Risk assessment of handling rigid carbon nanotubes at a technical centre in Berlin

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Abstract Emission of and inhalation exposure to multiwall carbon nanotubes (MWCNTs) were studied by air samples. Material samples and first air samples were taken in a test chamber during simulated work tasks and analysed under a scanning electron microscope (SEM). It was shown that due to careless handling an emission of the investigated MWCNT into air is possible. Consequently, workplace measurements were performed. Stationary sampling and sampling at the person were conducted during the handling and installation of discs coated with MWCNTs. The samples were analysed by a modified SEM analysis procedure to be able to compare the results with a suggested occupational exposure limit value (OELV) of 10,000 fibres per cubic meter (F/m³). The results show no emission of fibres above the limit of quantification; consequently, it could be assumed that there is neither a relevant exposure. The personal sampling results confessed this finding. Since mechanical damage of a MWCNT layer during the assembly may occur, risk management measures were suggested.

Gefährdungsbeurteilung für Tätigkeiten mit starren Kohlenstoffnanoröhrchen in einem Technikum in Berlin

Zusammenfassung Die Emission von und Exposition gegenüber mehrwandigen Kohlenstoffnanoröhren (MWCNT) wurden untersucht. Dabei wurden Luftproben, die während der Nachstellung verschiedener Tätigkeiten in einer Testkammer genommen wurden, sowie Materialproben mit einem Rasterelektronenmikroskop (REM) analysiert. Es konnte gezeigt werden, dass bei unvorsichtiger Handhabung eine Emission von MWCNT in die Luft möglich ist. Daher wurden auch Arbeitsplatzmessungen durchgeführt. Die Probenahme erfolgte sowohl stationär als auch an der Person während der Handhabung und des Einbaus von MWCNT-beschichteten Platten. Die Proben wurde mittels einer modifizierten REM-Analysenmethode ausgewertet, um die Messergebnisse mit dem vorgeschlagenen Beurteilungsmaßstab von 10 000 Fasern pro Kubikmetern (F/m³) vergleichen zu können. Die Ergebnisse wiesen aus, dass keine Fasern oberhalb der Bestimmungsgrenze emittiert wurden und daher auch von keiner relevanten Exposition am Arbeitsplatz auszugehen ist. Die Messungen an der Person bestätigten dies. Da bei Beschädigung der beschichteten Platten eine Emission von MWCNT nicht auszuschließen ist, wurden trotzdem Schutzmaßnahmen empfohlen.

1 Introduction

Normally, airborne fibre-shaped inorganic particles are measured in accordance with standard VDI 3492 for the assessment of indoor areas and workplaces in accordance with DGUV Information 213-546 [1; 2]. However, none of these measurement regulations is suitable for the measurement of multi-wall carbon nanotubes (MWCNT), since they solely require particles down to a fibre diameter of 0.2 μm to be detected and counted. In Germany an Announcement 527 for hazardous substances was published that provides recommendations for safety and health protection of persons working with nanomaterials [3]. As a precaution, in the case of tasks involving biologically resistant, rigid, fibre-shaped nanomaterials which correspond to the criteria of the World Health Organization (WHO) of length > 5 μm, diameter < 3 μm, and length-to-diameter ratio > 3 : 1, the effects should be considered to be similar to those of asbestos. In this context, assessment should take place on a case-by-case basis. In addition to the General Threshold Limit Values for the inhalable and the respirable fraction (10 mg/m³ respectively 1.25 mg/m³), also an assessment criterion of 0.5 mg/m³ has to be taken into account for nanoscale granular, biopersistent dusts [4]. For nanoscale fibres that correspond to the WHO criteria, here called WHO fibres, an assessment criterion of 10,000 fibres per cubic meter (F/m³) is recommended. In the announcement, the lack of a suitable measurement procedure for those fibres is mentioned, too.

In cooperation with the Unfallkasse Bund und Bahn (German Social Accident Insurance Institution of the Federal Government and for the railway services), the Bundesanstalt für Arbeitsschutz und Arbeitsmedizin (Federal Institute for Occupational Safety and Health, BAuA) and the Physikalisch-technische Bundesanstalt (National Metrology Institute of Germany, PTB), the Institut für Arbeitsschutz der DGUV (Institute for Occupational Safety and Health, IFA) investigated the emission of and exposure to nanosized fibres in air during the handling of discs coated with MWCNT. Although for the MWCNT material safety datasheets exist, no investigations have been carried out concerning the emission rate of MWCNTs from the surface into the interior air for the planned activities with the MWCNT. Therefore, initial investigations simulating the real conditions followed by workplace measurements in a laboratory setup at the PTB in Berlin had been carried out to find out whether MWCNTs are emitted when samples are handled.

After testing a possible emission simulating the application of those coated substrates in a small chamber, the following activities involving potential exposure in the laboratory were investigated at the workplace:

- removing the MWCNT coated substrate from its packaging underneath the exhaust hood,
- assembling the carrier material on a holder underneath the exhaust hood,
- transporting the carrier holder and fitting it into the test apparatus,
- operating the test apparatus by applying slightly pressurized air over the substrate,

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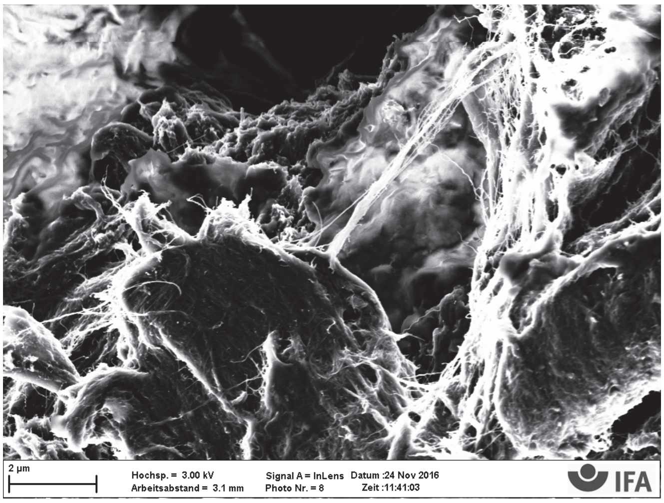

Figure 1. Fine structure of the Surrey NanoSystems MWCNT bundles.

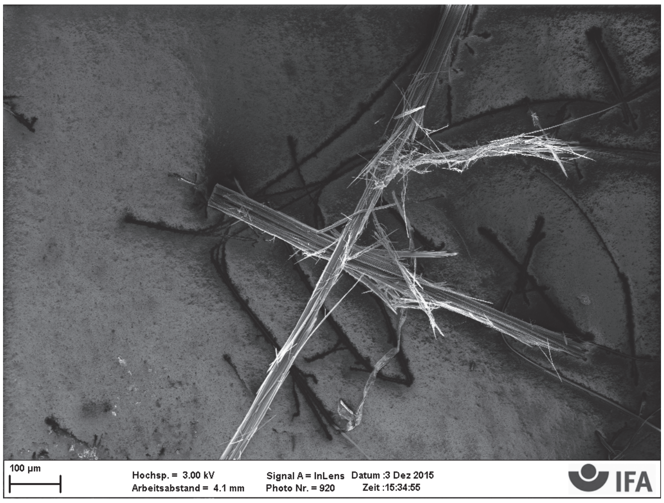

Figure 2. Torn MWCNT fibre bundles from NIST.

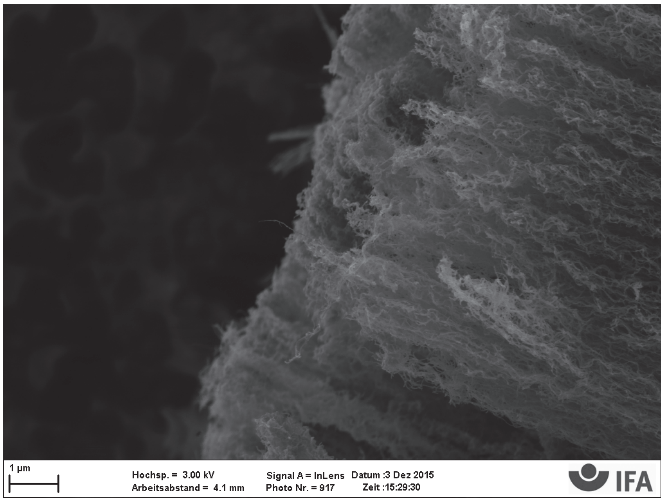

Figure 3. Fine structure of the MWCNT bundles from NIST.

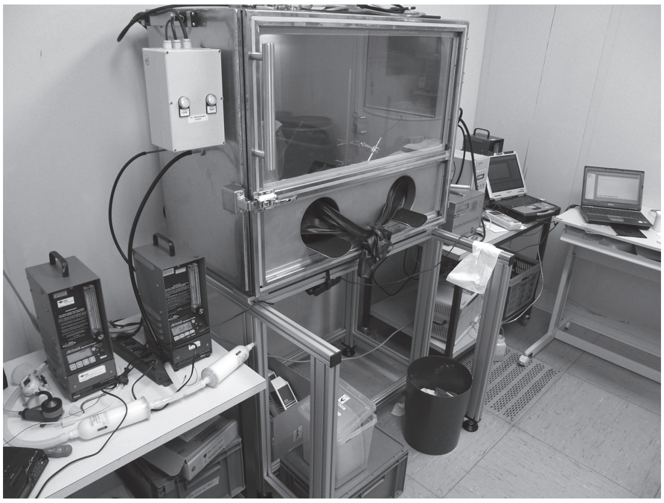

Figure 4. Test chamber for emission investigations.

- removing the carrier holder and transporting to the exhaust hood,
- dismantling the carrier material from the holder underneath the exhaust hood,
- packing the carrier material underneath the exhaust hood.

2 Materials

For the assessment of the emission and of the exposure, disc shaped samples in the following called "discs" with different MWCNT coatings from 2 manufacturers, the National Institute of Standards (NIST, USA) and Surrey NanoSystems (UK), were investigated.

One type of discs consists of a sandblasted aluminum alloy with a diameter of 100 mm and a thickness of 5 mm, coated with MWCNT Vantablack® (vertically aligned nanotube array black) from Surrey NanoSystems. The MWCNT used were 30 to 100 µm long single fibres with a diameter of 10 to 30 nm. Bundle length and thickness could not be sufficiently determined. Scanning electron microscope (SEM) images of typical particles taken from the layer are shown in **Figure 1**.

The other type of discs consists of silicon wafers (thin silicon discs) with a diameter of 100 mm and a thickness of 0.5 mm, coated with single MWCNT from NIST. The fibres are 10 to 100 µm long (partly longer), in bundles of 2, 4, and 6 mm in length. Diameter of the single fibres and bundle thickness could not be sufficiently determined. **Figures 2** and 3 show SEM images of different fibre bundles which were separated from the edge of the sample. These can have a length of up to 4 mm. The fine structure exhibits intertwined MWCNTs (Figure 3).

3 Methods

Simulations of work tasks with possible emissions of nano-objects were carried out in an IFA test chamber with a volume of approx. 400 l (dimensions: $L \times W \times H$: 100 cm × 50 cm × 80 cm, **Figure 4**). The in-coming air was fed in via high efficiency particulate air (HEPA) filters to prevent an excessive number of foreign particles from entering the test chamber. The airflow rate through the chamber was 17 l/min.

For the emission simulation of handling MWCNT coated discs in the lab, a disc was shaken circularly by means of an orbital shaker (300 turns/min) and an air stream of 2 to 4 m/s was applied onto the top of the disc. The air having passed above the disc was collected on a filter (PGP-FAP, approx. 5.8 l/min).

In a second step indicative workplace measurements had been performed at PTB before any activities involving the MWCNT coated discs were realized. For the workplace measurements a new determination procedure for nanofibres was used that is developed by BAuA and IFA within the scope of the „nanoGRAVUR“ project [5]. The measurements performed at PTB were based on the new measurement and analytical counting procedure, taking the requirements of an analytical determination of nanoscale fibres into account [6]. Workplace measurements were carried out for a different period of time at a total of 6 measurement points (**Figure 5**). Measurements were performed in the so-called „near field“, i.e. at two measurement points in the immediate vicinity of the main source. In addition, values were measured at two measurement points in the so-called „far field“. Here, the „far field“ means the area which is directly connected to the near field (with air being exchanged), in which the concentration of the emitted hazardous substance has, however, dropped significantly (from appr. 1/3 down to no longer detectable). What is designated as the „main source“ is in this case the aperture of the spherical radiation measuring device; correspondingly, measurements in the far field were performed in room 3. Since MWCNTs are also emitted during activities carried out under the exhaust hood (source), measurements were also performed in the „far field“ in room 1.
To determine the exposure of persons, measurements were carried out on the persons themselves and – for the time during which these persons left the room – person-related measurements (i.e. stationary measurements, but at the place where these persons typically spent most of their time) were conducted. Finally, the background contamination was determined by means of a measurement performed outside room 3 which is not directly connected with the source and does not exhibit any bilateral air exchange.
The measurements performed also take into account objects larger than 100 nm in order to detect aggregates and agglomerates of smaller particles. Direct-reading measurements were used to examine the particle number concentration.
MWCNT-coated discs are fitted onto a heating plate under the exhaust hood of a laboratory (room 1, see Figure 5) (activity 1), are then carried via room 2 to room 3 (activity 2) and are there mounted into the spherical radiation measuring device (activity 3). The person performing these tasks was wearing a DiSCmini particle monitor (Testo, Titisee-Neustadt, Germany) and one or two PGP-FAP sampling devices (GSA Gesellschaft für Schadstoffanalytik mbH, Ratingen, Germany). This sampling was occasionally pursued stationarily at the laboratory desk. Stationary PGP-FAPs were installed both in the corridor leading to room 3 and on the way from room 1 to room 3 as well as at the source itself. In addition, a second DiSCmini was located at the source and operated in stationary mode.
The sampling volume and the sampling duration were selected taking the prevailing dust concentrations on site into account in such a way that the analytical detection limit was, as far as possible, below 10.000 F/m³. The conditions for the air samples obtained by means of the PGP-FAP system while the different MWCNT coated materials were being handled are given in **Tables 1** and **2**.

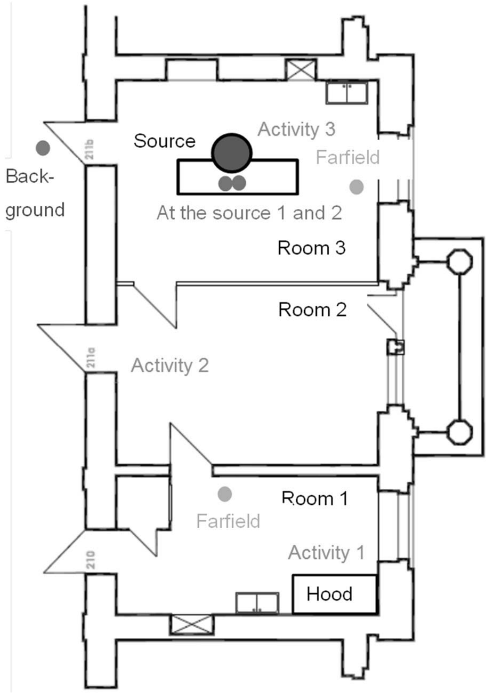

Figure 5. Positions of the stationary measurements in the laboratories. Measurements at the source, far field measurements and background measurement.

4 Measuring conditions and analytical instruments used

4.1 Collector for particulate matter PGP-FAP

The PGP-FAP was used to determine the particle concentration and the particle morphology. The particles were collected on a gold-coated filter (Nuclepore, 400 nm and 200 nm pore diameter, respectively) and were then analyzed by a scanning electron microscope (SEM). The airflow rate was approx. 5 l/min and 4 l/min, respectively.

Table 1. Surrey Nanosystems coated substrate.

Sampling position	Duration in h	Air flow rate in l/min
At the source 1	69.08	5.0
At the source 2	9.31	5.1
Background	69.11	4.9
Far field Room 1	69.06	5.1
Far field Room 3	69.08	5.0
Worn on the person	9.5	5.1
At the source 1	25.1	2.0
Far field	24.39	5.1

Table 2. NIST coated substrate.

Sampling position	Duration in h	Air flow rate in l/min
At the source 1	47.48	2.1
At the source 2	47.8	4
Far field Room 3	47.49	5.1
Worn on the person 1	6.33	5.0
Worn on the person 2	5.6	4

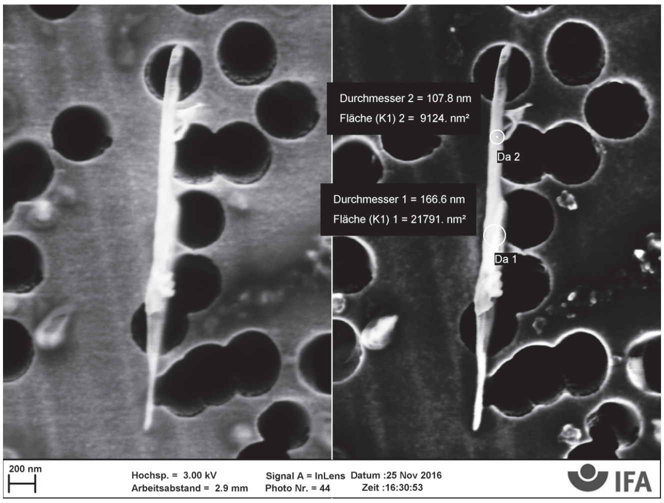

Figure 6. Non-WHO fibres with indications of diameters (surface indication: non relevant).

4.2 DiSCmini particle monitor

The particle number concentration was measured by means of the Testo DiSCmini. The principle of measurement is based on the electric charging of the particles and on detection by means of an electrometer in a small portable housing. Concentrations from 2,000 to 10^6 particles per cm^3 (at 20 nm) and a particle size range from 10 to 700 nm can be determined. The airflow rate is 1 l/min.

4.3 SEM analysis

The particles deposited on the Nuclepore filter were analyzed at IFA using a Zeiss Supra 40 P SEM. The images were generated with an acceleration voltage of 3 kV at a working distance of approx. 3 mm. From each sample, 100 randomly selected fields were analyzed at 20.000-fold magnification[1)]. At BAuA, the samples were examined using a Hitachi SU8230 SEM with similar magnification and acceleration voltage at a working distance of 6 mm.

1) Note concerning the detection limit: The detection limit is the upper limit of the concentration confidence interval at zero detected fibres, corresponding to the concentration at three detected fibres.

An elemental analysis was not performed since the particles detected would, on the one hand, not be differentiable from the carbon background of the filter material, and, on the other hand, the particles exhibited insufficient signal intensity in most cases.

5 Results

The simulation measurements in the small chamber have shown that exposure of the discs to vibration and airstream did not yield a detectable release of MWCNT. However, during handling of MWCNT coated plates mechanical damage of the layer can occur and it is possible that MWCNTs are emitted.
During the indicative workplace measurements no increased dust or fibre contamination was observed.
For the workplace measurements, three samples are represented since they best reflect the emission issue. In **Table 3**, C stands for the fibre concentration, C-low for the lower limit of the 95% confidence interval, and C-up for its upper limit.

5.1 Surrey Nanosystems (SN) sample

The results shown in Table 3 relate to the sample „at the source 1" (duration 69.08 h; air flow rate = 5.0 l/min), 100 fields were recorded and assessed at a 20,000-fold magnification. No single MWCNT were detected. Non-WHO fibres without MWCNTs of unknown origin (**Figure 6**) yielded a concentration of 2,700 F/m^3. Here, the diameter of the fibres was smaller than 200 nm, and the length was shorter than 5 µm (WHO convention). Numerous needle like residues/structures of questionable (possibly biological) origin were found. Their lenghts varied between approx. 0.5 and 1.5 µm with similar aspect ratio. However, they were not quantified since they considerably differed from the MWCNTs on the reference sample, with regard to both their shape and size.

5.2 NIST sample

The results shown in **Table 4** relate to the sample „at the source 1" (duration 47.48 h; airflow rate = 2.1 l/min) and at the person 2 (duration 5.6 h; airflow rate = 4 l/min). In these analyses, also the diameter range from 20 to 200 nm was taken into account as WHO fibres.

Table 3. Concentrations of particles of the SN sample; 20,000-fold magnification.

Pollutant	Objects found	Concentration C in m^{-3}		
		C	C-low	C-up
Non-WHO fibres (without CNTs)	1	2,700	100	15,200
WHO fibres (without CNTs)	0	0	0	8,200
WHO fibres with adhering CNTs	0	0	0	8,200
Granular particles with adhering CNTs	0	0	0	8,200
Agglomerates/aggregates with adhering CNTs	0	0	0	8,200
CNT pellets	0	0	0	8,200
CNTs adhering to particles/fibres/aggregates	0	0	0	8,200
Isolated CNTs (certain)	0	0	0	8,200
Nanofibres (questionable, biological)	uncounted			
Particles with nanofibers	0	0	0	8,200
Other oblong, nanoscale particles (incl. chain-like aggregate or agglomerate)	0	0	0	8,200
Pellets of nanofibers	0	0	0	8,200

Table 4. Concentrations of relevant particles of the NIST sample; different high magnification.

Sample/pollutant	Objects found	Concentration C in m^{-3}		
		C	C-low	C-up
At the source				
WHO fibres (with CNTs)	0	0	0	3,300
WHO fibre agglomerates (with CNTs)	0	0	0	3,300
Nanofibres (questionable, biological, length < 5 µm)	8	8,800	0	17,300
Worn on the person 2				
WHO fibres (with CNTs)	0	0	0	9,800
WHO fibre agglomerates (with CNTs)	0	0	0	9,800
Nanofibres (questionable, biological, length < 5 µm)	0	0	0	9,800

6 Discussion

The results shown are indicative and the assessment criteria not binding, since a validated measurement strategy assessing fibres with a diameter 20 nm < ∅ < 200 nm is not available yet. However, they show that no WHO fibres were detected at the workplace of the PTB. Due to the long measuring period of the stationary measurements the upper concentration limit of confidence show that at maximum a concentration of 3.300 fibres could be expected. Even for the shorter personal sampling, the expected maximum concentration of 9.800 F/m³ is below the recommended assessment criterion. Only "not WHO fibres/needles" of questionable (possibly biological) origin were found in a measurable amount. However, their appearance differs clearly from the MWCNT used and the concentration of 8.800 fibre-objects/m³ at the stationary sample is acceptable.

7 Conclusion

Due to the results of the workplace measurements, a contamination of the workplaces with MWCNT is considered improbable.

Since mechanical damage of a MWCNT layer during the assembly may well occur and in order to minimize the resulting exposure, protective measures were recommended. First of all it should be evaluated, if the desired function of the coating could be achieved by substituting the coating and using flexible and/or short MWCNT. Then all handling tasks should be conducted as far as possible in enclosed and ventilated workbenches. Likewise, the discs should be transported by carrying them in a closed box. The access to the lab should be restricted during the activities with MWCNT. The time and the number of persons handling MWCNT should be held at a minimum. Besides, for all staff performing tasks involving MWCNT materials personal protective equipment (such as respiratory protection of classes P2/FFP2) should be hold in readiness and the persons must be trained in handling the protective equipment correspondingly. Finally, there should exist a defined work procedure that includes cleaning and an emergency plan after the unintended release of MWCNT. All these measures will increase the workplace safety of handling MWCNT included in new products.

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