Occupational risk assessment during explosion severity tests of carbon black and MWCNT in a laboratory

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Abstract. Risk assessment has been conducted by quantitative and qualitative methods during explosion severity tests in a 20 L sphere for carbon black (N990) and MWCNT (NC7000™). The qualitative risk assessment was performed by control banding with CB Nanotool and StoffenManager Nano. The methodology for the quantitative assessment was based on general recommendations for exposure measurement assessment and an easy-to-use operational sampling approach. The results enabled to highlight a few sources of nanomaterials emission during the tests. It led also to the finding that the dynamic barrier provided by the local exhaust ventilation system can be temporarily weakened due to overpressure events. Based on the comparison of the measurements with the risk assessment results, the relevance of the selected control banding tools was assessed.

1. Introduction
The use of nanomaterials (NMs) in many innovative and commercial products has continuously increased in recent years. Belgian industries stock, use or produce important volumes of NMs. In 2016, 57,550 tons of NMs have been imported, 16,947 tons have been manufactured and 13,815 tons distributed in Belgium [1]. Some of these NMs might be explosive. In the light of past accidental events with powders explosions in industries, is it essential that explosion severity and sensitivity of nanopowders are characterized and that health and safety protection measures for workers manipulating those NMs are adapted when necessary. This study aims at comparing the results obtained with two different qualitative risk assessment tools, namely CB Nanotool and StoffenManager Nano, with the results from air particles concentration measurements during explosion severity tests on carbon black (N990) and MWCNT (NC7000™) in a laboratory.

2. Set up of a new laboratory dedicated to powders explosion severity tests
In the frame of its public service activities, ISSeP has set up in Colfontaine (Mons, Belgium) a new laboratory dedicated to the assessment of the risks associated with explosive NMs production and use in industrial facilities (figure 1). One of the applied tests is the characterization of the explosion severity of powders in a 20 L sphere, through the determination of the maximum pressure reached (Pmax) and the maximum rate of pressure rise (dP/dt max).

When designing the laboratory, collective and individual protection measures were taken to limit operator exposure as well as to mitigate the dissemination of nanoparticles (NP) into the environment. The laboratory is equipped with exhaust ventilation that sets up a depression in the airlock and in the...
work area. The local exhaust ventilation is equipped with 3 filters (one F7 and two HEPA H14) filtering the air before it is released to the outside environment. The entry to the laboratory is through an airlock where personal protective equipments (PPE) are stocked. They include a complete Tyvek combination, a FFP3 respiratory mask, security shoes and two pairs of nitrile gloves.

![Figure 1.](image)

(a) Configuration of test facilities with (b) entrance through an airlock and (c) the work area.

3. Qualitative risk assessment by control banding

Control banding tools like CB Nanotool [2], [3] and StoffenManager Nano [4] were designed to help NMs users in making a first assessment of their activities and to adapt their control measures when appropriate. The methodology consists in combining hazard and exposure levels within several risk levels (4 in CB Nanotool; 3 in StoffenManager Nano) in order to adjust workers’ protective measures. One of the major advantages of both tools is that they are applicable to substances where little knowledge exists on their intrinsic hazard or their emission potential through a simplified methodology accessible to non occupational health & safety (OSH) experts. The number and nature of input parameters differ between the two models. CB Nanotool includes more hazard parameters than StoffenManager Nano (15 hazard parameters versus 4) and less exposure parameters (5 versus 11). One distinctive feature of StoffenManager Nano is taking into account the protection measures in place, while CB Nanotool recommends the protection measures for the assessed tasks.

Both control banding tools have been applied to the scenario of explosion severity tests on carbon black (N990, provided by SkySpring Nanomaterials) and multi-walled carbon nanotubes (MWCNT, NC7000™, provided by Nanocyl). Tests on selected NMs have been conducted only a few times for research purposes, so an annual frequency (lowest available frequency) was chosen for the control banding assessment. However a risk assessment for a monthly frequency was also conducted in order to depict a standard use of the facilities. Results are presented in table 1.

| Nanopowder       | Frequency | CB Nanotool v2.0 | StoffenManager Nano 1.0 |
|------------------|-----------|------------------|------------------------|
| Carbon black (N990) | Yearly    | RL2 : Fume hood  | III : Lowest Risk      |
| Carbon black (N990) | Monthly   | RL2 : Fume hood  | II : Medium Risk       |
| MWCNT (NC7000™) | Yearly    | RL2 : Fume hood  | I : Highest Risk       |
| MWCNT (NC7000™) | Monthly   | RL3 : Containment| I : Highest Risk       |

In an annual frequency hypothesis, the estimated risks by the evaluation tools do not match. StoffenManager Nano leads to the highest risk level for MWCNT and the lowest risk levels for carbon black whereas CB Nanotool assesses a medium risk level for both NMs. For a monthly frequency, both tools estimate the highest risk level for MWCNT and the medium risk level for carbon black.
Some parameters strongly impact the assessed risk level, such as product’s dustiness, surface reactivity or carcinogenicity. However this information is not readily available in safety data sheets and is poorly documented in the literature [5], [6]. This lack of availability for some parameters increases uncertainties on risk assessments and therefore could lead to an overestimation of the control measures to apply on the basis of the precautionary principle. Hence it is important to be aware of those limits when using control banding tools. It is also crucial that further study is carried on to better characterize hazard properties and exposure potential of NMs placed on the market for a better knowledge of the risks associated to their use. Work on harmonized characterization protocols is needed [5].

4. Risk assessment with operator’s exposure measurements

A measurement campaign was performed in order to assess the relevance of assessed risks with control banding tools. The methodology was based on general recommendations for exposure measurement assessment [7] and an easy-to-use operational sampling approach [8].

The explosion severity test includes the following steps: powder weighing, tank filling with powder, explosion severity test, sphere and weighing area cleaning. The tested protocol was exactly the same for the 3 tests but the different steps of the procedure were intentionally separated by breaks to allow identifying the emitting activities.

4.1. Measurement strategy

The air flow through the laboratory (figure 1) was studied with a smoke generator. The results indicate that the main air flow comes from the ceiling to the hood placed in the workplace area. Therefore, a Condensation Particle Counter (CPC, TSI 3007) and a scanning mobility nanoparticle sizer (SMPS, Nanoscan, TSI 3910) were placed on a laboratory bench 2 m away from the working area to measure the background concentration.

The operator was equipped on the one hand with a portative particle counter DiscMini (Testo Inc.) and on the other hand with a Mini Particle Sampler (MPS) system (ECOMESURE) [9] in order to characterize the nature of measured particles by Transmission Electron Microscopy (TEM). Both instruments were sampling in the breathing zone.

In addition, a CPC 3007 was initially placed close to the worker (test on carbon black) and secondly handled by a technician (cf. figure 2) to measure particle concentrations in the operator’s breathing zone (tests on NTC). Nevertheless, as the operator is moving, both strategies were less reliable than the measurement provided by the DiscMini (carried by the operator). Figures 6 and 7 present an example of time series (third test, with MWCNT).

4.2. Explosion severity test with carbon black

No difference has been observed versus time between the two CPCs, indicating no major release of particles from the hood towards the laboratory. The total concentration remained below 100 particles/cm³. However, the DiscMini measured concentrations over 1.000 particles/cm³ during cleaning. MPS sampling in the operator’s breathing zone indicated that the aerosol was dominated by carbon black agglomerates with primary particles larger than 100 nm (figure 3). It has been noticed that high pressure air is used during the cleaning of the sphere: it would explain carbon black release out of the explosion severity testing system reaching the breathing zone of the operator.

4.3. Explosion severity test with CNT

The second CPC was carried by a technician to measure particles concentration in the operator’s breathing zone. It confirmed the findings from the first test, i.e. a release of particles while cleaning the sphere. Depressurization step during the explosion severity testing would also emit particles. However only one object related to MWCNT was observed by the TEM analysis (figure 4). The aerosol sampled during the cleaning phase appeared to be dominated by carbon black and by fiber-like...
particles (figure 5). They would be attributable respectively to carbon black deposits on clothes (from previous test) and to cleaning product.

Figure 2. Occupational exposure measurements in the breathing zone during explosion severity tests, with operator weighing on the right and a technician carrying the CPC on the left (Source: ISSeP).

Figure 3. Carbon black agglomerate on a MPS grid analyzed by TEM (Source: ISSeP).

Figure 4. MWCNT on a MPS grid analyzed by TEM (Source: ISSeP). Scale: 200 nm.

Figure 5. Fiber-like particles on a MPS grid analyzed by TEM (Source: ISSeP). Scale: 1 µm.

4.4. Explosion severity test with CNT, with improved protocols
During the two previous tests, it has been observed that the use of high pressurized air to clean the sphere was leading to particles emission. It has also been noticed that the operator was using a bin and changing his gloves outside the hood. Specific tests demonstrated that these operations were emissive. This third test was performed in order to assess remediation solutions: the bin was placed inside the work area; gloves change was carried out inside the hood; sphere cleaning was operated with a lower air pressure; operator was equipped with new PPE. The number concentration time series are presented in figures 6 and 7. Particles observed by TEM are mainly attributable to the cleaning product.
**Figure 6.** Particles number concentrations (particles/cm³) in the breathing zone and in the background during explosion severity tests with MWCNT with improved protocol: weighing, arms tapping, pressure rise and explosion in the sphere.

**Figure 7.** Particles number concentrations (particles/cm³) in the breathing zone and in the background during explosion severity tests with MWCNT with improved protocol: cleaning operations.
4.5. Conclusion

Findings of the measurement campaign carried out with INERIS are the following: (i) the entrance airlock is depressed compared to the exterior; the laboratory is depressed compared to the airlock; the aspiration velocity in the immediate vicinity of the work area is sufficient; (ii) the background concentration observed is around 10 particles/cm³ when the hood is working and around 1.000 particles/cm³ when the hood is in stand-by mode; (iii) cleaning activities generate particles emissions; (iv) the sphere reservoir filling step seems to not generate particles emissions.

An increase in particles number concentrations was observed following the sphere depressurization. A possible explanation is that the overpressure imposed during the sphere depressurization could temporarily lead to particles emissions inside and outside the hood.

At any time (except during tests with smoke) the number concentration of particles measured in the laboratory is lower than the threshold of 20,000 particles/cm³ proposed by BSI [10] and of 40,000 particles/cm³ proposed for carbon black by IFA [11], [12], [13], [14] for workers health protection. Even if those provisional reference values are under revision [15], no internationally approved reference values exist for the time being.

MPS grids are very slightly loaded with carbon black or MWCNT after weighing or cleaning operations. This indicates that worker exposure is limited. The measurements nevertheless allowed to identify a few sources of nanomaterials emission during the tests and to come up with recommendations to further reduce operator exposure.

5. Comparison of risk assessments results from qualitative and quantitative approaches

Results of the exposure measurements have enabled a further refinement of the risk assessment by control banding. In particular the dustiness has been adjusted. The results from comparing the measured carbon black concentrations are in line with those from control banding tools, both assigning a medium risk level (table 2). The level of control recommended by CB Nanotool corresponds to the existing measures (fume hood). On the other hand both tools assess the highest risk level for MWCNT while measurements of particles number showed that concentrations during tests are very low and that nearly no MWCNT fiber was detected on MPS grids. StoffenManager Nano automatically classifies fibers in the highest danger level, conducing to the highest risk category. This highlights a limitation in the use of this control banding tool for fibrous materials. However, MWCNT would deserve further investigation since their concentration measurement remains questionable due to their specific geometry.

Table 2. Risk assessment results by control banding for a monthly frequency compared to measured concentrations during corresponding tests on carbon black and MWCNT.

| Nanopowder                  | Carbon black (N990) | MWCNT (NC7000™) |
|-----------------------------|---------------------|------------------|
| CB Nanotool v2.0            | RL2 : Fume hood (Medium Risk) | RL3 : Containment (Highest Risk) |
| StoffenManager Nano 1.0     | II : Medium Risk    | I : Highest Risk  |
| Mean background concentrations¹ (part/cm³) – CPC² | 3                  | 20               |
| Mean background concentrations¹ (part/cm³) – NanoScan³ | 13                 | 14               |
| Mean concentrations¹ close to the operator (particles/cm³) – CPC² | 3                  | 21               |
| Mean concentrations¹ close to the operator (particles/cm³) – DiscMini² | 196                | 157              |
| MPS grids observation       | Slightly charged grids | Only one MWCNT   |
6. Discussion and conclusion
A measurements campaign during explosion severity tests with carbon black and MWCNT has confirmed the effectiveness of personal and collective protective measures in ensuring health protection of the worker in charge of the tests. Nevertheless the measurements allowed to identify a few sources of nanomaterials emission during the tests and to come up with recommendations to further reduce the operator exposure. A new measurements campaign could help validate the efficacy of the implementation of the new recommendations.

Selected control banding tools tend to overestimate the risk as shown by the comparison with measured air concentrations in the work area. Some parameters strongly influence the assessed risk level, such as product’s dustiness, surface reactivity or carcinogenicity. However these parameters are not readily available in safety data sheets or poorly documented in the literature. This lack of availability for some parameters increases uncertainties on risk assessments and therefore could lead to an overestimation of the measures applied for worker’s health and safety protection. Hence one must keep those limitations in mind when using control banding tools. In addition, agreed harmonized protocols and further studies are required to better characterize hazard properties and emission potential of NMs allowed on the market in order to get a better insight on the potential risks associated to their use.

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Acknowledgments
This study was funded by the Walloon Public Scientific Institute (ISSeP).