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An overview of the characterization of occupational exposure to nanoaerosols in workplaces

Paola Castellano¹, Riccardo Ferrante¹, Roberta Curini¹ and Silvia Canepari²

¹National Institute for Occupational Safety and Prevention, ISPESL, Via Fontana Candida 1, 00040 Monte Porzio Catone (Rome), Italy
²Chemistry Department, University of Rome “La Sapienza”, P.le Aldo Moro 5, 00184 Rome, Italy.

E-mail: paola.castellano@ispesl.it

Abstract. Currently, there is a lack of standardized sampling and metric methods that can be applied to measure the level of exposure to nanosized aerosols. Therefore, any attempt to characterize exposure to nanoparticles (NP) in a workplace must involve a multifaceted approach characterized by different sampling and analytical techniques to measure all relevant characteristics of NP exposure. Furthermore, as NP aerosols are always complex mixtures of multiple origins, sampling and analytical methods need to be improved to selectively evaluate the apportionment from specific sources to the final nanomaterials.

An open question at the world’s level is how to relate specific toxic effects of NP with one or more among several different parameters (such as particle size, mass, composition, surface area, number concentration, aggregation or agglomeration state, water solubility and surface chemistry).

As the evaluation of occupational exposure to NP in workplaces needs dimensional and chemical characterization, the main problem is the choice of the sampling and dimensional separation techniques. Therefore a convenient approach to allow a satisfactory risk assessment could be the contemporary use of different sampling and measuring techniques for particles with known toxicity in selected workplaces.

Despite the lack of specific NP exposure limit values, exposure metrics, appropriate to nanoaerosols, are discussed in the Technical Report ISO/TR 27628:2007 with the aim to enable occupational hygienists to characterize and monitor nanoaerosols in workplaces. Moreover, NIOSH has developed the Document Approaches to Safe Nanotechnology (intended to be an information exchange with NIOSH) in order to address current and future research needs to understanding the potential risks that nanotechnology may have to workers.

1. Introduction

Does exposure to nanoparticles (NP) pose a health risk to workers?

Many searches have demonstrated various specific health risks due to the absorption of NP, but data are still limited and numerous uncertainties remain. A number of studies are already available from the literature [1] on the toxicological properties of NP and on the risk associated to their exposure, but yet a classification of NP based on their relative level of risk for living species and the environment is far from being reached.
Different hazardous and toxic effects have been documented particularly in animals and have evidenced that some kinds of NP can pass through the various protective barriers of living organisms: the inhaled NP can end up in the bloodstream after passing through all the respiratory or gastrointestinal protective mechanisms and then are distributed in various organs and accumulated at specific sites. Few studies have also evidenced that NP can travel along the olfactory nerves and penetrate directly into the brain and in the various protective barriers of living organisms, inducing morphological changes in cells. Citotoxic, nephrotoxic, genotoxic effects and disturbs on the reproduction have been identified from studies in vitro and NP of different composition have been reported to cause granulomas, fibrosis and tumoral reactions in lungs.

However, in general the toxicological data specific to NP are insufficient due to the small number of studies, the short period of exposure, the different composition of NP tested and, in particular, the often unusual exposure routes in workplaces. Therefore additional researches (on absorption, translocation to other tissues or organs, biopersistence, carcinogenicity etc.) must be performed to assess the risk associated with inhalation and dermal exposure of workers to NP.

Aerosol exposure has been generally characterized by the mass concentration of airborne material usually associated with specific size ranges corresponding to different deposition regions in the respiratory system. So, in recognition of the potential importance of particle size, the term “ultrafine aerosol” refers to particles smaller than 100 nm in diameter and it is widely used to individuate incidental aerosols where there are potential particle size-dependent health effects.

As NP are developed in research laboratories and produced in industrial plants, the terms “engineered NP” and “engineered nanoaerosols” are used loosely to describe particles and aerosols associated with engineered nanometre-structured purposely generated particles with nanometre diameters or nanoscale structures [2]. For clarity in this work the term “NP” will be used to describe all aerosol particles with diameter smaller than approximately 100 nm with a potential inhalation health hazard.

Another special feature of NP is that their toxicity is probably linked also to the surface beside the product’s mass: NP are so tiny that small quantities could have major toxic effects due to their large surface. But, in addition, we have also to consider all the NP’s chemical-physical characteristics, such as the morphologic structure, which can be contribute to cause potential health effects.

Currently, there is a lack of standardized sampling and metric methods that can be applied to measure the level of exposure to nanosized aerosols and there are no specific data related to the measurements of NP concerning occupational exposure levels in workplaces. For this reason it is necessary to establish a structured approach dealing with hazard NP identification, exposure characterization, risk assessment and management with the objective of a standardisation and implementation of a prevention program to follow up and to refine through iterative approach as new data become available in this kind of studies. In particular must be considered which steps have to be done to protect the health of the identified workers exposed to NP, beginning from the characterization of nanoaerosols and from the consequent appropriate measurements of them in workplaces, in order to provide best safety and health practices to protect workers and the environment.

2. Approach to evaluation of the professional exposure to NP and nanoaerosols
The evaluation of occupational exposure to NP in workplaces needs dimensional and chemical characterization. Therefore, any attempt to characterize exposure to NP in a workplace must involve a multifaceted approach, including different sampling and analytical techniques for measuring all relevant characteristics of nanoparticle exposure. Furthermore, as NP aerosols are always complex mixtures of multiple origins, sampling and analytical methods need to be improved to selectively evaluate the portion from specific sources to the final nanomaterials.

An open question at the world’s level is how to relate specific toxic effects of NP with one or more among several different parameters, such as particle size and mass, composition, surface area, number concentration, aggregation or agglomeration state, water solubility and surface chemistry. In fact, for NP, a major difference from the usual situations exists, since their potential toxicity can not be
exclusively linked only to their mass. The evaluation of occupational exposure to NP in workplaces needs dimensional and chemical characterization. The main problem is linked to choice of the sampling and dimensional separation techniques. The EU Scientific Committee on Emerging and Newly Identified Health Risks [3] (which was requested to answer the question about the appropriateness of existing methodologies to assess the potential risks associated with engineered and adventitious products of nanotechnologies) has produced in 2006 and 2007 two documents suggesting that there is insufficient knowledge and data concerning nanoparticle characterisation, detection and measurement, to allow a satisfactory risk assessment. A convenient approach to improve the knowledge on NP, including all health, physical and chemical aspects, could be the contemporary use of different sampling and measuring techniques for particles with known toxicity in selected workplaces.

Exposure metrics appropriate to nanoaerosols are discussed in ISO/TR 27628:2007 [2], a Technical Report with the principal aim to provide the necessary background information and sampling guidelines to enable occupational hygienists to characterize and monitor nanoaerosol exposure in the workplaces before the specific exposure limits and standards are developed and implemented. Furthermore, to ensure worker protection as nanotechnology develops, the Document Approaches to Safe Nanotechnology [4] represents an information exchange with NIOSH in order to raise potential safety and health concerns from exposure to nanomaterials in the workplaces.

3. Characterization of the professional exposure to NP and nanoaerosols: environmental and analysis methodologies in workplaces

In this work we want to underline how the efforts in this field must be focused in increasing the present knowledge of crucial aspects of NP-related health risks and in providing valuable new tools for evaluating the professional exposure. In particular these objectives will be reached by:

1. developing new sampling procedures, selective for specific classes of particles (hydrophilic or hydrophobic, soluble or insoluble, agglomerated or aggregated);
2. studying aggregation and agglomeration dynamics and their relations with chemical composition and surface chemistry of NP;
3. applying suitable method of statistical analysis for source apportionment from bulk analytical data;
4. developing a standardized protocol for the evaluation of professional exposure;
5. individuating best practices for working with NP following a precautionary approach in order to minimize possible adverse outcomes, until the studies establish threshold limit values for NP or aggregate/agglomerate of NP that will not pose undue risk.

The effects on health of NP are related to their chemical and physical characteristics, whose evaluation requires use of different advanced sampling and analytical tools. An advanced particle characterization by an integrated approach is needed to understand the chemical-physical nature of particles, which involves chemical, morphological, dimensional and surface chemistry information. Surface extension and reactivity have been demonstrated to be the primary characteristic in determining NP interaction with cell barriers. Conventional surface analysis techniques, like BET (Brunauer, Emmett and Teller method) or epiphaniometer, give information not sufficiently detailed: advanced non-conventional spectroscopic techniques are needed for a full description of surface reactivity. This can help in understanding the strong inter-correlation among the different characteristics which address the interaction of NP among themselves, by accumulation, agglomeration and aggregation dynamics, and with the environment. The comprehension of accumulation, agglomeration and aggregation processes is the main objective, as they have a fundamental role in metrology. By now, there is not information about the possible differences in toxicity between aggregates/agglomerates and single NP, but when NP aggregates to ultrafine particles, the change of the dimensional distribution causes important artefacts in the measurements. In fact, all the measurements and sampling devices for NP are based on a dimensional fractionation which is sensible to the overall dimension.
Sufficiently detailed characterization is available only for exposure from production and manipulation of engineered nanomaterials, but NP are ubiquitous in many workplaces as they are produced from particular emission’s sources (such as hot processes, combustion, office machinery, cleaning fluids, mechanical processes, flame-based powder generation, material handling etc.) or can come by infiltration of outside air. In these cases, the identification and evaluation of the single sources is of primary importance, as differently produced particles are characterized by different toxicity. The available measurements systems are not able to distinguish the contribution from different sources: furthermore source apportionment may be obtained by the application of proper statistical analysis of bulk chemical analysis data, but the comparability of the results requires a harmonized approach.

The development of appropriate sampling and measurement procedures, selective to particular classes of particles (hydrophilic and hydrophobic, water-soluble or insoluble), would be then a relevant improvement in the risk evaluation.

For this reason it is necessary to develop a multifaceted protocol for the NP measurements and characterization in workplaces, in order to improve the evaluation of the professional exposure, by means of a full characterization of particles from a selected workplace, used to set up the methodological approach [5, 6]. The comprehension of relationship among morphological, chemical and dimensional characteristics and surface reactivity and the optimization of a measurement procedure able to distinguish among some chemical classes of particles will contribute, beside a proper statistical source apportionment tool based on bulk chemical analysis, to the identification of the main parameters which will need to be evaluated in routine NP monitoring activities.

4. Analytical procedure
The study design for developing the analytical procedure must start, after the selection of properly representative workplaces for the detailed study of particle characteristics, from parallel samplings with devices based on different physical principles and with different time resolution for the evaluation of the specific responses towards the same particle mixture. The following step must consist in the collection of dimensionally segregated samples (properly dimensioned considering the analytical techniques performances) and their preparation for bulk, morphological and surface analysis. In particular, for the acquisition of data based on particle dimensional distribution, also considering its time evolution must be used multistage cascade impactors and optical counters and, in order to evaluate NP number concentration, application of condensation particle counters (CPC) must be considered.

For the bulk analysis, used to evaluate organic and inorganic components expected in selected workplaces, different advanced hyphenated analytical techniques such as High Performance Liquid Chromatography (HPLC) interfaced with various detectors as Mass Spectrometer (HPLC-MS) and Diode Array Detector (HPLC-DAD), Gaschromatography - Mass Spectrometer (GC-MS) and Inductively Coupled Plasma – Mass Spectrometer (ICP-MS), are available. In addition electron microscopy analysis provides a wide range of qualitative and quantitative analysis methods that are suited for a morphological characterization of individual collected nanoaerosol: characteristic X-ray generated through atomic electron excitation and decay are routinely used in Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) analysis to detect elemental components through Energy Dispersive X-ray (EDX). The surface chemical composition and electronic structure are usually studied by application of conventional and advanced spectro/nanoscopic tools as PhotoElectron Emission Microscopy (PEEM), X-ray-photoemission-spectroscopy (XPS) and Ultraviolet Photoelectron Spectroscopy (UPS).

Finally, the evaluation of all the obtained results, performed with particular attention to the interrelations among measured physical-chemical properties, supported by the source apportionment approach, could contribute in the identification of ultrafine particles emission’s sources in workplaces and could help in the individuation of the more representative measurements which are needed for the exposure assessment.
Conclusions
The standardization of methodological approach in collecting and analyzing the composition regarding NP represent a useful tool for the evaluation of professional exposure. An improvement of the guidelines by now available (i.e. NIOSH - Approaches to safe nanotechnologies [4]) can be obtained only through an advanced and full characterization of particles, which allows the knowledge of the fundamental basis of the interaction with cells and environment. This approach has been attempted in the last years only for the exposure to some engineered nanomaterials, but the knowledge is poor about non-intentionally generated NP, despite of the number of exposed workers.

The approach protocol we have presented in this work, suitable in specific workplaces in which different non-intentional sources are expected, can be considered as a preliminary basis for settling specific Italian guidelines concerning evaluation of professional exposure to NP in workplaces. Furthermore, the identification of some of the main parameters which must be evaluated in routine NP monitoring activities, will furnish innovative opportunities for the development of new efficient Personal Protective Equipment (PPE) (gloves, respiratory protections, clothing etc.) and engineering controls (ventilation systems, fume hoods, etc.) and will allow to optimize all the procedural controls by means of appropriate working practices in workplaces characterized by NP exposures.

In this context it is also important to underline that for establishing threshold limit values for NP, exposure should be considered whether the biological impact of discrete NP depositing within the respiratory system is distinct from, or similar to, the impact of large agglomerates or aggregates of NP containing the same volume of material.

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