## Laser-induced Breakdown Detection (LIBD) with Field-Flow Fractionation (FFF): A Very Sensitive Method for the Direct Quantification of Nano-Particles

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The effect of nano-particles (colloids) on the migration of pollutants is of major concern in environmental research. Colloids are present in all aquatic systems [1], they are between 1nm and 1µm in size [2] and therefore have a high specific surface to mass ratio. Sorption of contaminants on colloid surfaces is an important mechanism in the transport behaviour of hazardous substances [3]. In addition, colloids can interfere with disinfection during water purification for drinking water production and provide a medium for microbial growth. Colloids may indicate the presence of disease-causing organisms, including bacteria, viruses, and parasites. Viruses in particular show a size spectrum down to only a few 10s of nm [4]. Within the context of quality assessment of aquatic systems it is necessary to quantify the colloids present, to determine their size, to assess their stability and to investigate their elemental composition.

Laser-induced breakdown detection (LIBD) is a sensitive nano-particle analysis method for the direct detection of colloids. During the detection process plasmas are generated on single particles by a focused laser beam and the plasma light emissions produced are detected [5]. The LIBD is based on the difference in the breakdown thresholds of liquid and solid matter [6]. The laser pulse energy is adjusted so 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 emission of single plasmas are detected by a microscope CCD-camera system. The resolved 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 [7]. With known mean particle diameter and breakdown

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probability the particle concentration can be calculated [8]. The laser-induced breakdown effect and the principal of LIBD are described in detail in the literature [5-10].

Field-flow fractionation (FFF) is a method used to separate colloids and suspended particles. Separation takes place in a flat channel, through which a carrier flow transporting the colloids is passed. Due to the channel geometry, a laminar flow profile develops. In sedimentation FFF (SdFFF), channel rotation results in a centrifugal force acting on the sample perpendicular to the direction of the carrier flow. Due to their larger diffusion coefficient, the smaller particles diffuse into the region of the higher flow velocities of the laminar flow and are therefore eluted prior to the larger particles [11]. The potential of FFF techniques are limited by the particle detection methods available. Especially in the lower nm colloidal size range detection methods like laser light scattering (LLS) are not sensitive enough to register colloids in low concentrations.

The LIBD is up to 1,000,000 times more sensitive in comparison to light scattering. Therefore the coupling of the SdFFF with LIBD is our future goal. Such SdFFF/LIBD instruments, or preferably all FFF/LIBD instrumentation will act as high resolution elution methods for separating and sizing a wide range of environmental and industrial samples. Further improvement in qualitative and quantitative colloid investigation can be expected.

- [1] Yariv, S., Cross, H.: Geochemistry of Colloid Systems for Earth Scientists. Springer, Berlin. 1979.
- [2] Shaw, D.J.: Introduction to Colloid and Surface Chemistry. Butterworth, London, 1980.
- [3] McCarthy, J.F., Zachara, J.M.: Surface Transport of Contaminants. Environ. Sci. Technol. 23, 496 (1989).
- [4] Stumm, W.: Chemical Interaction in Practical Separation. Environ. Sci. Technol. 11, 1066 (1977).
- [5] Bundschuh, T., Knopp, R., Kim, J.I.: Laser-Induced Breakdown Detection (LIBD) of aquatic colloids with different laser systems. Colloids and Surfaces A: Physicochem. Eng. Aspects 177, 47 (2001).
- [6] Bettis, J. R.: Correlation among the Laser-Induced Breakdown Tresholds in Solids, Liquids and Gases. Appl. Opt. 31 (18), 3448 (1992).
- [7] Hauser, W., Bundschuh, T.: Verfahren zur Bestimmung der Größe von Partikeln in einer Lösung. Patent DE 198 33 339 C1 (Method for Determining the Size of Particles in a Solution. International Publication No. WO 00/06993) (2000).
- [8] Bundschuh, T., Knopp, R., Winzenbacher, R., Kim, J.I., Köster, R.: Quantification of Aquatic Nano Particles after Different Steps of Bodensee Water Purification with Laser-induced Breakdown Detection (LIBD). Acta hydrochim. Hydrobiol. 29, 7 (2001).
- [9] Fujimori, H., Matsui, T., Ajiro, T., Yokose, K., Hsueh, Y., Izumi, S.: Detection of Fine Particles in Liquids by Laser Breakdown Method. Jpn. J. Appl. Phys. 31, 1514 (1992).
- [10] Scherbaum, F.J., Knopp, R., Kim, J.I.: Counting of Particles in Aqueous Solutions by Laser Induced Breakdown Photoacoustic Detection. Applied Physics B 63, 299 (1996).
- [11] Beckett, R., Hart, B.T.: Use of Field-Flow Fractionation Techniques to Characterize Aquatic Particles, Colloids, and Macromolecules. In: Buffle, J., van Leeuwen, H.P. (Eds.): Environmental Particles. Vol. 2, Lewis Publishers, Chelsea, 1993.