



# Asymmetric flow field-flow fractionation of manufactured silver nanoparticles spiked into soil solution



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## ABSTRACT

Manufactured metallic silver nanoparticles (AgNP) are intensively utilized in consumer products and this will inevitably lead to their release to soils. To assess the environmental risks of AgNP in soils, quantification of both their concentration and size in soil solution is essential. We developed a methodology consisting of asymmetric flow field-flow fractionation (AF4) in combination with on-line detection by UV–vis spectroscopy and off-line HR-ICP-MS measurements to quantify the concentration and size of AgNP, coated with either citrate or polyvinylpyrrolidone (PVP), in water extracts of three different soils. The type of mobile phase was a critical factor in the fractionation of AgNP by AF4. In synthetic systems, fractionation of a series of virgin citrate- and PVP-coated AgNP (10–90 nm) with reasonably high recoveries could only be achieved with ultrahigh purity water as a mobile phase. For the soil water extracts, 0.01% (w:v) sodium dodecyl sulfate (SDS) at pH 8 was the key to a successful fractionation of the AgNP. With SDS, the primary size of AgNP in all soil water extracts could be determined by AF4, except for PVP-coated AgNP when clay colloids were present. The PVP-coated AgNP interacted with colloidal clay minerals, leading to an overestimation of their primary size. Similar interactions between PVP-coated AgNP and clay colloids can take place in the environment and facilitate their transport in soils, aquifers, and surface waters. In conclusion, AF4 in combination with UV–vis spectroscopy and HR-ICP-MS measurements is a powerful tool to characterize AgNP in soil solution if the appropriate mobile phase is used.

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## 1. Introduction

Manufactured metallic silver nanoparticles (AgNP) are clusters of silver (Ag) atoms with a size ranging between 1 and 100 nm [1]. AgNP are among the most intensively utilized nanoparticles in a wide range of commercial products [2]. Examples of such products include cleaning agents, coatings, consumer electronics, cosmetics, paints, and textiles [2]. The use of AgNP in these products inevitably will cause their release to soils [3]. Examples of emission pathways of AgNP to soils are leaching from facade paints [4] or the application of sewage sludge from waste water treatment plants to agricultural land [5]. In a recent material-flow analysis of Sun et al. [3], the median AgNP content of soils amended with sewage sludge in the European Union was predicted at 0.3  $\mu\text{g Ag kg}^{-1}$  and expected to increase at a rate of 0.09–0.65  $\mu\text{g Ag kg}^{-1} \text{yr}^{-1}$ . The introduction of AgNP into soils can lead to the exposure of soil biota to these nanoparticles and the occurrence of toxic effects [6–8].

Once introduced into soil systems, AgNP can disperse into soil solution and subsequently further spread to ground- and surface waters by runoff and (subsurface) leaching [9,10]. The AgNP concentration in aqueous matrices depends on factors such as the ionic strength, electrolyte composition, pH, and the dissolved organic carbon (DOC) concentration [11–13]. These chemical characteristics are relevant for the colloidal stability of AgNP suspensions [11–13]. Moreover, the stability of AgNP suspensions can be influenced by the type of coating, which can include polymers or surfactants [12]. The interaction between AgNP and naturally present clay colloids in soil solution may play a role as well in determining the concentration of the AgNP, i.e., a process commonly referred to as hetero-aggregation [14–16].

To assess the risks of AgNP with respect to their toxicity and mobility in soils, quantification of both their concentration and size in soil solution is essential, which requires simple, sensitive, and robust analytical techniques [17]. Elemental quantification of Ag in soil solution can be achieved with techniques such as atomic absorption spectroscopy and inductively coupled plasma-mass spectroscopy (ICP-MS). With such techniques, metallic AgNP cannot be distinguished per se from other Ag species possibly present

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in soil solution including free ionic  $\text{Ag}^+$ , complexes of  $\text{Ag}^+$  with  $\text{Cl}^-$  or DOC, and  $\text{Ag}^+$  bound by natural clay colloids [14–16,18] while the bioavailability and toxicity of these Ag species may be very different. Emerging analytical techniques to detect the presence and size of metallic AgNP in environmental aqueous matrices include ICP-MS operated in a single-particle counting mode and asymmetric flow field-flow fractionation (AF4) [19–22]. In the present study, we focus solely on the use of AF4 as a technique for the continuous size fractionation of nanoparticles, which is based on size-dependent differences in their diffusion coefficient. This technique can be coupled on-line with a range of detectors [19–21]. Since metallic AgNP typically show surface plasmon resonance (SPR) absorbance in the UV–vis region [11], UV–vis spectroscopy is often used for their on-line detection with AF4. In addition to this, ICP-MS can be used for elemental quantification of Ag during the fractionation of metallic AgNP by AF4, either on-line [19–21] or off-line [23]. The main advantages of using ICP-MS instead of UV–vis spectroscopy as a detector coupled to AF4 are the higher sensitivity and the multi-element capability of the former analytical technique [20]. The latter advantage allows to measure the full elemental composition of nanoparticles during AF4 fractionation, which is especially helpful to unravel the speciation of Ag when both metallic AgNP and nano-sized Ag particles consisting of  $\text{Ag}^+$  bound to colloidal organic matter and clay minerals are present in soil solution.

An important work is from Delay et al. [11] who used AF4 coupled on-line to UV–vis spectroscopy and ICP-MS to characterize AgNP synthesized in bog water. The addition of  $\text{Na}^+$  to bog water with AgNP in the latter study had no effect on their elution time whereas  $\text{Ca}^{2+}$  addition at environmentally realistic concentrations led to longer elution times, and, therefore, a larger apparent size [11]. Similar findings were obtained in an AF4 study of Songsilawat et al. [24] who found strong peak shifts of the same citrate-coated AgNP when they were dispersed in different aqueous matrices including deionized water, tap water, groundwater, and sea water. Ideally, an analytical technique applicable for the detection of AgNP in environmental aqueous matrices should be able to quantify the primary size of these nanoparticles. This will be the main objective of our study in which we intend to develop a method to quantify the size as well as the concentration of metallic AgNP in soil solution by AF4 in combination with on-line UV–vis spectroscopy and off-line HR-ICP-MS measurements. Critical factors for a successful fractionation of AgNP in soil solution by AF4 will be identified. We selected citrate and polyvinylpyrrolidone (PVP) as a coating for the AgNP, because it is largely unknown how the type of coating influences the ability of AF4 to fractionate AgNP in soil solution and their behaviour in this aqueous matrix. Citrate is an example of an electrostatically stabilizing agent whereas PVP represents a steric stabilization mechanism [12]. Consequently, the interactions between citrate- or PVP-coated AgNP and natural colloids in soil solution and the effects thereof on the size distribution and mobility of these differently coated AgNP may vary. Citrate and PVP are most frequently studied as coatings for AgNP in the scientific literature.

For a good fractionation and recovery of AgNP by AF4, one important step is the evaluation and choice of the AF4 operating conditions such as variations in the mobile phase [19]. A wide range in mobile phases has been reported in the scientific literature to fractionate AgNP dispersed in various synthetic and environmental aqueous matrices by AF4 [11,21,23–28]. Since the selected mobile phase can have a profound impact on the AF4 results [17,29,30], we will start our research by testing a number of different mobile phases to fractionate virgin citrate- and PVP-coated AgNP (10–90 nm) in well-defined synthetic systems consisting of AgNP spiked into ultrahigh purity water (UPW). Fractionation of AgNP by AF4 is, amongst others, strongly influenced by their interaction with the AF4 membrane [19]. This interaction is, in turn, affected by the electric charge potential and the thickness

of the diffuse electrical double layer of both the AgNP and the AF4 membrane and will, therefore, depend on chemical characteristics of the mobile phase including the ionic strength, the concentration of potential determining ions such as charged detergents, and pH. Therefore, four different mobile phases will be tested in our study reflecting differences in ionic strength, electrolyte composition, and pH. We chose UPW [23,26], 5 mM solutions of  $\text{NaNO}_3$  [11] and  $\text{NaHCO}_3$  [31,32], and 0.01% (w:v) sodium dodecyl sulfate (SDS) at pH 8 [29]. These AF4 experiments will be performed to underpin the choice of a mobile phase for the subsequent experiments in which we will investigate the AF4 fractionation behaviour of citrate- and PVP-coated AgNP spiked into soil solution.

In our experimental approach, we used soil water extracts as a proxy for soil solution [33,34]. A relatively low ionic strength of the soil water extracts in the order of 1 mM was required, because AgNP tend to aggregate and settle in solutions at higher ionic strengths [11,12]. A low ionic strength can be achieved at a relatively low soil to solution ratio (SSR) of 1:10 (w:v) during the extraction of soil with water. Natural colloids of various origin may be present in soil solution, e.g., colloidal organic matter and clay minerals [35]. To cover this variability, we selected three representative agricultural topsoils. The aim of our study is two-fold: (i) to investigate the effects of different mobile phases on the fractionation of virgin citrate- and PVP-coated AgNP (10–90 nm) spiked into UPW by AF4 and (ii) to develop a method to quantify the size as well as the concentration of AgNP with the two different coatings in soil water extracts by AF4.

## 2. Materials and methods

### 2.1. AgNP

Stock suspensions of NanoXact Spherical Silver Nanoparticles (Nanocomposix, San Diego, CA, USA) were used, covering the size range of 10–90 nm with particle size increments of 20 nm. The AgNP were coated with either citrate or PVP. The citrate- and PVP-coated nanoparticles in the stock suspensions were present in a background electrolyte solution of 2 mM trisodium citrate ( $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$ ) solution or milli-Q water, respectively. The AgNP concentration of the stock suspensions varied between 19 and 23 mg  $\text{Ag L}^{-1}$ . The AgNP stock suspensions were stored in the dark at 5 °C during the experimental period. We measured the electrical conductivity (EC) of the stock suspensions and converted the EC into ionic strength [36]. The size of the AgNP in the stock suspensions was measured by transmission electron microscopy (TEM) and dynamic light scattering (DLS). In addition to this, the zeta potential and pH of the stock suspensions were measured. The data on TEM and DLS measurements, zeta potential, and pH and the analytical details of these measurements were provided by Nanocomposix (San Diego, CA, USA) [37]. The characteristics of the AgNP are presented in Table 1. The TEM- and DLS-measured size and zeta potential are discussed in the Supplementary data.

### 2.2. Selection of a mobile phase for AgNP spiked into UPW

The AgNP stock suspensions were ten-fold diluted in UPW obtained from a Milli-Q gradient water purification system (resistivity = 18.2  $\text{M}\Omega \text{cm}^{-1}$  at 25 °C; Millipore, Bedford, MA, USA) to a final AgNP concentration of about 2 mg  $\text{Ag L}^{-1}$ . In case of the citrate-coated AgNP, this resulted in a final background electrolyte concentration of about 0.2 mM trisodium citrate. Before dilution, the AgNP in the stock suspensions were homogenized by short sonication in an ultrasonic bath (30 s) and vigorous shaking (30 s). Each AF4 measurement day, fresh AgNP dilutions were made and the corresponding UV–vis spectrum of these dilutions was measured

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