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Field-flow fractionation coupled to multi-angle laser light scattering detectors: Applicability and analytical benefits for the analysis of environmental colloids

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Abstract

Results from the analysis of natural colloid with a coupling of field-flow fractionation (FFF) with multi-angle laser light scattering photometers (MALLS) are presented. The results indicate that after FFF of natural colloids MALLS is applicable to retrieve independent and absolute particle sizes (RMS radius or radius of gyration) for the colloids fractionated. For the analysed samples of soil colloids the appropriate data processing in MALLS is the linear or second order ZIMM fitting method for particle sizes up to 500 nm in diameter. This is in contrast to the MALLS analysis of latex beads, where the ZIMM fitting method produces reliable results only below ∼100 nm in diameter. The reason for the good results for the soil colloids can be found in the behaviour of the particle form factor $P(\theta)$ which was found to be linear function when plotted as $Kc/R(\theta)$ over $\sin^2(\theta/2)$.

Keywords: Field-flow fractionation (FFF); Light scattering; Non-spherical particles; Natural colloids; Environmental particles; MALLS

1. Introduction

Natural particles in the nanometer size range (also denoted natural colloids or environmental colloids) play a significant role in environmental processes (for extensive review, see [1–3]). If soil colloids are in situ mobilized they may alter, e.g. the hydraulic properties of aquifers [4] and due to the high surface to mass ratio mobile colloids can promote the transport of strong binding contaminants as radionuclides [5,6], polycyclic aromatic hydrocarbons [7] and heavy metals [8] in groundwater and seepage. Besides the colloid–contaminant interaction the mobility of the colloids itself is the limiting factor for colloid facilitated contaminant transport [9]. The increasing efforts to understand the behaviour of natural colloids in ground and surface waters are hampered by the lack of suitable methods for the analysis and characterisation of natural colloids [10]. Although numerous methods are available for colloid analysis and the determination of particle size distributions, the heterogeneity and broad size distributions of natural colloidal systems may lead to analytical artefacts or biased results. Especially light scattering techniques suffer from the heterogeneity of natural samples and may be suitable only after a pre-fractionation [3,10].

From about 1987 field-flow fractionation (FFF) was introduced for the analysis of natural colloids [11–13]. As a gentle and continuous hydrodynamic fractionation method, FFF proved to be very powerful in the size-based separation and subsequent characterization of size fractions, especially together with a coupling to a multi-element detection system as, e.g. ICP-MS [14,15].

In principle FFF comprises several chromatography-like separation methods based on the interaction of external forces with the respective analyte (molecules, colloids, particles) in a thin open channel. The method enables the continuous separation of molecules and particles in relation to their size-

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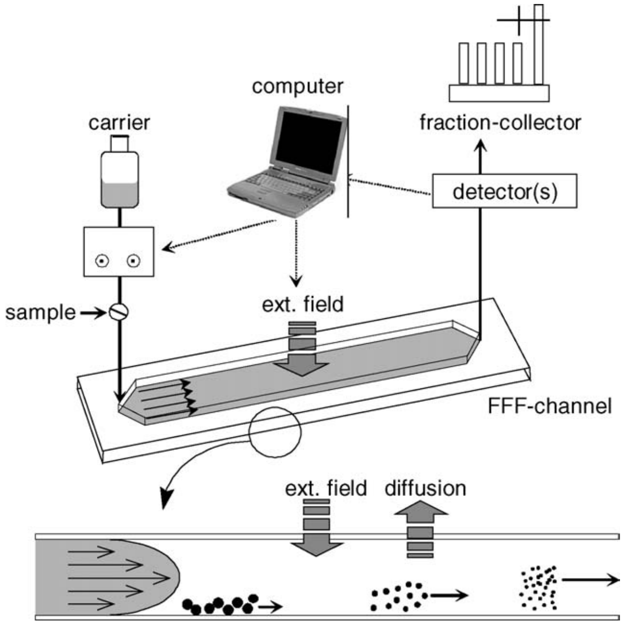

Fig. 1. Schematic plot of a conventional FFF system with carrier delivery, fractionation channel, external field control, detectors and data acquisition and processing. Separation principle of FFF is based on the balance of colloids translational diffusion against an external field force in a laminar flow. The retention of colloids in the FFF channel is a function of their diffusion coefficient/Stokes diameter (FlowFFF) or buoyant mass (SedimentationFFF).

related properties [13,16,17] (Fig. 1). Particle sizes and size distributions may be generated from first principles and the method proved powerful in the particle size range of a few nanometers to about 1 μm [18,19].

However, when FFF is used for the fractionation and analysis of natural colloids the FFF system is most likely not performing ideally. Particles in the samples may not be spherical or not even have a uniform shape and they will scarcely have a uniform density over particle size. Additionally, non-ideal behaviour as aggregation or particle–wall or particle–membrane interactions will cause errors in the determination of particle sizes. If data processing is based solely on the established theory of FFF [13,16] unperceived deviations from ideal fractionation behaviour may produce erroneous results.

Additionally, as soon as the analysed particles are non-spherical, the size distributions obtained from different FFF systems like FlowFFF or SedimentationFFF (SedFFF) will not match each other since both systems refer to a different equivalent spherical diameter [20].

FlowFFF in Brownian mode [21] is related to the diffusion coefficient of molecules/particles which can be transformed to a corresponding stokes particle diameter (equivalent hydrodynamic diameter).

SedFFF is related to particle volume and particles density difference to the carrier fluid (buoyant mass) which can be related to the equivalent volumetric diameter of a corresponding spherical particle.

It is therefore a straightforward approach to combine light scattering and continuous separation techniques by coupling flow-through light scattering detectors to a fractionation method as FFF. This coupling was successfully performed with FlowFFF and multi-angle laser light scattering detectors (MALLS) for latex nanobeads [22,23] and macromolecules [24–28]. Although the technique was already applied for the analysis of iron oxide colloids [29,30] and results from the MALLS analysis matched the expected values quite well, the general applicability and the appropriate data processing in the MALLS software have not been investigated yet.

In this paper it will be shown that for the analysis of natural colloids the combination of FFF with MALLS is capable of overcoming drawbacks which arise from the individual limitations of both systems. The focus of this study is on the independent determination of the RMS radius or radius of gyration (r_g) by MALLS. The FFF–MALLS coupling provides qualitative and quantitative data from which the accuracy of the fractionation can be evaluated and particle shapes may be assessed.

2. Theory

The theory of FFF is described elsewhere [13,16,17,21].

The general theory of light scattering is described in text books [30] and with special regard to environmental particles in [10,31]. Theory of MALLS is described in [23,24]. Due to the assumptions made in the application of MALLS, especially if environmental samples are concerned, the basic background will be given in the following section.

The net intensity of light scattered by a particle with dimensions smaller than the incident lights wavelength (Rayleigh ratio R as a function of the scattering angle θ, $R(\theta)$) is given by

$$R(\theta) = KcM_w P(\theta) \tag{1}$$

where M_w is the molecular weight of the particle, experimental constant K is given by

$$K = \frac{4\pi^2 n_0^2}{N_A \lambda_0^4}\left(\frac{dn}{dc}\right)^2 \tag{2}$$

with n_0 the refractive index of the medium, N_A the Avogadro's number, λ_0 the wavelength of the incident light in vacoo and dn/dc is the refractive index increment of the analyte. The particle form factor $P(\theta)$ (Guinier approximation) is given as

$$\underset{\theta\to 0}{P(\theta)} = 1 - \frac{q^2 r_g^2}{3} \tag{3}$$

with the scattering vector q

$$q = \frac{4\pi n_0}{\lambda_0} \sin\left(\frac{\theta}{2}\right) \tag{4}$$