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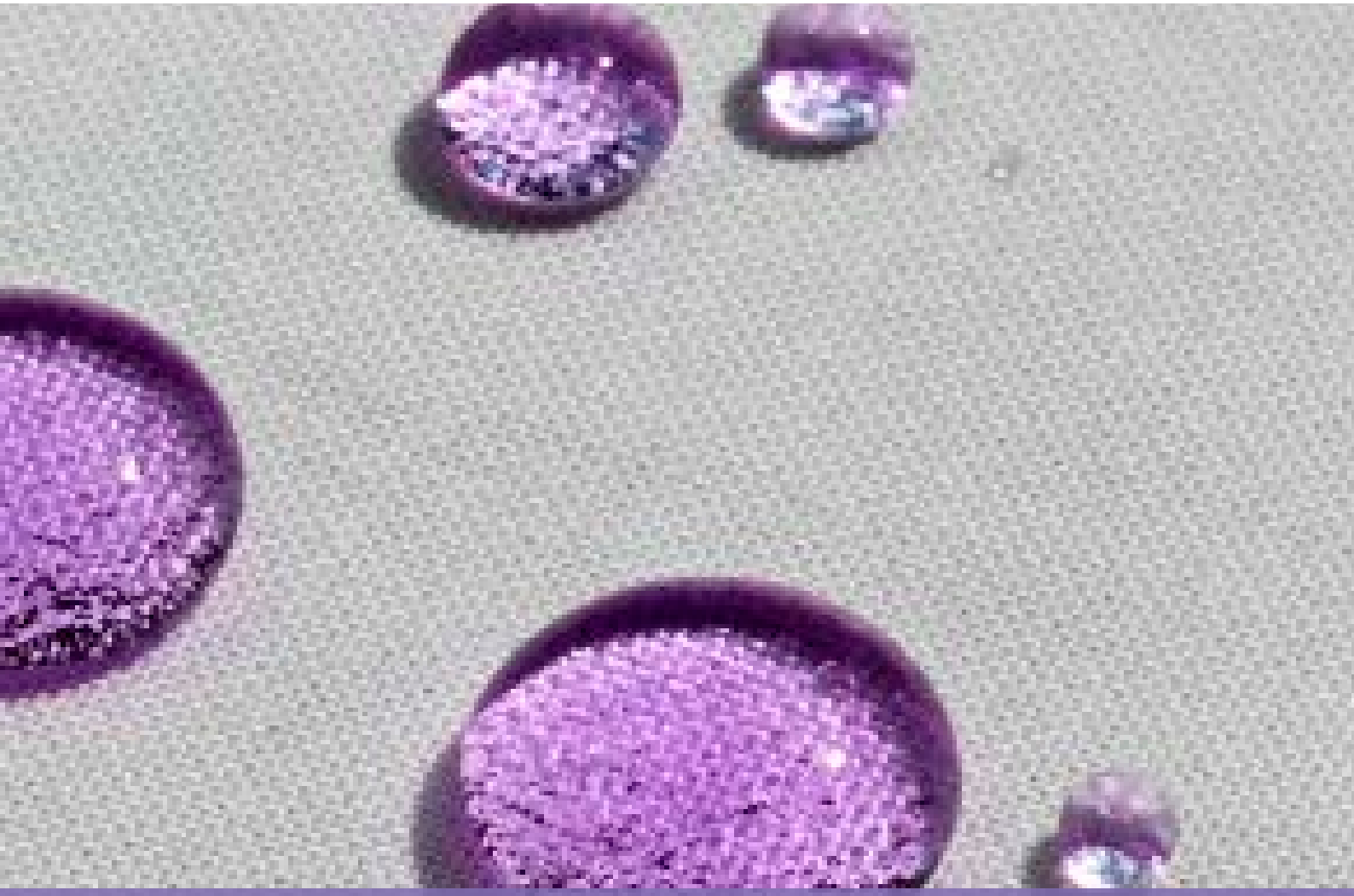
NanoValid

Developing Reference Methods for Nanomaterials



# Inhalation exposure during generation of multi-walled carbon nanotube (MWCNT) aerosols in a laboratory

## Field measurement report No 5

## Imprint

This report is a final product of the project NanoValid - project F2268 - and was generated under the lead responsibility of Miriam Baron (Federal Institute for Occupational Safety and Health).
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The responsibility for the contents of this publication lies with the authors.



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# Table of Contents



**The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under Grant Agreement n° 263147**

# Index of Figures



# Index of Tables

# 1 Abbreviations and acronyms

| | |
|---|---|
| A | alveolar |
| BAuA | Federal Institute for Occupational Safety and Health (in Germany) |
| CNT | Carbon Nanotubes |
| CPC | Condensation Particle Counter |
| DISC | Diffusion Size Classifier |
| DMA | Differential Mobility Analyser |
| EDX | Energy Dispersive X-ray Spectroscopy |
| ENM | Engineered Nanomaterials |
| HEPA | High Efficiency Particulate Airfilter |
| ICP-AES | Inductively Coupled Plasma Atomic Emission Spectroscopy |
| LDMA | Long Differential Mobility Analyser |
| LDSA | Lung-Deposited Surface Area |
| NanoGEM | Nanostructured Materials – Health, Exposure and Material properties |
| NAS | Nanoparticle Aerosol Sampler |
| NSAM | Nanoparticle Surface Aerosol Monitor |
| PGP | *Personengetragenes Gefahrstoff-Probenahmesystem* (Personal Sampling System for Hazardous Substances) |
| SEM | Scanning Electron Microscope |
| SD | Standard Deviation |
| SMPS | Sequential Mobility Particle Sizer |
| SOP | Standard Operating Procedure |
| TB | tracheobronchial |
| TEM | Transmission Electron Microscope |
| TP | Thermal Precipitator |
| TRGS | German Technical Rule for Hazardous Substances |

# 2 Summary

Within NanoValid, the BAuA laboratory for nanomaterials assessed and evaluated inhalative exposure to nanomaterials at different workplaces. The aim of these field studies was to check if the installed protective measures were effective and if a risk of the workers was sufficiently reduced. The present report refers to a workplace measurement in a laboratory, where multi-walled carbon nanotubes (MWCNT) were aerosolised into a large volume test chamber. Aim of this field study was to verify the effectiveness of the protection measures of the newly build test facility and to ensure that no particles leave the closed test chamber. For this, the particle number concentration was measured during operation of the test chamber and during subsequent cleaning of the equipment. Additionally, air samples from the laboratory were taken for subsequent optical analysis with scanning electron microscopy (SEM). Based on the measured particle number concentration and the optical analysis of the air samples, no single fibres or fibre agglomerates of used MWCNT were emitted from the operating test chamber or during cleaning. However, some microscaled fibrous agglomerates of unknown origin were found on the samples.

This report presents:

- A detailed measurement report, including morphological analysis of particles

# 3 Introduction

The manual "Nano to go!" compiles information and training material for people, who are responsible for the implementation of occupational safety and health issues at a company level. It contains valuable information on safe handling of nanomaterials and other advanced materials at workplaces.
In general, a specific workplace situation can be assessed either by using exposure measurements or by applying non-measurement methods like comparing the specific situation to standardised work routines and by using control banding tools. Since the reliability of the risk management depends highly on the quality of these approaches, it is important to provide professional advice on how to actually assess the workplace situation and how to perform adequate exposure measurements as potential efficiency control. "Nano to go!" aims to provide such advice in form of field study reports. The field study reports exemplify a way to address occupational safety and health issues when working with nanomaterials.
The present field study reports on exposure measurements at a laboratory where the release behaviour of multi-walled carbonanotubes (MWCNTs) was tested during research experiments.

a) The **exposure measurement** was performed according to standard operation procedures (SOP's), which were developed during the project NanoGEM (described in the section 4.3 sampling strategy). The measurements at the respective workplaces were carried out either according to tier 2 (basic assessment) or according to tier 3 (expert assessment) and take the background concentration into account. The aim of this field study measurement was to evaluate the particle number concentration and the particle size distribution. A morphological analysis of the samples was also performed.

# 4 Exposure measurements of fine and ultrafine dusts and fibres in a pilot plant

## 4.1 General

- Measuring task: Workplace measurements during experimental release of MWCNT at a test stand
- Company: 20141215
- Briefing participants: Company representative, BAuA representatives
- Measurement date: 15/12/2014 - 17/12/2014
- Receipt of samples: 17/12/2014
- Sample number: AP-2014-12-15-1 to AP-2014-12-17-04
- Analyses carried out by: BAuA representatives
- Date of analyses: March 2015
- Draft of measurement report: Sabine Plitzko

## 4.2 Description of measurement methods

**SMPS (Scanning Mobility Particle Sizer):**
The Scanning Mobility Particle Sizer (SMPS) is a stationary online measurement device. Depending on the used classifier (DMA, differential mobility analyser), it detects the particle number concentration in a mobility range analogous to spherical particles in a size range of 10 nm to 1000 nm (LDMA), respectively of 5 nm to 350 nm (MDMA). The preimpactor removes coarse particles out of the air volume flow before they enter the actual measuring system. With the aid of a neutralizer, the air volume flow is then brought into a state of defined charge distribution (charge equilibration). Subsequently, the particles are separated in the DMA (classifier) according to their mobility in an electrical field (44 size classes). Only particles of the respective charge and size move to the sample air outlet and enter the condensation particle counter (CPC). Within the CPC, the mono-disperse aerosol is directed in a heated saturation tube (N-butanol). The surfeited steam condenses onto the particles by a subsequent cooling. In this way, the particles are enlarged to a size of about 10 µm and counted by a laser beam. Measurements in this field study were carried out with a CPC type 5.403 from Grimm Aerosol Technik GmbH & Co. KG.

**CPC 3007 (Condensation Particle Counter):**
The CPC 3007 (Condensation Particle Counter) is a handheld measurement device from TSI GmbH. It detects the particle number concentration time resolved within a size range of 10 nm to 1000 nm. Compared to Grimm 5.403, the CPC 3007 works with a saturated isopropanol solution. The measurement system does not classify the particles, but provides a total number concentration for the whole measurement range.

**NSAM (Nanoparticle Surface Aerosol Monitor):**
The NSAM (Nanoparticle Surface Aerosol Monitor) from TSI GmbH detects the so-called lung-deposited surface area (LDSA, expressed in $\mu m^2/cm^3$) of particles, which are deposited in the tracheobronchial (TB) or alveolar (A) lung area.

**Aerosolspectrometer 1.109:**
Stationary online device that detects particles in a size range of 0.25 to more than 32 µm:

- Aerosolspectrometer 1.109 gravimetric - The measurement device detects the particles by light dispersion in a laser measurement chamber in 30 different size channels and shows the result as particle mass concentration, assuming an equivalent sphere.
- Aerosolspectrometer 1.109 numerical – The measurement device detects particles by light dispersion with a laser measurement chamber in 30 different size channels and shows the result as particle number concentration, assuming an equivalent sphere.

**NAS (Nanometer Aerosol Sampler):**
The Nanometer Aerosol Sampler (NAS) is a stationary electrostatic precipitator, which was used for subsequent morphological analysis of particles sampled from an aerosol. With the nanoparticles aerosol sampler (NAS), samples of charged particles (similar to those from the output of a differential mobility analyser (DMA)) can be transferred on substrate for further analyses. Due to the natural charge balance, such charged particles are present in every aerosol at room temperature.

**TP (Thermal Precipitator):**
The Thermal Precipitator (TP) is a portable offline collection system which works on the basis of thermophoresis. The particles of an aerosol pass between two metal heating plates and deposit onto the cold plate, which is laid out as a sample carrier (silicon wafer). The directed particle transport is caused by the higher thermal energy of the gas on the warm side of the chamber. As a result, there is a higher momentum transfer from the warm chamber side on the particles of the gas. Subsequently, the silicon wafer is analysed with scanning electron microscopy.

**PGP**
The PGP (*Personengetragenes Gefahrstoff-Probenahmesystem*) is a portable system for taking samples. It deposits components of aerosols on a gold evaporated nuclear-track membrane filter with a pore size of 200 nm. Here, a PGP-FAP is used for the collection of fibrous dusts.

**DiSCmini (Diffusion Size Classifier):**
The Diffusion Size Classifier (DiSCmini) is a portable online analyser from Testo AG used for the determination of particle number and average diameter. In addition, it provides an estimation of the lung deposited surface area (LDSA) of a particle.
The particle size estimation is based on a differentiation between highly diffusive light particles and less mobile heavier particles. For this purpose, the aerosol is charged unipolar and charge transport is measured at two electrodes. The more mobile particles are detected at the electrode which is closer to the charger.

**Partector:**
The partector is a portable online analyser by Naneos particle solutions GmbH and is used for the determination of the lung-deposited surface area (LDSA) of nanoparticles.

## 4.3 Sampling strategy

**Definitions:**
Background concentration – Particle number- or mass-concentration as measured inside (work area), while outside air conditions and further sources are largely excluded.
Outside air concentration – Particle number- or mass-concentration, which is measured outdoor (windward side) of the work area.

**Measurement routine:**
The sampling is made according to the standard operating procedures (SOPs) generated in the BMBF project nanoGEM.
Link:
http://www.nanogem.de/cms/nanogem/upload/Veroeffentlichungen/nanoGEM_SOPs_Tiered_Approach.pdf
A tiered exposure assessment serves as basis. The tiered approach applies as long as no legally binding, health-based limit values for the manufactured engineered nanomaterials (ENM) exist.

- **Tier 1 (Information gathering)**

The task in tier 1 is to clarify, e.g. during on-site inspection, whether nanomaterials are used in the workplace and if they can be released from the corresponding processes. If a release cannot be excluded, a potential exposure has to be determined in tier 2.

- **Tier 2 (Basic assessment)**

As long as no health based limit values exist for engineered nanomaterials, measurements are performed compared to an intervention level. These measurements can either be performed as a short-time screening or a temporary, respectively permanent, monitoring. If the intervention level is exceeded significantly, a potential exposure exists and has to be assessed in tier 3. Exposure measurements in tier 2 are carried out using handheld and easy-to-use devices and are performed to a limited extent. Important measurement parameters are particularly size-integrated particle concentrations, for instance the total number concentration. Typical measurement devices are handheld condensation particle counters (handheld CPCs) and devices based on electrical diffusion charging (DISCmini, nanoTracer, Aerotrak 9000).

- **Tier 3 (Expert assessment)**

Within tier 3, a potential exposure to ENM at the workplace is quantitatively assessed with extended measurement device expenditure. Measurement devices like the SMPS, CPC, NSAM or Aerosol spectrometer are applied. At the same time, collecting systems are applied, which collect samples for a subsequent morphological and/or chemical analysis by SEM, TEM or ICP-AES.
Measurements in tier 3 always include the determination of the particle background load either by a simultaneous measurement at a representative background location (two-devices-solution) or by a measurement of the load of the workplace itself before and after the process (one-device-solution).

**Quality check of the measurement devices in the laboratory and during the measurements on-site:**
Beside the annual calibrations from the producer, the particle number concentrations of the measurement devices were compared to identical measurement ranges before (in the nanofibre test centre) and during the measurements (on-site) according to the SOP in order to recognize and if necessary remove deviations. Figures 1 and 2 and tables 1 and 2 show the results of these comparisons.

Temporary deviations between the measured concentrations of air-carried particles are possible by the influence of temporal and spatial fluctuation of airflow between the place of release and the different located measurement devices.

**TABLE 1: RESULTS OF THE COMPARATIVE MEASUREMENT WITH THE CPC AND THE SMPS ON-SITE.**

| MEASUREMENT DEVICE | MEAN VALUE (PARTICLES/CM³) | STANDARD DEVIATION | CORRELATION COEFFICIENT | REGRESSION EQUATION |
|---|---|---|---|---|
| SMPS 1 | 609.9 | 313.7 | 0.854 | Y=1.21x-90.79 |
| SMPS 2 | 596.3 | 321.8 | | |
| SMPS 1 | 609.9 | 313.7 | 0.940 | Y=1.04x-40.4 |
| SMPS 3 | 799.9 | 293.3 | | |
| SMPS 2 | 596.3 | 321.8 | 0.636 | Y=0.76x+149 |
| SMPS 3 | 799.9 | 293.3 | | |

Comparative measurements in the test centre yielded very good correlations (see table 2). Due to the temporarily opened laboratory door and the work processes in the room, spatial fluctuation of the particle number concentrations were recorded. Nevertheless, the measured values of the devices are in the same size range and show the same distribution as shown in the boxplot (see figure 2). Only the SMPS 3 exhibits a higher variance of the particle number concentration in the boxplot-exposures which is probably caused by the device's shorter runtime and higher and fluctuating concentrations. Consequently, the devices work reliably and produce robust and representative measurement results.

**TABLE 2: RESULTS OF THE COMPARATIVE MEASUREMENT WITH THE CPC AND THE SMPS ON-SITE (MEASUREMENT FROM 29/09/14).**

| MEASUREMENT DEVICE | MEAN VALUE (PARTICLES/CM³) | STANDARD DEVIATION | CORRELATIONS COEFFICIENT | REGRESSION EQUATION |
|---|---|---|---|---|
| SMPS 1 | 5384 | 1659 | 0.99 | Y=0.97x-266 |
| SMPS 2 | 4938 | 1613 | | |
| SMPS 1 | 5384 | 1659 | 0.98 | Y=1.06x-73 |
| SMPS 3 | 5636 | 1778 | | |
| SMPS 2 | 4938 | 1613 | 0.99 | Y=1.10x+223 |
| SMPS 3 | 5636 | 1778 | | |

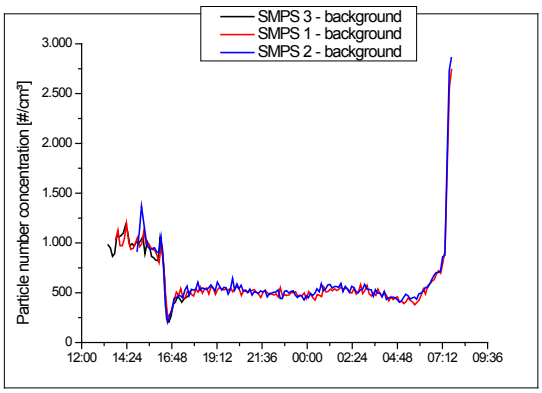


**FIGURE 1: TIME COURSE OF THE PARTICLE NUMBER CONCENTRATION OF THE SMPS (ON-SITE).**

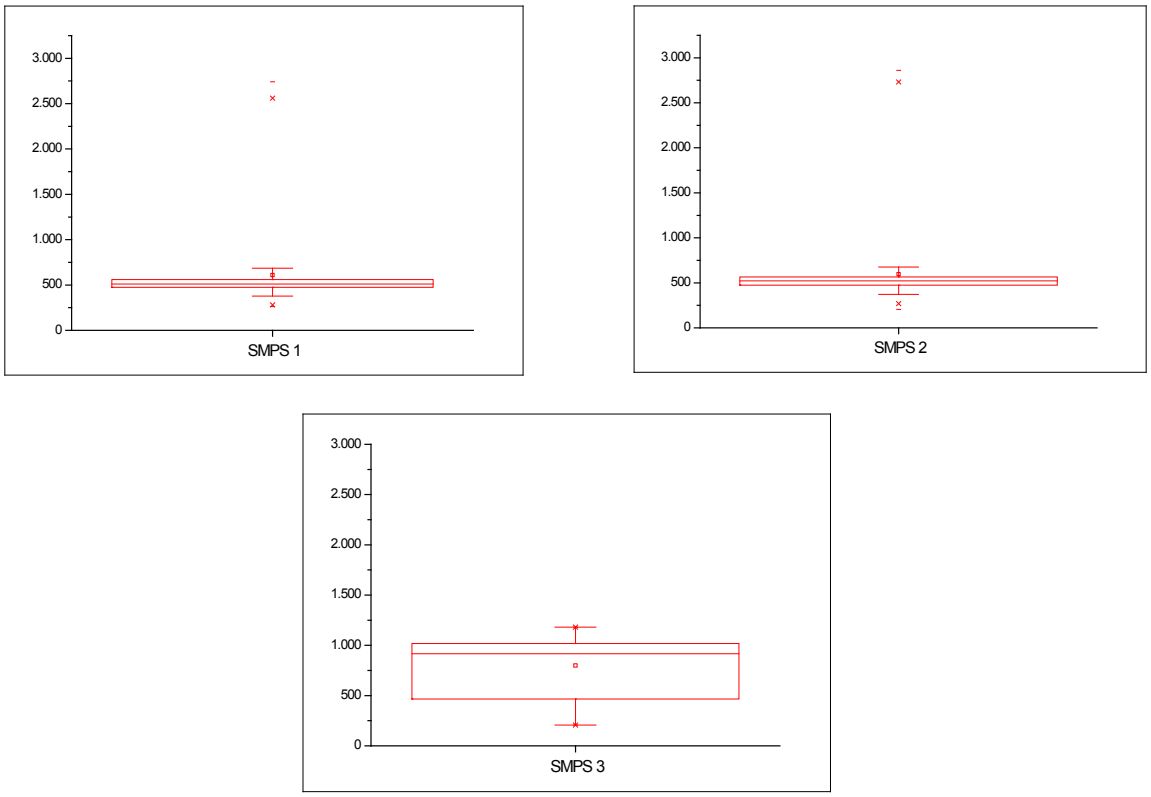


**FIGURE 2: BOXPLOT OF THE PARTICLE NUMBER CONCENTRATION COMPARING DIFFERENT SMPS DEVICES (ON-SITE).**

## 4.4 Workplace measurements during experiments with multi-walled carbonanotubes (MWCNT) at a test stand

**Sampling during experiments with MWCNT:**

The workplace measurements in the laboratory were carried out in accordance with the above-mentioned measurement strategy of tier 3 (expert assessment).

**Description of the workplace:**

The workplace measurements took place in a laboratory where the release behaviour of MWCNTs was tested during research projects. The release experiments with MWCNT (Arry ARIGM001, sold by Arry International) were performed at a fibre test bench. This served for a comparison of measurement devices for fibrous nanomaterials. A homogeneous distribution of MWCNT aerosols wihin the fibre test bench should be achieved at different concentrations.

The test bench was located in a laboratory with Laminar Flow Box in which activities with MWCNT (Arry 001) were performed. With the aid of an aerosol generator, which was also located in the Laminar Flow Box, the fibres were directed in the 400 L chamber of the test bench where they were spread homogeneously. The outgoing air was directed to the exhaust duct via a H14-HEPAfilter. Several measurement devices were mounted at the fibre test bench in order to control the parameters of the experiment.

During all activities respiratory protection, a laboratory coat and gloves were worn. The door of the laboratory was opened a few times. After finishing the experiments, the chamber was evacuated, the measurement devices were taken out of the chamber and the Laminar Flow Box was cleaned.

The particle number concentration and size distribution of airborne particles was detected stationary with the CPC 3007, the SMPS and an aerosol spectrometer. Simultaneously, the outdoor air concentration was determined outside the laboratory building. This allowed for a comparison of particle number concentrations during the activities with nanomaterials to the background concentration. Thus, emissions from the process could be identified.

Airborne particles were accumulated on a silicon-wafer with a NAS in order to characterise them morphologically afterwards.

Additionally, employees carried portable measurement and accumulation devices (DISCmini and a filter sampling with the FAP) during any activities. They were carried in a backpack (see figure 3, right). The device's accumulating aperture was installed directly in the employee's breathing area.

Further stationary and portable measurement and accumulation devices were installed for a comparison of measurement devices. They are only mentioned in the result section if they yielded relevant measuring results.

**FIGURE 3: TEST BENCH FOR RELEASE EXPERIMENTS WITH MWCNT (LEFT) AND PERSONAL SAMPLING WITH A PORTABLE DEVICE (RIGHT).**

**Room size:**
Laboratory area approximately 5.8 x 4.0 x 2.75 $m^3$

**Ventilation:**
- Supply air and exhaust in the ceiling area
- door of the technical laboratory open briefly, windows closed
- direct exhaust from the test chamber

**Handled substances and preparations:**
On the measurement day, MWCNT (Arry 01) were used during experiments. CNTs were handled in a Laminar Flow Box to prepare the experiments and were then analysed for their dustiness in a test chamber.

**TABLE 3: SAMPLING PROTOCOL FOR THE WORKPLACE AREA – RELEASE EXPERIMENTS OF MWCNT (ARRY 01) IN A FIBRE TEST BENCH.**

| DATE | SAMPLE NUMBER | MEASURE-MENT METHOD | MEASUREMENT TASK | VOLUME FLOW | SAMPLING PERIOD | | SAMPLING DURATION | SAMPLING MODE | CLIMATE |
|---|---|---|---|---|---|---|---|---|---|
| | | | | (l/min) | FROM | TO | (min) | | |
| 15.12.14 | AP-2014-12-15-1 | SMPS (LDMA) | Determinaion of particle number concentration outside/in the laboratory room (background measurement) | 0.3 | 13:20 | 17:48 | 268 | stationary | Measurement in the outside area: 4…5°C, 49 % humidity, calm to moderate wind, clouded<br><br>In the laboratory: 22,1°C, 31 % |
| 15.12.14 | AP-2014-12-15-5 | SMPS (LDMA) | Determinaion of particle number concentration outside/in the laboratory room (background measurement) | 0.3 | 13:24 | 07:49 | 1105 | stationary | |
| 15.12.14 | AP-2014-12-15-10 | SMPS (LDMA) | Determinaion of particle number concentration outside/in the laboratory room (background measurement) | 0.3 | 14:57 | 07:40 | 997 | stationary | |
| 16.12.14 | AP-2014-12-16-4 | CPC 3007 | Determination of particle number concentration during the experiments in the exhaust air of the test chamber (behind the HEPAfilter) | 1.2 | 08:26 | 14:51 | 385 | stationary | |
| 16.12.14 | AP-2014-12-16-5 | SMPS (LDMA) | Determination of the particle number concentration during the experiments in the employees' near field (beside the test chamber) | 0.3 | 08:26 | 14:51. | 385 | stationary | |
| 16.12.14 | AP-2014-12-16-6 | Aerosols-pektrom. 1.109 | Determination of the particle number concentration during the experiments in the employees' near field (beside the test chamber) | 1.2 | 08:26 | 14:50 | 384 | stationary | |
| 16.12.14 | AP-2014-12-16-8 | CPC 3007 | Determination of the particle number concentration during the experiments in the employees' near field (beside the test chamber) | 0.7 | 08:26 | 14:46 | 380 | stationary | |

| DATE | SAMPLE NUMBER | MEASURE-MENT METHOD | MEASUREMENT TASK | VOLUME FLOW | SAMPLING PERIOD | | SAMPLING DURATION | SAMPLING MODE | CLIMATE |
|---|---|---|---|---|---|---|---|---|---|
| | | | | (l/min) | FROM | TO | (min) | | |
| 16.12.14 | AP-2014-12-16-9 | DISCmini | Determination of the particle number concentration during the experiments at a person (rucksack) | 1.0 | 09:22 | 13:11. | 229 | personal related | |
| 16.12.14 | AP-2014-12-16-10 | SMPS (LDMA) | Determinaton of the particle number concentration during the experiments in the external air (external air concentration) | 0.3 | 08:05 | 13:20 | 315 | stationary | |
| 16.12.14 | AP-2014-12-16-11 | FAP | Particle accumulation for morphological characterisation, accumulation on gold evaporated filter during the experiments in the exhaust air of the test chamber (behind the HEPAfilter) | 2.0 | 10:17 | 13:08 | 171 | stationary | |
| 16.12.14 | AP-2014-12-16-12 | FAP | Particle accumulation at the person for morphological characterisation, accumulation on gold evaporated filter during the experiments (backpack) | 2.0 | 09:22 | 11:49 | 147 | personal related | |
| 16.12.14 | AP-2014-12-16-13 | NAS | Particle accumulation for morphological characterisation, accumulation on Si-Wafer during the experiments in the employees' near field (beside the test chamber) | 2.0 | 10:17 | 12:01 | 104 | stationary | |
| 16.12.14 | AP-2014-12-16-15 | NAS | Particle accumulation for morphological characterisation, accumulation on Si-Wafer in addition of the expriments (over-night measurement) | 2.0 | 15:04 | 08:40 | 1056 | stationary | |
| 16.12.14 | AP-2014-12-16-16 | SMPS (LDMA) | Determination of the particle number concentration during the experiments in the far field (in laboratory, next to the door) | 0.3 | 09:38 | 13:57 | 229 | stationary | |

## 4.5 Measurement results

**General:**

Product specific particle number concentrations are effected by emission sources in the outdoor area (e.g. increased traffic volume, particles from power plants and domestic fire), wheather influences (amongst others changing wind directions) and further sources in the interiors (e.g. smoking, welding, abrasion of electric motors). Without morphological and/or chemical analysis, the immediate effect of such other sources on the detected product specific particle number concentrations has to be generally taken into account.

Currently, there are no occupational exposure limits for ultrafine particles or nanomaterials. Accordingly, a correlation of measurement results to exposure limits cannot be given yet. In the present report, the measured workplace concentrations are therefore discussed in relation to the naturally occuring outside air concentrations and other background pollution.

**Analysis of experimental release of MWCNT (Arry 01) in a fibre test stand:**

The overnight measurements (background measurement before the process) with the different SMPS-systems yielded average particle number concentrations of 596 #/cm³, 609 #/cm³ and 799 #/cm³ in the laboratory.

During the actual activities, within the test chamber's near field, average particle number concentrations of 1,856 #/cm³ (SMPS, see figure 4, left) and 985 #/cm³ (CPC 3007, see figure 4, right) were measured. A parallel measurement of the background concentration at the laboratory door (far field) with a SMPS resulted in an average particle number concentration of 1,919 #/cm³ (see figure 4, left). The personal measurement with the DISCmini resulted in an average particle number concentration of 1,164 #/cm³ (see figure 4, right).

During the parallel outside air measurement on the same day, concentrations of 16,900 #/cm³ were detected (see figure 4, left). According to Voigtländer et al., average particle number concentrations from 6,000 #/cm³ up to 50,000 #/cm³ are detected in the vicinity of streets and highways. In contrast, 4,000 #/cm³ to 20,000 #/cm³ are common in the urban background [Voigtländer et al. (2006)]. Accordingly, the determined outside air concentrations correlate to the common measurement values of an urban background.

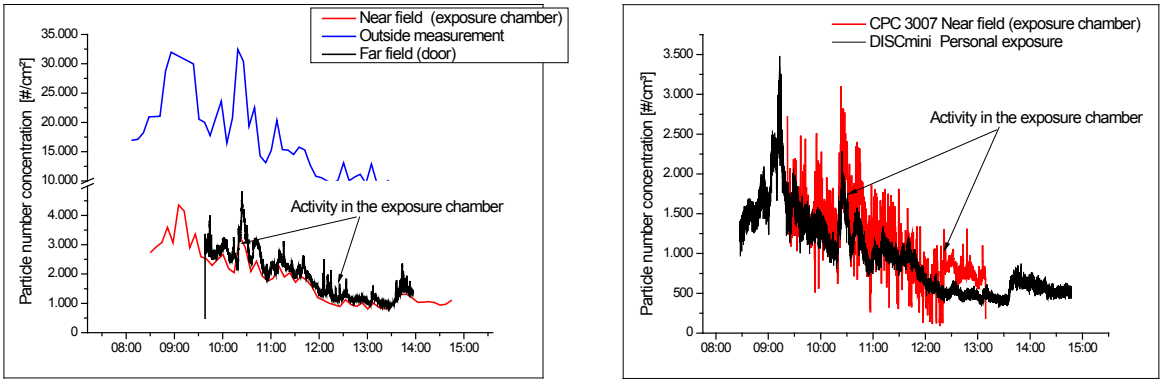


**FIGURE 4: TIME COURSE OF THE PARTICLE NUMBER CONCENTRATION DURING EXPERIMENTAL ACTIVITIES AS MEASURED WITH THE SMPS (LEFT SIDE) IN THE NEAR FIELD (RED), IN THE FAR FIELD (BLACK) AND OUTSIDE. PERSONAL MEASUREMENT DIRECTLY ON THE EMPLOYEE AND CPC-MEASUREMENTS (RIGHT SIDE), ALL MEASURED ON15/12/2014.**

The particle number concentrations in the laboratory area were significantly below concentrations of the outside area, both for the overnight measurement and for measurements during experimental activity. The time course of the particle number concentration shows that the fluctuations in the laboratory followed those in the outdoor area, but with lower particle number concentrations. This was possibly due to the filtered air supply.

The temporary peaks of the particle number concentrations were probably due to the influence of the outdoor air as the laboratory door was opened repeatedly. The distinct maxima around 9.00 and 9.30 a.m. were first detected in the outdoor area and then with the SMPS systems in the far and near field. Also the CPC 3007 and the portable DISCmini detected those peaks.

Neither the portable nor the stationary devices detected a general increase in the particle number concentration during experimental activities at the test stand. As evident from figure 4, there is rather a general decrease in the particle number concentration over time. Thus, judged from the measurements, there is no evidence for emission of MWCNT from the test stand.
Nevertheless, it cannot be fully excluded that single fibres were released during the experiments. Therefore, the focus of the discussion is on the morphological analyses with the scanning electron microscope which were carried out on collected samples (see below).

The geometric mean value of the particle size was 63 nm for the overnight measurement (background measurement before the process) and 55 nm for the measurement directly at the workplace (near field). For the outside air measurement an average particle size of 38 nm was detected. The average particle size which was detected at the employee with the DiSCmini during activity was 76 nm. This is a bit higher than the values detected with the stationary measurement devices.
Figure 5 shows the average particle size distribution for the outside air and the near field measurements.

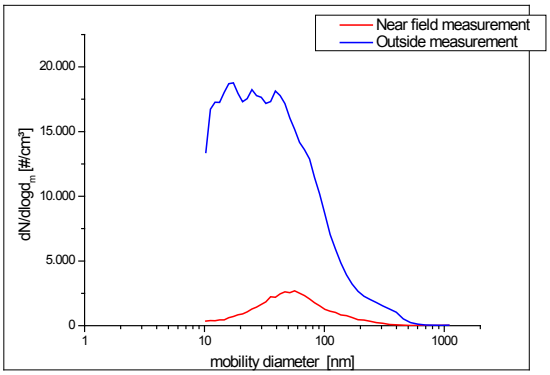


**FIGURE 5: AVERAGE PARTICLE SIZE DISTRIBUTION IN THE OUTSIDE AIR (BLUE) AND IN THE NEAR FIELD (RED) DURING ACTIVITES AT THE TEST STAND.**

**Morphological characterisation of particles:**
The online measurement devices (SMPS and CPC 3007) only detect the total particle number concentration without yielding morphological or chemical information. To obtain such information, several air samples from the different processes and work routines were collected with the NAS (stationary) and the portable FAP during the measurements at the laboratory workplace. Afterwards, scanning electron microscopic (SEM) analyses and energy-dispersive X-ray spectroscopy (EDX) were performed on those samples in order to find out whether nanoscaled carbonmaterial was released during the analysed processes.
A NAS-sample was collected directly at the test chamber in the near field during the experimental activity. A filter sample was collected directly in the breathing area of the employee (see figure 3). The SEM and EDX analyses are presented in figures 6 to 8.
The SEM analyses revealed compact respirable particles, single compact particles with fibrous adhesions and single fibre agglomerates on the NAS specimen from workplace samples (see figures 6-8). The fibre agglomerates and the fibrous adhesions on the compact particles were compared to NAS samples of the generated MWCNT aerosols. This

comparison showed that the fibrous substances were not MWCNT (Arry 001). They had different fibre morphologies and diameters as well as a different behaviour in the EDX analyses.
The analysis of specimen from the personal FAP sample (figure 9, left) showed some fibre agglomerates of unknown origin but with morphologies similar to those from the NAS sample.
Collected samples also cointained soot particles (probably from Diesel, see figure 9, right).

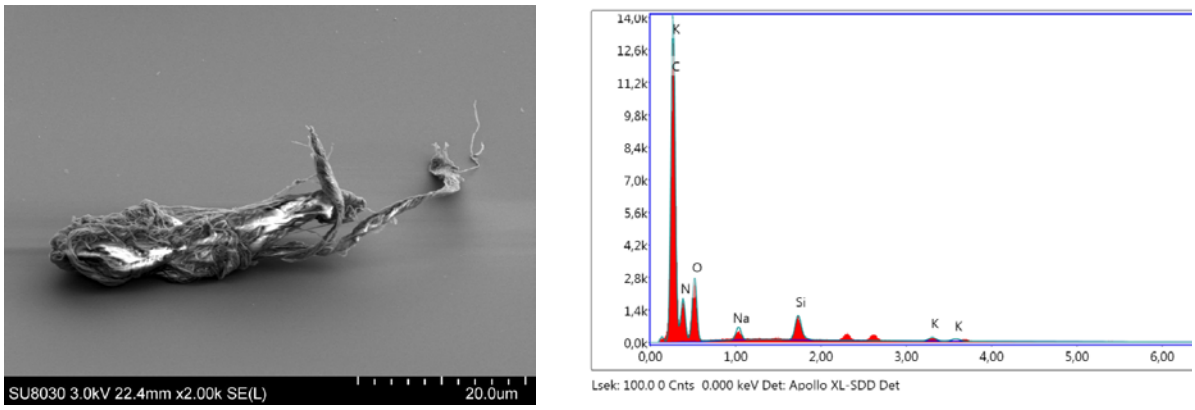


**FIGURE 6: COMPACT PARTICLE WITH FIBROUS ADHESIONS ON THE NAS SPECIMEN TAKEN DURING THE EXPERIMENTAL ACTIVITY (LEFT) WITH CORRESPONDING EDX ANALYSIS (RIGHT).**

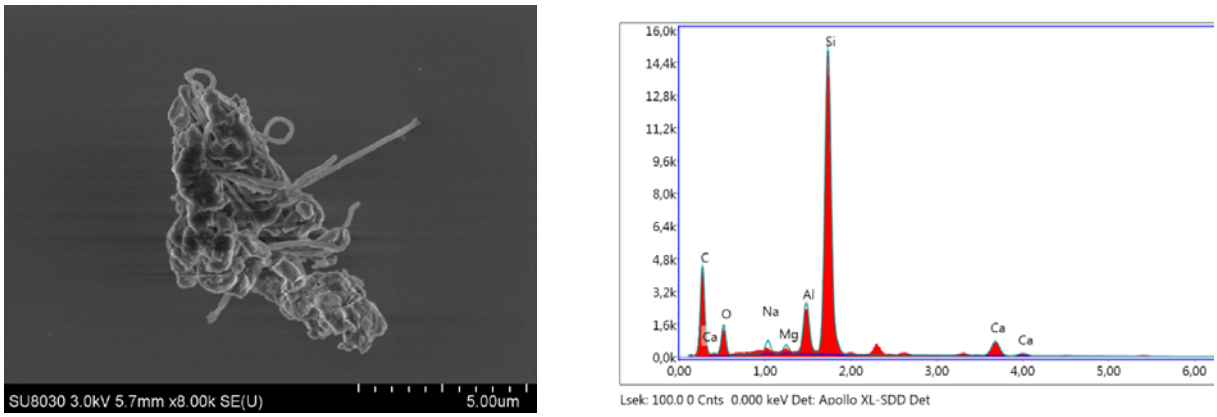


**FIGURE 7: FIBRE AGGLOMERATE ON THE NAS SPECIMEN TAKEN DURING THE EXPERIMENTAL ACTIVITY (LEFT) WITH CORRESPONDING EDX ANALYSIS (RIGHT).**

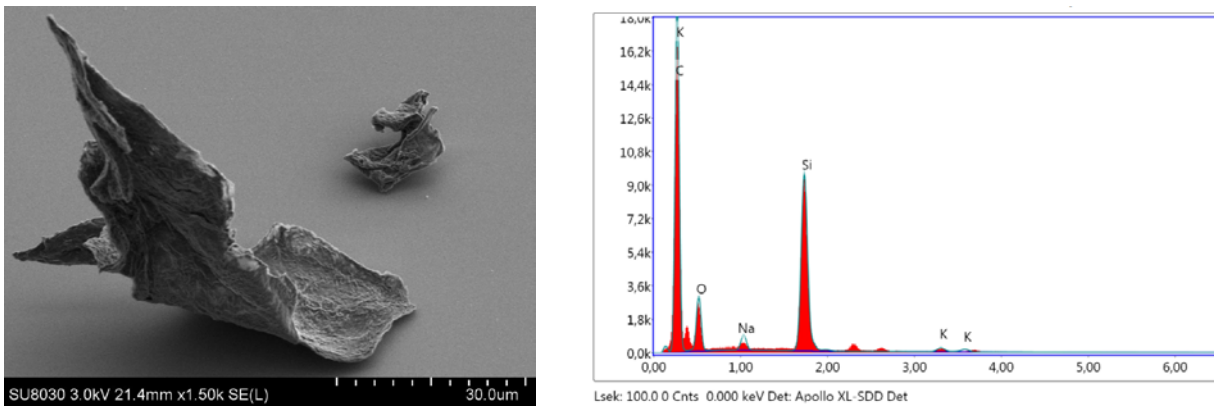


**FIGURE 8: COMPACT PARTICLE ON THE NAS SPECIMEN TAKEN DURING THE EXPERIMENTAL ACTIVITY (LEFT) WITH CORRESPONDING EDX ANALYSIS (RIGHT).**

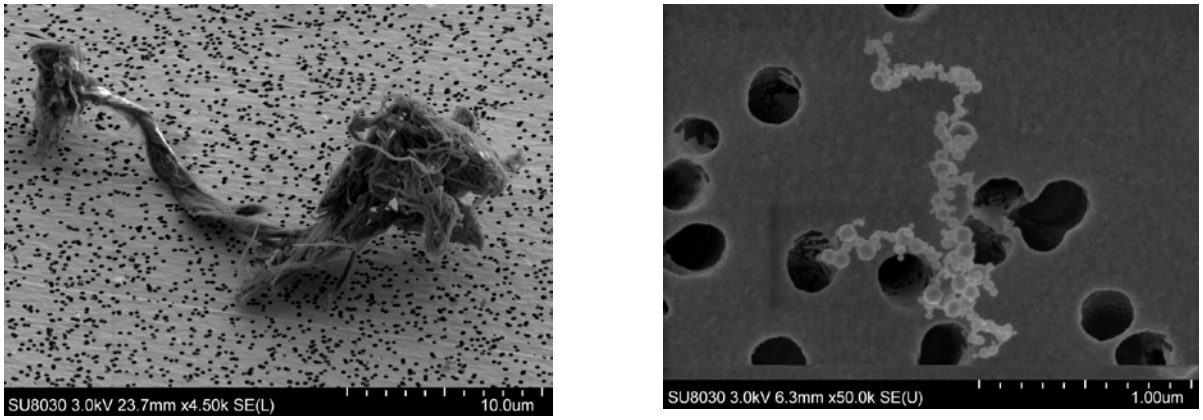


**FIGURE 9: FIBRE AGGLOMERATE ON THE FILTER SPECIMEN TAKEN DURING THE EXPERIMENTAL ACTIVITY (LEFT) AND SOOT PARTICLES (RIGHT).**

**Determination of mass concentration (gravimetric measurement):**
Gravimetric measurements were not performed.

**Discussion of measurement results - MWCNT (Arry 01) release experiments at a fibre test stand:**
The SEM and EDX analyses yielded no evidence that the fibre agglomerates analysed on the collective samples were Arry 001. Based on the measurement results and the morphological analyses one can therefore assume that neither single fibres nor fibre agglomerates were emitted from the test chamber or from the laminar flow box during the experimental activities. Thus, the protective measures of the test chamber, the laminar flow box and further organisational measures were efficient.

## 4.6 Workplace measurements during cleaning of the test stand

### 4.6.1 Sampling

The workplace measurements during the cleaning of the devices within the laminar flow box were carried out in accordance with the above-mentionend measurement strategy of tier 2 (basic assessment) and tier 3 (expert assessment).

**Description of the workplace:**

After the experiments for testing the dustiness of MWCNT (Arry 01) at the fibre test stand, all used devices, like the aerosol generator, flasks and tubes, were cleaned in the laminar flow box using an approved industrial vacuum cleaner (Nilfisk GM 80). In particular, the cyclone filter was opened and wet-cleaned. Subsequently, the waste was bagged in the laminar flow box and disposed of into specified waste containers.

During these cleaning activities, the particle number concentration was detected stationary with two CPC 3007 (left and right side of the laminar flow box, see figure 10, left).
In addition, personal measurement and sampling devices (DiSCmini and FAP) which were placed in and at a backpack, were used for measurements. The devices' collection apertures were positioned in the direct breathing area of the employee.
Further stationary and personal measurement and sampling devices were applied in order to compare the different devices. In this report they are only mentioned when they yielded relevant measurement results.

**Room size:**

Laboratory approx. 5.8 x 4.0 x 2.75 $m^3$

**Ventilation:**

- supply air and exhaust in the ceiling area
- door only temporaryly opened, windows closed
- direct exhaust from the test chamber

**FIGURE 10: CLEANING OF THE USED DEVICES IN THE LAMINAR FLOW BOX.**

**Description of handled substances and preperations:**

On the measurement day, MWCNT (Arry 01)-contaminated devices were cleaned. The entire cleaning took place within the safety cabinet.

**TABLE 4: SAMPLING PROTOCOL FOR THE WORKPLACE – CLEANING OF THE DEVICES IN THE LAMINAR FLOW BOX AFTER THE EXPERIMENTS.**

| DATE | SAMPLE NUMBER | MEASURE-MENT METHOD | MEASUREMENT TASK | VOLUME FLOW | SAMPLING PERIOD | | SAMPLING DURATION | SAMPLING MODE | CLIMATE |
|---|---|---|---|---|---|---|---|---|---|
| | | | | (l/min) | FROM | TO | (min) | | |
| 17.12.14 | AP-2014-12-17-1 | CPC 3007 | Determination of the particle number concentration in the laboratory during cleaning of the measurement devices left beside the safety cabinet (measurement in close-up range) | 0.7 | 10:02 | 12:57 | 175 | stationary | measurement in the outside area 2…5°C, cloudy, soft wind from NW<br><br>In the laboratory: 21 °C, 33 % |
| 17.12.14 | AP-2014-12-17-2 | CPC 3007 | Determination of the particle number concentration in the laboratory during cleaning of the measurement devices right beside the safety cabinet (measurement in close-up range) | 0.7 | 10:02 | 12:57 | 175 | stationary | |
| 17.12.14 | AP-2014-12-17-3 | DISCmini | Determination of the particle number concentration on the person during cleaning of the measurement devices | 1.0 | 09:16 | 12:57 | 221 | personal portable | |
| 17.12.14 | AP-2014-12-17-4 | FAP | Particles' accumulation for morphological characterisation, accumulation on a gold vaporised filter during cleaning of measurement devices (measurement on the person) | 2.0 | 10:00 | 11:53 | 113 | personal portable | |

### 4.6.2 Measurement results

**General:**

Product specific particle number concentrations are effected by emission sources in the outdoor area (e.g. increased traffic volume, particles from power plants and domestic fire), wheather influences (amongst others changing wind directions) and further sources in the interiors (e.g. smoking, welding, abrasion of electric motors). Without morphological and/or chemical analysis, the immediate effect of such other sources on the detected product specific particle number concentrations has to be generally taken into account.

Currently, there are no occupational exposure limits for ultrafine particles or nanomaterials. Accordingly, a correlation of measurement results to exposure limits cannot be given yet. In the present report, the measured workplace concentrations are therefore discussed in relation to the naturally occuring outside air concentrations and other background pollution.

**Cleaning of the devices in the Laminar Flow Box after the experiments:**

The time course of the particle number concentration during the cleaning activities is illustrated in figure 11.

Before cleaning, the average particle number concentration was 2,210 #/cm³ (DISCmini), 1,510 #/cm³ and 1,299 #/cm³ (CPC 3007). During the actual cleaning, average particle number concentrations of 1,284 #/cm³ (DISCmini), 1,158 #/cm³ and 940 #/cm³ (CPC 3007) were detected. Thus, higher concentrations were detected before the activities with both the DISCmini and the CPC 3007. A significant increase of the particle number concentration was not detected during cleaning (see table 3).

The geometric average value of the particle size was 65 nm as determined with the DISCmini.

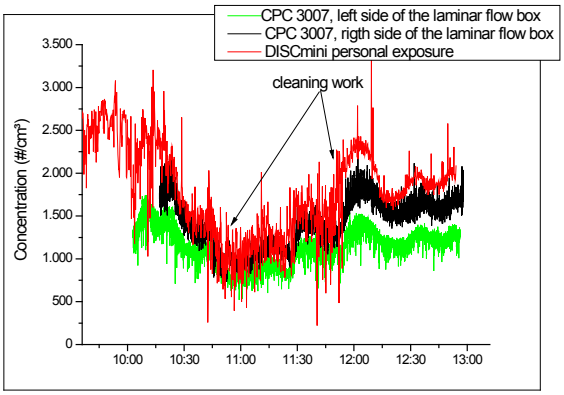


**FIGURE 11: MEASUREMENT OF THE PARTICLE NUMBER CONCENTRATION WITH THE CPC 3007 (FAR FIELD, GREEN AND BLACK) AND WITH THE PORTABLE DISCMINI (NEAR FIELD, RED) DURING CLEANING.**

**TABLE 5: PARTICLE NUMBER CONCENTRATIONS DURING CLEANING OF DEVICES (SIGNIFICANT PARTICLE INCREASE COMPARED TO THE BACKGROUND IS MARKED IN RED, IF VALUE IN COLUMN 4 IS > 0).**

| | | DISCMINI (CLEANING) (#/CM³) | DISCMINI (PRELIMINARY STUDIES) (#/CM³) | NETTO EXPOSITION (COLUMN 1-2) | SIGNIFICANCE (COLUMN 3 - 3X SD) |
|---|---|---|---|---|---|
| | | COLUMN 1 | COLUMN 2 | COLUMN 3 | COLUMN 4 |
| Cleaning 17.12.2014 | MW | 1,284 | 2,210 | -926 | -2,312 |
| | SD (3 x SD) | 924 | 1,386 | | |
| | min | 221 | 258 | | |
| | max | 2,274 | 3,206 | | |
| | | **CPC 3007 1 (CLEANING) (#/CM³)** | **CPC 3007 1 (PRELIMINARY STUDIES) (#/CM³)** | **NETTO EXPOSITION (COLUMN 1-2)** | **SIGNIFICANCE (COLUMN 3 - 3x SD)** |
| | | COLUMN 1 | COLUMN 2 | COLUMN 3 | COLUMN 4 |
| Cleaning 17.12.2014 | MW | 940 | 1,299 | -359 | -959 |
| | SD (3 x SD) | 411 | 594 | | |
| | min | 522 | 710 | | |
| | max | 1,296 | 1,742 | | |
| | | **CPC 3007 2 (CLEANING) (#/CM³)** | **CPC 3007 2 (PRELIMINARY STUDIES) (#/CM³)** | **NETTO EXPOSITION (COLUMN 1-2)** | **SIGNIFICANCE (COLUMN 3 - 3x SD)** |
| | | COLUMN1 | COLUMN 2 | COLUMN 3 | COLUMN 4 |
| Cleaning 17.12.2014 | MW | 1,158 | 1,510 | -352 | -1,134 |
| | SD (3 x SD) | 531 | 732 | | |
| | min | 731 | 782 | | |
| | max | 1,663 | 2,270 | | |

Nevertheless, it cannot be fully excluded that single fibres were released while cleaning. Therefore, the focus of the discussion is on the morphological analyses with the scanning electron microscope which were carried out on collected samples (see section below).

**Morphological characterisation of particles:**

Samples for the morphological characterisation were collected with an electric precipitator (NAS) and with a PGP-FAP-fibre sampling system on gold vaporised filters. The PGP sampling system was positioned in the employee's breathing area, so that an individual exposition could be detected. The NAS was run stationary in the near field. Results from the SEM and EDX analyses are presented in figures 12 and 13.

The analysis of the filter sample revealed soot particles (probably diesel exhaust particles from the outdoor area) and compact respirable particles in particular (see figure 12 and 13). Single fibres of the MWCNT (Arry001) or fibre agglomerates were not identified.

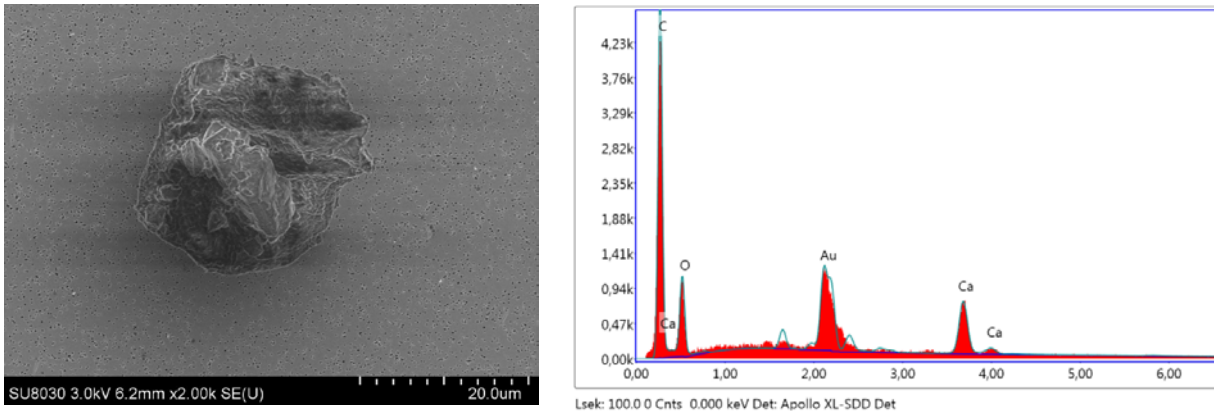


**FIGURE 12: COMPACT PARTICLE ON THE FILTER SAMPLE TAKEN DURING CLEANING ACTIVITIES (LEFT) AND CORRESPONDING EDX ANALYSIS (RIGHT).**

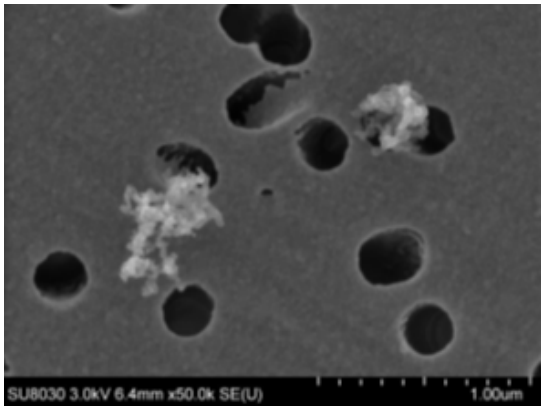


**FIGURE 13: SOOT PARTICLE ON THE FILTER SAMPLE TAKEN DURING CLEANING ACTIVITIES.**

**Determination of the mass concentration (gravimetric measurement):**
Gravimetric measurements were not carried out during cleaning of the devices.

**Discussion of the measurement results - Cleaning of the devices after the experiments:**
Based on the measurement results and the morphological analyses one can conclude that neither single fibres nor fibre agglomerates were emitted during cleaning activities. Thus, the protective measures of the laminar flow box and further organisational measures were efficient.

# 5 References

Voigtländer, J., Tuch, T., Birmili, W., and Wiedensohler, A.: **Correlation between traffic density and particle size distribution in a street canyon and the dependence on wind direction**, Atmos. Chem. Phys., 6, 4275-4286, doi:10.5194/acp-6-4275-2006, 2006.