Analytical chemistry of metallic nanoparticles in natural environments

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The use of metallic nanoparticles (NPs) has exponentially increased in the past decade due to their unique physical and chemical properties at nano-scales [1]. They are added to a myriad of materials and compositions. The key question is not if NPs will enter environmental compartments but rather when. The fate and the stability of NPs in the environment play important roles in determining their environmental distributions and probably control the risk to human health through exposure. Emissions of nanomaterials (NMs) could be intentional or unintentional but occur in particulate, aggregate or embedded states.

Despite environmental transformations and changes in their surrounding environment, metallic NPs (M-NPs) tend to exist as stable colloidal aggregates or dispersions. Characterizing NPs and NMs in environmental samples implies determination of their size, their chemical composition and their bulk concentrations in the matrix. Differential size filtration is the most commonly used method to isolate NPs from aqueous matrices. Micro-filtration, nano-filtration, cross-flow filtration, and ultracentrifugation are usually employed to achieve the highest degree of segregation.

Chemical characterization of NPs and NMs has traditionally been done using transmission/scanning electron microscopy (TEM/SEM) followed by energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). However, because of their intrinsic limitations, methods have also been combined and validated [e.g., size exclusion and ion chromatography (SEC and IC) with multi-element detection {inductively-coupled plasma mass spectrometry and optical emission spectroscopy (ICP-MS and ICP-OES)].

This review describes the current state and the challenges of isolating, segregating and detecting M-NPs in environmental samples. A simple case study shows a common procedure for the analysis of NPs in complex aqueous matrices.

Keywords: Aqueous matrix; Differential size filtration; Environmental fate; Environmental occurrence; Environmental sample; Environmental stability; Metallic nanoparticle; Multi-element detection; Nanomaterial; Nanoparticle analysis

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1. Introduction

The scientific interest in nanoparticles (NPs) or nanomaterials (NMs) mostly derives from the dramatic change in physical and chemical characteristics that substances experience at reduced length scales (~1–100 nM) [2] and their interactions with biotic and abiotic systems [3]. Size, but also other structural features (e.g., pore sizes) and tunable surface characteristics make them unique for both recognition and sensing. In addition, hollow or porous NPs are extremely important because of their capabilities in transporting materials through cellular membranes to protect substances from degradation or unintended interaction

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with non-target sites or simply for their enhancement of properties of common materials.

NMs could be broadly classified as naturally occurring (i.e. carbon black, fullerenes, iron oxides), processed (i.e. titanium, silicon or aluminum oxides) or man-made {e.g., silver NPs (AgNPs), carbon nanotubes, quantum dots, functionalized metallic NPs (M-NPs)}. Most NPs may also be broadly categorized as carbon-based (fullerenes, carbon NMs) or inorganic (mostly based on metals or metal oxides) [4].

Mainly due to their nature, but also because of their novelty, NPs or fabricated NMs are now used in many of the fields of science, ranging from analytical chemistry and medicine to agriculture, the construction industry and electronic fabrication. Although many of these disciplines have employed NMs for substantial periods of time (e.g., semiconductor industries), NPs were quickly brought into the global spotlight with the employment of Nano-Silver (AgNPs) as an antimicrobial in textiles, paints and a number of consumer products [5–8]. This boom in applications of AgNPs also coincides with increased concern for the environmental implications of the unintended release of AgNPs [9].

Due to the increasing use of M-NPs in consumer products and medical applications, a new concern has arisen about their presence in the environment. For example, the US Environmental Protection Agency (EPA) and the European Union are paying attention to the potential study of the fate, transport, and health effects of NPs in the environment. Although NPs are not yet regulated, they are already included in lists of emerging pollutants [10]. Despite that, there are very few reports on the presence and the behavior of NPs in the environment, because of the general lack of analytical methods able to detect and to quantify the rather wide range of NPs and the myriad of functionalities without changing their primary structure [11]. The methods of producing NPs and NMs are as varied as the materials themselves and their interactions with the environment are always complex. To overcome this challenge, analytical methods have to provide characterization of single nano-objects beyond their size and structure to include their chemical composition [12]. For example, in the case of silver, both the NP and ionic forms of silver are responsible of the effects associated with AgNPs, so complete speciation may be required to assess risk [13]. More commonly, only generalized estimations of the potential environmental concentrations of an array of NPs arising from consumer products have been produced through modeling and estimates of production and usage (Table 1) [14–16]. We clearly show that inorganic NPs and NMs have an unusually high contribution to the predicted concentrations, likely to derive from their volume of usage and the nature of industrial applications.

One of the biggest challenges in the analysis of NPs and NMs is that all their dimensions are important. Because of this, the environmental effects of an NP could be associated with its chemical composition, its two-dimensional cross section and its volume. A second challenge is that the fate of NPs in the environment (water column and sediments) as well as their separation from environmental matrices are greatly affected by their aggregation or stability. These phenomena are affected by pH, ionic strength (IS), ionic composition, the presence of natural organic matter (NOM), in particular bio-colloids, and other characteristics of the aqueous media [17]. The physico-chemical properties of NPs, especially their surface area, greatly affect their transport in the environment and their bioavailability [18]. Transport of aggregates can differ extremely from the primary constituent particles and control both fate and speciation [19].

Toxicological effects are also influenced by the composition, the size or the aggregation of NPs. Several groups in the literature clearly pointed to possible negative influences of NMs on the health of aquatic organisms [20,21].

Because of these difficulties, adequate and undisturbed separation of NPs or NMs from environmental matrices is imperative, and wet techniques relying on digestion of the material are no longer considered appropriate [12,22,23].

In summary, the complete characterization of single nano-objects beyond their size or shape is still greatly limited by the capabilities of current analytical technology and, in the best-case scenario, restricted to basic elemental composition. Although engineered NMs could be designed for easy detection, M-NPs and naturally-occurring nano-objects still present detection challenges.

2. Stability of metallic nanoparticles in the environment

The growing production and use of NPs and NMs will inevitably lead to their accumulation in the environment and will probably have major implications for human and environmental health. Exposure is always controlled by environmental fate and transport mechanisms. M-NPs have increasingly been incorporated into a wide range of products due to their potential for catalysis, transport and applications in biological, medical and material sciences [4].

Furthermore, the fate of commercial NPs in aqueous environments depends on their physical and chemical properties (e.g., surface characteristics and sizes) and other chemical species in water [24].

The partitioning of NMs into various environmental phases has been widely studied according to their mobility, their biodegradation and their persistence, among other factors. Even the most basic information concerning the behavior and the potential toxicity of