

Electrophoretic methods for the analysis of nanoparticles

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With the development of nanotechnology, there is a need for methodologies to determine and characterize nanomaterials. Electrophoresis has emerged as a useful tool, which has been employed in various formats (e.g., capillary-zone electrophoresis, gel electrophoresis or isotachopheresis) for the size- or shape-based separation of different types of nanoparticle (NP) (e.g., metallic, semi-metallic or carbon). This article reviews the main progress in electrophoresis techniques in order to achieve separation of NPs.

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1. Introduction

Nanotechnology is a growing area that attracts much attention due to the excellent properties of nanomaterials. Thanks to their potential, nanoparticles (NPs) – which are said to be particles that have at least one dimension in the nanoscale (~1–100 nm) – attract widespread attention in many scientific fields.

The sizes and the shapes of NPs are important factors that determine their physical and chemical properties. The difficulty in generating the desired size, shape, and monodispersity of NPs creates the need for new, refined techniques for synthesizing them. Synthesis of NPs is an active area of research, increasing their uses, with the potential for great advances in everyday life due to nanotechnology.

In addition, new tools are required for characterizing NPs [1]. Electron microscopy is one of the tools employed most in characterizing the size distribution of NPs. Transmission electron microscopy (TEM) suffers from the drawback of needing a lot of time for each analysis in order to assure sample representativeness. And, one of the most important shortcomings to be resolved in sample preparation is the aggregation of the NPs, which makes it difficult to analyze individual NPs. Moreover, there is statistical uncertainty because of the human subjectivity implied when deciding which parts of the grid are photographed.

To separate free from functionalized NPs, the use of size-exclusion chromatography (SEC) has been proposed. SEC has the advantages of being faster or coupling to optical spectroscopy, but there may be irreversible adsorption onto the stationary phase in some cases.

High-performance liquid chromatography (HPLC) have been also used in combination with TEM, although the resolution is not high enough [2].

For these reasons, from the diverse techniques employed for NP characterization, capillary electrophoresis (CE) has emerged as useful, potentially faster than electron microscopy, with fewer surface effects than in other techniques (e.g., SEC). Another advantage of CE is low consumption of sample and reagents.

CE has been used to separate a variety of differently sized materials, including inorganic oxide [3], latex [4], polystyrene [5], gold [6] and silver [7] NPs, carbon nanotubes (CNTs) [8], quantum dots (QDs) [9], etc. Capillary-zone electrophoresis (CZE) is easily applicable for the investigation of NPs due to their surface charges, which form electrical double layers, so their separation behavior is similar to that of charged molecular species in CZE. In other circumstances, when the electrical double layer is not enough to stabilize the NPs in the electrophoretic system, covalent functionalization is required. This strategy is useful if the covalent bond does not affect to the core of the NP.

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Gel electrophoresis has been extensively used in separating biological targets (e.g., DNA and proteins) with a remarkable resolution. This tool has gained exposure since it was employed for separation of nanomaterials [10,11]. However, several reasons may hinder use of polyacrylamide gel in preparative electrophoresis (e.g., pore size, which is typically $\sim 3\text{--}5$ nm or the heterogeneity in pore sizes). Preparative electrophoresis using agarose gels of $\sim 100\text{-nm}$ pore size has proved to separate gold NPs (AuNPs) based on size and shape.

Isoelectric focusing (IEF) is commonly employed to determine the isoelectric point of proteins and enzymes. Proteins move under the influence of an electric field in a pH gradient and come to rest at the isoelectric point. Colloid metal and semiconductor particles of different sizes derivatized with carboxylic groups can be rapidly separated from their mixtures in a home-made miniscale IEF unit [12]. The method is fast, inexpensive and highly sensitive. It shows potential for future modification and development in improving the monodispersity of colloidal particles.

This article is a general overview on determination and analysis of NPs by CE, focusing on the different strategies carried out in order to facilitate the determination of NPs of different sorts. Recently, several overviews have given theoretical descriptions of the physical mechanism involved in the electrophoretic transport of NPs and colloids [13–16]. We structure the article according to the target analyte, which may be the NP itself or a derivative of the NP. To improve electrophoretic resolution, there have been different approaches (e.g., functionalization of NPs, and use of gels or surfactants). In order to present a systematic view of strategies for solubilization and methodologies used to enhance resolution, this overview has been classified according to the nature of the NP. To be resolved by CE, NPs must be soluble, charged and stable in the background electrolyte (BGE) under the electrophoretic conditions.

2. Separation of nanoparticles by capillary electrophoresis

In this section, we describe the electrophoretic methodologies developed for the separation of NPs originally uncharged. Although strategies used to solubilize and separate NPs are similar, in our opinion, a classification according to the nature of the NP helps readers to have a general overview of the strategies, which can involve the solubilization, the detector or the electrophoretic separation.

2.1. Noble-metal nanoparticles

Metallic NPs (MNPs) display fascinating properties quite different from those of individual atoms, surfaces or bulk materials. For example, AuNPs have a characteristic red

color, while silver nanospheres are yellow. This color is due to the collective oscillation of the electrons in the conduction band, known as the surface-plasmon oscillation, whose frequency is usually in the visible region for gold and silver, giving rise to the strong surface-plasmon resonance (SPR) absorption. This property allows the determination of these NPs with UV/Vis detection. In this way, we need to take into account that characteristic absorption spectra are susceptible to be changed by the interaction of NPs with ligands. It means that the components of the BGE can change the color of the NPs. The change is normally a decrease of absorption. As a result, the UV/Vis detector has low sensitivity.

To be separated, MNPs must present a stable charge in the electrophoretic system. The charge can be the result of a colloidal stabilization with a ligand or the introduction of charged organic groups (e.g., through formation of thiol derivatives). AuNPs are normally synthesized by reduction of gold with citrate. As a result, a colloidal AuNP is obtained that arises from the sorption of citrate ions onto the NP surface during the preparation process that leads to the formation of an electric double layer, whose potential stabilizes NPs, preventing agglomeration and avoiding adsorptive interactions with the capillary wall when it is negatively charged.

Schnabel et al. [6] characterized colloidal AuNPs according to size by CZE using acetate buffer at pH 5.0 without any sieving additive. As they observed relatively broad peaks caused by the dispersion of the samples, a marker was introduced in order to simultaneously measure the electroosmotic flow (EOF) mobility and reduce possible bias of the colloid particle mobility data. They found a reduction of the ionic mobilities with decreasing ionic strength due to the increase of the thickness of the double layer affecting smaller particles more. Although the dependence on particle radius is complex, they demonstrated that electrophoretic properties can serve as a measure for size-based characterization.

Another strategy involves chemical functionalization of the MNPs. This can be a covalent bond or a hydrophobic interaction (e.g., with surfactant). For example, separation of MNPs by incorporating carboxylic groups was proposed using self-assembled bifunctional surfactant molecules. In this way, Gole et al. [12] developed a method for isolating MNPs (gold and silver) according to size by using a miniscale IEF technique. The pH at which the ionization of carboxylic groups begins is a strong function of the surface curvature of the colloidal particles, and, because it critically affects the number of surfactant molecules surrounding the NP, this property can be used to separate mixtures of colloidal particles according to their sizes.

Surfactants have been widely employed as stabilizers for the size-selective preparation of MNPs, since they

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