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Report on the measurement of particulate matter when handling MWCNT-coated plates

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Type of application:	Testing of MWCNT-coated plates	
Inspection carried out by:	Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung (IFA) Alte Heerstr. 111, 53757 Sankt Augustin Bundesanstalt für Arbeitsschutz und Arbeitsmedizin (BAuA), Nöldnerstr. 40-42, 10317 Berlin	

Motive/measurement task:
Investigation of the particle emission during the handling of MWCNT-coated plates

Number of pages of the report:	17

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1 Task Definition

In cooperation with the *Unfallversicherung Bund und Bahn* in Berlin (contact person: Mrs. Jäkel) and the Federal Institute for Occupational Safety and Health (*BAuA – Bundesanstalt für Arbeitsschutz und Arbeitsmedizin*), the *Institut für Arbeitsschutz* (IFA) investigated the emission of and exposure to nano-sized objects in air during the handling of plates coated with multiwall carbon nanotubes (MWCNTs) at the working place (PTB lab).

2 Activities and materials

Within the scope of a research project, the *Physikalisch-Technische Bundesanstalt* (PTB) is planning to perform activities involving so-called vertical multiwall carbon nanotubes (MWCNTs) grown on silicon, aluminum or lithiumtantalate carrier material. Hereby, the following activities involving potential exposure are performed:

- Removing the carrier material from its packaging underneath the exhaust hood
- Assembling the carrier material on a holder of the test setup underneath the exhaust hood
- Transporting the carrier holder to the test station and fitting it into the test apparatus
- Removing the carrier holder from the test apparatus 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

For the assessment of the emission and of the exposure, three samples with different MWCNT coatings from 2 manufacturers (one from the National Institute of Standards (NIST, USA) and one from Surrey NanoSystems (UK)) were selected:

2.1 Vertically Aligned NanoTube Array Black - VBS 2225 (Surrey NanoSystems)

Carrier material (manufacturer's specifications): aluminum alloy discs with a diameter of 100 mm and a thickness of 5 mm, sandblasted.

Nanomaterial (manufacturer's specifications): 30 - 100 µm long single fibers with a diameter of 10 - 30 nm. Bundle length and thickness not sufficiently determined. Scanning electron microscope (SEM) images of typical particles taken from the layer are shown in Figure 1.

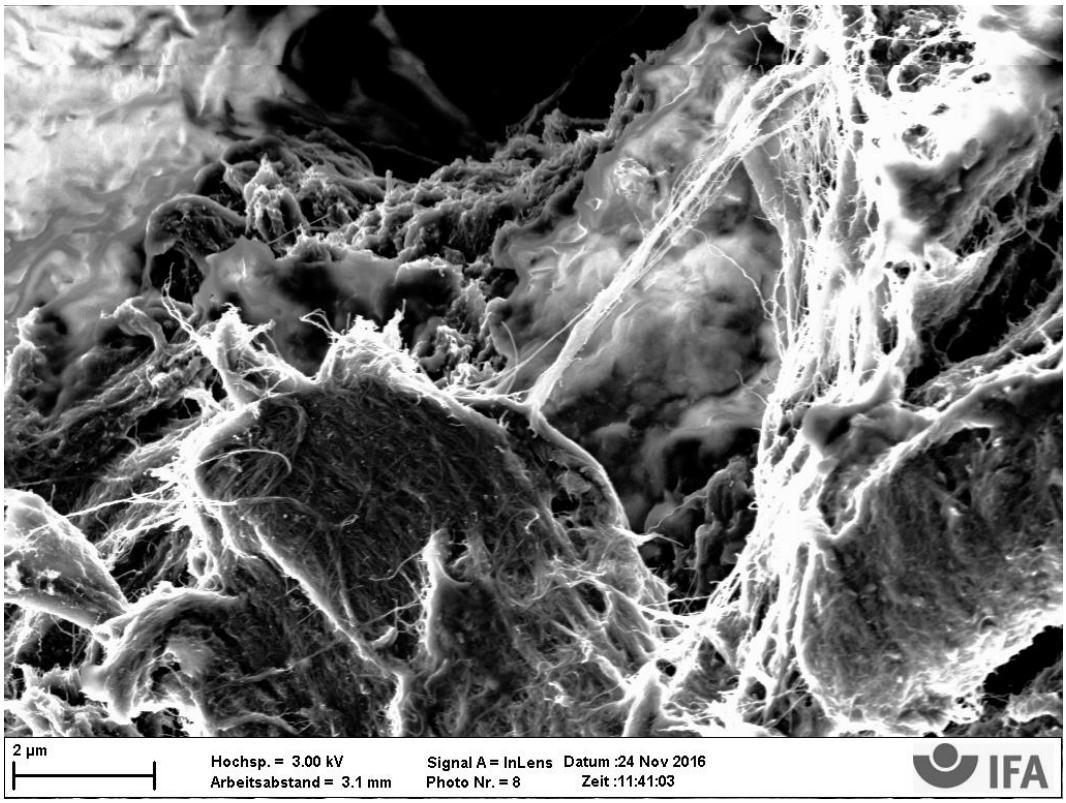

Figure 1: VBS 2225, fine structure of the MWCNT bundles

2.2 Vertically Aligned NanoTube Array – VANTA, 4 mm (NIST)

Carrier material (manufacturer's specifications): silicon wafer (thin silicon discs) with a diameter of 100 mm and a thickness of 0.5 mm.

Nanomaterial (manufacturer's specifications): single fibers of 10 - 100 µm in length (partly longer) in bundles of 2, 4 and 6 mm in length. Diameter of the single fibers and bundle thickness not sufficiently determined. Figures 2 and 3 show scanning electron microscope (SEM) images of different fiber bundles which were taken from the side of the sample. These can have a length of up to 4 mm. The fine structure exhibits intertwined MWCNTs (Fig. 3).

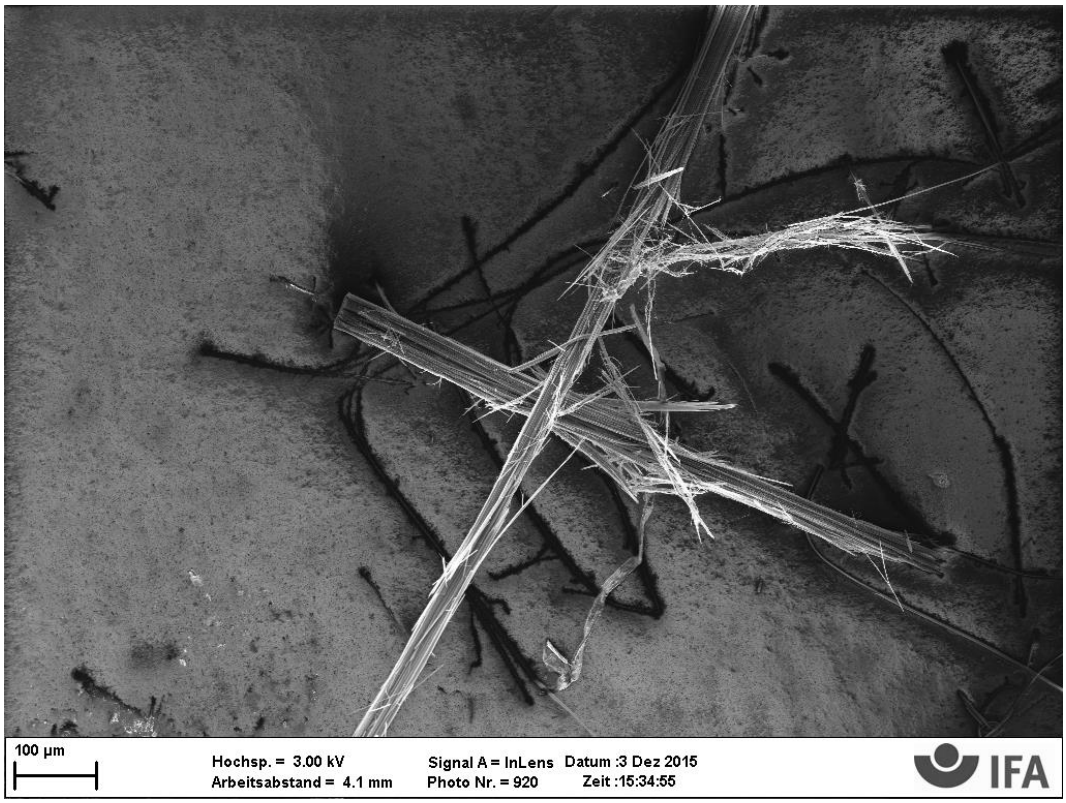

Figure 2: VANTA 4 mm, torn MWCNT fiber bundles

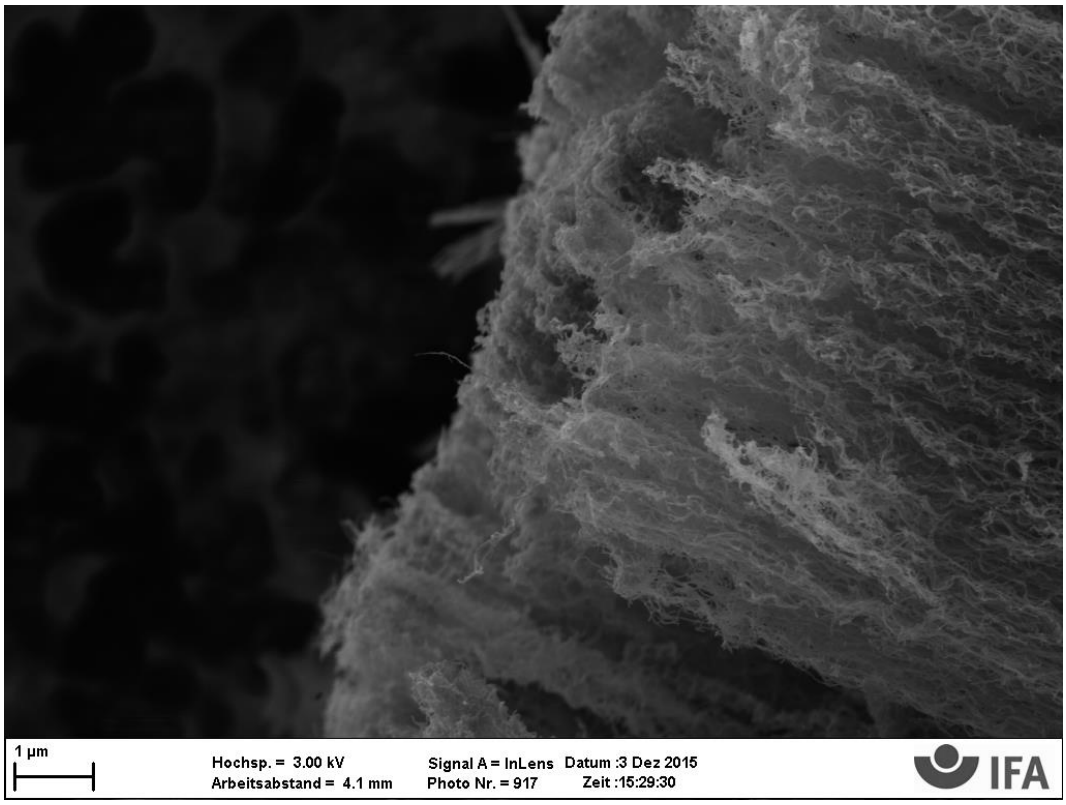

Figure 3: VANTA 4 mm, fine structure of the MWCNT bundles

3 Classification, hazardous substances and threshold values

In 2013 an Announcement 527 for hazardous substances "Manufactured nanomaterials" (BekGS 527) was published that provides recommendations for safety and health protection of persons working with nanomaterials. As a precaution, in the case of tasks involving biologically resistant, rigid, fiber-shaped nanomaterials which correspond to the WHO criteria (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. The assessment of flexible, biologically resistant fibers is still being discussed. In this context, assessment should take place on a case-by-case basis. BekGS 527 also provides risk assessment for biologically resistant, fiber-shaped nanomaterials and recommends not only technical, but also personal protective measures. Concentration measurements are carried out in order to check the efficiency of such measures. A fiber concentration in air below 10,000 F/m^3 at the place of work would be desirable.
In addition to the General Threshold Limit Values for the inhalable (and the respirablefraction, also an assessment criteria of 0.5 µm/m^3 has to be taken into account for nanoscale granular, biopersistent dusts.

4 Measurement strategy

For the materials used within the scope of the project, safety datasheets (potential hazard) exist (essentially labeled "Irritating to eyes and respiratory system"), but to our knowledge, no investigations have ever been carried out concerning the emission rate of MWCNTs from the surface into the interior air. Initial recreating investigations have therefore been carried out in a laboratory setup to find out whether MWCNTs are emitted when samples are handled. The investigation has shown that MWCNTs may be emitted into the air if the samples are not handled correctly and/or if the coating material is damaged.
Thus, measurements were subsequently performed at the workplace at PTB.
A measurement convention of several European institutes in the field of safety at work states, in coordination with the MAK Commission, that ultrafine particles (UFPs) designate particles that are smaller than 100 nm = 0.1 µm. According to ISO/TS 80004-2:2015 "Nanotechnologies – Vocabulary – Part 2: Nano-objects", nano-objects are particles which, in one to three dimensions, have a size from 1 to 100 nm and are manufactured specifically for their particular materials properties. In the EU Commission's recommendations for the definition of nanomaterials (10/2011), a nanomaterial designates "a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm - 100 nm". This recommendation thus does not differentiate between UFPs and nanoparticles.

Also, differentiating between UFPs and nanoparticles from a metrological viewpoint is difficult, since most of the direct-reading measuring instruments used for this purpose determine the particle number concentration without indicating the specific substance detected. Substance-specific information can, to date, only be obtained by means of data-collecting measurement procedures and complex subsequent analysis. It is therefore very important to be able to allocate changes (such as an increase in the particle concentration in the ambient air of the workstation during certain processes). Hence, an increase in the particle concentration occurring simultaneously with an activity involving nanoparticles can be assigned to the latter if the background nanoparticle concentration is lower and there are no disturbing influences.

For this purpose, indicative measurements were performed at PTB from 15 to 20 June 2016 without activities involving the MWCNT material being carried out. Hereby, no increased dust or fiber contamination was observed. Thus, solely the possible fiber emission and exposure were then metrologically assessed.

The measurements performed, which are described below, also take objects larger than 100 nm into account in order to detect aggregates and agglomerates of smaller particles.

Fiber-shaped inorganic particles are measured in accordance with VDI 3492 for the assessment of indoor areas and workplaces in accordance with DGUV Information 213-546 "Procedures for the separate determination of the concentrations of respirable inorganic fibers in workspaces – SEM procedures". None of these measurement regulations is suitable for the measurement of airborne, nanoscale, fiber-shaped materials, since they solely require particles down to a fiber diameter of 0.2 µm to be detected and counted, so that they provide no information on the fraction of nanoscale particles in an aerosol containing fibers.

With a sensitivity of 1 particle/cm^3 at best, alternative online measurement procedures for the determination of the particle number concentration of airborne nanoparticles (such as SMPS or CPC) are not sensitive enough for the verification of the strict assessment standards of 10,000 fibers/m^3. Moreover, they are not selective when it comes to the type of fibers detected, i.e. they provide no information whatsoever on the morphology of a count, so that particle-shaped and fiber-shaped objects as well as short and WHO fibers are not differentiated and can thus not be counted separately.

A new measurement procedure for nanofibers is currently being developed by BAuA and IFA within the scope of BMBF's "nanoGRAVUR" project. These activities are based on an amendment of the afore-mentioned regulations. The measurements performed at PTB were based on the new measurement procedure, taking the requirements of an analytical determination of nanoscale fibers into account.

For this purpose, measurements were carried out for a different period of time at a total of 6 measurement points. In order to assess the emission, measurements were performed in the so-

called "near field", i.e. at two measurement points in the immediate vicinity of the 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 (1/3 down to no longer detectable). What is designated as the "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, 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 spend most of their time) were conducted.

Finally, the background contamination was determined by means of a measurement performed in a room which is not directly connected with the source and does not exhibit any bilateral air exchange.

5 Measurement setup

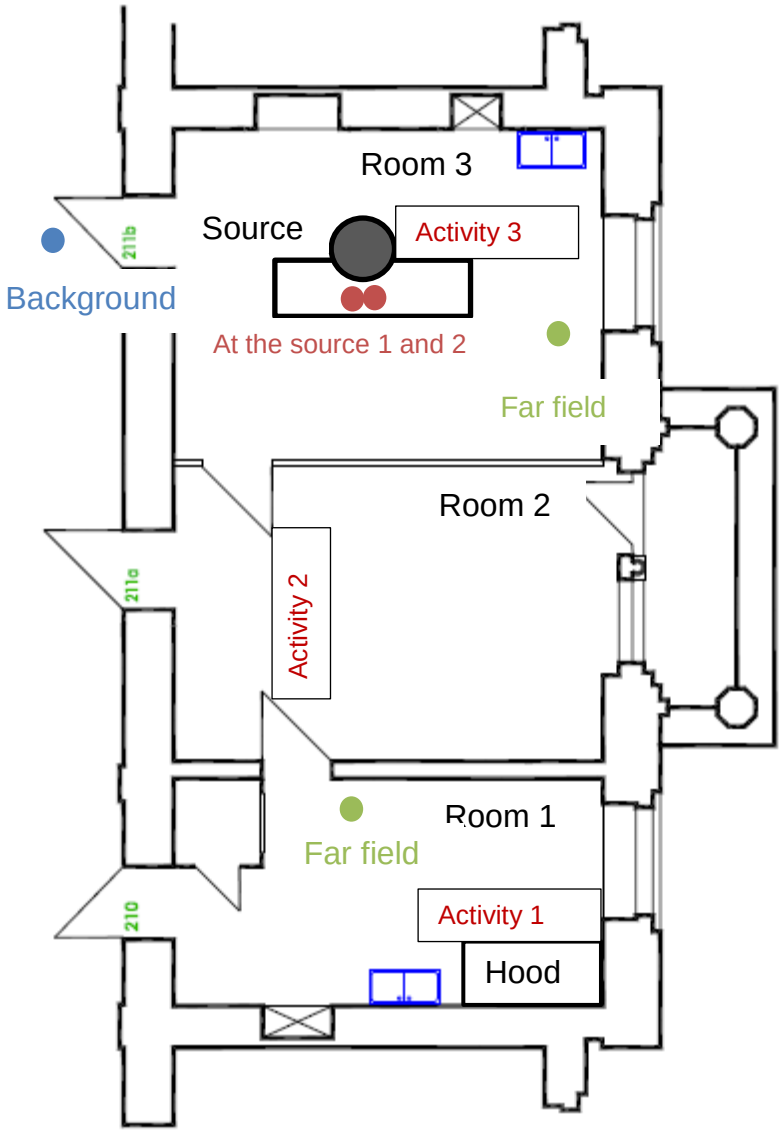

Figure 4: Positions of the stationary measurements in the laboratories

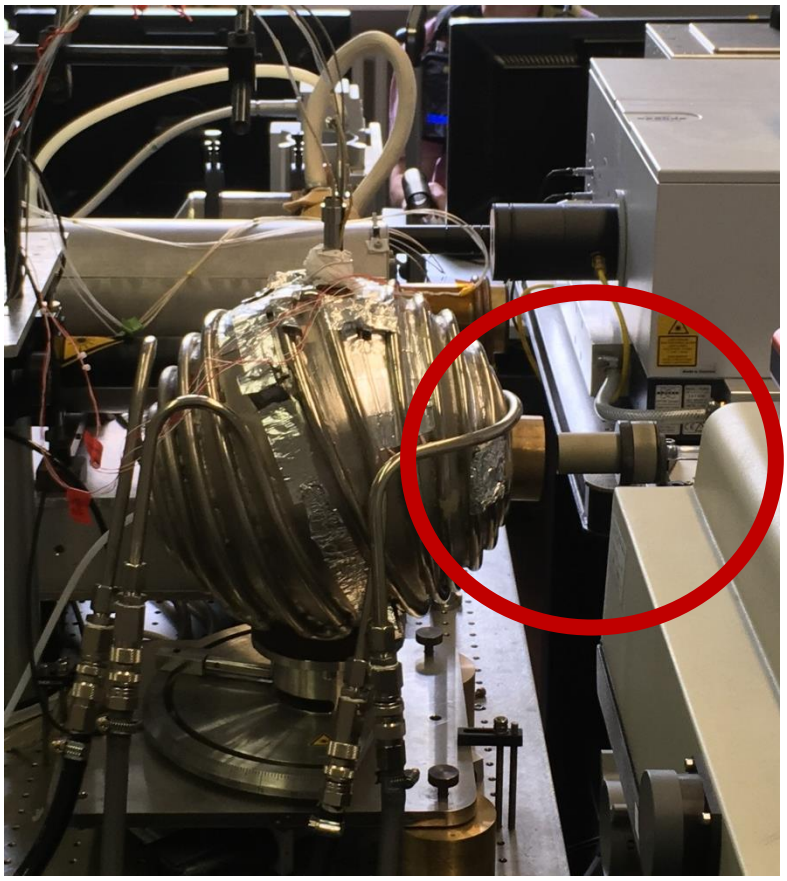

Figure 5: Position of the PGP-FAP, sampling "at the source 1"

Figure 6: Sampling location Room 3, desk/far field

MWCNT-coated disks are fitted onto a plate under the exhaust hood of a laboratory (Room 1, see Figure 4) (Activity 1), are then carried to Room 2 and to Room 3 (Activity 2) and are there fitted into the spherical radiation measuring device (Figure 5) (Activity 3). The person performing these tasks was wearing a DiSCmini particle monitor and one or two PGP-FAP sampling devices. This sampling was occasionally pursued stationarily at the laboratory desk (Figure 6). 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 fibers/m^3.

6 Measuring and analytical instruments used

6.1 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 nuclear core filter (Nuclepore, 400 nm and 200 nm pore diameter, respectively) and were then analyzed in the SEM (scanning electron microscope). The volume rate was approx. 5 l/min and 4 l/min, respectively.

6.2 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 1000 to 10^6 particles per cm^3 with a size ranging from 10 to 700 nm can be determined. The volume rate was 1 l/min.

6.3 SEM analysis

The particles deposited on the nuclear pore filter were analyzed at IFA using a Zeiss Supra 40P SEM. The images are generated with an accelerating voltage of 3 kV at a working distance of approx. 3 mm. From each sample, 100 selected fields generated at random were analyzed at 20,000-fold magnification.

Note concerning the detection limit: The detection limit is the upper limit of the concentration confidence interval at 0 detected fibers, correspondingly to the concentration at 3 detected fibers.

At BAuA, the samples were examined using a Hitachi SU8230 with similar magnification and accelerating voltage at a working distance of 6 mm.

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.

7 Performing the measurements

The following air samples were obtained by means of the PGP-FAP while the different MWCNT-coated materials were being handled:

7.1 VBS-2225 (Surrey Nanosystems' sample)

Sampling date: beginning on 11 July 2016

Sampling position	**Duration**	**Volume rate**
At the source 1	*69.08 h*	*5.0 l/min*
At the source 2	9.31 h	5.1 l/min
Background	69.11 h	4.9 l/min
Far field Room 1	69.06 h	5.1 l/min
Far field Room 3	69.08 h	5.0 l/min
Worn on the person	9.5 h	5.1 l/min

Sampling date: beginning on 14 July 2016

At the source	25.1 h	2.0 l/min
Far field	24.39 h	5.1 l/min

7.2 VANTA 4 mm (NIST sample, designation: PTB-Si-1)

Sampling date: beginning on 18 July 2016

At the source 1	47.48 h	2.1 l/min
At the source 2 (BAuA, AP_2016_07_18_001)	*47.8 h*	*4 l/min*
Far field Room 3	47.49 h	5.1 l/min
Worn on the person 1	6.33 h	5.0 l/min
Worn on the person 2 (BAuA, AP_2016_07_18_002)	*5.6 h*	*4 l/min*

In this report, results concerning the three identified samples are represented since they reflect the emission issue best.

8 Results

In the results table, C stands for the fiber concentration, C-u for the lower limit of the 95 % confidence interval, and C-o for its upper limit.

8.1 VBS-2225 (Surrey Nanosystems' sample)

The following evaluation belongs to the sample "at the source 1" (duration 69.08 h; volume rate = 5.0 l/min). 100 fields were recorded and assessed at a 20,000-fold magnification. No MWCNTs were detected with certainty on the fields considered. Non-WHO fibers without MWCNTs of unknown origin (Figures 7 and 8) yield a concentration of 2,700 fibers/m³. Here, the diameter of the fibers is smaller than 200 nm, and the length is shorter than 5 µm (WHO Convention). Numerous fibers of questionable (possibly biological) origin were found (also visible in Figure 7); they were, however, not counted since they considerably differed from the MWCNTs on the reference sample, with regard to both their shape and size.

Table 1: Concentrations of relevant particles of the sample VBS 2225; 20,000-fold magnification

Pollutant	**Objects found**	**Concentration C [1/m³]**		
		C	C-u	C-o
Non-WHO fibers (without CNTs)	1	2,700	100	15,200
WHO fibers (without CNTs)	0	0	0	8,200
WHO fibers 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/fibers/aggr.	0	0	0	8,200
Isolated CNTs (certain)	0	0	0	8,200
Nanofibers (questionable, biological)	uncounted			
Particles with nanofibers	0	0	0	8,200
Other oblong, nanoscale particles (e.g. "smoke chain" – chain-like aggregate or agglomerate of primary particles originating from combustion or evaporation processes)	0	0	0	8,200
Pellets of nanofibers	0	0	0	8,200

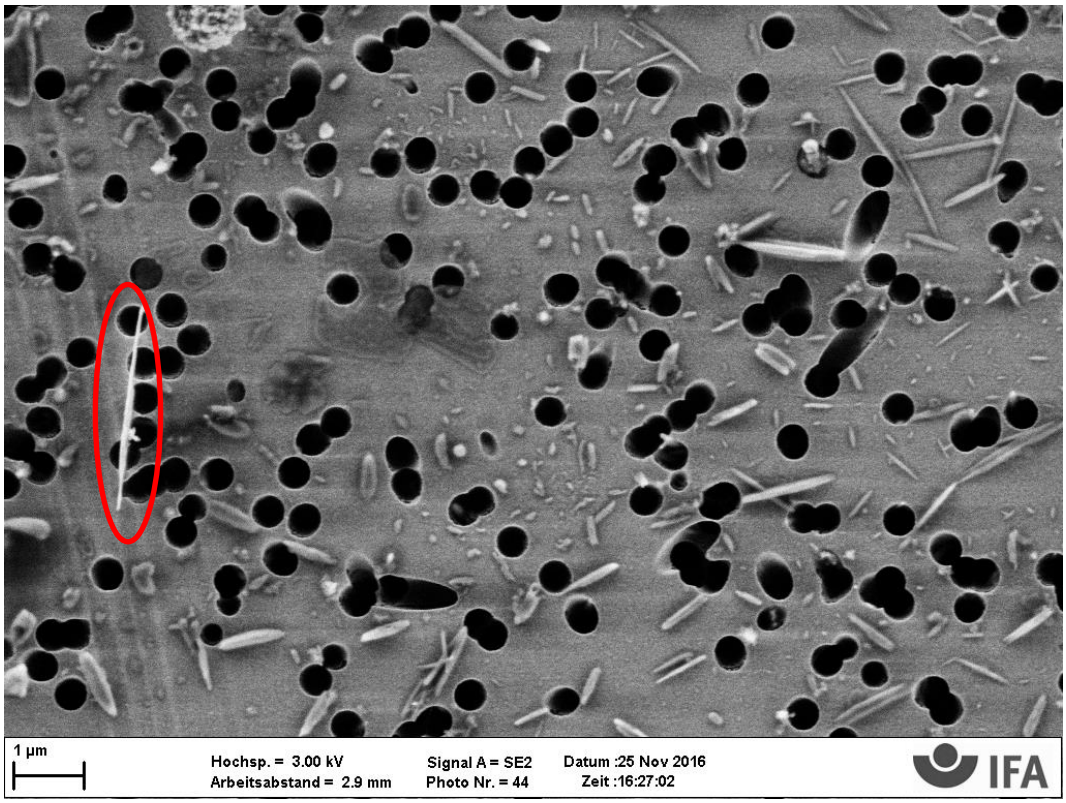

Figure 7: Non-WHO fibers (outlined in red)

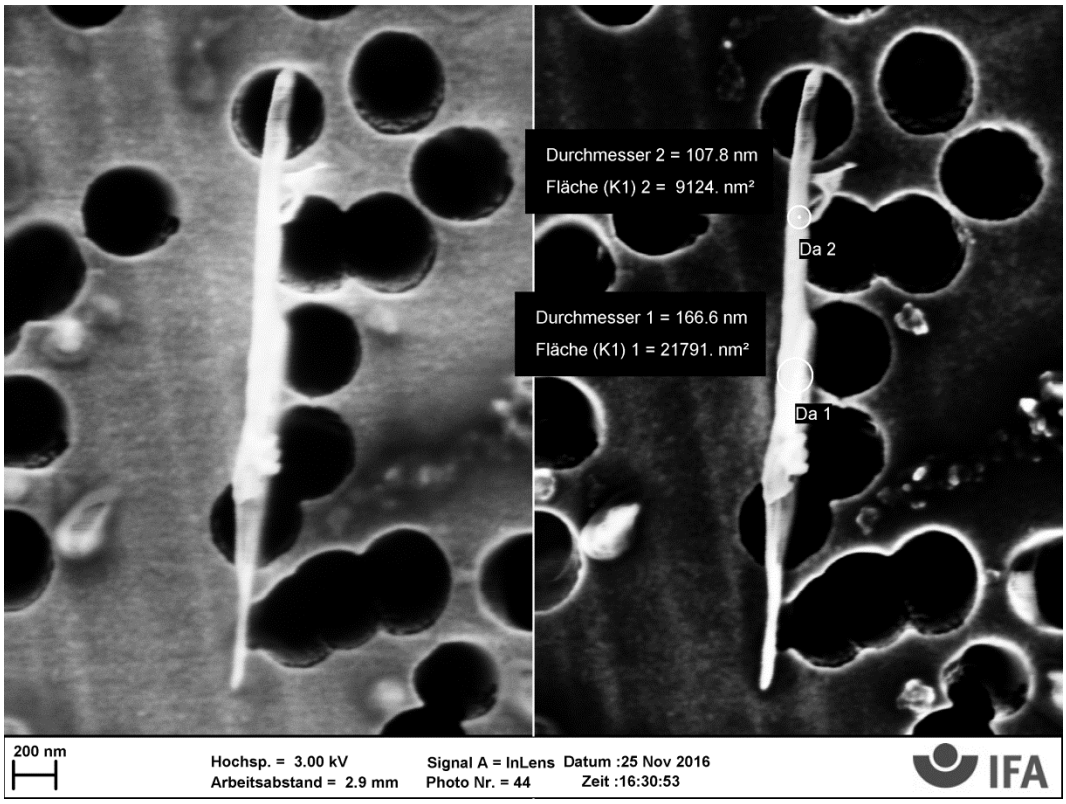

Figure 8: Non-WHO fibers with diameters indications (surface indication: non relevant)

8.2 VANTA 4 mm (NIST sample, designation: PTB-Si-1)

The two samples below were analyzed by BAuA.
Sample AP_2016_07_18_001
Filter surface assessed: 0.056 mm² with 1,623 l/cm² (0.91 l air volume sample assessed)
Sample AP_2016_07_18_002
Filter surface assessed: 0.161 mm² with 190 l/cm² (0.31 l air volume sample assessed)

The results are shown in Table 2 as the concentrations of airborne fibers. The fibers of questionable (possibly biological) origin, which are, however, atypical for MWCNTs, were assessed with 8,800 fibers/m^3 at the stationary sample by the source. In addition, also the diameter range from 20 to 200 nm was taken into account as WHO fibers.

Table 2: Concentrations of relevant particles of the sample VANTA 4 mm; high magnification

Sample/pollutant	**Objects found**	**Concentration C [1/m³]**		
		C	C-u	C-o
At the source 2, AP_2016_07_18_001				
WHO fibers (with CNTs)	0	0	0	3,300
WHO fiber agglomerates (with CNTs)	0	0	0	3,300
Nanofibers (questionable, biological, length < 5 µm)	8	8,800		17,300
Worn on the person 2, AP_2016_07_18_002				
WHO fibers (with CNTs)	0	0	0	9,800
WHO fiber agglomerates (with CNTs)	0	0	0	9,800
Nanofibers (questionable, biological, length < 5 µm)	0	0	0	9,800

9 Summary

The measurements were carried out on the basis of VDI 3492 (Measuring indoor air impurities, measuring of inorganic fiber-shaped particles – SEM procedure) and DGUV Information 213-546 (Procedures for the separate determination of the concentrations of respirable inorganic fibers in workspaces – SEM procedure). The measurements at workspaces were indicative measurements, since a validated measurement strategy assessing fibers with a diameter 20 nm < Ø < 200 nm is not available yet. The results stated are therefore to be considered as indicative exposure values.
The results obtained for the three samples (when handling two MWCNT-coated plates – VBS 2225 and VANTA 4 mm) are stated as these reflect best the issue of emissions. MWCNTs were detected on none of the three samples investigated. A contamination of the workplaces with MWCNTs is thus considered very improbable. Also, the concentrations of all assessed samples

were below the assessment standard of 10,000 F/m^3. On two samples, however, numerous fibers of questionable (possibly biological) origin were found, but only on one of the samples (AP_2016_07_18_001) were they counted, since they considerably differed from the MWCNTs on the reference sample, with regard to both their shape and size.

Since mechanical damage of a MWCNT layer during the assembly may well occur, in order to minimize the resulting exposure of staff to emitted fibers or fiber bundles, we recommend that protective measures (such as working under a lab exhaust hood and in an enclosed and exhausted processing area, and encapsulating the carrier material for transport) be taken when handling such materials. Besides, all staff performing tasks involving MWCNT materials should wear personal protective equipment (such as respiratory protection of classes P2/FFP2) and be trained correspondingly.

Sankt Augustin, 20 December 2016
By order

M.Sc. Christian Schumacher gez. M.Sc. Bianca Oeffling