Size Determination and Quantification of Colloids by Sedimentation Field-Flow Fractionation coupled with Laser-induced Breakdown Detection

T. Bundschuh, T. Wagner, R. Köster

Introduction

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 surface to mass ratio. Colloids may increase the total amount of pollutants in water beyond what can be expected from the thermodynamic solubility product of their respective chemical compounds [3, 4]. Thus, 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 [5]. Nano-particles as such are often unwanted particulate contaminants reducing the product quality in many modern production processes (e.g. semiconductor industry), too. 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.

Forschungszentrum Karlsruhe GmbH, Institute for Technical Chemistry, Water Technology and Geotechnology, PO Box 3640, 76021 Karlsruhe, Germany

tobias.bundschuh@itc-wgt.fzk.de

Particle Fractionation by SdFFF

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 [6]. The schematic setup of a SdFFF instrumentation and the principle of particle fractionation by FFF are shown in Fig. 1.

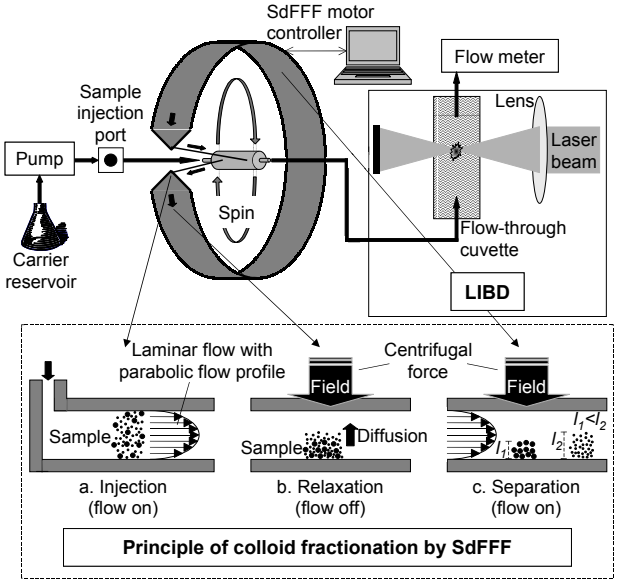

Fig. 1: Setup of the SdFFF/LIBD instrumentation and principle of particle fractionation by FFF.

The potential of FFF techniques are limited by the particle detection methods available. Especially in the lower nm size range detection methods like laser light scattering (LLS) are not sensitive enough to register colloids in low concentrations.

Particle detection by LIBD

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 fo-

cussed laser beam and the plasma light emissions produced are detected [7]. The LIBD is based on the difference in breakdown thresholds of liquid and solid matter, it is approximately one order of magnitude lower for solid material [8]. 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 the particle size the light emissions of single plasmas are detected by a microscope CCD-camera system. The spatial distribution of the recorded plasma flashes within the focal volume gives information about the colloid size [9]. With known mean particle diameter and breakdown probability the particle concentration can be calculated [10]. A schematic setup of the laser-induced breakdown detection instrumentation is shown in Fig. 2.

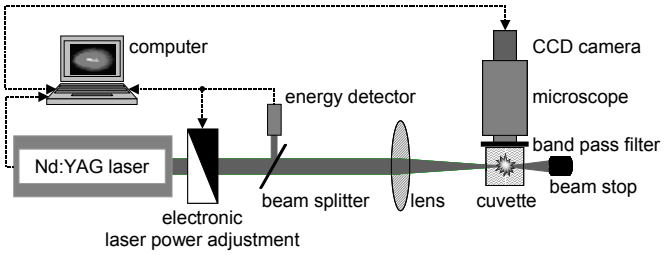

Fig. 2: An experimental setup of LIBD [11].

The LIBD is up to 1,000,000 times more sensitive compared to light scattering methods (see Fig. 3). Therefore the direct on-line coupling of SdFFF with the mobile constructed LIBD is the future objective. Such SdFFF/LIBD instruments (or preferably all FFF/LIBD instrumentations) can act as high resolution elution methods for the separation and size determination of a wide range of environmental and industrial samples. First off-line measurements of FFF fractions by means of LIBD showed an enhancement of sensitivity, especially for particles smaller than 0.1 µm [12].

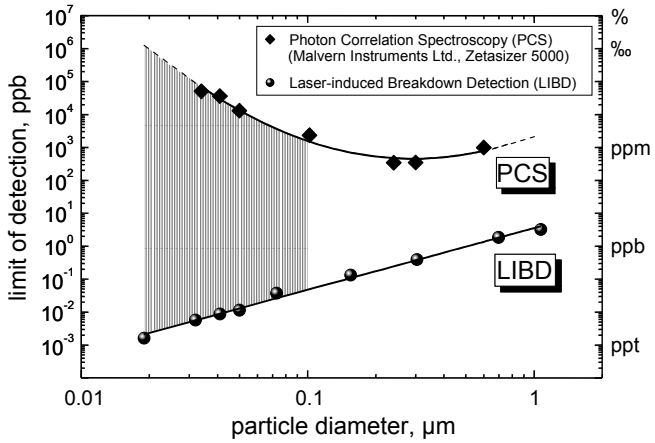

Fig. 3: Detection limits of LIBD in comparison to PCS.

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