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Comparison of on-line detectors for field flow fractionation analysis of nanomaterials

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ABSTRACT

Characterization of nanomaterials must include analysis of both size and chemical composition. Many analytical techniques, such as dynamic light scattering (DLS), are capable of measuring the size of suspended nanometer-sized particles, yet provide no information on the composition of the particle. While field flow fractionation (FFF) is a powerful nanoparticle sizing technique, common detectors used in conjunction with the size separation, including UV, light-scattering, and fluorescence spectroscopy, do not provide the needed particle compositional information. Further, these detectors do not respond directly to the mass concentration of nanoparticles. The present work describes the advantages achieved when interfacing sensitive and elemental specific detectors, such as inductively coupled plasma atomic emission spectroscopy and mass spectrometry, to FFF separation analysis to provide high resolution nanoparticle sizing and compositional analysis at the $\mu\text{g/L}$ concentration level, a detection at least 10–100-fold lower than DLS or FFF-UV techniques. The full benefits are only achieved by utilization of all detector capabilities, such as dynamic reaction cell (DRC) ICP-MS. Such low-level detection and characterization capability is critical to nanomaterial investigations at biologically and environmentally relevant concentrations. The techniques have been modified and applied to characterization of all four elemental constituents of cadmium selenide–zinc sulfide core–shell quantum dots, and silver nanoparticles with gold seed cores. Additionally, sulfide coatings on silver nanoparticles can be detected as a potential means to determine environmental aging of nanoparticles.

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1. Introduction

Nanotechnology offers potential advancements for both industrial and commercial sectors, including useful products either when used alone or when integrated with other materials into larger products (e.g., consumer goods, foods, pesticides, pharmaceuticals, and personal care products, among others). Specifically, it is particularly important to develop improved detection techniques for metal-containing nanoparticles (NPs) since they are the fastest growing category of engineered NPs (ENPs). With the list of applications growing rapidly, the use of nanomaterials could potentially impact environmental systems. In fact, a number of life cycle assessments concluded that a significant amount of metal bearing NPs is likely to enter aquatic systems [1–3]. Despite the rapid progress, use, and probable

release of nanoproducts to the environment, questions remain on the potential toxicological risk to the biome [4,5].

Understanding nanoparticle fate in the environment is difficult, due in part to challenges associated with detecting small amounts in complex environmental and biological matrices. These complex, heterogeneous matrices may confound detection of very low ($\mu\text{g/L}$ or less) levels of engineered nanomaterials. Spectrometry techniques, including a very new method, single particle ICP-MS (SP-ICP-MS), have been applied for the detection of NP determining both concentration and size simultaneously [6–8]. However, the most commonly used detection and characterization methods available to assess particle concentration and size distributions are not adequate for the study of NPs in complex systems or at low concentrations [9]. These include microscopy [10], chromatography [11], centrifugation [12], laser light scattering [13], and filtration [14,15]. One particular analytical challenge is distinguishing engineered nanoparticles from other constituents of the matrix such as natural particles, humic substances, and debris [16]. Perhaps the major problem identified

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with most techniques relates to method sensitivity, which is generally insufficient compared to environmentally and toxicologically relevant concentrations ($\mu\text{g/L}$ to ng/L ranges) [17,18].

One of the most commonly used approaches to study nanoparticles is microscopy, either Transmission Electron Microscopy (TEM) or scanning probe microscopy. Theoretically, microscopy offers the ultimate sensitivity, with the ability to detect/image a single nanoparticle; however, accomplishing this practically is equivalent to the proverbial 'needle in a haystack'. These techniques create images of single particles but their shortcomings include unrepresentative sampling, changes during the preparative process (i.e., agglomeration), and inability to find particles in very dilute samples. Another common approach that has long been used to study colloidal solutions is Dynamic Light Scattering (DLS), which measures the particle hydrodynamic diameter. However, limitations for the study of nanoparticles are numerous including: poor sensitivity at dilute concentrations, nonselective material detection, failure to differentiate between nanoparticles and other matrix components, and the inability to reliably quantify the relative proportions of particle or aggregate sizes in multi-modal distributions. Multi-modal populations are particularly problematic for DLS as intensity-normalized results will characteristically be disproportionately skewed to the larger particles/aggregates in suspension even if smaller sizes predominate. Furthermore, many analytical techniques have difficulty distinguishing organic coatings that may be present on nanoparticles.

Field flow fractionation (FFF) consists of a suite of high resolution sizing techniques which allows separation and sizing of macromolecules, submicron colloids, and nanoparticles of 1–100 nm, depending on the type of field applied and mode of operation [19]. The separation process is similar to chromatography except that it is based on physical forces (e.g., diffusion) as opposed to chemical interactions. Particle separation is preformed in a thin channel with laminar flow under the influence of a perpendicular field. Depending on the type of analysis that is being performed, a different member of the FFF family would be chosen to achieve optimal separation results. The three techniques that are the most commercially available and thus most commonly used include thermal, sedimentation and flow FFF. Applications of FFF have become increasingly diverse in the recent years to include separation and characterization of proteins [20], polymers [21], cells [22], natural nanoparticles [23] and more recently manufactured nanoparticles [24].

Flow FFF (FIFFF) was chosen for this research because it is the most widely used subset of techniques for environmental analysis and is highly versatile for a range of both natural and manufactured NPs. As outlined in Baalousha and Lead [25], the increased use of FIFFF can be related to the wide size range that can be fractionated either of natural colloids (1–1000 nm) or natural and manufactured NP (1–100 nm) [26]. Many FFF techniques, including FIFFF, are also adaptive, allowing the ability to change carrier solutions with respect to pH and ionic strength as to match the carrier solution with sample composition [27], and the possibility of both on-line hyphenation to a wide range of detectors as well as collection of sample fractions for further off-line analysis [25,28–31,8].

UV absorbance is a common non-destructive detector for on-line processes; therefore, FFF–UV hyphenation has been used extensively. However, with the sensitivity limited generally to particle concentrations in the mg/L range, FFF–UV is not suitable for many environmental studies since aggregation behavior may be vastly different at low $\mu\text{g/L}$ levels where the probability of particle-to-particle collisions is lower. Additionally, the UV detector lacks specificity, even when multiple wavelengths are employed. Interfacing FFF with ICP–MS or ICP–AES, however, allows element specific detection at trace concentration levels

[32] when studying metal-containing NP [33]. Several reviews have been published discussing the broad range of environmental [32,34], biological [35,36], and nanoparticle [18,37–39] applications for FFF–ICP–MS [40]. Furthermore, the capability of multi-metal analysis is an added benefit when using these detection techniques.

Though literature is scarce to engineered nano-specific studies, there is a growing potential for the use of FFF in nanotoxicity studies with increasing interest concerning characterization methodology for environmental and biological risk evaluation. Notably, recent studies to characterize quantum dots [41] and NP [42–44] in biological media before and after exposure, as well as environmental samples [28,45,46] have shown promising results when using FFF–ICP–MS and FFF–ICP–AES. The resultant hyphenated techniques of FFF–ICP–MS and FFF–ICP–AES described in the present study provide nanoparticle detection, sizing, and compositional analysis capabilities at the $\mu\text{g/L}$ level for multiple elements present within the nanoparticle, which is critical to environmental and toxicological investigations of nanomaterials [14,40]. We demonstrate the advantages of using dynamic reaction cell ICP–MS and ICP–AES detectors for non-metallic analytes present in nanomaterials in addition to standard ICP–MS in comparison to UV absorbance detection. The methodology developed in the current work expands detection capabilities for multiple components of nanoparticle systems, including core-shell gold–silver nanoparticles, Cd–Se–Zn–S quantum dots, and silver nanoparticles after sulfidation, these methods can be used for more descriptive nanoparticle fate and characterization.

2. Materials and methods

2.1. Reagents and nanoparticles

All nanoparticles were obtained from commercially available sources. Aqueous NanoXact silver nanoparticle suspensions (nominal primary particle sizes of 10, 20, 30, and 60 nm) were purchased from Nanocomposix (San Diego, CA) at 20 mg/L stock concentration stabilized with either citrate or tannic acid. These particles were nearly monodisperse in size as determined by Transmission Electron Microscopy, DLS, and FFF–ICP–MS analyses [42]. Aqueous suspensions of gold nanoparticles were purchased from the National Institute of Standards and Technology (NIST, Standard Reference Materials 8011, 8012, and 8013) at nominal 50 mg/L stock concentrations. These particles were also monodisperse as determined by Atomic Force Microscopy, DLS, and FFF–ICP–MS analyses.

All nanosilver and nanogold stock solutions were diluted in 18.2 $\text{M}\Omega\text{-cm}$ deionized water and used immediately after dilution. UV–vis spectra were obtained for the Ag and Au particles using a Beckman-Coulter DU 800 spectrometer. Cadmium selenide–zinc sulfide core–shell quantum dots (eFluor™605NC carboxyl functionalized) were purchased from eBioscience, Inc. (San Diego, CA) at a reported 10 μM concentration stabilized with DSPEPEG lipid (1,2-distearoyl-sn-glycero-3-phosphoethanolamine-N-[carboxy-(polyethylene glycol)-2000]) and received in 0.1 M borate, 0.3 M NaCl, ~0.01% Sodium Azide at pH 8.3. This stock solution was diluted 1:200 in 18.2 $\text{M}\Omega\text{-cm}$ deionized water for all FFF analyses presented below (which results in cadmium, zinc, selenium, and sulfur concentrations of 7.73, 4.12, 1.72, and 43.9 mg/L , respectively, as determined by ICP–MS and ICP–AES analysis).

2.2. Asymmetrical FFF(AF4) and DLS

AF4–UV and AF4–light scattering analysis was performed to provide a comparison to the use of ICP–MS and ICP–AES detection

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