Improved sensitivity for the direct quantification of nano-particles by means of Laser-induced Breakdown Detection (LIBD)

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Colloids (sizes 1 nm - 1 µm) are present in all aquatic systems. They are chemically surface active and they therefore readily absorb e.g. heavy metal ions. The generation of colloids may increase the amount of mobile heavy metals in water over what is expected by their thermodynamic solubility [1]. In addition, disease-causing microbial impurities (algae, bacteria, viruses, …) themselves are colloids, and nano-particles as such are often unwanted particulate contaminants reducing the product quality in many modern production processes. The possible environmentally relevant impact of colloids in natural aquatic systems as well as the relevance of nano-particles in technical processes therefore needs to be investigated and new analytical methods like Laser-induced Breakdown Detection (LIBD) are developed.

For the quantification of low concentration (< 1 µg/L) nano particles smaller than 100 nm in size, the LIBD is a very sensitive analytical tool [2, 3]. The method is based on the generation of plasmas on colloidal particles by using an intense, pulsed laser beam and the detection of the produced plasma light emission and/or the generated shock wave. The minimally required critical power density, $P_{A,crit}$, for the generation of breakdown events (breakdown threshold) depends on the state of aggregation of matter. Breakdown thresholds of different materials follow the qualitative order [4].

$$P_{A,\,crit}(\text{solid}) < P_{A,\,crit}(\text{liquid}) < P_{A,\,crit}(\text{gas})$$

The LIBD is based on the difference in the breakdown thresholds of liquid and solid matter. The laser beam energy is attenuated so far that in the pure liquid no breakdown events occur, and only in the presence of colloidal particles the breakdown threshold in the focal volume is exceeded. The evaluation of the number of breakdown events per number of laser shots results in a breakdown probability, dependent on particle concentration and size. For the determination of colloid sizes the light emissions of single plasmas are detected by a microscope/camera system. The optical detection of the plasma light emissions results in a spatial distribution of breakdown events within the focal volume, dependent on particle size and not dependent on

concentration. By comparison to the distribution width of reference particles (calibration curves) a mean particle diameter of colloids can be derived. With known mean particle diameter and breakdown probability the particle concentration can be calculated [5].

The schematic setup of the LIBD instrumentation is represented in fig. 1. The main part of a pulsed laser beam at 20 Hz is focussed into the sample cell (cuvette). The laser pulse energy is monitored and kept constant by a newly developed, electronically controlled servo-motor attenuator. The plasma light emissions caused by the breakdown process are magnified by a microscope and detected by means of a IEEE1394 camera connected to a personnel computer for data storage and evaluation. The laser pulse energy, the plasma pictures and the x,z-coordinates of the single events are determined by means of a specially designed image processing software. The complete measurement is fully automated, and the system can be controlled remotely via a LAN or the Internet if necessary.

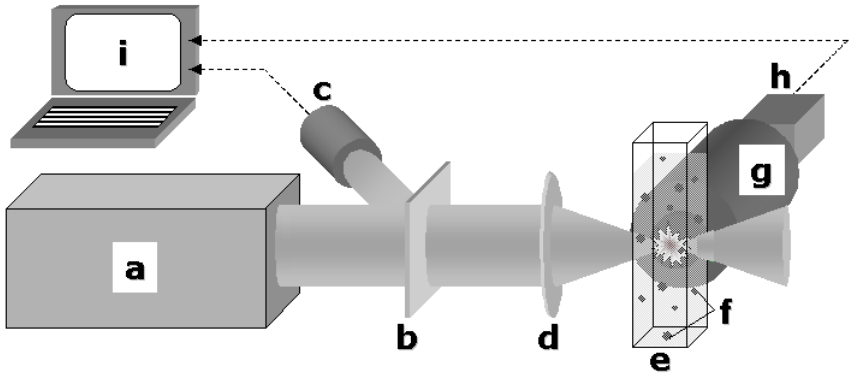

Fig. 1: Schematic setup of the LIBD instrumentation.
(a: laser, b: beam splitter, c: energy detector, d: lens, e: sample cell, f: colloids, g: microscope, h: camera, i: personal computer)

REFERENCES

1. J. F. McCarthy and J. M. Zachara. *Environ. Sci. Technol.*, 23**:** 496-502 (1989)
2. T. Bundschuh, T. Wagner and R. Köster. *Chem. Ing. Tech.*, 75: 386-390 (2003)
3. T. Wagner, T. Bundschuh, R. Schick, T. Schwartz and R. Köster. *Acta Hydrochim. Hydrobiol.*, accepted (2003)
4. J. R. Bettis. *Appl. Opt.*, 31: 3448-3452 (1992)
5. T. Bundschuh, R. Knopp, R. Winzenbacher, J.-I. Kim and R. Köster. *Acta Hydrochim. Hydrobiol.*, 29: 7-15 (2001)