All the particles that were located above the mark at the beginning of the experiment, (hereafter at time 0) will fall below the laser beam level in time t if they have a velocity bigger than $v_m(t)$, given by equation (6):

$$v_m(t) = \frac{L}{t} \tag{6}$$

This dictates that at time t, only the particles having a velocity smaller than $v_m(t)$ in equation (6), are still remaining in suspension, above the line and hence a diameter smaller than d_{max} found by reverting equation (5):

$$d_{max} = 2 \cdot R_{max} = \sqrt{\frac{9\eta v_m}{2(\rho - \rho_0)g}} \tag{7}$$

A plot of the d_{max} versus time, considering L = 1 cm, as was used in the work described here, and the suspensions whether it was silt or sand, with a density ρ = 2,600 kg/m^3, is presented in figure 3.

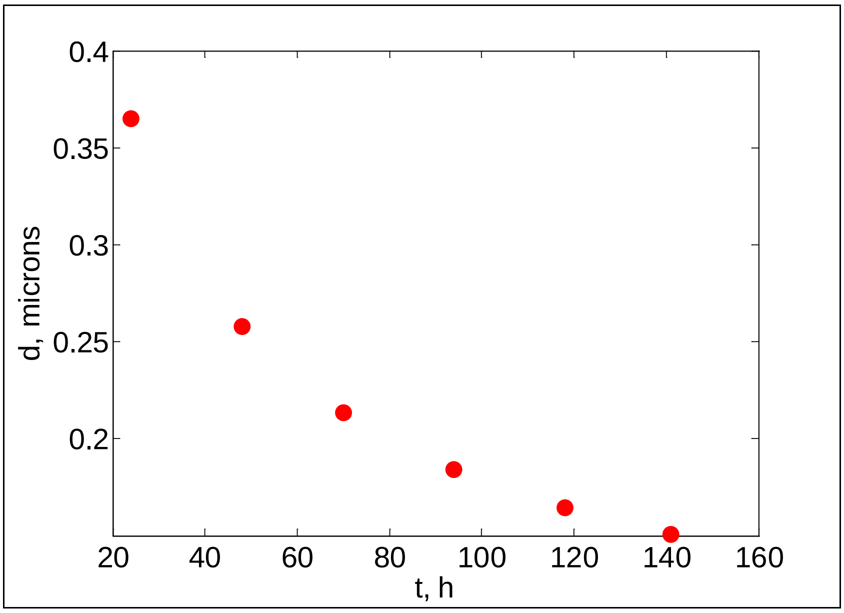

Figure 3: The maximum diameter, in microns,
of the particles still being in suspension above the line, after time t, in hours.

These considerations allow us to assess the type of suspensions in water, together with another complimentary procedure to measure the diameter of the particles at time t. This complimentary procedure is a modified Dynamic Light Scattering procedure and is described in the following subsection.

Dynamic Light Scattering

Dynamic Light Scattering (DLS hereafter) is an optical procedure used for assessing the size of the particles in suspension (Chicea, 2010). When coherent light crosses a medium having scattering centers (SC) an un-uniformly illuminated image is obtained, currently named speckled image, as explained in a report of previous work on this subject (Chicea, 2013a, b). The image is not static, but changes in time giving the aspect of “boiling speckles” (Goodman, 1984; Briers, 2001).

The speckled image can be observed either in free space and is named objective speckle (Goodman, 1984) or far field speckle (Briers, 2001) or on the image plane of a diffuse object and it is named subjective speckle (Goodman, 1984) or image speckle (Briers, 2001). The dynamics of the speckle field was analyzed by correlometric methods (Boas and Yodh, 1997; Aizu and Asakura, 1991; Fedosov and Tuchin, 2001) or by laser speckle contrast analysis (Briers et al., 1999; Zimnyakov et al., 2002). The far field statistics, as speckle size, can be used to measure the roughness of a surface (Lehmann, 1999; da Costa and Ferrari, 1997; Berlasso et al., 2000) or to assess the thickness of a semi-transparent thin slab (Sadhwani et al., 1996). Other papers (Giglio et al., 2001) report on using the near-field speckle dependence of the particles size. The work reported by Piederrière et al. (2004a, b) and Chicea, (2010) used a transmission optical set-up to analyze the far field, and this type of experimental setup was used in the work reported here, which is a continuation of the previous experimental work (Chicea, 2013a, b, c), but using a different procedure for data recording and processing, called DLS.

As the SCs are moving, the image presents fluctuations, hence variations of the intensity in each locations. An image of the far interference field covering an area of 0.5 x 0.5 cm is presented in figure 4.

If we place a detector in a location, the time variations of the intensity are recorded and a time series is the result. The schematic of the experimental setup is presented in figure 5.

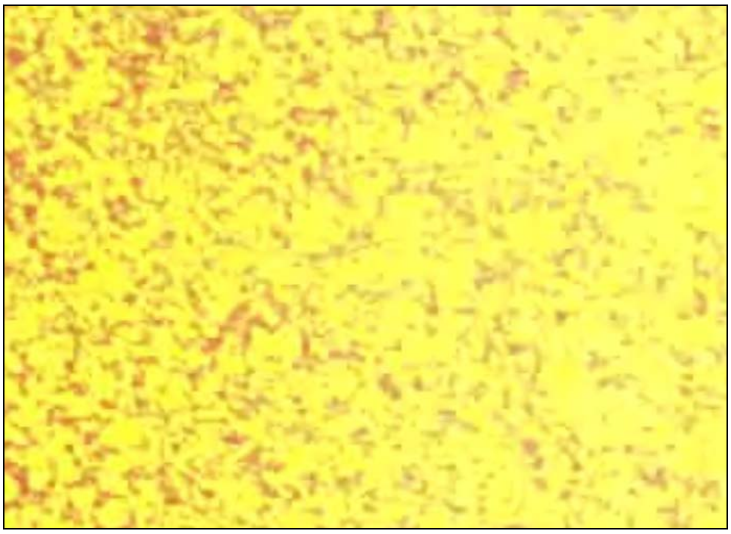

Figure 4: An image of the far interference field covering an area of 0.5 x 0.5.

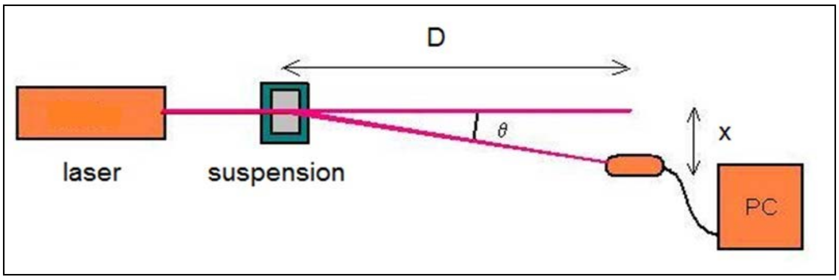

Figure 5: The schematic of the experimental setup.

The power spectrum of the intensity of the light scattered by particles in suspension can be linked to the probability density function (here after PDF) (Clark, 1970; Tscharnuter, 2000). This link between the PDF and the power spectrum is a consequence of the translation of the relative motion of the scattering particles into phase differences of the scattered light. Thus spatial correlations are translated into phase correlations. As already proved (Clark, 1970; Tscharnuter, 2000) 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. The power spectrum of the intensity of the light scattered by particles in suspension can be linked to the probability density function. This link between the PDF and the power spectrum is a consequence of the translation of the relative motion of the scattering particles into phase differences of the scattered light. Thus spatial correlations are translated into phase correlations, relating the power spectrum to the autocorrelation function of a process.

By subtracting the average intensity from the recorded time series and calculating the square of the intensity we obtain the power time series. The Fourier transform of the power time series is the power spectrum. We can compare the spectrum calculated from the experimental data with the theoretically expected spectrum, namely the functional form of the Lorentzian line S(f) (8):

$$S(f) = a_0 \frac{a_1}{(2\pi f)^2 + a1^2} \tag{8}$$

The Lorentzian line S(f) has two free parameters a_0 and a_1 and is fit to the power spectrum using a non-linear minimization procedure to minimize the distance between the data-set and the line. We notice that a_0 performs a scaling of the function in the range, which translates into a shift in the logarithmic representation.

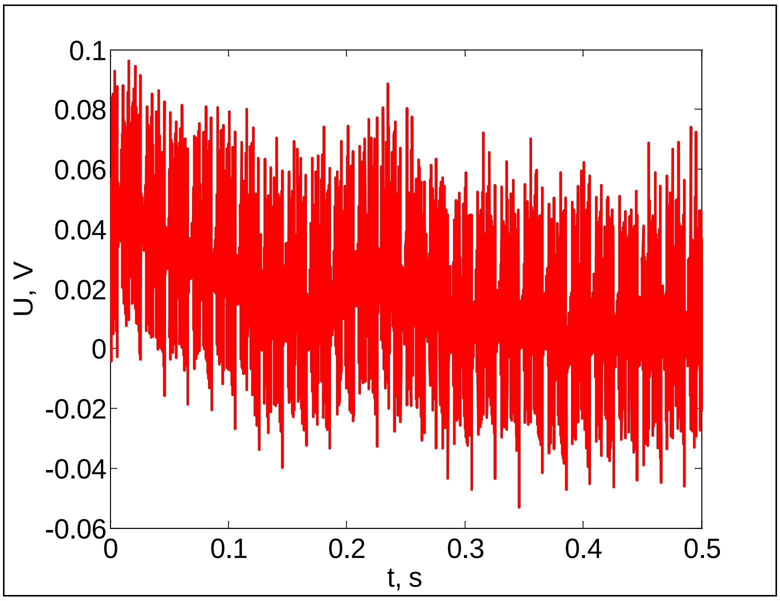

Figure 6: The first second of a time series.

The a_1 parameter enters nonlinearly into the function. Once the fit is completed and the parameters are found, the diameter of the SCs can be assessed as the double of the radius R. The radius can be derived as a function of the fitted parameter a_1 and other known quantities using (9):

$$R = \frac{2k_B T K^2}{6\pi\eta a_1} \tag{9}$$

where

$$K = \frac{4\pi n}{\lambda} \cdot \sin\left(\frac{\theta}{2}\right) \tag{10}$$

In (9) k_B is Boltzman's constant, T is the absolute temperature of the sample, η is the dynamic viscosity of the solvent. In (10), θ is the scattering angle, n is the refractive index of the scattering particles and λ is the wavelength of the laser radiation in vacuum.

The scattering angle θ is equal to 4°58'11". This is not typical for DLS where a bigger angle is chosen, usually 90°. This setup shifts the rollover point in the Lorentzian line towards smaller a_1 values, hence smaller frequencies, where the noise is considerably smaller (Chicea, 2012a, b). For this reason, and for fitting the Lorentzian line rather than the autocorrelation function, the above mentioned DLS procedure is called a modified DLS. The wavelength was 633 nm, the light source was a laser diode and the power was 18 mW. The data acquisition rate was 8,000 Hz and the DLS experiment was carried on at 20°C. Figure 7 presents the power spectrum and the fitted Lorentzian line.

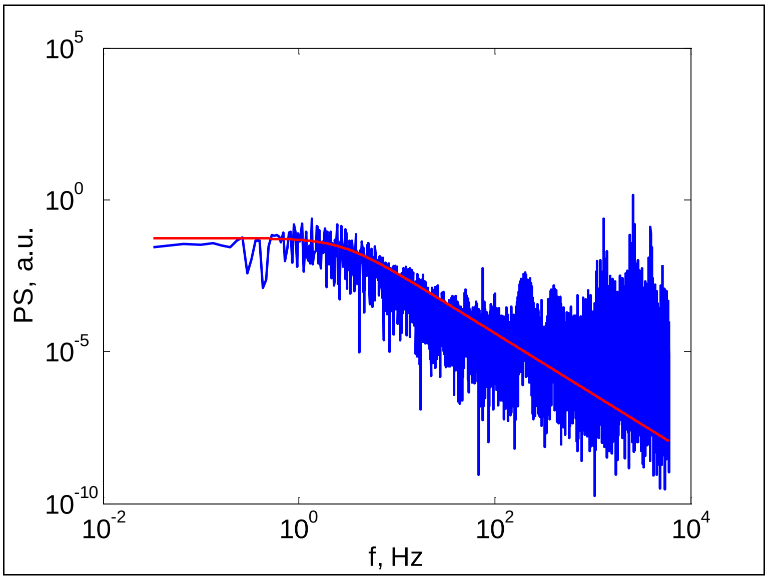

Figure 7: The power spectrum (shattered line) and the fitted Lorentzian line (continuous).

Experimental procedure and data processing

River water samples from the Trinkbach River were taken and each one was placed in the 1 x 1 cm cuvette. The DLS experiment was started and time series were recorded with a time interval of 24 hours for each sample. The time series were processed using the modified DLS procedure and the average diameter of the suspended particles was computed using the least squares procedure, as described above. The diameter considering sedimentation was computed as well, and compared with the measured DLS diameter. The results are presented in the next section.

RESULTS AND DISCUSSION

Figure 8 presents the variation of the diameter calculated using the sedimentation assumption, considering the particles to be sand and silt, and the variation of the measured DLS diameter, with the time elapsed from the beginning of the experiment.

If the particles are sand or silt, the sedimentation and the diameter variation is described by the red circles. If the particles are organic suspension, their density is comparable with the density of water and they remain in suspension. In this case the diameter is described by a constant set of data.

The variation of the average diameter, as results from the DLS sizing over five days, described by the blue squares, indicates that the initial sediment consisted of both organic and mineral particles. During the first 24 hours the mineral suspension, most probably sand or silt became sediment and the remaining particles were organic, which is proved by the constant diameter over the next days.

Moreover, the diameter of the sand and silt particles is smaller, which is proved by the increase of the average diameter after sedimentation.

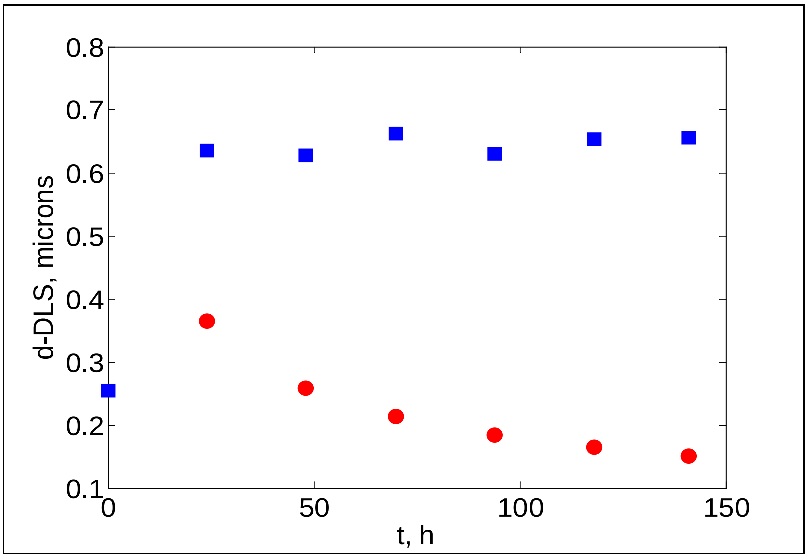

Figure 8: The variation of the sedimentation diameter (circles) and of the measured DLS diameter (squares) with the time elapsed from the beginning of the experiment.

CONCLUSIONS

Using the combination of DLS with sedimentation can be a simple, but useful tool in describing the type of suspension in natural water. The combined procedure does not provide the amount of particle suspended, hence turbidity, but the type and the average diameter of the particles. The combined procedure is relative insensitive to the concentration of particles and works well even for extremely diluted samples, completely transparent. If the concentration of particles is too big and the sample becomes opaque, the sample can be diluted to achieve transparency, without altering the results.

The DLS procedure is an absolute procedure, which means that a calibration is not required. This procedure can be used in combination with other optical techniques, like average speckle size and intensity to assess the amount of particles in suspension, these procedures require calibration though.

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