

Proposal of a new risk assessment method for the handling of powders and nanomaterials

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Abstract: A new approach to assess the risks inherent in the implementation of powders, including nanomaterials, has been developed, based on the OHB (Occupational Hazard Band) method which is widely spread in the chemical industry. Hazard classification has not been modified; only the control of exposure has been worked at. The method applies essentially to the prevention of the exposures to airborne materials, whatever their particle size. The method considers exposure based on seven parameters which take into account the characteristics of the materials used, their emission potential, the conditions of use, as well as classic parameters of exposure characterization like duration and frequency. The method is a pragmatic exploitation of the state-of-art and of available data, bearing in mind that a lot of them are not easily accessible to factory operators. The result of the reflection is then positioned on a hazard versus exposure matrix from which 4 levels of priority of action are defined, as in the classical OHB method used to manage pure chemical risk. This approach fills a gap in terms of risk assessment and avoids jeopardizing all that has been set up for years, while introducing new elements of decision making accessible to all operators.

Key words: Control banding, Occupational risk, Powders, Nanomaterials

Introduction

The evaluation of the risks at the workplace is inescapable in the approach of control of the risks inherent in a professional activity. In most cases, and specifically with chemical risk, the risk assessment is a regulatory deliverable^{1, 2}. It has to be the object of a validation process under the responsibility of the employer. Although the

properties and characters of powders especially at the nanometric scale are still being discussed³, it must not be forgotten that these are chemicals and that they must be considered as such in terms of risk assessment. The fact that the toxicology of nanomaterials is still poorly known stresses on the importance of risk analysis in order to prevent dreaded events.

The risk assessment methods associated to the implementation of dangerous chemical agents are numerous and have been available for a long time. The peculiarity of powders, and more particularly nanomaterials, both in their physical characteristics and in their ability to react, leads to the conclusion that the existing methods need to

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be adapted to the current goals in health and in industrial hygiene⁴⁻⁷).

The purpose of this document is to provide the professionals in charge of conducting the risk evaluations with information allowing them to manage the discussions that they may have with their colleagues, during the construction of the scenario of dreaded events and to prioritize the appropriate arrangements. This method has been built based on the information that could be made available for operators thus allowing them to be strongly implicated in the risk assessment process.

The method is not intended to substitute existing methods currently in use to manage the chemical risk or the risk of explosion.

The proposed method is based on a “control banding” (CB) approach⁸) used in the industry for several decades, and which is easily accessible to the operators. Principally, it crosses the data of toxicology with the conclusions of the scenarios of exposure. If some methods have already been derived for nanomaterials e.g. by Paik *et al.*⁹), the report RIP-oN 3¹⁰) concluded on the necessity to develop risk evaluation tools.

In that context, the new method uses the pieces of information that are available in practical situations, which often is not much, and aims to be applicable for industrial implementation for all powders.

Existing Control Banding Approaches

Because of the increase of concern about nanomaterials over the past years, the main developments in control banding methods have been focusing on powders of this size. A critical review of some of these methods was recently published by Brouwer *et al.*¹¹).

One of the first robust tools was proposed by Paik *et al.*⁹) with the CB Nanotool that was updated in 2009¹²). This method presents the advantage of being easy to use with simple additive parameters related to intrinsic properties (e.g. size, shape, toxicity) and to the probability of exposure (e.g. dustiness, frequency of operations). It is recognized nowadays as a reference amongst existing methods¹⁰). One main drawback of this method for industrial applications is related to the scale of quantities, limited to laboratory situations (<100 mg) whereas industrial operations can necessitate quantities in kilograms.

To supplement its web-based control banding tool to assess hazardous substances, called Stoffenmanager¹³), TNO developed a nano-specific module (Stoffenmanager Nano) dedicated to nanomaterials¹⁴) (<http://nano.stof->

fenmanger.nl). The hazard bands are completely based on the COSHH Essentials¹⁵) based on a series of equations between the various criteria of hazard and exposure which make its implementation difficult in an industrial context.

The French ANSES agency^{16, 17}) uses a standard CB framework by applying incremental factors on the hazard classification of the parent material or an analogous material. The emission potential relies only on the physical form of the nanomaterial (solid, liquid, powder or aerosols). The process characteristics and safety issues are not considered. This method leads, in most cases, to the highest hazard bands.

The Precautionary Matrix for Synthetic Nanomaterials¹⁸) aims to guide producers or users of nanomaterials to identify the safety issues, during production, handling and waste disposal, in order to limit the personal exposure but it is not a risk assessment method as such.

The decision tree based method of Groso *et al.*¹⁹) more particularly addresses research laboratory situation. Although it is very handy, this method is difficult to adapt to an industrial environment.

In the above mentioned methods, uncertainty, availability of toxicological data and precautionary approaches lead to allocating of hazard bands in a conservative way. The consequence is a high level risk with no distinction between tasks even if strong safety measures (e.g. full containment) have been applied. Moreover, laboratory scale quantities of materials are considered at the laboratory scale (<100 mg), allowing no scaling in industrial operations.

Risk Assessment Method

Objectives and scope of the method

The present method aims to evaluate the risks for health issued at the workplace implying the solid materials, the powders, solid aerosols, and beyond particles of nanometric size (i.e. a material that contains primary particles with a diameter below 100 nm). It has not been intended to apply this method to fibers. This is due to the difference in aerodynamic behavior between spherical particles and fibers that shall be treated with an adapted approach.

This method is based on the “control banding” approach that classifies on several levels the toxicological hazard of the materials implemented, and the potential exposure issued by the use of these materials. For the hazard banding part of it, it takes up an existing scale of toxicological hazard called OHB (Occupational Hazard Band) very common in management of the chemical risk^{20, 21}). Indeed,

it has been chosen to keep unchanged the existing hazard classification whilst waiting for robust and validated data of occupational risks of nanomaterials which is currently in progress^{6, 7}.

The evaluation of the exposure takes into consideration the conditions of use of materials, their properties, the used quantities, as well as the frequency and the duration of implementation. The approach of the evaluation of risks is schematized in Fig. 1. The method focuses on exposure by inhalation. The skin exposure is not treated for the time being.

The calculation of the exposure index must be performed for every unit task, from the delivery of materials, down to their elimination as waste or as effluents. Every process must be divided into as many single tasks as necessary to allow a preliminary and detailed examination of all potential exposures in all working situation.

This method is not dedicated to the preliminary evaluations of risks inherent to the phases of maintenance, as well as maintenance/cleaning of collective protection equipment which have to be the object of dedicated procedures, specifically in the case of accidental situations. It could usefully be supplemented by specific measures of the exposure at the workplace by means of appropriate techniques^{22, 23}.

It has been deliberately decided not to mention the PPEs (Personal Protection Equipments) in this risk assessment method. Indeed, the evaluation of the risks must be ideally realized without PPEs that must be considered only in the last resort, when the preventive and corrective actions of collective protection have been deployed to reduce the initial risk.

It has to be noticed that, in conformance with the maximal potential of emission, some of the evoked situations of process taken as examples in the present document describe conditions degraded like leaks or spillage. These are simply examples that do not exempt in any way specific studies using appropriate methods (e.g. what if, HAZOP, MADS-MOSAR)^{24, 25}. It is reminded that if the present method does not apply to the accidental situations or to abnormal working conditions, it can nevertheless be used to fuel the process in place to prevent those situations.

The co-occupancy must be also taken into account for the workers in the handling zone and being the object of the risk evaluation. Even if they are not using these materials themselves they can be exposed to them.

Hazard banding

As already mentioned, the scale of toxicological hazard

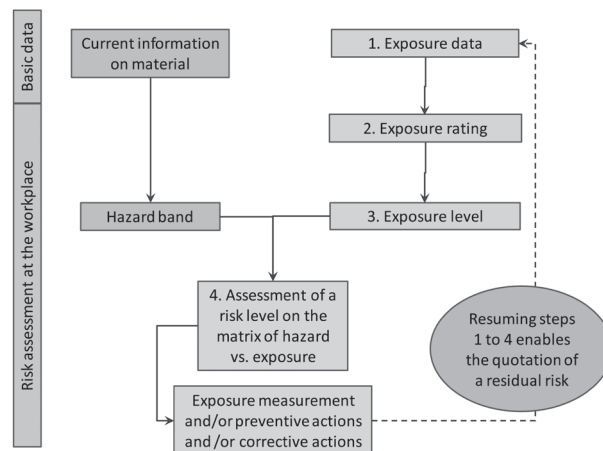


Fig. 1. Overview of the implementation of the method.

used in the present method is the existing OHB method, very wide-spread in the industry, and which comprises 5 bands. The threshold from one another band of danger is given by the interpretation of the current standards DSD²⁶ (Dangerous Substances Directive) before 2010, and CLP²⁷ (Chemical Labelling and Packaging) since 2010.

The principle of hazard banding is to assign values from 1 to 5 of chemicals, depending on the available toxicological data. Like all classification scales, the hazard banding scale depends heavily on how reliable the available data are. In other words, this scale shall be revised according to new scientific insights, and can be considered more as a “certainty scale” regarding the toxicity of chemicals than an absolute and final measurement of hazard.

At the beginning of 2010, the OHB scale of classification was revised as a step in the implementation of European regulation related to the classification, labeling and packaging of substances and mixtures (CLP)²⁷.

Several reasons have led us to keep the OHB scale unchanged for the time being. First of all, the scientific knowledge on nanomaterials is in continual motion, as much as the associated toxicological data²⁸. In the absence of threshold limit value (TLV) or even of indicative data that are not imposed by regulation, it is premature to adopt standards shifted from the reality, and that could give place to unsuitable actions. In any case, it is necessary to consult all supplier data and to gather as much information as possible before the implementation of any process on any material.

Moreover, the implementation of the CLP regulation is hardly 2 yr old. It has redistributed the toxicological data on a finer scale comprising a supplementary category compared to the DSD. The phase of transition between the

DSD and CLP regulations is not finished yet. Therefore, it seems desirable to let the industrialists achieve their upgrade process, at least till the end of the deadline setup for substances, i.e. in June 2015. Once this upgrade has been finished, it shall be planned to deeply modify the scale of toxicological danger OHB for the specific consideration of nanomaterials covered by the present risk assessment method.

The above assumptions as well as the details of the OHB classification presented in Table 1 are in line with the publications of NIOSH⁸⁾ and in agreement with the most recent position defended by the EC that says that the nanomaterials are also present in conventional chemicals, which means that current risk assessment methods need to be adapted to the nanometric scale²⁹⁾. These considerations have led us to concentrate on the control of exposure at the workplace rather than reassessing the toxicology scale applicable to nanoparticles.

In the OHB table (Table 1), the first step consists in analyzing the carcinogenic and mutagenic properties of chemicals together with those of toxicity for reproduction. Next the sensitizing power and the irritating power are examined, and afterwards the data of lethal concentration to 50% or lethal dose to 50%. The mentions H or EUH of the CLP²⁷⁾ are then used before reviewing the exposure limit values provided by regulation or any other source. The lowest hazard correspond to OHB1 and OHB5 compounds are the worst in terms of toxicological hazards and need the highest safety measures.

In practice, in the absence of knowledge of the toxicological properties of the materials, their OHB classification is proposed at the value of 4. The value of OHB 5 is applied to the most worrisome materials by application of the precautionary principle, e.g. in the particular case of nanomaterials with parent materials having an OHB value of 4.

Exposure levels

In order to facilitate the assessment of the exposure, the method has been proposed as a tool as simple as possible and sharp enough to enable anyone to make the difference in terms of risks between various situations. It is based on parameters that are easily accessible to operators who are often missing information. Therefore, a very complicated tool that would require a lot of sophisticated input data would be of no use on the shop floor and would not be put into practice.

The choice of the parameters was driven by very trivial questions that operators may very frequently ask such as:

- Am I going to open my container of nanoparticles so

that the content shall have a high probability of being put into suspension in air or is it hermetically closed most of the time and opened at the very last time?

- What is the shape of the solid material that I am going to handle? Is it made of nano particles 100% engineered?

• Since the MSDS is not saying anything about the particle size distribution, what information shall I use to assess what is inside the bag that I am about to open? And once my bag is open? Is there any behavior or any shape of the powder that shall warn me even if I have no accurate data about it?

• What about the operations that I am going to do with this material? Could they lead to aerosolization of material? And what about the liquid phase in which I am going to pour my nanomaterial? Is there any chance that my process temperature could vaporize my solvent and that I shall then be exposed to an aerosol containing nanoparticles?

• Is the confinement sufficient to protect me and my team-mates? What kind of data shall I read on the manometer or on the anemometer? Or what data shall I ask the maintenance team so that I can check that the confinement is within specifications before commencing my process?

• Is the current group protection sufficient for the operations I shall conduct?

All these questions and many other ones that had been collected on the shop floor have led to define a set of parameters that make sense at industrial scale, allow to assess correctly exposure at workplace whilst bearing in mind that the resulting tool must remain practical and practicable so that it can be practiced. Otherwise the method will not be used.

For these reasons, seven parameters have been proposed and assessed with different values corresponding to the description of actual situations seen on the shop floor and included in several models. The levels on each parameter are proposed on the analysis of practical industrial and laboratory situations based on the experience return of the authors and of a group of industrial and academic users of powders down to nanometer sizes.

In existing methods, various mathematical forms were used to qualify exposure levels, e.g. addition in Paik's method or a combination of equations in the Stoffenmanager Nano. Models involving different mathematical forms were tested (sum of parameters, combined sum and multiplication, weighing coefficients). The simple combination of multiplication and addition of seven selected parameters was found as the most convenient to get a final score that can be easily exploited by operators and to make

Table 1. Definition of Occupational Hazard Bands (OHB) of divided materials

OHB	Mutagenicity Carcinogenicity	Toxicity for Reproduction	Sensitizing power	Irritating power	DL50 (skin) mg/kg	CL50 (inhalation) mg/l/4 h	DL50 (oral) mg/kg	Mention H or EUH of hazard ⁽⁷⁾	OEL (dust) mg / m ³	OEL (vapors) ppm
1	Negative	Negative	Negative	No or little irritating	>2,000	>5	>2,000	Not classified	≥1	≥1000
2	Negative	Inadequate evidence of effects to the animal	Slightly skin sensitiz- ing	Irritating eyes and/ or skin	400–2,000	1–5	200–2,000	H302, H304, H312, H315, H319, H332, H336, EUH066	1–0.1	1000–100
3	Mutagenic positive in vitro not confirmed in vivo Carcinogenic, Mutagenic Cat. 2 (CLP) or 3 (DSD)	Effects moderated to the animal Reprotoxic Cat. 2 (CLP) or 3 (DSD)	Moderately to severely skin sensitizing Slightly allergenic of respiratory tract	Severely irritating eyes / skin Irritating of respiratory tract Corrosive	50–400	0.25–1	25–200	H301, H311, H315, H317, H319, H331, H335, H341, H351, H361, H362, H371, H373, EUH029, EUH 031, EUH070, EUH071, EUH203, EUH204, EUH205, EUH 208	0.1–0.01	100–10
4	Mutagenic positive in several tests in vitro and in vivo Carcinogenic, Mutagenic Cat. 1a and 1b (CLP) or 1 and 2 (DSD)	Severe effects to the animal and/or suspected or turned out at the man Reprotoxic Cat. 1a and 1b (CLP) or 1 and 2 (DSD)	Moderately to severely sensitizing of the respiratory tract	Corrosive with severe burns	1–50	0.005–0.25	0.5–25	H300, H310, H314, H318, H334, H340, H350, H360, H370, H372, H330, EUH032	0.01–0.001	10–1
5	An OHB can be attributed in case of high mutagenic or carcinogenic potential				<1	<0.005	<0.5		<0.001	<1

a difference between an acceptable working situation, and a situation to be improved.

The exposure indices are calculated as follows:

$$\text{IEx} = H \times S \times E \times C \times Q \times (F + D) \quad (1)$$

where H, S, E, C, Q, F, D (detailed in the following) are the seven parameters based on a pragmatic approach of assessing risks in labs and plants.

These parameters were chosen as the main characteristics of the materials and of the process that better describe the worker's exposure. They were also chosen as the most accessible ones at the shop floor level. All parameters are multiplied except the Frequency and the Duration parameters that are both related to time and therefore added.

Hermeticity of the source of particles (H). The hermeticity (tightness) parameter takes into account the fact that the emitting point of material stays hermetically closed (or not) during the implementation, enabling to put into practice the principle that no exposure means no risk in normal operating conditions. This parameter allows simplification in the assessment of the risk of systematic industrial operations in which the material remains in a sealed container (e.g. in original sealed supplier big bags). The counterpart of this approach is in the difficulty of guaranteeing the integrity of the containment of the materials as long as they are not in a state preventing them from showing any hazard, as for example the dispersion in a non volatile liquid. It also has to be noted that this parameter is only valid when considering normal working conditions and that it does not substitute the identification of potential accidental scenarios that could lead to exposure. Finally, it should be noted that apart from situations showing no exposure by definition (like sealed containers), an assessment of H at zero can also be achieved if sufficient physical measurements of particle concentration lead to the conclusion that there is no exposure. The same result can be obtained if a constant monitoring of the ventilation parameters is correlated to the same documented and measured observation of non-exposure. There are only two values for H:

H=0: Hermetic. The material is implemented in a container hermetically closed throughout the tasks that are applied to it, or there are sufficient physical measurements to conclude that there is no exposure.

H=1: Non-hermetic. The container is opened or has been opened (non guaranteed air tightness, repackaging, transfer).

Characteristics of the material (S). The intrinsic properties of solid particles are influenced by their particle size. It does not only affect hazards but also dispersion properties and consequently exposure by inhalation. However,

reliable data on the size of nanoparticles are often not available. Moreover, no definitive conclusion has emerged yet from the on-going debates on how to qualify particles with sizes between nanometers and micrometers. Without a complete definition, the lowest particle size value should be used to determine the S parameter, even if little information is commonly available in the Materials Safety Data Sheets^{30, 31}). In the absence of information on particle size, the S parameter also includes practical descriptive considerations on the behavior of powders.

S=1: Compact material. Substance in the state of block, granular, granular coated with wax; no emission of dust without alteration of the surface of the material.

S=2: Divided material. Primary particles of size grading <1 mm measured or according to the data provided by the supplier; material divided without formation of a cloud of material.

S=3: Unrefined powder. Primary particles of size grading <100 μm measured or according to the data provided by the supplier; possible formation of a cloud of material which falls down immediately under the influence of the gravity.

S=4: Fine powder. Primary particles of size grading <10 μm measured or according to the data provided by the supplier; formation of a cloud of dust that remains in the air during several seconds before observing a deposit (e.g. micronized powder).

S=5: Ultrafine particles or having a speed of fall almost nil. Primary particles of size grading <100 nm measured or according to the data provided by the supplier; a cloud of dust suspended in the air and clearly visible during a long moment. It has to be noticed that the materials of nanometric size being invisible, the cloud of ultrafine particles remains suspended in the air much longer than the one of the visible particles.

Emission potential of the material during its usage (E). This parameter is related to the potential emission of materials during usage. A lot of materials can generate a dust cloud of particles size up to nanometric scale when they are being used. This is due to all the combined conditions of implementation and mostly because of mechanical forces applied in the process. Even a steam distillation can drag particles away, and quite particularly during the relief of pressure of a tank, as the solvent being used is getting closer to its boiling point.

A distance of 2 meters was also assigned as the threshold between 'near field' and 'far field'. This value was calculated based on the work of Cherrie³²) which had been endorsed by the Stoffenmanager¹³). Instead of considering

the source of particles at the center of a 8 m³ cube, it was decided to apply a multiplicative factor of 3 to allow for the dustiness of nanoparticles. This means a volume of 24 m³ taken as a sphere that leads to consider a distance of 2 meters as a threshold between ‘near field’ and ‘far field’ in order to discriminate some working situations.

Although most solids dispersed in a liquid are not supposed to evaporate when temperature raises, the observation of working situations when releasing the pressure of tanks or reactors containing fine particles in a liquid shows some deposits of solid material at the venting port. This is particularly true when the liquid is getting close to the boiling point. An analogous observation can be made when operators are pouring some fluffy material or a dusty powder into a reactor (or a standard beaker at the lab scale) that contains a hot liquid, with some dust being generated and mixed with vapors which leads to an occupational exposure. In order to reinforce best practices and to make operators aware of the risks at stake when handling and mixing powders with liquids, something simple and practical had to be implemented with accessible parameters that do not necessitate any other detector than those already in place.

The partial pressure of the different constituents of an industrial mixture is not easily accessible, not as easily measured as a temperature, even when using a simple solvent like water. Taking water as a reference medium for the mixing with powders, it was easy to arbitrarily divide the 0–100 °C range using temperature thresholds commonly seen in industrial processes. From these temperatures, the corresponding pressure values have been calculated through the Antoine’s equation and then rounded for simplification. Doing the same exercise for ethanol leads to another set of pressure values for the same temperatures (Table 2).

The reading of Table 2 gives the same E value of 4 for water at a maximum temperature of 80 °C than for ethanol at 60 °C. Emission potential values can be calculated for other solvents used in the handling of powders through the same relationship^{36, 37}.

Five levels are proposed depending on the type of operation involved in the workplace.

E=1: Unlikely emission of material. Any operation (storage, transportation, weighing, etc.) in closed packaging.

E=2: Very low emission of material, not exceeding the emission point. E.g. Fractionated weighing, or Quality Assurance (QA) sampling, implementation in a wet medium in a QA or analytical laboratory, cleaning of closed industrial lines, implementation of material of nanometric size

Table 2. Emission potential (E) of Water and Ethanol based on the temperature / pressure relationship through the simplified Antoine’s equation^a

Maximum T (°C)	Ethanol		Water	
	P/P _{atm}	E	P/P _{atm}	E
20	0.1	2	0.0	---
40	0.2	3	0.1	2
60	0.5	4	0.2	3
80	1.0	5	0.5	4
100	---	---	1.0	5

^a The simplified Antoine’s equation is $\log(P) = A - B / (T + C)$ with P is the vapour pressure in mmHg, P_{atm} is the atmospheric pressure (760 mmHg), A=8.2133, B=1652.56, C=231.48 for ethanol and A=8.07131, B=1730.63, C=233.426 for water³⁷.

in water up to 40 °C or in ethanol up to 20 °C.

3=3: Possible emission of material, not exceeding 2 m around the emission point. E.g. Introduction in a liquid through a ventilated manhole, carefully fold of empty bags after unloading, lab scale implementation (by transfer, pouring, manual stirring, etc.) of material of nanometric size in a lab hood in water at 40–60 °C or in ethanol at 20–40 °C.

E=4: Likely emission material, being able to exceed sporadically 2 m around the emission point. E.g. Draining of big bag, compacting of packaging soiled in compactor with waste, handling of unsealed containers, transfer of a liquid under vacuum in non leakproof conditions, mixes or dilution under mechanical stirring, wet cleaning of packaging, or of equipments or of working surfaces or of clothes, implementation of material of nanometric size in water at 60–80 °C or in ethanol at 40–60 °C.

E=5: Very likely emission of material: permanent presence of a cloud of particles in the working zone because of the processes and of the mechanical forces involved. E.g. Non leakproof conveying of material finely divided by pneumatic mean or by vacuum, manipulation by dry way of soiled packaging, dry mixing of finely divided material, transfer by dry way of finely divided material whatever the quantity involved; hot sampling on tank, decompression of any packaging containing a material of nanometric size in a liquid, implementation of material of nanometric size in water above 80 °C or in ethanol above 60 °C.

Containment by ventilation / efficiency of capture (C). In some cases, the process needs to be hermetically and entirely closed (i.e. usage or fabrication of very sensitive particles), and there is no possible exposure. However, most operations are conducted at open atmosphere and the ventilation remains among the most essential tools of

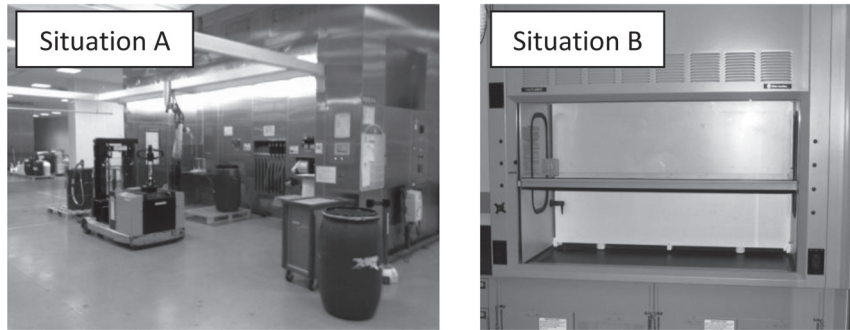


Fig. 2. Industrial booth (A) and lab fume cupboard (B).

protection in the workplace against all types of chemicals. Especially when handling powders, it is essential that the particles are conveyed in such a way that the pulmonary tract of the operator is constantly protected.

An originality of the present method compared to the other risk assessment methods is the air containment by ventilation that is taken into account as an essential parameter to drive or prevent the exposure to airborne materials. Based on the current state of the art, a dynamic barrier like a top-down air flow generated at the ceiling combined with a specific extraction that enables a slight depression at the workplace is amongst the best ways to protect operators from the exposure to materials by inhalation.

Given all the different configurations that may be encountered in an occupational environment, ventilation parameters were selected based on the authors experience on their efficiency since no normative rules have been yet proposed for large equipments of air containment. For this reason, the values mentioned in existing standards for containment^{33, 34)} expressed in ppm of sulfur hexafluoride (SF₆) and for the efficiency of capture³⁵⁾ have been fitted to fulfill the purpose of the risk assessment process, and have been experienced on practical industrial and laboratory workplaces. These suggested parameters should be continuously improved. Moreover, in the industrial safety management process, procedures can be introduced to allow workers to check that the containment equipment fulfills these criteria.

However, these parameters take into account engineering, general ventilation, characteristics of the equipments, operating method, distance from the capture point to the emission point, maintenance, periodic controls, etc. When standards exist, the agreement of the recommendation in terms of ventilation parameters with these standards was respected. These levels of containment or capture efficiency are indicative and can be adjusted on the basis of

more detailed study.

Finally, air containment systems used in industrial environments and in laboratories are distinguished to represent as the best onsite practical situations. All mentioned values of tracer gas concentration, flow out and flow in consider front air velocity, measured at the sash opening. In this parameter, open air conditions of work, without any containment are not accepted in the perspective of the manipulation of materials divided down to nanometric sizes. In the same manner, the general building ventilation is not taken into account in the estimation of containment levels although it can have a major impact on the efficiency of containment.

Given the large choice in the existing technologies, especially at the lab scale, it is important to bear in mind that a protective equipment has to be checked by the user before all operations, and that all the operational parameters (air speed, flow, etc) must be easy to access. The C parameter is therefore a combination of different conditions that need to be checked regularly and maintained as a whole to avoid any drift in an industrial environment as well as in a lab.

For the C parameter, two areas are considered in an industrial environment (C_A) and a lab environment (C_B), as illustrated in Fig. 2, with 5 values from 1 to 5 for each condition. For the containment by ventilation in an industrial environment, the following levels are proposed:

C_A=1. Total containment. Airtight static barrier or completely closed industrial process.

C_A=2. Ventilated industrial large-sized booth in dynamic barrier satisfying the following criteria (Type 1):

- Vertical flow in through ceiling with rate of renewal in extracted air ≥ 30 .
- Efficiency of capture $\geq 95\%$ at the point of emission of particles.
- Depression expressed by Flow in / Flow out $\leq 70\%$.

- Air speed from 0.25 to 0.35 m/s at a distance ≤ 60 cm of the closest point of venting out (60 cm is taken as the average most comfortable working distance between an operator and the vented wall of an industrial booth)

$C_A=3$. Ventilated industrial large-sized booth in dynamic barrier satisfying the following criteria (Type 2):

- Vertical flow in through ceiling with rate of renewal in extracted air ≥ 30 .

- Efficiency of capture $\geq 90\%$ at the point of emission of particles.

- Depression expressed by Flow in / Flow out $\leq 80\%$.

- Air speed from 0.15 to 0.25 m/s at a distance ≤ 60 cm of the closest point of venting out.

$C_A=4$. Dedicated local ventilation. Static barrier limiting the scattering of the materials and the influence of the disturbances in the workshop, rate of renewal ≤ 30 , efficiency of capture $\geq 85\%$.

$C_A=5$. Ordinary local ventilation. Efficiency of capture between 70 and 85%.

For the containment by ventilation in laboratory, the following levels are proposed:

$C_B=1$. Total containment. Glove box, insulator, totally closed process.

$C_B=2$. Dynamic barrier suitable for a containment ≤ 0.1 ppm of SF₆^{33, 34}.

Depending on technologies:

- Vertical flow in through ceiling at >0.35 m/s and flow out >0.4 m/s (safety weighing booth, biosafety cabinet (BSC) class II a/b, ...).

- Without controlled flow in but with flow out at >0.4 m/s (standard fume cupboard, ventilated booth, booth with recycled and filtered air, biosafety cabinet (BSC) class I...).

$C_B=3$. Dynamic barrier suitable for a containment ≤ 0.5 ppm of SF₆^{33, 34}.

Depending on technologies:

- Vertical flow in through ceiling at ≤ 0.35 m/s and flow out ≥ 0.4 m/s (safety weighing booth, biosafety cabinet (BSC) class II a/b, ...).

- Without controlled flow in but with flow out at $0.2 \leq v \leq 0.4$ m/s (standard fume cupboard, ventilated booth, booth with recycled and filtered air, ...).

$C_B=4$. Dedicated local ventilation. Flow out ≤ 0.2 m/s or containment >0.5 ppm of SF₆^{33, 34}.

$C_B=5$. Ordinary local ventilation. E.g. Open booth without specific ventilation, articulated arms (schnörkel).

Quantity of material used (Q). Given the intention to see the present method applied in industry at all scales, it is important to be able to make the difference between the

quantities used in production and those used at the laboratory scale. So, the Q parameter stands for the quantity of material used and it has been proportioned so that it can fit all possible environments, from the analytical lab up to the minimal bag size of material in a production area.

Q=1: Below 1 g.

Q=2: 1–10 g.

Q=3: 10 g–1 kg.

Q=4: 1–10 kg.

Q=5: Above 10 kg.

Operation frequency (F). The frequency of operation is classically used in existing CB methods. It considers the fact that more frequent operations result in a more likely exposure.

F=1: Less than monthly.

F=2: Monthly.

F=3: Weekly.

F=4: Daily tasks or tasks repeated over several days.

F=5: Tasks repeated several times per day.

Daily usage duration (D). The duration of operation is considered on a daily basis. As for the frequency parameter, it takes into account the fact that longer operations are more likely to result in employee exposition.

D=1: Less than 5 min.

D=2: 5–30 min.

D=3: 30 min–2 h.

D=4: 2–4 h.

D=5: More than 4 h.

Finally, these seven parameters (Table 3) are included in Eq. 1 to define the exposure index IEx. It has to be noted that the two parameters of time (the frequency of operation F and the duration of implementation D) are added together before multiplication with the other parameters. This is to avoid taking the time of exposure twice with the same weight in the same calculation of IEx. The calculation of the exposure index is made for all unit operations, from the delivery of materials to their elimination as wastes. Each process is decomposed in as much unit tasks as necessary to allow the examination of all potential exposures in all involved work situations. Moreover, co-activity has to be considered for workers in the material handling area under investigation, even if they do not handle directly this material.

Risk evaluation

The construction of a table IEx/OHB sheds light on the levels of risk that correspond with the priorities of action of identical rank. Once IEx has been assessed for a given material with a specific OHB, the crossing of the suitable

Table 3. Summary of exposure parameters

Hermeticity at source	Characteristics of the solid divided material	Emission potential	Air containment	Quantity of used divided materials	Frequency of operation	Duration of operation
H	S	E	C	Q	F	D
0 Airtightness guaranteed	1 Compact material	Unlikely emission	Total containment	<1 g	< Monthly	<5 min
1 Airtightness not guaranteed	2 Divided material < 1 mm	Very low emission	Type 1 dynamic barrier	<10 g	Monthly	<30 min
	3 Unrefined powder < 100 µm	Emission possible	Type 2 dynamic barrier	<1 kg	Weekly	<2 h
	4 Fine powder < 10 µm	Likely emission	Dedicated local aspiration	<10 kg	Daily	<4 h
	5 Ultra-fine powder < 100 nm	Very likely emission	Ordinary local aspiration	≥10 kg	More than Daily	≥4 h

IEx row with the right OHB column gives the semi quantitative level of risk as shown on Fig. 3.

The calculated IEx is comprised between 0 and 6,250. The value of 0 refers to any situation with no exposure in normal condition, corresponding to the cases of handling in hermetic conditions (H=0). The scale of IEx has been shaped to obtain a satisfactory discrimination on a large number of working situations in various existing manufacturing areas.

Four risk levels (RL) are defined:

RL blue: No action required given the justified lack of exposure in the work situation. This justification is based on the configuration of the work situation that does not allow for exposure. The same assessment can be performed by an expert when all metrological data associated with the task being examined enable to conclude a total absence of exposure. This encompasses exposure measurements as well as constant monitoring of the efficiency of the ventilation.

RL green: Acceptable situation provided there is no drift, neither in the working situation being examined, nor in any of the exposure parameters.

RL yellow: Situation to be looked at carefully. The task being examined shall not be commenced before technical and / or organizational arrangements have been taken and documented so that a new assessment enables to conclude that the level of exposure shows no risk for the health of operators according to local standards.

RL red: Unacceptable situation. Immediate action required before commencing the task being preliminarily examined.

To illustrate how the method is applied on a practical case, application to an operation of weighing of nanomate-

		Toxicity of chemicals (OHB values)				
		1	2	3	4	5
Calculated IEx	> 1800	Yellow	Yellow	Red	Red	Red
	1001 - 1800	Yellow	Yellow	Yellow	Red	Red
	601 - 1000	Green	Green	Yellow	Yellow	Yellow
	401 - 600	Green	Green	Green	Yellow	Yellow
	201 - 400	Green	Green	Green	Green	Yellow
	1 - 200	Green	Green	Green	Green	Green
0	NO EXPOSURE MEANS NO RISK IN NORMAL CONDITIONS					

Fig. 3. Risk matrix based on calculated exposure indices (IEx) and Occupational Hazard Band (OHB) values

Risk levels:

Risk Level Blue: No action required given the justified lack of exposure in the work situation. This justification is based on the configuration of the work situation that does not allow for exposure. The same assessment can be performed by an expert when all metrological data associated with the task being examined enable to conclude a total absence of exposure. This encompasses exposure measurements as well as constant monitoring of the efficiency of the ventilation.

Risk Level Green: Acceptable situation provided there is no drift, neither in the working situation being examined, nor in any of the exposure parameters nor in the efficiency of the protection at the workplace.

Risk Level Yellow: Situation to be looked at carefully. The task being examined shall not be commenced before technical and / or organizational arrangements have been taken and documented so that a new assessment enables to conclude that the level of exposure shows no risk for the health of operators according to local standards.

Risk Level Red: Unacceptable situation. Immediate action required before commencing the task being preliminarily examined.

rials (original particle size <100 nm) in an industrial large size booth of type 1 is proposed.

In this case, the quotation in each parameter is the following: H=1 since the bags are opened before weighing, S=5 since the material is <100 nm, E=2 since the material is weighed gently, C=2 since the booth used for this operation is of type 1, Q=5 since we assume an amount of mate-

rial >10 kg, F=5 since the operation is performed daily, D=2 since the total duration of the task is less than 30 min.

The equation (1) gives:

$$I_{EX} = H \times S \times E \times C \times Q \times (F + D) \\ = 1 \times 5 \times 2 \times 2 \times 5 \times (5 + 2) = 700.$$

$I_{EX}=700$ which means a risk level green for a material of OHB 1, a risk level yellow for a material of OHB comprised between 2 and 4, and a risk level red for a material of OHB 5.

Discussion on residual risk, risk management and documentation

The residual risk shall be assessed after all the relevant measures have been taken. Group protection measures must of course be preferred to individual ones so that the new calculation of exposure index is leading at least to an acceptable level. Ideally, a measurement of exposure shall be performed to substantiate the efficiency of the corrective actions taken.

Only the measurements at the workplace can lead to the conclusion that there is no exposure. These measurements can focus on direct exposure by particle counting or on the efficiency of the ventilation if an expert has previously quantified and calibrated the expectable exposure as a function of ventilation. Relying on ventilation requires a constant monitoring of the performance of the installation.

The risk assessor shall also remain aware that local ventilation can be very efficient and bring to a conclusion of non-exposure if all the dust is very properly collected at the point of emission with a very remote probability of drifting. In other words, a calculated I_{EX} only means a potential exposure. Only measurements at the workplace can lead to the conclusion that the exposure is or is not there.

If individual protection measures are to be implemented, the risk assessor shall take into consideration the protection of all the workers exposed, which means those handling the material as well as all colleagues working in an area where they can be affected by the dust then generated. Because inhalation is the main risk associated with powders, the efficiency of the personal protection equipment (PPE) shall be very thoroughly checked, especially the tightness of masks and how they fit on the face. It shall also be taken into account that the choice of masks is of critical importance. A mask suitable for the filtration of minimum 99.95% of particles allows an excellent protection, and it is often preferable to a chemical cartridge respirator when handling powders. Again, measurements

of exposure at the work place shall be of relevant help to better choose suitable protection.

The rest of the personal protection equipment depends a lot on the nature of the business. It shall be adapted to the tasks to be performed and shall allocate some comfort in use, bearing in mind that the handling of fine powders requires some logical industrial hygiene practices due to their tendency to stick any kind of surface. These practices encompass dedicated long sleeves clothes, vacuum cleaning the clothes after use, goggles, hair protection, safety shoes and gloves.

For each task identified in the analyzed process, a risk level and a priority of action have to be documented. All the necessary information has to be gathered to ensure the site management that the regulation requirements have been fulfilled. It is necessary to assess the risk on each elementary task, and not on a working post, in order to make sure that the parameters of the exposure would not differ from one situation another without being thoroughly analyzed. For instance, weighing shall not be considered as such as an elementary task. It should be decomposed at least in (1) opening of a container, (2) taking the right amount of material, (3) gently pouring into another dedicated container, (4) closing both containers and (5) cleaning the weighing scale. In all these situations, the different parameters of the calculated I_{EX} shall differ from one another and lead to different prevention measures.

Moreover, the risk assessment has to be revised regularly, not only to take into account the modifications of the process equipments and parameters but also take into account potential new pieces of information available on the properties of the materials. Regardless of local requirements by law, the risk assessment process on a whole plant shall be visited at least annually.

Conclusion

In this paper, a new control banding method is proposed for the risk assessment in the workplace of solid material down to the nanometric scale. The involved parameters have been selected to take into account all factors leading to exposure, from lab activities up to the industrial scale situations. They have been defined based on industrial information currently and practically available.

In particular, this method takes into account the ventilation barriers applied at the workplace with detailed functional parameters (air speed, flow, etc.). Moreover, a hermeticity parameter (H) is introduced to concentrate the evaluation of the risks on working situations which can

reasonably lead to exposure.

This method is a practical tool for assessing workplaces up to the industrial scale for powders and nanoparticles. Advances in scientific knowledge of nanomaterials, both physical characteristics and toxicology, will inevitably drive improvements and modification to this risk assessment method.

References

- 1) EC (1989) Council Directive 89/391/EEC of the 12 June 1989 on the introduction of measures to encourage improvements in the safety and health of workers at work.
- 2) EC (1998) Council Directive 98/24/EC of the 7 April 1998 on the protection of the health and safety of workers from the risks related to chemical agents at work (fourteenth individual Directive within the meaning of Article 16(1) of Directive 89/391/EEC).
- 3) Borm PJA, Robbins D, Haubold S, Kuhlbusch T, Fissan H, Donaldson K, Schins R, Stone V, Kreyling W, Lademann J, Krutmann J, Warheit D, Oberdorster E (2006) The potential risks of nanomaterials: a review carried out for ECETOC. *Part Fibre Toxicol* **3**, 11.
- 4) Maynard AD, Aitken RJ, Butz T, Colvin V, Donaldson K, Oberdorster G, Philbert MA, Ryan J, Seaton A, Stone V, Tinkle SS, Tran L, Walker NJ, Warheit DB (2006) Safe handling of nanotechnology. *Nature* **444**, 267–9.
- 5) Ricaud M, Witschger O (2009) Nanomaterials – Definitions, toxicological risk, characterisation of occupational exposure and prevention measures. INRS, ED 6050.
- 6) NIOSH (2010) Progress Toward Safe Nanotechnology in the Workplace. National Institute for Occupational Safety and Health (NIOSH), No. 2010–104.
- 7) NIOSH (2013) Filling the Knowledge Gaps for Safe Nanotechnology in the Workplace. National Institute for Occupational Safety and Health (NIOSH), No. 2013–101.
- 8) NIOSH (2009) Qualitative Risk Characterization and Management of Occupational Hazards: Control Banding (CB) – A Literature Review and Critical Analysis. National Institute for Occupational Safety and Health (NIOSH), No. 2009–152.
- 9) Paik SY, Zalk DM, Swuste P (2008) Application of a pilot control banding tool for risk level assessment and control of nanoparticle exposures. *Ann Occup Hyg* **52**, 419–28.
- 10) Aitken RA, Bassan A, Friedrichs S, Hankin SM, Hansen SF, Holmqvist J, Peters SAK, Poland CA, Tran CL (2011) Specific Advice on Exposure Assessment and Hazard/Risk Characterisation for Nanomaterials under REACH (RIP-oN 3), Final Project Report.
- 11) Brouwer DH (2012) Control banding approaches for nanomaterials. *Ann Occup Hyg* **56**, 506–14.
- 12) Zalk DM, Paik SY, Swuste P (2009) Evaluating the control banding nanotool: a qualitative risk assessment method for controlling nanoparticle exposures. *J Nanopart Res* **11**, 1685–704.
- 13) Marquart H, Heussen H, Le Feber M, Noy D, Tielemans E, Schinkel J, West J, Van Der Schaaf D (2008) ‘Stoffenmanager’, a web-based control banding tool using an exposure process model. *Ann Occup Hyg* **52**, 429–41.
- 14) Van Duuren-Stuurman B, Vink SR, Verbist KJM, Heussen HGA, Brouwer DH, Kroese DED, Van Niftrik MFJ, Tielemans E, Fransman W (2012) Stoffenmanager Nano version 1.0: a web-based tool for risk prioritization of airborne manufactured nano objects. *Ann Occup Hyg* **56**, 525–41.
- 15) Brooke IM (1998) A UK scheme to help small firms control health risks from chemicals: toxicological considerations. *Ann Occup Hyg* **42**, 377–90.
- 16) Ostiguy C, Roberge B, Woods C, Soucy B (2010) Development of a specific Control Banding Tool for Nanomaterials. French Agency for food, environmental and occupational health and safety (ANSES).
- 17) Riediker M, Ostiguy C, Triolet J, Troisfontaine P, Vernez D, Bourdel G, Thieriet N, Cadene A (2012) Development of a control banding tool for nanomaterials. *J Nanomater* **2012**, 879671.
- 18) Höck J, Hofmann H, Krug H, Höhner K, Krug H, Lorenz C, Limbach L, Gehr P, Nowack B, Riedeker M, Schirmer K, Schmid B, Som C, Stark W, Studer C, Ulrich A, van Götz N, Wengert S, Wick P (2010) Guidelines on the Precautionary Matrix for synthetic nanomaterials. Bern, Switzerland: Federal Office for Public Health and Federal Office for the Environment.
- 19) Groso A, Petri-Fink A, Magrez A, Riediker M, Meyer T (2010) Management of nanomaterials safety in research environment. *Part Fibre Toxicol* **7**, 40.
- 20) Rhoditech (2001) Chemical risk assessment and control (*Evaluation et maîtrise du risque chimique*).
- 21) Sanofi Aventis CRVA (2007) Risk assessment at the workplace (*Evaluation des risques au poste de travail – ERPT*), version 5.
- 22) Fleury D, Bomfim JAS, Vignes A, Girard C, Metz S, Muñoz F, R’Mili B, Ustache A, Guiot A, Bouillard JX (2013) Identification of the Main Exposure Scenarios in the Production of CNT-polymer Nanocomposites by Melt-moulding Process. *J Clean Prod* **53**, 22–36.
- 23) Witschger O, Le Bihan O, Reynier M, Durand C, Charpentier D (2012) Recommendations for characterizing potential emissions and exposure to aerosols released from nanomaterials in workplace operations. INRS, Hygiène et sécurité au travail, 226, ND 2355, 41–55.
- 24) Tixier J, Dusserre G, Salvi O, Gaston D (2002) Review of 62 risk analysis methodologies of industrial plants. *J Loss Prev* **15**, 291–303.
- 25) Périllon P (2003) MOSAR, présentation de la méthode. Techniques de l’ingénieur; SE 4060.
- 26) EC (1967) Council Directive 67/548/EEC of 27 June 1967 on the approximation of laws, regulations and

- administrative provisions relating to the classification, packaging and labelling of dangerous substances.
- 27) EC (2008) Regulation N°1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labeling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) N° 1907/2006.
 - 28) Schulte PA, Murashov V, Zumwalde R, Kuempel ED, Geraci CL (2010) Occupational exposure limits for nanomaterials: state of the art. *J Nanopart Res* **12**, 1971–87.
 - 29) Linher O (2013) Où en sommes nous de la réglementation sur les nanomatériaux en Europe? Afnor, Plaine Saint-Denis (France), 05/07/2013.
 - 30) Lee JH, Kuk WK, Kwon M, Lee JH, Lee KS, Yu IJ (2013) Evaluation of information in nanomaterial safety data sheets and development of international standard for guidance on preparation of nanomaterial safety data sheets. *Nanotoxicology* **7**, 338–45.
 - 31) Eastlake A, Hodson L, Geraci C, Crawford C (2012) A critical evaluation of materials safety data sheets (MSDSs) for engineered materials. *J Chem Health Saf* **19**, 1–8.
 - 32) Cherrie JW (1999) The effect of room size and general ventilation on the relationship between near and far-field concentrations. *Appl Occup Environ Hyg* **14**, 539–46.
 - 33) EN 14175 (2003) Fume cupboards. Safety and performance requirements. EN 14175 Standard.
 - 34) NF 15206 (2010) Sorbonnes de laboratoire—Seuil pour l'essai de confinement, installation et maintenance. NF 15206 Standard.
 - 35) EN 1093-4 (2008) Safety of machinery. Evaluation of the emission of airborne hazardous substances. Capture efficiency of an exhaust system. Tracer method. EN 1093–4 Standard.
 - 36) Yaws CL, Yang HC (1989) To estimate vapor pressure easily. Antoine coefficients relate vapor pressure to temperature for almost 700 major organic compounds. *Hydrocarbon Proc* **68**, 65–8.
 - 37) Lide DR (2005) *CRC Handbook of Chemistry and Physics*, Boca Raton.