Sampling and characterization of nanoaerosols in different environments

Celine I.L. Justino, Teresa A. Rocha-Santos, Armando C. Duarte

Efficient sampling and characterization of nanoparticles have been challenging tasks in environmental research due to the limitations of regular analytical techniques (e.g., dynamic light scattering, and nuclear magnetic resonance and UV-Vis spectroscopies) – especially the difficulties in their application to *in situ* and real-time monitoring, which are intrinsically related to the nanometer-size range.

This critical overview aims at characterizing recent instrumental techniques (e.g., hygroscopic tandem-differential mobility analysis, thermal desorption-gas chromatography-mass spectrometry, and time-of-flight secondary ion mass spectrometry) for sampling and characterization of individual nanoaerosols in terms of their general operation principles, analytical parameters, advantages and limitations. We also discuss classification of this instrumentation based on off-line and/or *in situ* methods, and on physical and chemical characterization of nanoaerosols. Further, we summarize recent air-quality studies aimed at understanding the physical and chemical behavior of aerosols in different environments.

Keywords: Aerosol mass spectrometry; Condensation particle counter; Differential mobility analyzer; Epiphaniometer; In situ characterization; Mobility particle sizer; Nanoaerosol; Nanoerosol characterization; Nanoerosol sampling; Off-line characterization

Celine I.L. Justino*, Teresa A. Rocha-Santos, Armando C. Duarte
Department of Chemistry & CESAM, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal
Teresa A. Rocha-Santos
ISEIT/Viseu, Instituto Piaget, Estrada do Alto do Gaio, Galifonge, 3515-776 Lordosa, Viseu, Portugal

*Corresponding author.
Tel.: +351 232910100;
Fax: +351 232910183;
E-mail: celinejustino@ua.pt

1. Introduction

Atmospheric aerosols are dispersions of solid and liquid particles suspended in the air, which can have a major impact on regional and global climate changes due to their influence on Earth's radiation balance. They can also play an important role in human health and atmospheric visibility. The major sources of primary particles in the atmosphere are road traffic, coal combustion, windblown dust, and salts from sea spray. Secondary particles are generated from sulfate and nitrate salts formed by the oxidation of SO_2 and NO_x. Most of these particles, especially those from diesel vehicles, are at the nanoscale size, so they can enter into the alveolar region, with consequent risks for human health. The prefix nano is associated to particles with sizes up to 100 nm, and it is related to the concept of nanotechnology defined by The Royal Society [1] as ''the design, characterization, production and application of structures, devices and systems by controlling shape and size at nanometer scale''. Nanoaerosols [also known as airborne nanoparticles (NPs)] are particles in a gas; consequently, the NPs suspended in a liquid are named colloids or nanohydrosols, and NPs embedded in a matrix are called nanocomposites.

Among the large range of sizes of airborne particles, nanoaerosols are the least studied due to the difficulty of developing instrumentation for efficient sampling and characterization that could lead to representative statistical distributions. Another challenge in the characterization of nanoaerosol analysis relates to their mass. According to Nash et al. [2], a particle of 10 μm can have around 500 pg that can be measured by any mass spectrometer, but, in terms of particles of 10 nm, their mass can drop by nine orders of magnitude, and then their individual molecular identification is beyond the current range of instrumentation.

The small sizes of nanoaerosols, their high chemical reactivity and consequent rapid changes represent the main issues in their chemical characterization. Thus, the development of efficient instrumentation to characterize accurately the variety of

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nanoaerosol properties has become a research priority, since the qualitative and quantitative understanding of physical and chemical properties of nanoaerosols, as well as their temporal and spatial trends in the lower atmosphere are very important parameters that should be taken into account in determining their potential risks to human health and climate change.

Recently, some progress has been made in nanoaerosol science regarding the electrical, optical, and/or magnetic properties of nanoaerosols that are perceived to be attractive for nanotechnology applications. Over time, emerging instrumentation and analytical improvements, for both sampling and characterization of NPs, have produced data with better sensitivity and greater time resolution. Continual progress has also been made to ensure that characterization is performed within the nanoaerosol environments (*in situ*) in order to collect and to characterize the samples in real-time.

We start with a short discussion about the general characteristics, main sources and formation processes of airborne particles, especially in the nanoscale range, emphasizing their impact on climate and human health, but excluding engineered NPs. The heart of this critical overview is updating the instrumentation for sampling and characterization of nanoaerosols, a challenging task in aerosol science. We also discuss the general operation principles, analytical parameters, advantages and limitations, and classification of this instrumentation based on *in situ* and off-line methods, and on physical and chemical characterization, together with recent air-quality studies in terms of monitoring nanoaerosols in different environments.

2. Types and general characteristics of nanoaerosols

Nanoaerosols, as any other airborne particles, are generally characterized by their number concentration (number of particles per unit volume of air), surface-area concentration (total surface area of particles per unit volume), mass concentration (mass of particles per unit volume), particle-size distribution and chemical composition.

Aerosols exist in four classes, which are related to their processes of formation, and commonly known [3] as the nucleation mode, the Aitken mode, the accumulation mode, and the coarse mode. The nucleation mode includes a distribution of NPs in the range 10–100 nm, which can grow rapidly through processes (e.g., coagulation and/or condensation) and have a very short life (a few seconds to minutes). The nucleation mode includes the Aitken mode, where the majority of NPs have diameters of 25–90 nm. Due to their high surface area, NPs are very reactive, and, by condensing and coagulating, they change in size distribution and composition from primary sources to form larger particles. According to Harrison [4], the surface area of NPs can be 10^2–10^3 times greater than larger particles, at a given mass. The accumulation mode includes particles with a size distribution of 0.1–2 μm; they are unlikely to grow any further and they have a longer atmospheric lifetime than those in the nucleation mode. Finally, the coarse mode includes particles with diameter above 2 μm.

In medical and toxicological terminology, aerosols are classified as ultrafine (up to 100 nm), fine (100–1000 nm) and coarse (>1000 nm) particles, according

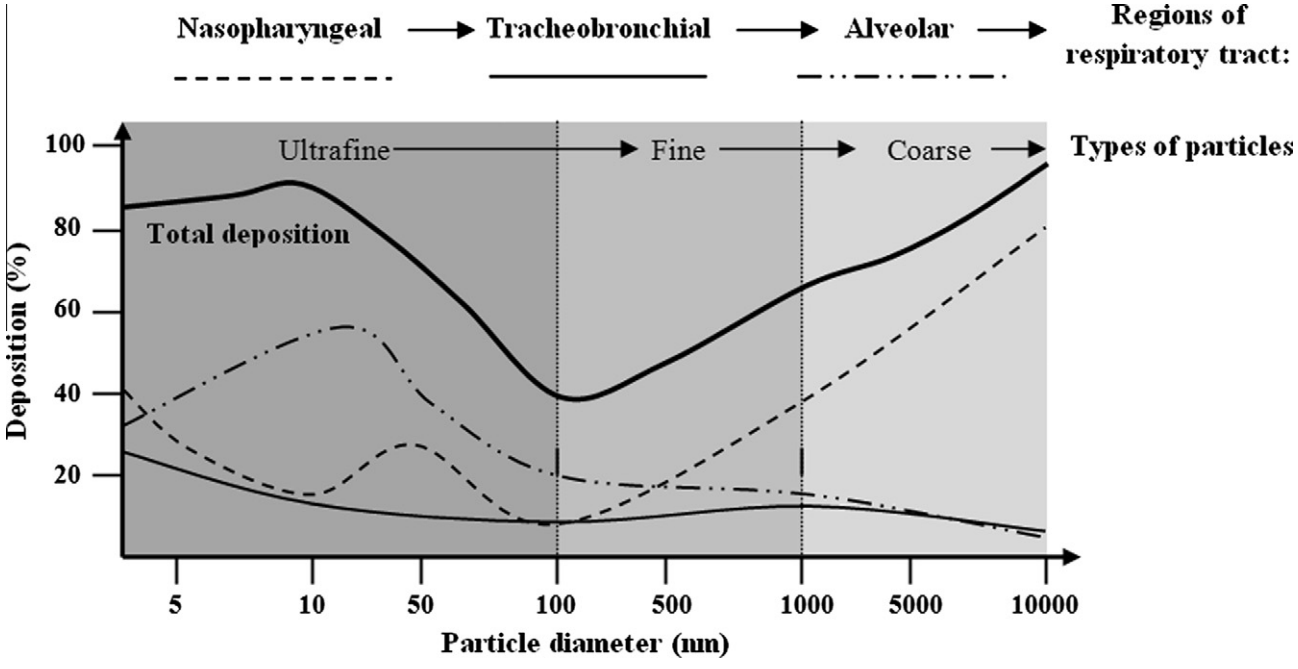

Figure 1. Deposition of aerosols in regions of the human respiratory tract (adapted from [6]).