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Abstract. The handling of carbon nanotube (CNT) powders is a plausible scenario during the course of the CNT life-cycle. However, related exposure data remain limited. In this context, information about the dustiness of CNT is therefore of great interest, for example for control banding or exposure modelling. Here, we investigate the dustiness of fourteen CNT powders using the Vortex Shaker (VS) method. The central component of the VS method is a stainless steel cylindrical tube, continuously shaken in a circular orbital motion, in which a small volume (0.5 cm^3) of the powder to be tested is placed. All samples were obtained through the NANoREG Nanomaterials Information and Web-Order system. The test procedure that we have developed is based on four principal components: (i) a respirable cyclone for gravimetric sampling, (ii) a CPC as a reference instrument for number concentration measurement, (iii) an MPS for collection of particles for EM observations/analysis, and (iv) an ELPI for size-resolved aerosol measurement. In this paper, the data were evaluated using two parameters: (i) the mass-based dustiness index in the respirable fraction; and (ii) the number-based dustiness index in the respirable fraction. The results indicate that the method leads to relatively accurate mass- and number-based dustiness indices. The indices obtained span wide ranges, of 2 and 3 orders of magnitude variation for mass and number respectively, suggesting a corresponding significant difference in terms of potential exposure. EM observations reveal that airborne CNTs are mostly released as bundles of different shapes ranging from a few tens of nanometers up to tens of micrometers in size.

1. Introduction

Dustiness is a generic term used to define the ability of a powdered material (e.g., loose, granulated, or pelletized powders) to generate an aerosol (airborne particles) during handling. The dustiness of a powder is an important determinant for worker exposure and should be considered during the design and operation of many industrial or research processes [1]. For some years now, dustiness has been a required input parameter in control banding (CB) tools used to evaluate and control the risk of exposure to nanomaterials [2, 3]. Its use is also increasing in risk assessment, for example for the carbon nanotube group [4].

In response to the particular requirements associated with testing and measuring the dustiness of nanomaterials, a number of recent studies have aimed either to modify the two methods (the rotating drum and the continuous drop) described in the EN15051-1 European standard [5] or to develop new approaches [6]. One such approach is the Vortex Shaker (VS) method described in this work. Our motivations for developing this method were based on three main issues simulating different (including worst-case) workplace scenarios to those addressed by the EN15051-1 methods [5]; performing dustiness experiments with small amounts of nanomaterials that are either potentially very toxic and/or costly; and developing smaller set-ups that can be used in ventilated enclosures or fume hoods, thus better protecting operators in charge of experiments.

The expected widespread use of carbon nanotube (CNT) composites in industrial and commercial applications across industry calls for an assessment of their possible release and of potential worker exposure [7]. The handling of CNT powders is plausible throughout the entire life-cycle of CNTs, but in spite of evidence that shows that workers are exposed to CNTs [8], exposure data obtained in workplaces are unfortunately scarce. Consequently, there is a real interest in developing dustiness test methods in order to produce data for CNTs and rank them according to their ability to generate aerosols.

The current consensus in the literature is that particle mass on its own is not an adequate metric for evaluating aerosol exposure in situations where nanomaterials are handled. Instead, a multi-metric approach is now recommended, especially for carbon nanotubes [9]. A multi-metric approach includes other aerosol properties, including airborne particle number concentration, size distribution and morphology. In addition, the usefulness of real-time data for providing information about particle emission kinetics is also now well-established because new procedures for data-analysis are being developed [6].

Given this context, the VS method was established here in order to provide relevant dustiness indices as well as information about size distribution and morphology. The dustiness of fourteen CNTs was investigated. Only results in terms of mass- or number-based dustiness indices are reported here; particle emission kinetics and size distribution of the released aerosols will be presented in a separate paper.

2. Material and methods
The vortex shaker (VS) method is a recent method in terms of standard dustiness testing, however several configurations of this method have been proposed over time [6, 10]. The technique was derived from an original concept that was developed as part of a field study devoted to evaluating the release of aerosols during the handling of single-walled carbon nanotubes (SWCNT) [11].

2.1. Vortex shaker design and aerosol measurement
The central component of the experimental set-up consists of a specially designed stainless steel cylindrical tube (inner diameter of 31 mm, volume of 102 cm^3) with a conical bottom that is continuously shaken in a circular orbital motion (displacement amplitude: 4 mm; angular frequency: 30 Hz), into which a small volume (0.5 cm^3) of the test sample is placed (Figure 1).

HEPA-filtered air is passed through the cylindrical tube at a flow-rate Q_{VS} of 8.4 l/min in order to transfer the emitted aerosol inside the tube to the sampling and measurement section. The aerosol emitted during the vibration is drawn from the outlet tube to the real-time instruments and sampling devices through an initial flow splitter, which divides the aerosol flow into two flows directed toward two identical respirable cyclones (GK2.69, SKC) operating at Q_C = 4.2 l/min. One of these respirable cyclones is equipped with a cassette containing a pre-weighed filter for gravimetric analysis. The sampled particle mass is then used to determine the respirable mass dustiness index. The second respirable cyclone acts as a particle selector for the real-time instruments and the TEM grid sampler positioned downstream. Due to the short sampling time (~10 s), the TEM grid sampler requires a by-pass system (equipped with a 25-mm filter cassette) in order to maintain a constant flow through the respirable selector. To prevent exposure of the operator during tests as well as during the disassembly

and cleaning sequences between each test, the entire test bench is housed within an approved ventilated enclosure that has been specially designed for the safe handling of powders (LEV systems, Safetech).

Because (i) the entire range of particle sizes corresponding to the respirable size fraction should be assessed for the risk of exposure by inhalation [12], (ii) a single, rather than two, size-resolved instrument is preferred, and (iii) the size-resolved instrument should have a high time resolution (~1 s), the Electrical Low Pressure Impactor (ELPI™, Dekati Ltd) was selected for the size-resolved instrument. As a reference instrument for counting particles, a condensation particle counter (CPC Model 3007, TSI Inc.) was used.

To collect airborne particles for subsequent observation and analysis by electron microscopy, a specific TEM grid sampler (MPS, Ecomesure) equipped with Holey Carbon Film on 400 Mesh Copper Grids (S147-A, Agar Scientific) was used. The electron microscopy observations were conducted at the Laboratoire Amiante Fibres Particules (LAFP) with a transmission electron microscope (120 kV JEM-1400, Jeol) equipped with a CCD camera (ES500 Erlangshen ES500, Gatan Inc.). The JEM-1400 is also equipped with an EDS microanalysis system (Oxford Instruments). Prior to each observation, a size calibration at the magnification used for EM observation of the samples was performed with certified polystyrene latex spheres of 0.88 µm diameter. The collected particles was not counted and sized in this study as our intention was only to characterize the samples from a qualitative and global point of view.

Carbon impregnated conductive flexible tubing was used to connect the different parts of the set-up as well as the instruments.

In compliance with the requirements of EN15051-1 [5], the air in the experimental set-up was controlled for humidity (RH = 50.9 ± 0.6 %) and monitored for temperature (22.1 ± 0.3 °C) for the duration of the experiments.
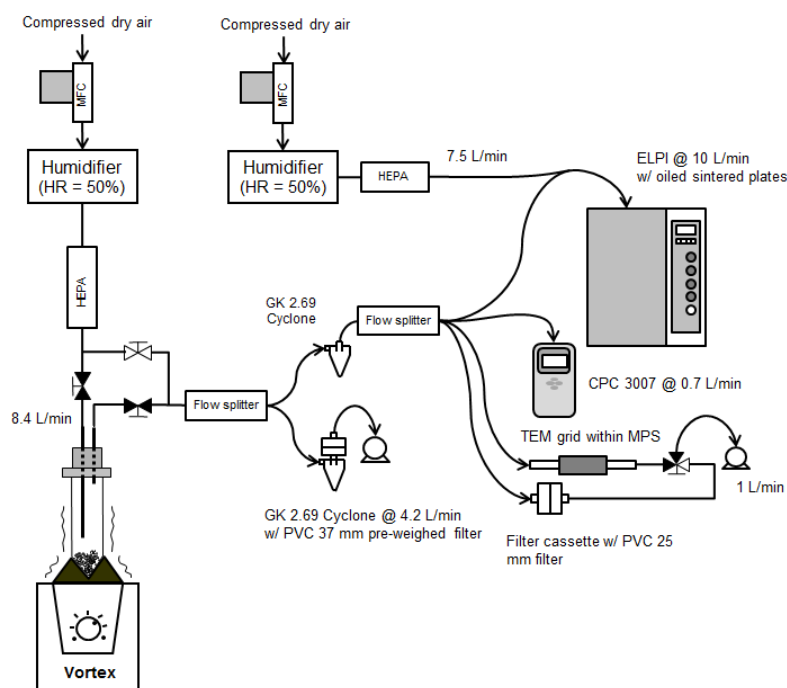

Figure 1: Experimental set-up of the vortex shaker method for determining the number-based and mass-based dustiness indices, characterizing the particle size distribution of the aerosol emitted, and collecting airborne particles for subsequent EM observations.

The test samples were weighed with a XP205 analytical balance (10 µg readability, Mettler Toledo), and the 37-mm filters used for the respirable cyclone were weighed with a MX5 microbalance (1 µg readability, Mettler Toledo). The filters used in this study are PVC membrane filters with a pore size of 5 µm (GLA 5000, SKC Inc.). This type of filter was chosen because of its low tare weight and low moisture pickup for gravimetric stability.

2.2. Test protocol

The test samples were prepared by pouring 0.5 cm^3 of powder into an Eppendorf® microtube. After filling, the tubes were weighed to the nearest 10 µg. The samples were then conditioned for at least 24 h prior to the dustiness test in a laboratory-made humidity-controlled chamber at 50 ± 2 % RH.

After cleaning the entire test bench, and/or, if necessary, changing the tubing and connections, and having equipped the cyclone with a pre-weighed filter for gravimetric analysis, the airflows were checked using a flow calibrator. The cleanliness of the air through the test bench was then assessed from CPC measurements. The by-pass line was then opened and the main line closed in order to fill the pre-conditioned 0.5 cm^3 test sample into the cylindrical tube. The mass of the test sample M_0 was obtained from the difference between the mass of the filled microtube and mass of the microtube after emptying.

In parallel, the real-time instruments started recording the background level, over about 180 s. Finally, at the same time, the incoming air flow was switched on in the main line and the agitation was turned on. The test sequence comprised 60 s of agitation, with the measurement continuing for another 540 s, thus giving a total of 600 s for the sampling (respirable cyclone) and real-time measurement (CPC and ELPI). Sampling with the MPS was carried out for around 10 s after the peak in concentration.

After each test, the respirable sampling filter was gently removed from the cassette and gravimetric analysis was then performed according to the laboratory protocol in order to obtain the mass Δm_f of the collected particles. This mass was used to determine the mass-based dustiness index (see section 2.3.

Real-time instrument data files from the CPC and the ELPI™ were saved and the data were subsequently analysed using specific calculation tools developed in the laboratory in order to determine the number-based dustiness index, emission rate and size distribution (see section 2.3.

During cleaning of the test bench and measurement instruments, the operator wore a powered respirator, protective gloves with sleeves and a cotton laboratory coat.

2.3. Data processing

In this work, the data for the vortex shaker method were evaluated using two parameters derived from the respirable filter sampling and CPC measurements. As mentioned in the introduction, the emission rate and size distribution data will be presented in a separate paper.

The mass-based dustiness index in the respirable fraction ($DI_{M,R}$), reported in milligrams of aerosol per kilogram of powder, was calculated by dividing the mass collected by the respirable sampling filter (in milligrams), by the mass M_0 of the powder placed in the cylindrical tube (in milligrams) :

$$DI_{M,R} = \frac{\Delta m_f}{M_0} \cdot \frac{Q_{VS}}{Q_C} \cdot 10^6$$

The number-based dustiness index in the respirable fraction ($DI_{N,R}$), given in particles per milligram of powder, was calculated by dividing the number of particles emitted over the duration of the vibration period (60 s) (in particles) by the mass M_0 of the powder placed in the cylindrical tube (in milligrams) :

$$DI_{N,R} = \frac{1}{M_0} \cdot \sum_{0}^{T} C_{CPC}(t) \cdot Q_{VS} \cdot \Delta t_{CPC} \cdot \frac{10^3}{60}$$

where $C_{CPC}(t)$ is the number concentration recorded by the CPC at time t, in particles per cm^3, and Δt_{CPC} is the time step of the CPC (1 s in this work).

2.4. Carbon nanotubes

Fourteen CNTs were evaluated. These candidate CNTs were supplied by the European Commission's Joint Research Centre (JRC), who have established a repository of Representative Test Materials (RTMs), which hosts industrially manufactured nanomaterials that are distributed worldwide for the safety testing of nanomaterials [13]. The CNTs were received in vials, each containing about 100 mg of CNTs. One or more vials were used for each experiment, depending on the bulk density of the sample. Given the subsampling procedure from a single batch by the JRC, the vials provided can be considered identical.

The different test CNTs, their main physical properties and the basic characteristics of the test samples are given in Table 1, below.

Table 1: Designation and main properties of the test CNTs and test samples.

CNT Designation*			JRC Data**			Test Sample	
Type*	NM	MW or SW	Diameter (nm)	Length (μm)	Surface area (m²/g)	Mass (mg)	Bulk density (g/cm³)
Core	400	MW	13.6	0.846	254	29.7	0.06
	401		64.2	4.048	18	4.8	0.01
	46000a	SW	n/a	n/a	n/a	95.6	0.19
Alternative	402	MW	12.7	2.2	226	47.1	0.09
	403		12	0.62	189	70.0	0.14
	40001a		15	50	>233	24.3	0.05
	40002a		15	50	>233	27.5	0.05
	40003a		20-30	10-30	>110	48.7	0.10
	40004a		<8	10-30	>500	198.3	0.40
	40005a		8-15	50	>233	31.1	0.06
	40006a		20-30	10-30	>110	63.3	0.13
	40007a		8	30	>500	129.9	0.26
	40008a		8-15	50	>233	24.9	0.05
	40009a		20-30	20-30	N.A	44.3	0.09

*Type according to the NanoREG project and identification code used by JRC.

Only one of the fourteen CNTs was a single-walled CNT (SWCNT); the other thirteen were multi-walled CNTs (MWCNT). According to the JRC data, the CNTs cover a wide range of diameters, lengths and surface areas.

The mass of the test samples ranged from about 200 mg down to 5 mg. These masses correspond to the volume of 0.5 cm^3 used as the reference volume in the VS method. The large variations in mass are due to the differences in the bulk density of the CNTs; the minimum and maximum bulk densities obtained were 0.01 and 0.4 g/cm^3, respectively. It is interesting to note that these values are 5 to 235 times lower than the theoretical graphite solid density of 2.27 g/cm^3.

Results and discussion

A total of 42 experiments were conducted on the fourteen CNTs using the VS method (i.e. three replicates of each CNT were tested).

Figure 2 presents the mass-based ($DI_{M,R}$) and number-based ($DI_{N,R}$) dustiness indices (average values and 95 % confidence intervals) of the respirable fraction. The limit of detection of the mass-based dustiness index (LOD($DI_{M,R}$)) is also shown. The LOD($DI_{M,R}$) corresponds to the ratio of the gravimetric detection limit to the mass of the test sample, thus the LOD($DI_{M,R}$) was determined for each experiment. The limit of detection associated with the gravimetric analysis was obtained from the reproducibility of the blank PVC membrane weights as measured before and after their assembly within a 37 mm sampling cassette used with the respirable cyclone. The repeat weight measurements took place over a period of about 1 month and were performed on six series of five PVC membranes from the same batch. The gravimetric limit of detection finally obtained was 17 µg. Assuming a mass M_0 of 100 mg, this corresponds to a LOD($DI_{M,R}$) of 340 mg/kg.

A first observation concerns the low scatter of the results obtained for each CNT. The median coefficient of variation (CV) of the $DI_{N,R}$ is 10 %, with minimum and maximum values of 1 % and 29 %, respectively. This CV is the same as that of the $DI_{M,R}$ (10 %) but the range of the latter is a little wider, with minimum and maximum values of 4 % and 63 %, respectively. Overall, these results demonstrate that the protocol developed in this study yields accurate dustiness indices.
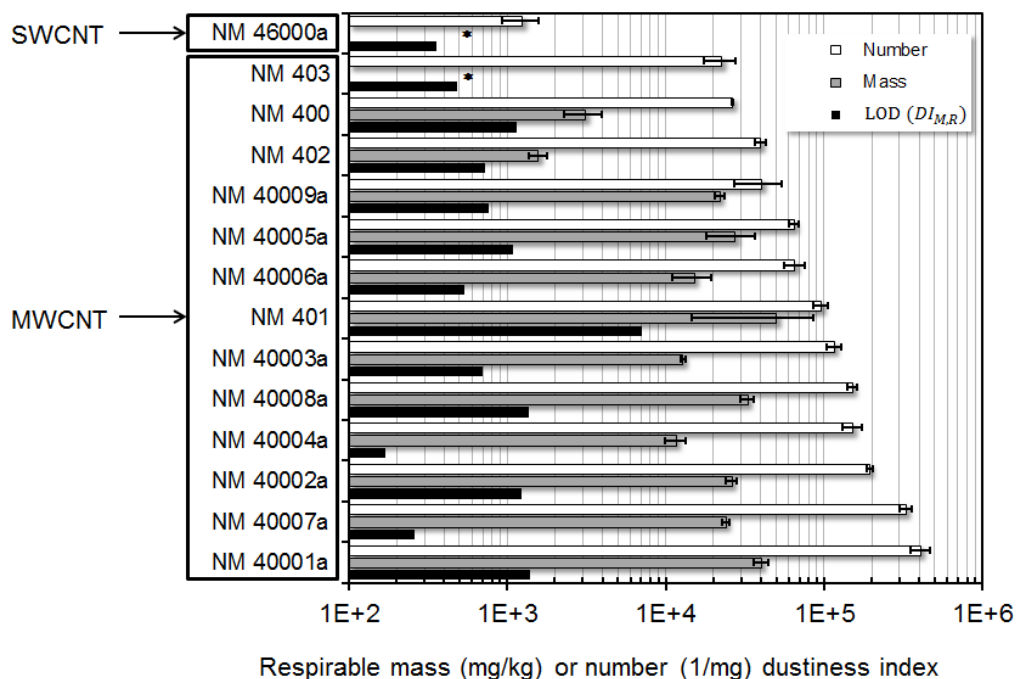

Figure 2: Respirable mass dustiness indices (in mg/kg) and respirable number dustiness indices (in 1/mg) for the fourteen CNTs, obtained using the VS method. Average values are presented with their 95% confidence interval. Black bars correspond to the LOD($DI_{M,R}$). *: mass dustiness indices were below the LOD($DI_{M,R}$).

A second observation concerns the values of the dustiness indices obtained using the VS method. The $DI_{N,R}$ values of the CNTs vary by three orders of magnitude, with a median value ~8.1 10^4 1/mg, while the $DI_{M,R}$ values span a narrower range, covering two orders of magnitude variation, with a median value of ~2.3 10^4 mg/kg. If the SWCNT is excluded, a narrower range of $DI_{N,R}$ values is observed the $DI_{N,R}$ values of only the MWCNT vary by one order of magnitude, with a median value ~9.6 10^5 1/mg. However, exclusion of the SWCNT does not change the result for the $DI_{M,R}$ as the

index obtained for the SWCNT was below the LOD($DI_{M,R}$). From these results, it seems clear that the particle releases are considerably lower for the SWCNT than for the MWCNT, suggesting that there is a corresponding significant difference in terms of potential exposure, all other things being equal. Concerning the $DI_{M,R}$, the situation is somewhat different as the SWCNT is characterized by a mass dustiness index below the LOD($DI_{M,R}$). Only one of the MWCNT samples (NM 403) had a value below the LOD($DI_{M,R}$). The ratio $DI_{M,R}$/ LOD($DI_{M,R}$) varies widely among the other twelve MWCNTs, ranging from about 2 to 92.

Although a number of experimental studies have been carried out on the dustiness of carbon nanotubes [6], only two produced dustiness data that can be compared to the results of this work [14, 15]. The data available for comparison are shown in Figure 3. In one of the studies, the dustiness test method was somewhat different to the VS method, based instead on the Venturi dustiness testing device initially developed for pharmaceutical powders [16]. In the other study, the dustiness method was also based on the use of a vortex shaker, but a different configuration and measurement protocol were used [15]. Moreover, the trade names of the JRC CNT samples cannot be determined (for the second study), though the names are given for the three CNTs used in the other study [14]. For these reasons, our interpretation of the comparison remains very limited. Of the dustiness values presented in Figure 3, only two are categorized as SWCNT. Overall, the dustiness values vary by a little more than two orders of magnitude, from about ~1.6 10^3 mg/kg up to about ~3.2 10^5 mg/kg. Interestingly, only one link can be made on NM 402. The difference between the two $DI_{M,R}$ determined for NM 402 is quite important: the value obtained in this work is ~20 times lower than the value obtained in the previous study [15]. As stated earlier, this is essentially due to differences in the test protocol. In the earlier study, bronze micro-beads were added to the test samples in the cylindrical tube in order to promote de-agglomeration and release of airborne particles during the agitation. Moreover, the test sequence involved 3600 s of agitation and sampling, and thus was very different from the protocol used in this work.
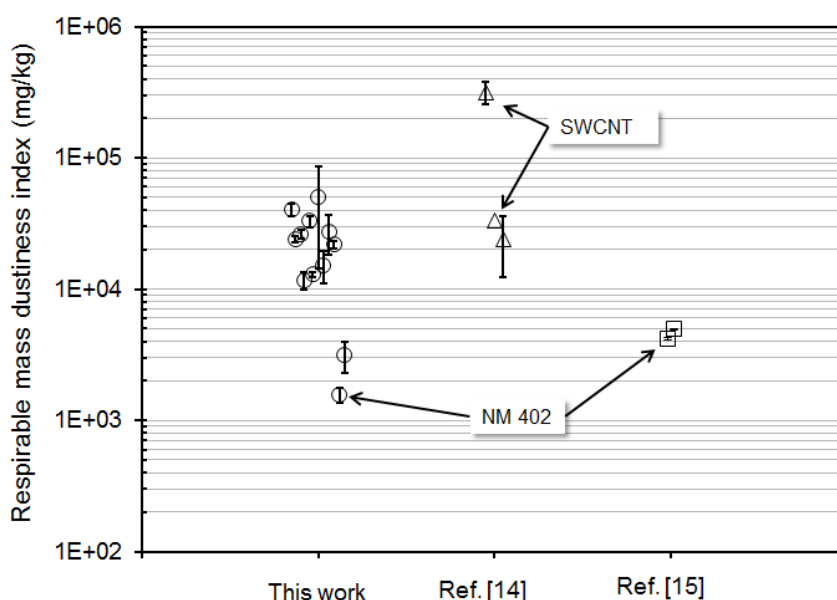

Figure 3: Comparison of the respirable mass-based dustiness indices (in mg/kg) obtained in this work with available published indices from [14, 15].

The last observation concerns the ranking of the different CNTs. In Figure 3, the dustiness data are ranked according to $DI_{N,R}$, from the highest (NM 40001a) to the lowest (NM 46000a). The lowest

$DI_{N,R}$ was obtained on the SWCNT. It can be observed that the ranking order differs according to which of the dustiness metrics, mass- or number-based, is considered. Moreover, there appears to be no correlation between the two dustiness metrics. This suggests that the choice of a dustiness metric will have significant implications for exposure modeling or when comparing powders. This supports our initial decision to develop a dustiness method following a multi-metric approach.

Figures 4, 5 and 6 present transmission electron microscopy (TEM) images of collected airborne CNTs (MWCNT 401, SWCNT 46000a, MWCNT 40002a) at different magnifications. MWCNT 401 was selected for TEM analysis because of its singular morphology compare to the others CNTs. SWCNT 46000a was selected because it was the only SWCNT included in the study. MWCNT 40002a was chosen as it is representative of the other CNTs.
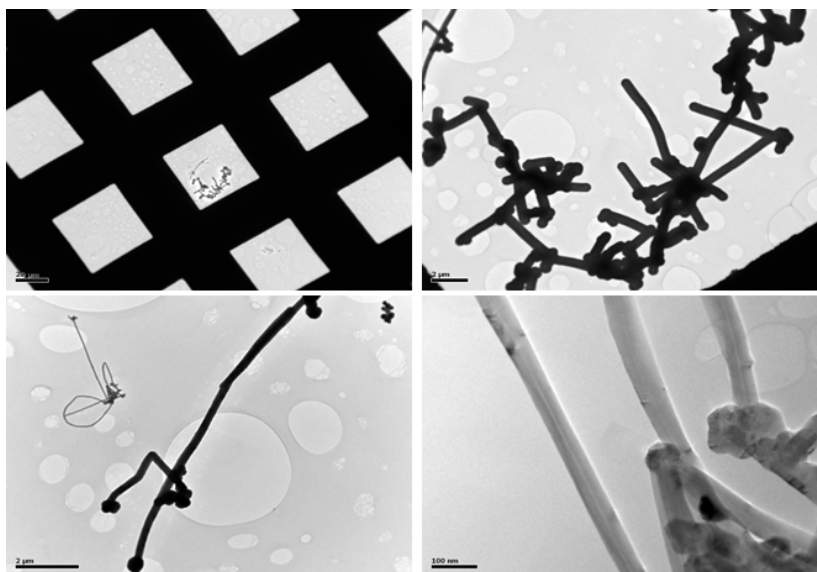

Figure 4: TEM images of airborne CNTs sampled during the MWCNT 401 experiments. Sampling duration of 10 s with the MPS equipped with 400 Mesh Holey Carbon Film TEM grids. Images © LAFP.
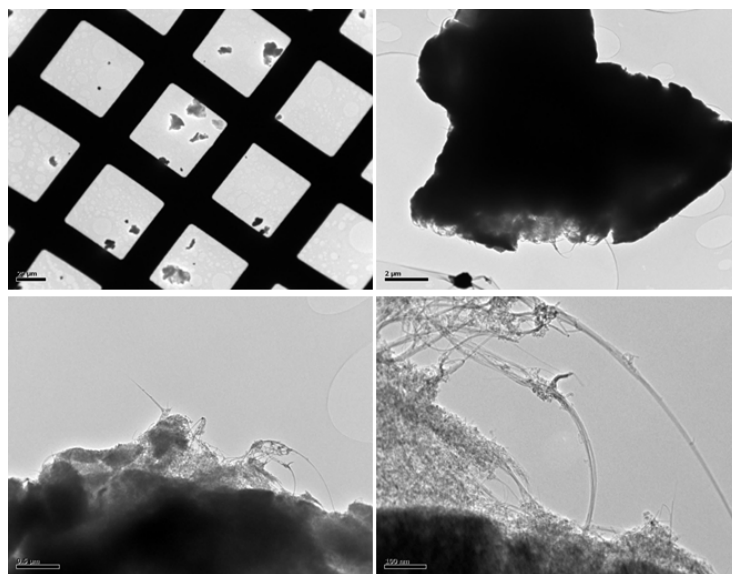
Figure 5: TEM images of airborne CNTs sampled during the SWCNT 46000a experiments. Sampling duration of 10 s with the MPS equipped with 400 Mesh Holey Carbon Film TEM grids. Images © LAFP.

The image on the top left shows the structure of the square mesh grid (openings of 40 x 40 μm^2) and the particles that were collected. The images demonstrate that the protocol used here makes it possible to obtain TEM grids that are not overloaded, i.e. the number of particles per unit of area is low enough to allow straightforward observation.

The images also illustrate that the particles that comprise the released aerosols vary greatly in terms of the size and morphology of the CNT aggregate structures. Only MWCNT 401 exhibited any individual fibers in the images (Fig. 4). Some of these fibers appear to be knotted, as shown in Figure 4. The remainder of the CNT images all show nanotubes with different diameters and aspect ratios, tied or wrapped up together in bundles (Figs. 5 and 6). The bundles, of variable density, exhibit different shapes and range from a few tens of nm to several tens of micrometers in size. Several nanotubes, either straight or curved, typically protrude from these bundles. Closer examination of the bundles reveals that some of the nanotubes have metal catalyst particles attached to them. EDS analysis indicates that these particles are essentially Fe.
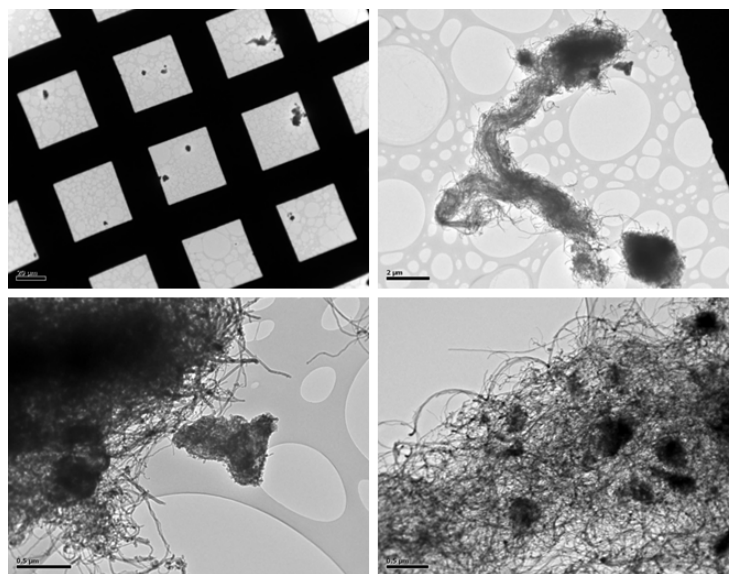
Figure 6: TEM images of airborne CNTs sampled during the MWCNT 40002a experiments. Sampling duration of 10 s with the MPS equipped with 400 Mesh Holey Carbon Film TEM grids. Images made © LAFP.

Conclusion

In this work, the VS method was developed following a multi-metric approach, in order to obtain relevant dustiness indices as well as information about size distribution and morphology. The dustiness of fourteen industrially manufactured CNTs provided by JRC was then investigated. The results indicate that the method provides relatively accurate mass- and number-based dustiness indices. The dustiness indices cover a wide range, of 2 and 3 orders of magnitude variation for mass and number metrics, respectively, suggesting a corresponding significant difference in terms of the potential for exposure. When the CNTs are ranked in order of dustiness, the order is different depending on which of the two metrics is considered, and there appears to be no correlation between the two indices. Electron microscopy observations show that CNTs are mostly released as bundles of different shapes, ranging from a few tens of nanometers up to several tens of micrometers in size. Individual nanotubes were observed to protrude from these bundles. The particle emission kinetics and size distributions of the released aerosols will be presented in a separate paper.

The few existing studies on the dustiness of powders (including CNTs) show that there is still a need for further work on the harmonization of methods and the processing of data. Moreover, efforts should be made to improve our understanding of the factors that control the dustiness of powders. These different elements are important as requests for relevant dustiness data are likely to increase in the future, particularly for risk assessments using exposure modeling or control banding tools.

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