Characterization of manufactured nanoparticles at workplace

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Abstract. French government has launched a dedicated program on nanotechnologies in May 2009. One of the topics was to develop measurements and characterisations at workplace, with the aim of getting the experience over 100 of them, either in research centres, universities and industries. At this time, about 80 have been realized. The methodology is based on the study of nanoparticles emission, during the whole duration of the process and/or operation, in real time, by comparison between background level and process ones. Parameters such as number of particles, size and developed surface are obtained. Shape, agglomerate state and chemical composition are obtained by further microscopy analysis. Currently, dustiness and surface state are not characterized and future developments are needed. It has to be pointed out that, at this time, and thanks to very various scenarios met, data collected from this program lead in a field database already used in different European research programs.

1. Introduction

Nanoparticles are or are about to be present in various and numerous fields and activities (medicine, cosmetology, building materials…). As a result, the number of workers in contact with nanoparticles is increasing and it becomes necessary to be able to measure and prevent potential exposure during processes. Different initiatives’ and work groups are already in process, either at international, European or national scale.

In May 2009, French government has announced an important and specific program dedicated to Nanotechnologies: NanoINNOV. The aim of this plan is to give to industry all the abilities in order to catch all the benefits of “nanorevolution”, while research would continue to explore intimate properties of matter, and find technical applications.

Over 3 integration centres, based in Paris, Toulouse and Grenoble, NanoINNOV topics are covering 4 axis:
- build a national device joining international standards,
- focus means on technology, heart of innovation process,
- bring this French ambition to European and international level,
- inscribe this process in a societal and timeless dynamism.

Nanoparticles’s safety is one of the topics involved in this last item, such as the building of a dedicated nanocenter or training as well.

Since the beginning of 2010, CEA, INERIS and CNRS have joined their efforts and have worked together, in order to be able to propose an innovatory offer to industrials, research centres and
universities: measure and characterize manufactured nanoparticles in workplace air, and improve safety on work stations.

2. Experimental Setup

2.1. Campaign sequence

Each campaign sequence obeys different compulsory steps. The first one is a pre-assessment on site in which the adequation between operating conditions and our methodology and equipments range is established. For example, the workstation layout, aerodynamics, the timing of each operation, the safety settings are checked. Moreover, during this meeting, data concerning the manufactured nanoparticles are also collected: scale, shape, chemical composition. The second step, which is the measurement on site, is completely described in point 2.2 and 2.3. The final stage consists in a restitution which is done through a technical report including all the results obtained on site completed by a list of recommendations in order to improve the safety and environment working conditions.

2.2. Equipments

To study the nanoparticles liable to be released in air at workplace, we used several techniques to characterize particles aerosol in terms of volume concentration, size distribution, specific surface area shape and chemical properties.

Particles counting is performed using water-based Condensation Particle Sizers (CPC 3785) manufactured by TSI Inc. [1], operating on the principle of enlarging small particles using a condensation technique to a size allowing optical detection. The CPC detects particles in the size range from 5 nm to 3 µm and provides measurements over a particle concentration range from 0 to $10^7$ p.cm$^{-3}$ with time resolutions in the order of one second.

This tool is continuously used during the measurement at workplace because of its high sensitivity and its quick response time. As it will be detailed in the methodology section, we made the choice of using two CPC in parallel to evaluate the influence of surrounding environment on each operation at the workplace.

To go further and get information on size distribution of particles, different granulometric techniques were used.

We used a GRIMM 5.416 Scanning Mobility Particle Sizer (SMPS) [2] consisting of a particle neutralizer (Am241), a short-column Differential Mobility Analyzer (DMA) and a CPC. In such a configuration, the SMPS provides the size distribution of nanoparticles in the range 5-350 nm up to a concentration of $10^7$ p.cm$^{-3}$.

We performed real-time measurements by using a Fast Mobility Particle Sizer (FMPS). The FMPS 3091 from TSI measures the particle mobility diameter in the range 5.6-560 nm with a time resolution of 1 s using a flow rate of 10 l.min$^{-1}$. A detailed description of the FMPS can be found in reference [3].

An Electrical Low Pressure Impactor (ELPI) [4,5] manufactured by DEKATI Ltd was used. It combines both size distribution measurements with time resolutions in the order of seconds and the possibility of size resolved particle collection on impaction substrates for subsequent chemical analysis. The 12 stages cover a size range from 30 nm to 10 µm and the lower size limit can be extended to a cut-off diameter of 7 nm by using an electrical filter stage.

In order to get an information of the specific surface area of particles, we sometimes used a Nanoparticle Surface Area Monitor (NSAM) that indicates the human lung-deposited surface area of particles in units of square micrometers per cubic centimetre (µm$^2$.cm$^{-3}$), corresponding both to tracheobronchial and alveolar regions of the lung. The instrument used is the NSAM 3550 manufactured by TSI.

The NSAM 3550 matches the corresponding lung deposition criteria of particles for a reference worker as predicted by human lung deposition models published by the International Commission on Radiological Protection (ICRP, 1995). The lung deposition is calculated for a reference worker as
defined in a publication by the American Conference of Governmental Industrial Hygienists (ACGIH, ed. Vincent J.H., 1999).

For the qualitative side of the characterization, we use a Scanning Electronic Microscopy (SEM) 5500 from HITACHI. The high resolution of this tool allows the visualization of the nanoparticles for size measurement and shape determination. Associated to the SEM, we used an EDX (Energy Dispersive X-Ray Spectroscopy) tool from THERMO SCIENTIFIC Inc. to get information on the chemical composition of the nanoparticles collected during the previous step.

2.3. Methodology
When emission of nanoparticles is suspected during an operation at a workplace, three characterization steps are conducted. The first one is a real time quantitative characterization, as close as possible to the operation taking place, to have access to the number of particles emitted per unit of volume (CPC), the size distribution (SMPS, FMPS, ELPI) and the associated specific surface area (NSAM). This initial step also includes sampling on dedicated membranes (within the ELPI). The second step of the methodology is the chemical characterization of the nanoparticles emitted, which is done offline from the samples collected in step one and using dedicated analysis instruments (SEM, EDX). This second set of characterization gives access to new and very important data. Are we in front of isolated species or agglomerates? What is the chemical composition? Those fundamental questions are answered through this qualification step.

It is important to point out that our methodology was built from the beginning with the rule of conduct that each operation at the workplace should not be disturbed from the possible variations of the surrounding ambiance. For this purpose, we established a protocol where each operation measurement should be completed by a real time comparison with the air of the local.

One CPC is set to a fixed position to measure continually the ambient air in the workplace. Another one is linked to the sampling stick to follow the operator activity and to measure the potential sources of nanoparticles release in air. The measurements performed by the CPC tools in parallel (so called CPC_{source} and CPC_{ambient air}) bring information about the global concentration variations, over the whole duration of the process, between the ambient air of the workplace and the different steps of the process that could be sources of nanoparticles release in air.

This is different from the NEAT method (Nanoparticle Emission Assessment Technique) developed by the National Institute for Occupational Safety and Health (NIOSH) [6, 7]. This last method includes a first run to draw a baseline or a background picture of the nanoparticles already in the environment before any operation. The second step is then to run the same measurements but this time with the operation taking place. If measurements during the process indicate particles concentration higher than the background level, then further analytical information are conducted to identify the nanoparticles. The complete comparison of the two methodologies will be the topic of a coming publication in the following months.

3. Results - Example
A workstation is defined as a process or a process step, involving nanomaterials and liable to release nanoparticles in air due to operator activity.

The case we consider here is the preparation of a solution for CMP (Chemical and Mechanical Polishing) (Figure 1). This process consists of several steps among them we were particularly interested in the dry ones: the weighing phase of a nanometric AlO\textsubscript{2} powder and the decanting of the powder in a bowl. These operations were performed in a class 10000 - ISO 4 clean room environment under a laboratory fume hoods.
First, we sampled in the lab near the polishing zone and both the CPC measured a concentration of 0.1 p.cm$^{-3}$ (Figure 2). Then, a measurement with the so called CPC$_{source}$ was performed in the introduction airlock (number 1 on figure 2) while the other CPC was still in the lab but next to half-opened airlock. We observe a concentration of 2800 p.cm$^{-3}$ in the airlock while the second CPC indicates a concentration increase from to 0.1 to 1 p.cm$^{-3}$. As a comparison, the ambient concentration level generally measured in an office with normal human activity is around $10^4$ p.cm$^{-3}$.

Respectively at 11:28 and 11:32 two peaks were detected (79 p.cm$^{-3}$ and 27 p.cm$^{-3}$) and seem to be related to equipments movements. At 11:33 the sampling under the fume hoods was started. During this phase, the fume hoods aspiration was on (light blue on figure 1). The particulate concentration before the beginning of the operator activity is constant between 1 and 10 p.cm$^{-3}$. At 11:41 the decanting of the AlO$_2$ powder in a bowl was started by the operator (number 2 on figure 2). During this short operation, a concentration peak of 179 p.cm$^{-3}$ was measured while the ambient air particles concentration keeps constant around 1 p.cm$^{-3}$. Then, a sampling was immediately performed very close to the operator respiratory tracts. A level equal to the ambient air one was detected. This may reveal that the particles release in air keeps very close to the source emission point and that the fume hoods provides a well-adapted air recirculation.

At 11:47, the aspiration of the fume hoods was turned off. During the first five minutes of this phase (light orange on figure 2), no operations from the operator were done and we measured under the fume hoods with the CPC$_{source}$ while the other CPC was still measuring the ambient air nearby the workplace of interest. We observe an increase of the particles concentration under the fume hoods, from 1 to several 10 p.cm$^{-3}$. The ambient air particles concentration is constant and lower than 1 p.cm$^{-3}$.

From 12 a.m., the same operations than with the fume hoods turned on were performed. A general increase (factor 10) of the concentration of particles present in the ambient air was observed. However, no significant increase of the concentration due to the different steps of the process was emphasized, as shown by the CPC$_{source}$ signal. It seems that under no air aspiration, the fact that the air is more charged in particles entails a lack of sensitivity whereas a cleaner environment allows the identification of more variations phases.
Figure 2. Concentration (p.cm$^{-3}$) of particles within the size range 5-3000 nm as measured in parallel by two CPC. The blue line corresponds to the potential source of particles release, the pink one corresponds to the ambient air of the workplace. The first part of the graph (light blue) corresponds to measurements with the fume hoods on, the second part (light orange) with fume hoods off.

The decanting phase of the powder in a bowl was identified by the CPC measurements as a potential source of nanoparticles release in air. The distribution size of those particles was studied by means of FMPS (Figure 3). Considering the quickness of the decanting of the powder, the SMPS which needs 4 minutes to record a spectrum, does not provide a granulometry representative of the phase of interest. The FMPS measurement shows a monodispersed aerosol with a size distribution centred on 250 nm.

Figure 3. Size distribution of the aerosol as measured by FMPS during the decanting of the powder in the bowl.

To get information about the specific surface area of particles, we performed a real-time NSAM measurement indicating the human lung-deposited surface area of particles, corresponding in that case to alveolar regions (Figure 4). At the day of redaction of this paper, NSAM data are still not totally understood in some cases. Nevertheless, presently, we identified three principal peaks that all correspond to well-known events. Indeed, the two first significant peaks at 11:50 and 11:52 (28 and 51 µm$^2$.cm$^{-3}$) correspond to the moment when the fume hoods aspiration was turned off, as shown by the CPC measurements. The highest peak at 12:02 (77 µm$^2$.cm$^{-3}$) corresponds to the moment when the operator started to sand the powder under the fume hoods off. Here we point out the fact that surface deposition of particles in the alveolar region of lung seems correlated to the presence or not of air aspiration and so collective protection.
A batch of Aluminium impaction substrates were placed on the ELPI stages for subsequent chemical analysis. We specially concerned our interest on samples to stage 4 and 5, corresponding respectively to theoretical aerodynamic diameters 155 nm and 260 nm. These samples were then analyzed by means of SEM-EDX giving access to both structural and chemical information on the particles. The SEM measurements revealed that particles impacted on stage 4 had aerodynamic diameters between 170 and 210 nm and on stage 5 between 210 and 280 nm. A SEM observation of a particle impacted on stage 5 of the ELPI is shown on Figure 5. This particle has a critical size of 226 nm and EDX spectra were recorded inside and outside of it to get information about its chemical composition (Figure 6).

The EDX analysis revealed the presence of oxygen only inside the particle. Moreover, the same Al peak was detected both on the Al substrate and in the particle. The EDX analysis confirmed that the particle consists of alumina and oxygen.

**Figure 4.** Deposited Surface Area (µm$^2$.cm$^{-3}$) of particles as measured by NSAM in alveolar mode.

**Figure 5.** SEM observation of a particle measured on stage 5 of the ELPI.

**Figure 6.** EDX spectrum inside the AlO$_2$ particle (black) and outside, on the Al substrate (red).
Our methodology allowed us to provide a complete characterization of a workplace in terms of nanoparticles released in air in the form of aerosol and liable to be inhaled by the operator.

4. Conclusion
Over the last 10 months, 76 workstations and/or operations have been studied and characterized following our strategy. The objective of NanoINNOV is to join the aim of 100 till the end of 2010 and this target is about to be reached.

Different scenarios and type of nanoparticles have been characterized that way:

- As type of conditions:
  - Processes such as weighing, grinding, pelleting, repackaging, scraping, evaporation, cleaving, …
  - Operations such as ink preparation, maintenance, cleaning, furnace opening, …
  - Use of equipments such as sandblaster…

- As type of nano-objects: nanopowders, nanotubes, nanowires,

- As type of substances: titanium dioxide, carbon, carbon black, silicon, silicon dioxide, titanium, alumina, zinc oxide, copper, iron phosphates, arsenic, …

- As amounts used: from few micrograms to some kilograms

For the next months, one of our objectives is to continue to collect on-site data on a national scale while continuing to improve the methodology in order to be able to measure complementary parameters such as surface properties, dustiness. In the same way, measurement on colloids could be developed.

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