



Analytical strategies to the determination of metal-containing nanoparticles in environmental waters



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ABSTRACT

Metal-containing nanoparticles (MNPs) represent emerging pollutants that still pose analytical challenges for their determination in environmentally relevant samples, including extremely low MNPs' concentrations, high colloidal background and the need to perform speciation analysis. Complementary to traditional state-of-the-art techniques evaluated elsewhere, this review additionally evaluates less conventional approaches for sample pretreatment, preconcentration, on- and offline detection, size characterisation and quantification of MNPs in environmental samples.

Preconcentration techniques, like cloud point extraction and solid phase extraction, provide high preconcentration factors and recoveries. Electrothermal atomic absorption spectrometry opens interesting perspectives in the still unresolved distinction between dissolved ions and nanoparticles. Combination of single particle ICP-MS with size fractionation techniques, like hydrodynamic chromatography or electrospray-differential mobility analysis, is highly promising for assessment of shape and structure-related information of MNPs and their aggregates. Although highly relevant, the validation and production of reference materials and quantitative criteria on measurement certainty still require further development.

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Abbreviations: AAS, atomic absorption spectrometry; AF4, asymmetric flow field flow fractionation; AFS, atomic fluorescence spectrometry; AUC, analytical ultracentrifugation; CE, capillary electrophoresis; CHDC, capillary hydrodynamic chromatography; CPE, cloud point extraction; CRM, certified reference material; DLS, dynamic light scattering; DMA, differential mobility analysis; ERM, European reference material; ES, electrospray; ESI, electrospray ionisation; ETAAS, electrothermal atomic absorption spectrometry; FFF, field flow fractionation; FI, flow injection; GE, gel electrophoresis; HDC, hydrodynamic chromatography; HPLC, high performance liquid chromatography; ICP, inductively coupled plasma; LPE, liquid phase extraction; MALS, multi-angle light scattering; MNP, metal-containing nanoparticle; MS, mass spectrometry; NIP, nanoparticle-imprinted polymer; NIST, national institute of standards and technology; NOM, natural organic matter; NP, nanoparticle; PGM, platinum group metal; PVP, polyvinylpyrrolidone; RM, reference material; SdFFF, sedimentation field flow fractionation; SEC, size exclusion chromatography; SP, single particle; SPE, solid phase extraction; SPR, surface plasmon resonance; TEM, transmission electron microscopy; TXRF, total reflection x-ray fluorescence analysis; UC, ultracentrifugation; UV, ultra violet.

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1. Introduction

Nanoparticles (NPs) are defined as objects with three dimensions in the nano-scale, *i.e.* ranging from 1 to 100 nm [1]. Generally, NPs can be of natural origin (*e.g.* nanoclays), unintentionally formed (*e.g.* soot), or produced and specifically engineered to provide particular nano-size/shape related features [2]. These engineered NPs show unique properties and are used widely in commercial products nowadays. Most common NPs and their application fields have been summarised *e.g.* by López-Serrano et al. [3] in a recent review. In March 2015 the consumer products inventory *nanotechproject* listed 1,814 products containing nanomaterials [4]. Amongst these engineered NPs, the group of metal-containing nanoparticles (MNPs), *i.e.* NPs consisting of a zero-valent metal, (semi-)metal oxide, metal sulphide or other metal compound core, amounts to the largest portion [5]. The application of MNPs covers a broad variety of fields including consumer products, medicine, industry, and research.

A very common representative of MNPs are TiO₂ NPs. These are extensively used in the fabrication of paints and dye as well as in cosmetic industry, namely for UV-blocking sunscreen [2,3]. Moreover, construction industry uses layers of photo-catalytic TiO₂ NPs as antifouling agent [6,7]. A future field of application of TiO₂ NPs is the “*intelligent food packaging*” [8]. If considering pyrogenic silica, which has been produced since 1943 as “*Aerosil*” [9], as engineered SiO₂ NPs with silicon being a semi-metal, its application is vast in construction, pharmaceutical, and food industry [6,10]. Further metal oxide NPs, such as cerium, copper or iron oxide NPs, are applied in energy industry, as catalysts, or in sensing applications in biomedicine [3,5].

The group of engineered zero-valent MNPs comprises the noble metals – gold (Au), silver (Ag), platinum group metals (PGMs) and iron (Fe). Ag is produced in nanoparticulate form since the late 19th century [11] and Ag NPs are nowadays enclosed in about 24% of all listed nanomaterial-containing products [4]. They are added to textiles and coatings because of their unique antimicrobial effects [5,12]. The application of Au NPs is inspired by a variety of unique features, such as optical, thermal, and catalytic properties as well as their chemical inertness and easy surface functionalization. Amongst other applications they are used in medicine as drug carrier, contrast agent or in hypothermic therapeutics [13,14], in analytical separation [15] and atomic spectrometry [16], in optical sensors [17], *etc.*

PGMs are well-known for their excellent catalytic properties and are applied in automotive, pharmaceutical, and chemical industry [18–20] as well as in chemistry research (*e.g.* [21]).

With increasing fields of application and rising production of MNPs, concerns about probable environmental and health risks have arisen [3,22]. In this regard, it is important to identify potential emission sources and study distribution and chemistry of MNPs in the environment. Despite high uncertainties about the future MNPs production and use, some sources were clearly identified [23–26]. For instance, TiO₂ NPs can run off from painted facades during rain events [24] or be dispersed in natural water by swimmers using sunscreens [27] and Ag NPs can be washed out from cloths [28]. Most of the emitted MNPs are expected to attach to biosolids during waste water treatment [29–32] and therefore, biosolids amendment could also be a source of MNPs in the environment [33]. Intentional releases such as for soil remediation purposes (*e.g.* with Fe⁽⁰⁾ NPs) and acute release due to industrial accidents are also expected in the future [34,35]. Efforts to model NPs fate in environmental compartments resulted in several preliminary estimations of their

concentrations in various environmental compartments [23,26]. For instance, typical concentrations are expected to range from 10 mg kg⁻¹ of TiO₂ and 0.1 µg kg⁻¹ of Ag⁽⁰⁾ in sediment and from 2 ng L⁻¹ of TiO₂ and 0.01 ng L⁻¹ of ZnO in surface waters [23].

The largest amount of MNPs is predicted to be released into the wastewater and to sediment due to homo- or hetero-agglomeration [23]. However, both agglomeration and disagglomeration of MNPs in natural waters is subject to variations in ionic strength, pH, type of cations, temperature, concentration and type of organic matter and natural colloids (clays, iron oxides, organic colloids, *etc.*) [36–39]. Furthermore, MNPs' coating is in often replaced or over-coated by natural organic matter resulting in new surface properties [37]. In addition, MNPs can be reactive towards natural components of water and, therefore, undergo chemical transformations, in particular oxidation, sulfidation, and dissolution [24,40]. This high diversity of physico-chemical processes, triggering the fate of NPs in environmental samples, is one of the most challenging aspects in the development of dedicated analytical methods.

2. Analytical strategies for metallic NPs determination

2.1. General aspects

Providing suitable analytical procedures for a reliable study of fate and pathways of MNPs in the environment is a prerequisite to assess potential risks for environmental and human health arising from nanomaterial production, application and disposal. Particularly, quantitative analysis is necessary in order to characterize the flux of MNPs from emission sources to environmental compartments and their possible entry into biota. Depending on the measurement method, quantification can be either mass-based, volume-based or particle number-based. Qualitative analysis of the NPs should reveal their chemical composition and thereby provide in most cases also discrimination between engineered and natural NPs. The determination of the particle size distribution is also highly important for data interpretation. At least distinguishing MNPs from dissolved species of the same metal, *i.e.* free ions, complexes, or compounds is required (which is further referred to as ‘speciation’). Other relevant parameters of high relevance are particle shape, surface area, surface charge, surface functionality, nature, stability, and structure of coating, *etc.* A variety of different analytical techniques is required in order to determine those numerous metrics. These techniques can be sorted into five main categories:

- Quantitative techniques providing mass- or particle number-based concentrations;
- Qualitative techniques revealing chemical composition;
- Characterisation techniques of particle sizes (distribution, fractionation or speciation);
- Visualisation techniques for identification of (individual) NPs' size, shape, *etc.*;
- Surface characterisation techniques to determine surface area, charge, coating, *etc.*

Visualisation and surface characterisation techniques for NPs have been comprehensively reviewed by several other authors [41–44] and, therefore, are not included here. In this review we have focused on the first three categories, *i.e.* on analytical strategies that provide information on MNPs concentration, composition, and/or speciation and on fractionation techniques. Figure 1 describes the general analytical procedure, starting with sample pretreatment, followed

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