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# Novel techniques for detection and characterization of nanomaterials based on aerosol science supporting environmental applications

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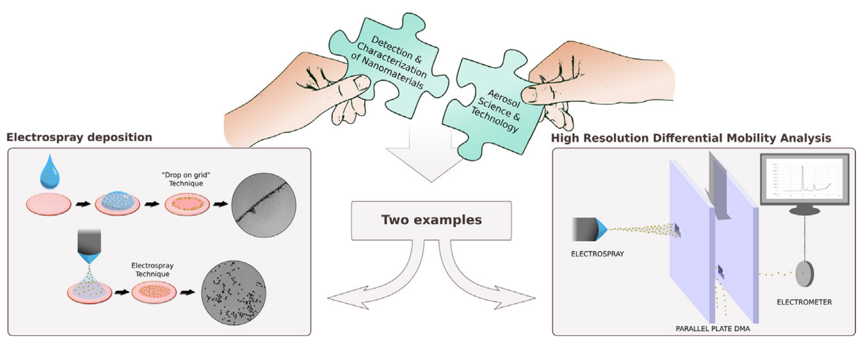
## HIGHLIGHTS

- There is a technology gap for sampling and characterizing engineered nanomaterial.
- Electron microscopy is the most accepted method for characterizing, but it has important shortcomings.
- Electrospray techniques allow avoiding multilayer deposition in sample preparation.
- New DMA developments have led to some promising results regarding size characterization of the smallest nanoparticles.
- Aerosol techniques would fulfil some exposure assessment requirements.

## GRAPHICAL ABSTRACT

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## ABSTRACT

The number of people exposed to nanoparticles is growing accordingly to the production and development of new nanomaterials. Moreover, this increase is expected to continue in the future. However, there is a lack of standardized sampling and metric methods to measure the level of exposure to nanoparticles, and the information related to possible adverse health effects is scarce. Aerosol technology has been detecting and characterizing nanoparticles for decades and some of their developments can be of use in nanotechnology characterization. We present here two current developments based on used principles in aerosol science, which can widen its application to the characterization of nanomaterials. On the one hand, a sample preparation technique for nanoparticle analysis by electron microscopy based on electrospray atomization technology. Several samples prepared in this way have been analysed and compared to more traditional sample preparation strategies like the "drop on grid" method. It was found that the particles deposited by electrospray generally show a much more homogeneous spatial distribution on the substrate and the number of single particles increases substantially. On the other hand, it is presented an electrical mobility classification system, DMA, with enormous possibilities for the quick and economic size characterization of suspensions of nanoparticles, thanks to its injection system by electrospray and to its high resolution in the lower range of the nanoscale. The first assessment of the abovementioned devices highlights its potential applications in exposure assessment and nanotechnological contexts.



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**Abbreviations**

| | |
|---|---|
| CPC | Condensation Particle Counters |
| DMA | Differential Mobility Analyser |
| ENM | engineered nanomaterial |
| EL | electrometer |
| EM | electron microscopy |
| ES | electrospray |
| FWHH | full width at half height |
| HV | high voltage |
| NM | nanomaterial |
| LOD | limit of detection |
| LOQ | limit of quantitation |
| NEAT | Nanoparticle Emission Assessment Technique |
| NF/FF | Near Field/Far Field |
| NFWHM | normalized full with at half maximum |
| NIOSH | National Institute for Occupational Safety and Health |
| NP | nanoparticles |
| OPC | Optical Particle Counters |
| PSD | particle size distribution |
| PM1 | particulate matter particles of diameter <1 μm |
| PM10 | particulate matter particles of diameter <10 μm |
| PM2.5 | particulate matter particles of diameter <2.5 μm |
| SMPS | Scanning Mobility Particle Sizers |
| SAM | Surface Area Monitor |
| TDDABr | tetra-dodecyl ammonium bromide |
| TEM | Transmission Electron Microscopy |
| THABr | tetra-heptyl ammonium bromide |

*Symbols*

| | |
|---|---|
| $B_j$ | flow in the capillary, $m^3 \cdot s^{-1}$ |
| $C_c$ | Cunningham slip correction |
| $C_{THABr}$ | THABr concentration, ppm |
| $D_p$ | diameter of particle, m |
| $E$ | electric field, $V \cdot m^{-1}$ |
| $e$ | elementary charge, C |
| $K$ | electrical conductivity, $S \cdot m^{-1}$ |
| $n$ | number of charges on the particle |
| $P_{cz}$ | pressure at the classification zone, mm Hg |
| $Q_0$ | minimum flow rate, $m^3 \cdot s^{-1}$ |
| $Q_i$ | inlet flow rate, $m^3 \cdot s^{-1}$ |
| $Q_o$ | outlet flow rate, $m^3 \cdot s^{-1}$ |
| $Q_a$ | aerosol flow rate, $m^3 \cdot s^{-1}$ |
| $Q_{sh}$ | DMA sheath flow rate, $m^3 \cdot s^{-1}$ |
| R | resolution of the DMA |
| $T_{cz}$ | temperature at the classification zone, K |
| V | applied voltage, V |
| v | particle velocity, $m \cdot s^{-1}$ |
| $Z_p$ | electrical mobility of the particle or ion, $m^2 \cdot V^{-1} \cdot s^{-1}$ |
| $Z_0$ | reduced electrical mobility, $m^2 \cdot V^{-1} \cdot s^{-1}$ |
| $\Delta x$ | distance from the ion inlet slit to the ion outlet slit, m |
| $\Delta y$ | separation between the electrodes, m |
| $\Delta x$ | width (in the direction perpendicular to the plane) of the DMA classification zone, m |
| $\varepsilon$ | sample permittivity, $F \cdot m^{-1}$ |
| $\varepsilon_0$ | permittivity in vacuum, $F \cdot m^{-1}$ |
| $\gamma$ | surface tension, $N \cdot m^{-1}$ |
| $\eta$ | dynamic viscosity of air, $Pa \cdot s^{-1}$ |
| $\rho$ | density, $kg \cdot m^{-3}$ |

## 1. Introduction

Nanotechnology is considered to be one of the most relevant technologies of the last decades. Both from its economic potential on new or optimised products as well as its capacity to meet new social demands and needs. Nanotechnology includes the study and application of nanomaterials (NMs), understood as "materials with any external dimensions in the nanoscale or having internal structure or surface structure in the nanoscale" than can be used across all the other science fields, such as chemistry, biology, physics, materials science, and engineering. The definition of the terms 'nanotechnology' and 'nanomaterial' has been the subject of a number of discussions in the last 10 years. A recommended, though not legally binding, definition of a 'nanomaterial' has also been provided by the European Commission (2011/696/EU).

When the dimensions of a material become very small its physical and chemical properties can become very different from those of the same material in bulk form (Ray et al., 2009),which confers special properties and characteristics to engineer new products and services, providing an opportunity to explore new possibilities and solutions. New nanotechnology consumer products are coming on the market; however, there are open questions about how the NMs may affect the human health and environment. To solve these questions, a proper risk assessment framework based on validated methodologies, tools, and guidance for monitoring the potential exposure, together with methods for characterizing adverse effects on human health and biota, is urgently needed (Maynard and Aitken, 2016).

Despite the large investments carried out in nanotechnology, corresponding investments in environmental, adverse health effects and safety aspects of this technology have not been as high (Ramachandran et al., 2011). Therefore, little is known about the toxicity and hazards of NMs, and some questions related to the penetration routes into the human body are still unanswered (Klöpffer et al., 2007; Kuempel et al., 2012; Amoabediny et al., 2009).

The potential routes of exposure to NMs for humans include inhalation, dermal and oral (Amoabediny et al., 2009), although inhalation is the most critical pathway during human exposure to a nanostructured aerosol (Cesard et al., 2013; Evans et al., 2013). Larger particles enter the respiratory tract and are deposited in the upper airways, being rapidly removed (Ferron et al., 1993; ICRP, 1994; Schmid et al., 2008; Ferron et al., 2013). Nevertheless, NMs are deposited deep in the lung and can enter from the bloodstreams, being able to be translocated to other organs (Amoabediny et al., 2009; Stephenson et al., 2003; Maynard and Aitken, 2007). Limitations in NM size characterization methods as well as difficulties in sampling are a current scientific challenge (Löndahl et al., 2014; Fissan et al., 2014; Charvet et al., 2014).

These limitations are partly due to the wide size range covered by the term nanomaterial, as well as to the lack of techniques suitable for collecting, measuring, preserving, and storing samples containing NMs (Lin et al., 2010).

As a result of this lack of information, several projects such as NanoREG (FP7-G.A n° 310584), GuideNANO (FP7 – GA n° 60438) and Calibrate (H2020 – G.A. 686239) are currently working in developing frameworks for the safety assessment of NMs. All these projects suggest that risks should be reduced to the lowest reasonably practicable level by taking preventative measures following the principles of the hierarchy of controls (Bergamaschi, 2009; Vinches et al., 2013).

Human exposure to engineered nanomaterials (ENMs) and its release to the environment may in principle occur during any stage of the material's lifecycle, although it is most likely in workplaces, where these materials are produced or handled in large quantities or over long periods of time (Asbach et al., 2017). Many tasks require the manual handling of NMs in dusty form, contributing to the potential release of NPs to the environment (Evans et al., 2013; Gomez et al., 2014). Furthermore, accidental spills, falling powders or transferring processes can also generate airborne NPs (Evans et al., 2013). Therefore, there is a need to evaluate exposure to NMs in order to establish accurate exposure scenarios.

Assessing the human end environmental impact of NPs is not an easy task, due conventional exposure monitoring techniques may not adequately characterize NMs (Abbott and Maynard, 2010). Besides, it involves a multifaceted approach, incorporating many different