
NANOTRANSPORT-Project



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NANOTRANSPORT

The Behaviour of Aerosols Released to Ambient Air from Nanoparticle Manufacturing
- A Pre-normative Study

Recommendations to the European Commission

- Transport of Nanoparticles in the Workplace Environment and its Effects on
the Size Spectrum

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Transport of nanoparticle aerosols in the workplace environment, its effects on the size spectrum, and consequences for hazard evaluation strategies

This document summarizes the principal conclusions from the experimental part of the NANOTRANSPORT study and derives recommendations to the European Commission regarding

- Characteristics of suitable test aerosols for nano-toxicological studies,
- Testing of filters and protective equipment in the workplace,
- Assessment strategies for ENP aerosols in the workplace,
- Knowledge deficits and research priorities.

The recommendations are constrained by the scope of the project, and in particular the exclusion of other ways of exposure than inhalation; thus only airborne engineered nanoparticles (“nano-aerosols”) were investigated, and only particles of fairly isometric shape (i.e. not nano-fibers or CNTs).

The study focuses on the evolution of “particle size“ and “concentration“ with time spent in the aerosol phase („history“) between source and receptor (defined as the entrance to the human respiratory system), and its strategic implications for measurement, testing, abatement, and hazard evaluation.

This time is determined by distance as well as magnitude and direction of air currents in a given workplace environment. These will be highly location specific. Therefore, the subject is discussed in terms of scenarios.

The study concentrates only on the aspect of ENP number concentration vs. size as a key metric describing the evolution of the aerosol, particle number being the primary descriptor for aerosol dynamics. Other metrics such as aerosol mass and surface area distribution are undoubtedly important for the correlation of particle concentration with toxicological effects. However, changes in these metrics due to the aerosol evolution can be derived from the changes occurring in particle number distribution.

Key results

The experimental results, together with our general knowledge background of aerosol science, lead to a number of key conclusions regarding the evolution on nano-aerosols with time. Nano-aerosols emitted from an ENP source evolve considerably with time, both due to auto-agglomeration and/or due to attachment to pre-existing background aerosol particles. Which one of these two mechanisms will prevail depends on the given workplace scenario (i.e. the strength of a primary ENP source relative to background concentration, and the elapsed time during transport from source to receptor). For simplicity and without limiting the conclusions, we disregard the attachment of ENP to macroscopic surfaces such as “walls” or workbenches.

There is no workplace without an ambient background aerosol: concentrations are typically reported in the range of 10^3 to less than 10^5 particles per cm^3 ; sizes are in the range of about 0.1 – 1 μm . Coarser aerosol particles may exist, but their concentrations are typically too low to act as effective scavengers.

Aerosol dynamic processes are driven largely by concentration, with size (or size differences) being a relatively minor factor. If the source strength is high compared to the typical background concentration, then auto-agglomeration will initially dominate the evolution of size and concentration, forming a significant new population of agglomerates ENP. If source and background are comparable in concentration, then both mechanisms are likely to run concurrently, producing both agglomerates of ENP and mixed particles; if the source is relatively weak, the scavenging will prevail.

Both mechanisms cause the average particle size to increase significantly on a time scale ranging from minutes to about an hour, while the number concentration decreases, first rapidly and with decreasing concentration more slowly. The auto-agglomeration process stabilizes typically in the 100-200 nm size range, where collision processes slow down. On the other hand, the attachment of small ENP to background aerosol particles leaves the size of the latter practically unchanged. The scavenged ENP therefore merge into the ambient aerosol between about 0.1 and 1 μ m. The attachment of ENP to pre-existing background aerosols as well as auto-agglomeration thus lead to the physical/chemical presence of nanoparticles in size classes well above the one in which they were originally produced and emitted.

The aerosol agglomeration and/or attachment process is driven predominantly by thermal ("Brownian") collisions. Hence the adhesion forces within the agglomerates will be mostly of the van der Waals type and thus fairly weak. (Adhesion within an agglomerate may be enhanced by adsorption of water vapor; however this should not affect its behavior once it becomes immersed into cellular fluid.)

Filtration of nanometer sized aerosol particles can be done with high efficiency using state of the art filter media. The effectiveness of filters for NP increases continually down to sizes on the order of 1-2 nm. However, the shift of nanoparticles to larger size classes by the two above-mentioned mechanisms may transfer them into the size range where filters are least efficient, the most penetrating particle size (MPPS), typically in the range of about 80-200 nm.

Suitable test aerosols for nano-toxicology studies

Based on the results of the study, two scenarios must be considered in emulating exposure to NP in the workplace. In one limit, the receptor is located immediately at the source of a NP aerosol (the nose near the "leak", so to speak); in the other, the receptor is located further away (e.g. a person working elsewhere in the lab). Scenario 1 requires testing with primary, un-agglomerated NP, while Scenario 2 requires aged aerosols, either auto-agglomerated or adhering to neutral particles, or both. Scenario 2 may well be the more prevalent case for many exposure situations. Studying the deposition and effects of "aged" nano-aerosols is thus at least as important as those of un-agglomerated particles from a primary ENP source.

A point of clarification with regard to the above mentioned scenarios: the range within which a receptor will likely be exposed to predominantly un-agglomerated NP (the "near-field exposure" radius) can be expressed in terms of the average distance traveled by the aerosol during the time required for the primary aerosol to become significantly agglomerated. The "near-field" exposure radius is thus a function of the primary emitted concentration (hence the agglomeration rate) as well as air velocity. Analogous considerations apply to the far-field exposure scenario.

For either scenario it becomes critical to control the state of agglomeration of the particles at the receptor: either as little agglomeration as possible, or a significant but defined state of agglomeration with corresponding, well defined structural characteristics of the aged particles.

The state of agglomeration matters of course for exposure assessment studies, because deposition is governed by aerosol particle size. However a well controlled state of particle agglomeration is also important for toxicological studies, considering our current, rather limited knowledge about the toxicological effects of the agglomeration state of NP, their potential for deagglomeration in cellular environments, or how the structure of the airborne agglomerate carries over into the liquid state.

Liquid NP suspensions or pre-prepared powders are generally difficult to aerosolize with controlled particle sizes. Particle structures and agglomerate strengths obtained

via redispersion are generally not representative of those formed in the aerosol state, except in cases where NP redispersion is the release mechanism to be investigated.

For exposure and toxicology studies it is therefore recommended to produce and age NP directly via on-line aerosol processes, including aging the presence of a relevant background aerosol. Aerosol processes best ensure NP structures and size distributions representative of workplace releases into the air. Only after the effects of agglomerate structure in cellular tissue environments, the transport processes of agglomerates in such environments, possible deagglomeration mechanisms etc. have been understood may it become possible to relax these requirements.

Testing of filters & protective equipment

The mechanisms of particle filtration in air are well understood. In particular we know that the efficiency of filters increases steadily with decreasing particle size in the submicron range. Recent studies confirm this down to sizes of about 1 or 2 nm [eigene Zitate]. We can thus conclude that a filter deemed sufficient for larger particles will be even more effective in capturing "true" NP (<10 nm).

On the other hand, the growth of aged NP by auto-agglomeration or their attachment to ambient background particles can shift their size into the range of the Most Penetrating Particle Size (MPPS) of typical filter media, which is typically in the range of 80 - 200 nm. If adequate protection against nano-aerosols is required, it becomes critical to assure adequate filter efficiencies also in the MPPS region.

The methods for filter testing, and in particular for testing at the MPPS, are well developed and have been incorporated into various standards; aerosol generation and testing equipment for the submicron size range such as mobility spectrometers and CPCs are also available on the market. Mobility spectrometers classify irregularly shaped particles by their mobility size, which is also the relevant parameter for diffusion deposition in filters.

The chemical or surface composition of the particles is of no importance for the deposition efficiency in filters and other protective equipment and need not be considered in the choice of test aerosols.

A notable exception to this statement are nano-fibers and carbon nano-tubes (CNTs), which by virtue of their highly non-spherical shape do not behave in the same way as isometric particles during deposition in a filter. Filtration behavior of fibrous particles merits a more detailed investigation. The agglomeration state of CNTs is again critical for such tests.

Metrology of nano-aerosols

The fact that aging nano-aerosols can move up the size scale rapidly by various agglomeration processes has important implications in choosing suitable metrological strategies for purposes of workplace assessments.

Aged NP aerosols are not recognizable by a specific particle size range, such as "<10 nm". Moreover, it is not sufficient to look for NP in the "nano size range" where they may have originally been generated/emitted, unless one measures near a primary source. Agglomerated or scavenged NP will populate a size range where they become nearly indistinguishable from ubiquitous background aerosol by straightforward size distribution measurements. It is well known that additional ENP concentrations are often marginal, unless there are gross emission sources.

One alternative are highly selective real-time (!) analytical techniques with some kind of species sensitivity. This would allow detecting the presence of a NP even when it is attached to other particles. Today such methods are not broadly available and those

which exist, such as single particle mass spectrometry or aerosol catalysis, are untested in the context of workplace assessments. A significant effort is necessary in this critical area, akin to the development of real-time detection for bio-aerosols, which seemed nearly impossible a decade ago but has made great strides since then for well known reasons.

An alternative strategy to hazard assessment of NP emissions is based on the use of aerosol dynamic models to predict relevant information for specific workplace scenarios such as concentrations and size range of the NP aerosol at the receptor. Such models have been developed in past years to predict the evolution of an aerosol during catastrophic releases of radioactive material. Although not yet validated for such new applications, aerosol dynamic codes require as input

- the background aerosol size distribution,
- the characteristics of an emission source (strength, primary size range), hence the identification of release mechanisms for each specific NP hazard;
- and assumptions about an age distribution and possible dilution of the aerosol during transport to the receptor. This can be done via model scenarios.

Finally, the prevalence of aged and therefore agglomerated NP brings up the question of their ability to fragment, which presumably has a strong influence on biological effects. Thus there is a need for effective techniques to quantify agglomerate strength in aerosol particles.

Open questions & priorities for future research

As a result of the preceding analyses, a number of important open questions can be formulated.

The *release mechanisms and sources of ENP* into ambient workplace air need to be characterized and typified regarding source strength, size range and agglomerate structure. This is relevant for the development of realistic aerosol generators, realistic doses, as well as for the effective use of predictive aerosol dynamic models.

The development of *model aerosol sources* for exposure and toxicological studies needs more focus and effort. Simultaneously, a systematic effort should be undertaken to use aerosol sources for such studies, rather than powders or liquid suspensions and to advance the appropriate techniques for their application. Model aerosol sources are required for relevant classes of species and release mechanisms, including aging and scavenging methods where appropriate.

Existing *predictive dynamic models* for nano-aerosol evolution between source and receptor need to be adapted, validated and further developed as needed. While the basic mechanisms are known, the specific input parameters for the workplace environment are not.

Real-time methods for highly selective, species-specific ENP detection in the aerosol state are not broadly available and require a major effort, including the sustained funding of basic research to develop and validate new concepts. This includes methods capable of detecting NP attached to background particles as well as new methods to characterize the surface chemical state of airborne particles.

The fate of *structure and strength of nano-agglomerates* during their transition from the aerosol to the cellular liquid phase, and the influence of these structural parameters on their toxicological effects needs a concerted investigation. Techniques for quantifying the strength of homogeneous and heterogeneous agglomerates, especially on-line methods would be very useful.