Evaluating performance of containment equipment designed for handling manufactured nanomaterials by use of nanoparticle tracer

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Abstract. The implementation in many products of manufactured nanoparticles is in strong growth 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 working group Nano-CERT/MTD, driven by INERIS, federates actors of the sector: experts, research organizations, industrial users and manufacturers of collective protection. The main activity of this group is to establish specific guidelines or a voluntary certification of collective protection, at a national scale, but with the possibility of a further extension at an European level. The group aims to establish an experimental protocol of certification to characterize collective protections for workers faced with nanomaterials potential exposure. The NanoSafety Platform provides in this presentation a method of collective protection characterization based on the developments in nanoparticles metrology and on the study of existing standards and practices in related areas (chemicals, dust, microbiological and nuclear). This study presents the results obtained during the experimental characterization of a potential nanoparticles transfer in a prototype laboratory fume hood by the use of a particulate tracer of sodium-fluorescein. The efficiency of the equipment and more specifically the efficiency of dynamical air barrier is evaluated, with the experimental results, by calculating the backward diffusion coefficient.

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 is increasing. 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 (NSP) 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 knowledge and skills in the field of nanosafety.

In this objective the NanoSafety Platform is developing various research topics for health and safety, environment and nanoparticles exposure in professional activities. One of this topic is to determine the best available method to characterize protection techniques for workers faced with nanomaterials exposure. For this purpose the NSP joined the working group Nano-CERT/MTD, driven by INERIS. The working group brings together various stakeholders, experts, research organizations, industrial users and manufacturers of collective protection.

The main activity of this group is to establish specific guidelines for a voluntary certification of collective protections, at a national scale, but with the possibility of a further extension at a European level. The first certifications with an experimental evaluating of performance of containment equipment by a particulate tracer, are expected for 2013.

The NSP provides a method of collective protections characterization based on the use of a particulate tracer of sodium-fluorescein. This study presents the results obtained during the experimental characterization of a potential nanoparticles transfer in a prototype laboratory fume hood. The efficiency of the equipment and more specifically the efficiency of dynamical air barrier are evaluated, with the experimental results, by calculating the backward diffusion coefficient.

2. Principle of determination of Aeraulic parameters with a tracer

2.1. Extraction airflow

The principle of the method is based on the dilution of a tracer injected at a constant flow rate in the pipe. The determination of mass balance (equation 1) allows to calculate the extraction airflow of the equipment.

\[
Q = \frac{q C_{inj}}{C_{mes} - C_0} \quad \text{with } q \ll Q
\]

With :
- Q the flow in the pipe in m³/h
- q the flow of tracer in m³/h
- \(C_{inj}\) injected volume concentration of tracer
- \(C_0\) volume concentration of tracer in ambient air
- \(C_{mes}\) the volume concentration of the tracer at the measurement point

2.2. Air renewal

The residence time distribution (RTD) of a chemical reactor is a probability distribution function that describes the amount of time a fluid element could spend inside a reactor or, for this study, in the containment equipment. The RTD characterizes the mixing and flow in the equipment and allows comparing the behavior of real equipment to his ideal models.

The theory of residence time distributions generally begins with three assumptions:

- the reactor or equipment is at steady-state,
- flow where no random event happens at the macroscopic scale,
- the fluid is incompressible.

If ventilation is assumed to be homogeneous, the equipment is considered equivalent to a perfectly stirred reactor. The theoretical system response (here the equipment) to an inverse step experiment is resulting in equation 2.
\[
\ln \left( \frac{C(t)}{C_0} \right) = -\frac{1}{\tau} = -Rt \tag{2}
\]

The plot of \(\ln((C-C_0) / (C^*-C_0)) = f(t)\) gives a straight line whose slope represents, except for the sign, the renewal rate \(R\). The renewal rate \(R\) (equation 3) is equal to the inverse of renewal time \(\tau\) (equation 4).

\[
R(h^{-1}) = \frac{Q \left( \text{m}^3 h^{-1} \right)}{V \left( \text{m}^3 \right)} \tag{3}
\]

\[
\tau(h) = \frac{1}{R} \tag{4}
\]

With:
- \(Q\) the flow in the pipe \(\text{m}^3/\text{h}\)
- \(C\) the concentration at the instant \(t\)
- \(C^*\) the equilibrium concentration
- \(C_0\) the concentration of tracer in ambient air
- \(V\) the volume of the equipment

2.3. Backward diffusion coefficient

The backward diffusion coefficient \(K\) is defined as the ratio of the concentration at the point of measurement “m” (plane of the fume hood, respiratory tract or at the level of a nanoparticulate detection device...) on the flow of pollutant. This coefficient is used to characterize the potential transfer of pollutant used in the equipment.

\[
K = \frac{C_m}{q_s} \tag{5}
\]

With:
- \(C_m\) the concentration at the point of measurement \(\text{m} \text{ g/m}^3\)
- \(q_s\) the flow of pollutant or tracer at its source \(S\) in \(\text{g/h}\)

3. Materials and method

3.1. Containment equipment

The prototype of containment equipment of FAURE QEI company has two configurations. The first without the front panel is called “fume hood mode”. The second with the front panel in place, is called “glove box mode”. A removable filtration / ventilation block allows to filtrate air with a HEPA filter and set the extraction airflow (Figure 1-a). The exhaust of equipment is driven in a laboratory fume hood. The Figure 1-b shows the localization of the measurement points for the determination of backward diffusion coefficients. The sampler used for gas and particulate tracer is defined by the French standard NF EN 14175 [1].

For determining the air renewal, the injection takes place at the entrance to the equipment using a cable entry at the side and by using various injection sites in order to homogenize the concentration inside the equipment. Measuring the gas concentration is carried out downstream of the filtration unit. Measuring by counting or by sampling on a filter for fluorescein is performed immediately upstream of the filtration unit.
1.1. Method

3.1.1. The helium tracer
The injection of helium is controlled by a mass flow meter ANALYT MTC-358 (Figure 2). The localization of injection is adjusted according to the desired information (extraction flowrate, air renewal, backward diffusion coefficient). The concentration of tracer gas is measured by a mass spectrometer adixen - type ASM 102S. The sampling point is adjusted according to the desired information (extraction flowrate, air renewal, backward diffusion coefficient).

3.1.2. The sodium fluorescein tracer
The principle of measurement is to inject a solid aerosol of sodium fluorescein. The number median diameter of aerosol is 60 nm (Figure 3). The generator is described in the French standard NFX44-011 [2]. The injection point is adjusted according to the desired information (extraction flowrate, air renewal, backward diffusion coefficient). The mass flow rate of generator is of the order of 30 mg/h.
Figure 3. Fluorescein generator and size distribution obtained by FMPS of TSI

4. Results

4.1. Aeraulic characterization
The figure 4-a shows the curves of RTD obtained for two extraction airflows in fume hood mode and in glove box mode. The set of curves shows that the renewal is homogeneous in fume hood mode and in glove box mode. The exploitation of results gives renewal time around 20 s in glove box mode. For the fume hood mode the renewal time is around 4 s with an extraction airflow at 450 m$^3$/h and around 7 s with a extraction airflow at 280 m$^3$/h. The values of renewal and extraction airflow allow to calculate the volume of equipment. The result is of the order of 0.5 m$^3$.

The figure 4-b shows the curves of RTD obtained in fume hood mode and in glove box mode with helium and Fluorescein tracer. The set of curves shows that the renewal is similar with a nanoparticulate tracer and a gaseous tracer. This result is interesting for the characterization of equipment. In fact, several equipments have an exhaust in the room. Gas is not retained by the filters and is sent back in the room. Thus it’s not possible to characterize the aeraulic with a gaseous tracer.

The table 1 summarizes the results obtained when measuring RTD for different modes of equipment and for the two types of tracer. The values obtained with a gaseous or a particulate tracer, for a same configuration of the equipment (fume hood mode or glove box mode) are similar.
Table 1. Synthesis of determination of aeraulic parameters

| Mode               | Tracer    | Extraction airflow (m$^3$/h) | Hourly renewal (R/h) | Renewal time (s) | Volume of equipment (m$^3$) |
|--------------------|-----------|-----------------------------|----------------------|------------------|----------------------------|
| Fume hood (280 m$^3$/h) | helium    | 280                         | 539 et 476           | 6.6 et 7.7       | 0.52 et 0.6                |
|                    | fluorescein| 250                         | 537 et 581           | 6.7 et 6.2       | 0.43 et 0.47               |
| Fume hood (450 m$^3$/h) | helium    | 450                         | 944                  | 4.6 et 3.8       | 0.57 et 0.48               |
| Glove box          | fluorescein| 102                         | 187 et 203           | 17 et 19         | 0.49                       |

4.2. Backward diffusion coefficient

The Figure 5-a shows the backward diffusion coefficients obtained in fume hood mode for two extraction airflows (280 m$^3$/h and 450 m$^3$/h) for localizations A and B (Figure 1-b). The lower the value of backward diffusion coefficient at the measurement point is, the more efficient is the equipment.

The results show that helium tracer method is near from the detection limit. The consequence is that there’s no significant difference between values of backward diffusion coefficients between extraction airflow at 280 m$^3$/h and extraction airflow at 450 m$^3$/h. For the extraction airflow at 280 m$^3$/h, the values of backward diffusion coefficients obtain with the gas or particulate tracer are similar. The results show that, for this operating point, it’s possible to use a tracer gas to account of the behavior of a nanoparticle pollutant.

The Figure 5-b compares the backward diffusion coefficients obtained in fume hood mode for two extraction airflow and in glove box mode with the fluorescein tracer. The results show that the glove box mode is 100 times more efficient than the fume hood mode. Finally the low limit detection of fluorescein allows determining the decrease of the backward diffusion coefficients with the increase of extraction airflow in fume hood mode.

Figure 5. Backward diffusion coefficients

5. Conclusion

This study shows the importance of carrying out tests for characterizing ventilation (extraction airflow, RTD, renewal) because these parameters have a significant influence on the performance of containment equipment. In addition, the study shows that this characterization can be performed both with a gas or nanoparticulate tracer. The feasibility of study the renewal of equipement using a
A nanoparticle tracer, is particularly advantageous when the extraction airflow is in the room where the equipment is located.

These measures have to be completed by measurements of coefficients either gaseous or particulate tracers in the plane of equipment. The values of backward diffusion show that a gas tracer can account of the behavior of a nanoparticulate pollutant if the backward diffusion is high enough to be above the detection limit of the method of gas analysis. However, the analytical method with a nanoparticulate tracer of fluorescein is more sensitive and allows to differentiate changes in the operating point of the equipment.

In conclusion the method using a solid aerosol fluorescein is robust, reliable and sensitive. Moreover, sodium fluorescein does not present any danger to humans until today.

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