Strategy for the lowering and the assessment of exposure to nanoparticles at workspace – Case of study concerning the potential emission of nanoparticles of Lead in an epitaxy laboratory

Sébastien Artous¹, Eric Zimmermann¹, Paul-Antoine Douissard², Dominique Locatelli¹, Sylvie Motellier¹, Samir Derrough¹

¹ Univ. Grenoble Alpes, F-38000 Grenoble, France
CEA-Grenoble, NanoSafety Platform, F-38054 Grenoble, France

² ESRF, F-38043, Grenoble, France

E-mail: sebastien.artous@cea.fr

Abstract. The implementation in many products of manufactured nanoparticles is growing fast and raises new questions. For this purpose, the CEA - NanoSafety Platform is developing various research topics for health and safety, environment and nanoparticles exposure in professional activities. The containment optimisation for the exposition lowering, then the exposure assessment to nanoparticles is a strategy for safety improvement at workplace and workspace. The lowering step consists in an optimisation of dynamic and static containment at workplace and/or workspace. Generally, the exposure risk due to the presence of nanoparticles substances does not allow modifying the parameters of containment at workplace and/or workspace. Therefore, gaseous or nanoparticulate tracers are used to evaluate performances of containment. Using a tracer allows to modify safely the parameters of the dynamic containment (ventilation, flow, speed) and to study several configurations of static containment. Moreover, a tracer allows simulating accidental or incidental situation. As a result, a safety procedure can be written more easily in order to manage this type of situation. The step of measurement and characterization of aerosols can therefore be used to assess the exposition at workplace and workspace. The case of study, aim of this paper, concerns the potential emission of Lead nanoparticles at the exhaust of a furnace in an epitaxy laboratory. The use of Helium tracer to evaluate the performance of containment is firstly studied. Secondly, the exposure assessment is characterised in accordance with the French guide “recommendations for characterizing potential emissions and exposure to aerosols released from nanomaterials in workplace operations”. Thirdly the aerosols are sampled, on several places, using collection membranes to try to detect traces of Lead in air.

1. Introduction

Nanoparticles are present in various and numerous fields and activities (medicine, cosmetology, building materials, ...). As a result, the number of workers in contact with nanoparticles increases. As collective protections are the first one to be implemented, before individual protections, it becomes necessary to be able to test their efficiency for nanoparticles.

The CEA - NanoSafety Platform (PNS) located in Grenoble works on all matters of safety and security related to the handling of nanomaterials. It conducts in parallel actions of R & D and services missions of measurement and characterisation, expertise, training and intervention in accidental situations. It employs nearly 150 professionals, researchers and experts, whose jobs are to provide a strong support to researchers and partners using nanotechnology, while maintaining the highest level of knowledge and skills in the field of nanosafety.

For this purpose the NanoSafety Platform is developing various research topics for health and safety, environment and nanoparticles exposure in professional activities. The optimisation of containment for lowering the exposition, then the assessment of exposure to nanoparticles is a strategy for safety improvement at workplace and workspace. The lowering step consists in an optimisation of dynamic and static containment at workplace and/or workspace. Generally, the exposure risk due to...
the presence of substances containing nanoparticles does not allow modifying the parameters of containment at workplace and/or workspace. Therefore, gaseous or nanoparticulate tracers are used to evaluate performances of containment. Using a tracer allows to modify safely the parameters of the dynamic containment (ventilation, flow, speed) and to study several configurations of static containment. Moreover, a tracer allows simulating accidental or incidental situation. As a result, a security procedure can be written more easily in order to manage this type of situation. The step of measurement and characterization of aerosols can therefore be used to assess the exposition at workplace and workspace.

The case of study, aim of this paper, concerns the potential emission of Lead nanoparticles at the exhaust of a furnace in an epitaxy laboratory: The laboratory makes Lead crystal growth in furnaces. The use of Helium tracer to evaluate the performance of containment is firstly studied. The efficiency of two extraction systems, located at the exhaust of an epitaxy furnace, is evaluated. In addition, the influence of a refractory component, placed at the exhaust of the furnace, to canalise the Lead vapour is studied.

Secondly, the exposure assessment is characterised in accordance with the French guide “recommendations for characterizing potential emissions and exposure to aerosols released from nanomaterials in workplace operations”. These recommendations should be proposed to international regulation. The characterization of aerosols includes measurements of the concentration using condensation particle counters and measurements of the size distribution based on electrical mobility of particles.

Thirdly the aerosols are sampled, on several places, using collection membranes to try to detect traces of Lead in air by atomic absorption and X-Ray Fluorescence (XRF).

2. 2.1. Characterization of containment

2.1. Characterization of containment by a gaseous tracer – leak detection
The implementation of an air blowing associated to an extraction of air with an HEPA filter is the classical configuration of a lab where nanoparticles are handled. This configuration enables to maintaining the pressure in the laboratory lower than the pressure outside to contain inside the lab a potential contamination of nanoparticles. In addition, close to the source of nanoparticles, an extracting system is usually used.

The evaluation principle of the performance of containment is based on the diffusion of a tracer injected at a constant flow rate instead of the source of nanoparticles (Figure 1). An analyser of leak allows detecting the tracer in several areas to determine if a diffusion of nanoparticles in the laboratory might occur in a real configuration. Representative results were obtained with a gaseous tracer when the aeraulic parameters (air blowing, extracting air of room and process, temperature of furnace…) are the same that when the source of nanoparticles is handled. This characterisation is based on the hypothesis that the transport of nanoparticles is principally due to the turbulent diffusion and that the concentration of gaseous tracer in the room is low. Helium tracer is used in this study (see paragraph 3.1.1). Using a gaseous tracer instead of a nanoparticles source enables to optimising aeraulic parameters in complete safety.
2.2. Containment characterisation by real-time measurement of potential aerosol emission and by aerosol sampling

The methodology, first validated by the NanoSafety Platform (PNS), has been deployed at a large scale since the end of 2009 (up 270 workstations have been measured and analysed up to date).

The goals of an aerosols measurement are the identification, the characterization and the assessment of nanosize and microsize aerosols potentially generated, intentionally or unintentionally, during the normal working phases (studied size range: 5nm – 32µm).

At this stage, there is no real consensus on the most representative unit of measure to assess the exposure of workers. The evaluation principle of the exposure in a located area is to use a sampling tube connected to the instruments measuring both concentration and distribution (Figure 2). Thus, the equipments used in this study are detailed in paragraphs 3.1.2 [2]. Nevertheless these equipment cannot detect specifically the Lead.

Besides the aerosol measurement, the aerosols are sampled at several places, using collection membranes to detect potential traces of Lead in air by atomic absorption and X-Ray Fluorescence (XRF), see paragraph 3.1.3.
3. Materials and method

3.1. Method

3.1.1. The Helium tracer
The injection of Helium is controlled by a mass flow meter ANALYT MTC-358 (Figure 3-a). The injection flow is 1 L/min at 20°C and is located in the centre of the furnace for simulating an emission of Lead. The concentration of tracer gas is measured by a mass spectrometer Adixen - type ASM 102S. The sampling point is moved into several areas according to the method presented at the paragraph 2.1.

![Figure 3. Mass flow meter and mass spectrometer](image)

3.1.2. The equipment for the aerosols measurement
The particles concentration is determined by a Condensation Particle Counters (CPC) 3785 of TSI. The size range of particles detected is from 5nm to 3µm. If an emission of particles is detected when analyzing the CPC results, the next step is the determination of the size distribution of the aerosol emission. A FMPS (model 3091 - TSI) is used in this study. The size range of particles detected is from 5.6nm to 560nm. In addition an optical counter (Dustmonitor model 1.109 – GRIMM) is used to obtain the distribution of submicronic and micrometric particles (range from 250nm to 32µm).

![Figure 4. Equipment for the aerosols measurement](image)
3.1.3. The equipment for the determination of Lead

i. XRF Characterization
X-Ray Fluorescence (XRF) is used for the characterisation of the samples made at workplace and/or workspace. This analytical method is a non-destructive method. The XRF analyses are realised on a Rigaku spectrometer of NanoHunter bench-top apparatus type. The XRF analysis is a surface characterisation technique where a beam of primary X-rays hits a sample with a very small incidence angle (typically 1mrad). The depth of penetration of primary X-rays being very small, the secondary X-ray photons are transmitted through a depth of about 3nm to 5nm. This enables a chemical characterisation of the constitutive elements of the particles which are at the surface of the sample.

ii. ICP-MS
Inductively coupled plasma mass spectrometry (ICP-MS) is used for the characterization of the samples which have been realised at workplace and/or workspace. This analytical method is a destructive method. ICP-MS analysis are realised on an Agilent Technologies 7700 Series. Before analysis the membranes of collection are mineralised by concentrated HNO₃.

3.2. Epitaxy laboratory – Asterix furnace
The Figure 5 describes the Epitaxy laboratory. Three furnaces are located in the laboratory, Asterix, Solarix and Obelix. For this study only Asterix and Solarix furnaces work. In this paper, only the results concerning Asterix furnace are given. The aeraulic system of the laboratory is made up by three air intakes associated to an air extraction wall with a flow of 1,600 m³/h. Moreover, a dynamic containment is created at the exhaust of each furnace by an extracting system. Two types of extraction systems, an extracting box (Figure 6-a) and an extracting slot (Figure 6-b) located at the exhaust of Asterix furnace, are evaluated with the Helium tracer. The Figure 7-a presents the injection of Helium located in the centre of the furnace to simulate a potential emission of lead. Afterwards, the measurement of a potential aerosol emission is conducted. The Figure 7-b presents an example of localisation of the sampling tube for the aerosol measurement. Finally three sampling are performed on filters exposed for 7 days to the laboratory atmosphere (Figure 5).

Figure 5. Schematic view of the epitaxy laboratory
4. Results

4.1. Containment characterisation by a gaseous tracer – leak detection

Figure 8 shows the evolution of the helium concentration in the area of the Asterix furnace with the extracting box and for a fan extraction speed of 32Hz. A significant concentration of Helium is recorded when the probe is located: at the opposite of the extraction air; between the extraction air and the opening of the furnace; at the back of the furnace; 10cm above the furnace and also at the upper part of the agitator of the furnace. Using the extracting box creates a large area of extraction where Helium is significantly measured. In a normal operation of the furnace some Lead nanoparticles could deposit at the surface of this area. The fan extraction speed increase to 45Hz to increase the extraction flow does not reflect into a significant decrease of the helium concentration for the same measurement locations. Then the fan extraction speed is gradually decreased. The fan extraction speed where significant helium concentration is recorded in the laboratory corresponds to a loss of dynamic containment. This loss of dynamic containment is recorded for a variation of the fan below 15Hz.
Afterward, the evolution of the Helium concentration in the area of the Asterix furnace with the extracting slot for several fan extraction speed is studied (Figure 9). No significant Helium concentration is recorded apart from the measurement realized above the opening of the furnace and at the level of the extracting slot. The concentrations recorded at the opening of the furnace are 10 times lower than the concentrations recorded in the configuration with the extracting box.

A test of a gradual decreasing of the fan extraction speed is conducted to evaluate the los of dynamic containment. This limit is reached when the Helium is extracted by the air laboratory extracting (extraction wall) and not by the air process extracting. With the extracting slot, this limit is around a fan extraction speed of 5Hz.

As a result, the characterisation of a potential aerosol emission will be realised only in the configuration with the extracting slot.

**Figure 8.** Helium concentration with the extracting box for a 32Hz fan extraction speed
Figure 9. Concentration of Helium with the extracting slot for several speed variations of the fan

4.1. Characterisation by the measurement of a potential aerosol emission

Figure 10 shows the evolution of the particles concentration in the area of the Asterix furnace with the extracting slot and for several fan extraction speed. The blue curve shows the evolution of the particles concentration from 5nm to 3µm and the red curve shows the evolution of the particles concentration from 250nm to 32µm. For a fan extraction speed of 32Hz, no significant nanoparticles emission is recorded apart from the measurement realised between the opening of the furnace and a lid. An increase of 1,500 p/cm³ is recorded. Figure 11 shows the distribution at the emission point and in the aerosol background. The emission is characterised by a significant increase of the nanoparticles number around 10nm.

This increase is probably due to the turbulent movement of air caused by the high speed of extracting air associated with a lid. Indeed, this lid was not present at the step of characterisation with a gaseous tracer (see the difference between Figure 7-a and Figure 7-b). This result underlines that the characterisation with the gaseous tracer has to be realised strictly in the same configuration as the configuration where nanoparticles are handled. However, this increase is not recorded for a fan extraction speed at 25Hz or 20Hz. For these two fan extraction speeds no significant nanoparticles emission is recorded.
4.2. Aerosol sampling

The last step of characterisation is the sampling step. The sampling step is conducted for the furnaces with the extraction slot and for a fan speed at 20Hz. Three collection membranes are used to seek traces of Lead in air. The sampling lasts 7 days with a sampling flow between 3 L/min and 7 L/min. The analysis by X-Ray Fluorescence (XRF) does not highlight the presence of Lead on membrane. Then Analysis by ICP-MS are also conducted. Like the XRF, the ICP-MS does not highlight the presence of Lead on collection membranes. The detection limit of analysis by atomic absorption is 1 ppb. The detection limit resulting for the concentration of Lead in the laboratory is evaluated at 15ng/m³.
5. Conclusion
This study shows the strategy for the lowering and the assessment of exposure to nanoparticles at workspace and workplace. The step of containment optimisation with a gaseous tracer determines the success of the lowering of the exposition. In this case of study, using a gaseous tracer enable to optimise the aeraulic parameters with the selection between two types of extraction system (box or slot) for the extracting process and with the optimisation of the fan extraction speed to select the lowest speed as possible. This last parameter is important for the growth process of single crystal films, in maintaining a safer environment.

The study underlines that the characterisation with the gaseous tracer to represent the behaviour of aerosol and nanoparticles has to be realised strictly in the same configuration (aeraulic and geometric) as the configuration where nanoparticles are handled. In this case of study, regardless of the method used, no lead was found in the air of epitaxy laboratory.

The three steps of characterisation with using a gaseous tracer with a measurement of aerosol and with a sampling on membrane, ensures a safer environment at the workplace and workspace.

References
[1] Durand, C., Witschger, O., Le Bihan, O., Reynier, M., Marchetto, A., Zimmermann, E., Charpentier, D. “French approach for characterizing potential emissions and exposure to aerosols released from nanomaterials in workplace operations”, Nanosafe 2012
[2] Zimmermann, E., S. Derrough, D. Locatelli, C. Durand, J. L. Fromaget, E. Lefranc, X. Ravanel, and J. Garrione. “Results of Potential Exposure Assessments during the Maintenance and Cleanout of Deposition Equipment.” Journal of Nanoparticle Research 14, no. 10 (October 1, 2012): 1–17. doi:10.1007/s11051-012-1209-6.
[3] Août 2004, French standard, Sorbonnes - Partie 3 : méthodes d'essai de type, NF EN 14175-3, AFNOR
[4] Mai 1972, French standard, Méthode de mesure de l’efficacité des filtres au moyen d’un aérosol d’uranyne (Fluorescène), NF X44-011, AFNOR