

Sensitive Quantification of Colloids using Laser-induced Breakdown Detection

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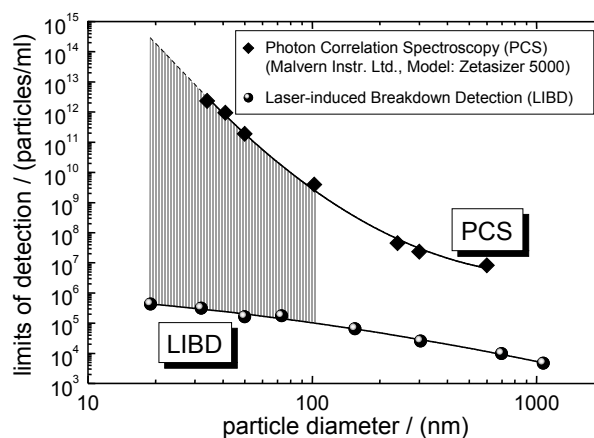
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Colloids (size typically between 1 and 1000 nm) are present in all aquatic systems. Due to their very small size, colloids have got a large surface in relation to their mass and therefore have a large sorption capacity¹ for both pollutants and microbial water impurities. Disease-causing microbial impurities (bacteria, viruses) themselves are colloids. It is vitally important, e.g. for drinking water purification, to effectively remove such particulate water contents². Hence, the impact of colloids on aquatic systems needs to be investigated.

The quantification of aquatic colloids is quite a difficult task because they are often found in small concentrations and show a colloid size distribution where small particles ($d < 100$ nm) dominate. Using commercially available light scattering techniques a direct, non-invasive quantification is possible. However, the disadvantage of all light scattering methods is that the detection limits for particles with diameters in the lower nanometer size range are not sufficient in many cases.

For the direct quantification of colloids smaller than 100 nm in low-concentrated suspensions ($< 1 \mu\text{g/l}$) the Laser-induced Breakdown Detection (LIBD) is a very sensitive analytical tool^{3,4}. The method is based on the generation and counting of plasmas (breakdown events) on colloidal particles using an intense, pulsed laser beam. Due to the difference in breakdown threshold (laser pulse power density necessary for the production of a plasma) of solid, liquid and gaseous matter (it is lowest for solids), plasmas can be selectively generated on particles in liquids⁵. The laser beam energy is attenuated so that only in the presence of colloidal particles the breakdown threshold in the focal volume is exceeded, whereas in the pure liquid no breakdown events occur. The number of breakdown events per number of laser pulses is defined as breakdown probability and dependent both on particle concentration and size. For the determination of the particle size, plasmas are recorded by means of an image processing system and the distribution of the plasma events along the laser beam axis is determined. This distribution of plasma blobs is dependent solely on the particle size⁶, hence a number weighted mean diameter can be calculated by means of calibration with reference standards of known particle size. With known size and breakdown probability the colloid concentration can be calculated^{7,8}. The main advantage of LIBD compared to light scattering techniques such as Photon Correlation Spectroscopy (PCS) is a higher sensitivity of several orders of magnitude, especially in the particle size range $< 100 \text{ nm}$ ^{2,8} (see graph below).

Fig.1: Limits of detection from Photon Correlation Spectroscopy (PCS) and Laser-induced Breakdown Detection (LIBD).



Biological material can add to the particulate content of natural waters, as mentioned above. Since the LIBD technique is based on the different breakdown thresholds of solid and liquid matter, structures like bacteria that mainly consist of water are hard to detect. To test whether the LIBD instrumentation is capable of detecting microbial material in low concentrations, suspended in water, *Enterococcus durans* as a rather easy to both cultivate and handle spherical bacterium was used⁹. The breakdown threshold of the bacteria suspension is shifted to lower laser pulse energy compared to the threshold of ultra pure water used for suspending the bacteria. This demonstrates the capability of the LIBD technique to not only detect solid particles, but also colloids in the transition sphere between solid and liquid matter like bacteria².

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