

**Production of nanoscaled
zinc oxide particles in a
laboratory**

Field measurement report No 3

Imprint

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1 Abbreviations and acronyms

A	alveolar
BAuA	Federal Institute for Occupational Safety and Health (in Germany)
CPC	Condensation Particle Counter
DISC	Diffusion Size Classifier
DMA	Differential Mobility Analyzer
EDX	Energy-Dispersive X-ray spectroscopy
ENM	Engineered Nanomaterials
FFP	Filtering Face Piece
HEPA	High Efficiency Particulate Airfilter
LEV	Local Exhaust Ventilation
MSDS	Material Safety Data Sheet
NanoGEM	Nanostructured materials – Health, Exposure and Material properties
NAS	Nanoparticle Aerosol Sampler
NSAM	Nanoparticle Surface Aerosol Monitor
PPE	Personal Protective Equipment
SEM	Scanning Electron Microscope
SMPS	Sequential Mobility Particle Sizer
SOP	Standard Operating Procedure
TEM	Transmission Electron Microscopy
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. In all studies, the risk assessment combined measurements and a non-measurement approach in terms of an additional inspection of the specific workplace situation. The present report refers to laboratory, where nanoscaled zinc oxide particles were produced in a closed system. They were then harvested in the laboratory by scraping an agglomerated powder layer from a plate and filling it into a glass bottle. The occupational safety and health situation was evaluated both by measurements and by an additional assessment of the specific workplace situation and during activities with nanomaterials.

This report presents:

- an example for a guided dialogue (non-measurement method)
- a note on first impressions by a safety expert (non-measurement method)
- a detailed measurement report
- a conclusion combining the findings of both approaches

The dialogue guide is a short check list with questions that provide an overview of workplace activities, nanoscaled substances and installed protection measures. It covers nanospecific issues as well as general occupational safety and health aspects.

The measurement report summarises results from measurements in the zinc oxide production laboratory and from measurements during the dispersion of zinc oxide.

Zinc oxide particles were found during several activities, but in general the amount of background particles (e.g. soot), was always higher than the specifically generated zinc oxide particles.

Several recommendations for technical and organisational measures were given, like vacuum cleaning with HEPA filter and the removal of devices positioned near the exhaust ventilation inside the enclosure.

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 advance 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 was performed at a laboratory, where nanoscaled zinc oxide particles were produced, harvested and filled into a glass bottle. The report includes an exposure measurement and a non-measurement method.

- a) The selection of the **non-measurement method**, here a **guided dialogue** and a **note on first impressions by a safety expert**, is based on the approach of the brochure, which focusses on safety strategies for occupational safety and health for handling nanomaterials at workplaces. The dialogue guide can also be found among the supplementary items compiled for “Nano to go!”.
- b) The **exposure measurement** was performed according to standard operation procedures (SOP’s), which were developed during the project NanoGEM (described in the section 5.3 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 including the particle size distribution and the surface area of the alveolar dust fraction (A-dust) as well as the mass concentration. Measurements included personal exposure monitoring with novel portable monitors.

4 Dialogue guide for occupational safety and health aspects for handling nanomaterials

DIALOGUE GUIDE FOR OCCUPATIONAL SAFETY AND HEALTH ASPECTS FOR HANDLING NANOMATERIALS (NM)		
Company/Institution:	Contact data: Contact person:	Date:

Question 1: Are NM

- Produced
- Processed
- Released during production / processing
in your company / institution?

NM are produced in this department and in another department further processed and possibly analytically-chemically characterised.....

Question 2: How many employees come into contact with NM in your company / institution?

- < 10
- 10 to < 50
- 50 to < 100
- ≥ 100

In this department, up to ten persons (7 permanent employees, 3 students) come into contact with nanomaterials. For the other tests, probably 10-20 employees more are handling NM.....

Question 3: In which form are the NM produced / processed / released?

- Fibre
- Dust

Aerosols

Liquids

The production takes place in the closed oven.

A release of dust is maybe possible during sampling.

Question 4: Which NM is (are) produced / processed / released during the working procedures?

In this case, diethylzinc (liquid) is combusted and forms nanoscaled zinc oxide. On other occasions, nanoscaled copper or aluminium oxide is produced.

Question 5.1: What is the quantity of NM handled on a daily basis?

g/day (ml/day)

kg/day (l/day)

t/day (m³/day)

Question 5.2: What is the quantity of NM handled on a yearly basis?

g/year (ml/year)

kg/year (l/year)

t/year (m³/year)

Question 6.1: Are MSDS for the produced / processed nanomaterials available in your company? (Can the MSDS be shown? Can they be delivered? Are they accessible for all employees?)

Yes

No

Although MSDS for all raw materials are accessible online, it is not clear if a MSDS for nanoscaled zinc oxide exists.

Question 6.2: Do the MSDS refer specifically to NM?

- Yes No

.....

.....

.....

Question 6.3: Do the MSDS contain the following information?:

- Does the classification of the hazardous properties (see below) refer specifically to the nanoscaled form?

.....

.....

- Are there values for alveolar dust (A-dust) and / or particle number concentration?

.....

.....

- Morphological information (form, structure, i.e. is it for example a stiff fibre...)

.....

.....

- Solubility in water (g/l range → well soluble, below 100 mg/l → insoluble)

.....

.....

- Information about dustiness / dust number

.....

.....

- Information about human toxicity

- Acute toxic (R23, R24, R25; H301, H311, H331)
- Chronic toxic (R48)
- Carcinogenicity (carc. 3) (R68)
- Irritating to skin (R38; H315)

Sensitisation by inhalation (R42, R43; H317)

.....

.....

Question 7: Do you include NM safety information in training courses and occupational-medical and toxicological advice?

Yes No

Are there any specials?

New employees are instructed with a laboratory rules document, where all specifications how to handle NM are integrated (including PPE).

.....

.....

Question 8: Which of the following operations are performed on NM?

1. mixing and dispersion
 ... Control guidance sheet 215: Mixing of solids with other solids or liquids (additional measures)

.....

.....

2. filling and bagging
 ... Control guidance sheet 204: Removing waste from a dust extraction unit (additional measures)

.....

.....

3. charging and decanting

.....

.....

4. weighing

.....

.....

... Control guidance sheet 214: Weighing solids (additional measures)

.....

.....

5. spraying

6. coating (of surfaces)

7. other

After condensation on the cooling surface, the NM are sampled (scraped and swept).

❖ Control guidance sheet 240: Dust workplaces (principles)

Question 9: Which of the following protection measures are used when handling NM?

Technical protection measures – ventilation:

- Function and efficiency is regularly inspected, at least once per year.
- Before starting work the ventilation is switched on and tested.
- The ambient air movement is across or away from the employee.
- Is data on the amount of alveolar dust (A- dust) and /or particle number concentration at the workplace available respectively does data on the fibre amount exist?
 - Yes
 - How high was the exposure?
 - No

Which of the following technical measures are used when working with NM?:

- Local exhaust ventilation (LEV)
- Fume hood (the devices are (partly) closed - see figures)
- Glove box
- Safety cabinet

Which of the following technical measures are used when working with NM in form of aerosols:

- Closed facility

- Closed spray booth with automated change of moulded part
- Open spray booth, the spray dusts are captured by exhaust ventilation
- If spraying is performed manually, the spray lance is as long as possible. The drop size is preferably $>100\ \mu\text{m}$ (no inhalable mist)

❖ **Control guidance sheet 100:** General ventilation (minimum requirements)

❖ **Control guidance sheet 200:** Local exhaust ventilation (source extraction) (additional measures)

❖ **Control guidance sheet 301:** Glove box (closed system)

Technical protection measures - processes:

- Low-dust drop and dump areas
- Low-dust processing and disposal methods

The condensed material is very sticky and agglomerates. Hence, it is not dusty during the sampling. The situation for the further handling is not known.

Organisational protection measures:

- Hazardous substances are clearly labelled
- Containers for waste disposal are clearly marked and labelled

-> *Since the CNTs are completely processed, no waste disposal took place yet. In the case concerned, CNTs would not be disposed separately, but in containers for plastic waste.*

- Surfaces are easily cleaned (*partly*)
- Possibilities for dust deposits are minimised. (*unfortunately some dust deposit possibilities exist*)
- Wet cleaning is mandatory. (*with water*)
- Industrial vacuum cleaners are available. (*one special vacuum cleaner for CNTs is present*)

Type of filter: (*not known*)

- M
- H
- Appropriate clean-up equipment for leaking or spilled agents are available and easily accessible. -> *are disposed separately*
- Cleansing wipes are not kept in pockets.

Dusty protection clothes are not shaken out or blown off -> *not applicable, since disposable suits are worn one time and then disposed.*

In case of dusty activities, only clean filtered air (filter type H) is recycled.

Bulk goods and open containers are covered.

Dusty agents are stored in closed containers.

Basic occupational hygiene standards are adhered to.

🔗 **Control guidance sheet 110:** Inhalation - Basic Safety Precautions (Principles)

Personal protective measures:

Instructions on how to use, maintain and properly store protective equipment, are readily available. (see remark on gloves below)

Chemical-resistant gloves are used.

Type: *For handling NM, dermatril is used, for activities at the oven wool cotton (or similar) is worn.*

Protective equipment is correctly stored in a dedicated area.

The behavioural measures for handling gloves shall be optimised (see figures, for instance box on the laboratory table)

Is protective clothing worn?

Material of protective clothing (if a high amount of material is handled) *Only the normal laboratory coat*

Dust: Type 3 (*not known*)

Aerosols: Type 4

Is a respirator used for short-term activities?

Type of respirator? Type of filter?:

P2 P3

FFP2 FFP3

Other

5 Notes from an inspection of occupational safety and health aspects in a particle production laboratory

These questions and notes were taken in addition to the dialogue guide.

1. Aim of occupational safety and health & communication:
It was not asked in this case.
2. Responsibility:
Mr. XXX is working as PhD in the laboratory. The superior in the legal sense is not specified.
3. Training and documentation:
Laboratory rules with all instructions do obviously exist. Operating instructions do refer to the respective activity / device, not to single substances.
4. Operating instructions accessible on-site:
No
5. Classification & labelling of chemicals:
Old and new labeling is found, depending on the age of the chemical.



FIGURE 1: LABELLED DIETHYLZINC VESSEL

6. Used PPE (personal protective equipment):
 - Dermatrill gloves are used for handling nanomaterials, wool cotton gloves for hot surfaces.
 - The behavioural measures for handling gloves shall be optimized.
 - Respiratory dust mask is worn for actually handling nanomaterials.
 - On the measurement day, the employee wore a measurement device (DiSCmini¹ (Diffusion Size Classifier)) for continuous measurement of the particle number concentration.

¹ Trademark of the company Matter Aerosol AG



FIGURE 2: LEFT - PPE OF EMPLOYEE, RIGHT – BEHAVIOURAL MEASURES FOR HANDLING GLOVES NEED TO BE OPTIMIZED

7. Orderliness and cleanliness at work:

It is a typical research laboratory full of devices (actually too full). However, everything makes a clean impression.



FIGURE 3: LABORATORY FULL OF MANY DEVICES AND CABLES

8. Emergency measures

- Emergency measures are posted in the hall (emergency phone numbers and first aid instructions).
- No evacuation plan is posted in the laboratory or hall (only in the entrance hall near the staircase).

9. Ergonomics at the workplace

The do-it-yourself processes result in a close and overfilled workplace. For this reason, certain areas are difficult to reach.

10. Do products go externally? MSDS or information sheet accessible?

It was not asked.

11. Further remarks

- All devices are generally located in a plexiglass enclosure (approx. 5x3x3 m). The exhaust ventilation of the enclosure is continuous. Two doors allow access to the interior. However, the enclosure is not completely tight and several enclosure panel-units are missing.
- In order to facilitate the experiments, many devices are located within the enclosure. However, it is unclear if they possibly distract the volume flow inside the enclosure.
- Both mentioned points result in doubts regarding the efficacy of the exhaust ventilation.
- An access restriction sign to the laboratory does not exist. Access is only possible with the respective key. It is unclear whether the door can be opened by a rescuer in case of emergency.

6 Exposure measurements of fine and ultrafine dusts in a laboratory

6.1 General

■ Measuring task:	Workplace measurements in the field: Generation of ZnO, weighing and dispersing of ZnO
■ Company:	20131007
■ Participants in the preliminary discussion:	Company representatives, BAuA representatives
■ Measurement date:	From 07.10.2013 to 09.10.2013
■ Receipt of samples at:	09.10.2013
■ Sample number:	From AP-2013-10-07-1 to AP-2013-10-09-07 (BAuA dust laboratory Berlin)
■ Analyses carried out by:	BAuA representatives
■ date:	November/December 2013
■ Preparation of measurement report:	BAuA representative

6.2 Description of the measurement procedure

SMPS – Sequential Mobility Particle Sizer:

The SMPS detects the particle number concentration in a size range of 10 nm to 1000 nm (LDMA) respectively of 5 nm to 350 nm (MDMA). The pre-impactor 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.

CPC 3007 (Condensations Particle Counter):

The handheld measurement device detects the particle number concentration time-resolved within a size range of 10 nm to 1000 nm. Within the CPC 3007, the particles condense on 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 surface monitor for nanoparticles detects the surface of the particle (expressed in µm²/cm³), which are deposited in the tracheobronchial (TB) or alveolar (A) lung area.

NAS (Nanoparticle Aerosol Sampler):

With the nanoparticles aerosol sampler (NAS), samples of charged particles (similar like those from the output of a differential mobility analyser (DMA)) can be transferred on substrate for further analyses.

Aerosolspectrometer 1.109 - particles in a size range of 0.25 to more than 32 µm are detected:

- Aerosolspectrometer 1.109 gravimetric - The measurement device detects the particles in a laser measurement chamber in 30 different size channels and shows the result as particle mass concentration.
- Aerosolspectrometer 1.109 numerical – The measurement device detects the fine particles with a laser measurement chamber in 30 different size channels and shows the result as particle number concentration.

TP (Thermal Precipitator):

The TP is applied as collection system and works on the basis of thermophoresis. The airflow passes between two heating plates and condenses on a cold heating plate, which is laid out as a sample carrier (Si plate). Subsequently, the sample carrier is analyzed with scanning electron microscopy.

6.3 Sampling strategy

Definitions:

- Background concentration – Particle number- or mass-concentration, which is achieved in inner rooms (work area), while outside air conditions and further sources are largely excluded.
- Outside air concentration – Particle number- or mass-concentration, which is measured outside (windward side) the work area.

Measurement strategy:

The sampling is made according to the standard operating procedures 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 engineered manufactured nanomaterials (ENM) exist.

- Tier 1 (Information gathering)

The task in tier 1 is to clarify, e.g. through on-site inspection, whether nanomaterials are used in the workplace and if they can be released during 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 conducted using handheld and easy-to-use devices and are performed to a limited extent. Measurement parameters coming into consideration can be 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 assessed with extended measurement device expenditure. In this case, 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 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 are compared with identical measurement ranges before (in the laboratory) and during the measurements (on-site) according to the SOP in order to recognize and – if necessary – remove deviations. Table 1 and 2 show the results of these comparisons.

TABLE 1: RESULTS OF THE COMPARATIVE MEASUREMENT WITH THE CPC, THE SMPS AND THE OPC ON-SITE

MEASUREMENT DEVICE	MEAN VALUE (particles/cm ³)	STANDARD DEVIATION	CORRELATIONS COEFFICIENT	GRADIENT
CPC 1	3,957	3,530	0.997	0.92
CPC 2	4,368	3,830		
SMPS 2	2,976	1,149	0.993	1.02
SMPS 3	2,961	1,179		
OPC 1	116	182	0.891	1.02
OPC 2	113	168		

TABLE 2: RESULTS OF THE COMPARATIVE MEASUREMENT WITH THE CPC AND THE SMPS IN THE LABORATORY

MEASUREMENT DEVICE	MEAN VALUE (particles/cm ³)	STANDARD DEVIATION	CORRELATIONS COEFFICIENT	GRADIENT
CPC 1	4,116	2,575	0.985	0.99
CPC 2	4,321	2,582		
SMPS 2	923	625	0.990	1.03
SMPS 3	985	650		

As an example for quality assurance measures, figure 4 illustrates the comparative measurement of the CPC measurement devices on-site.

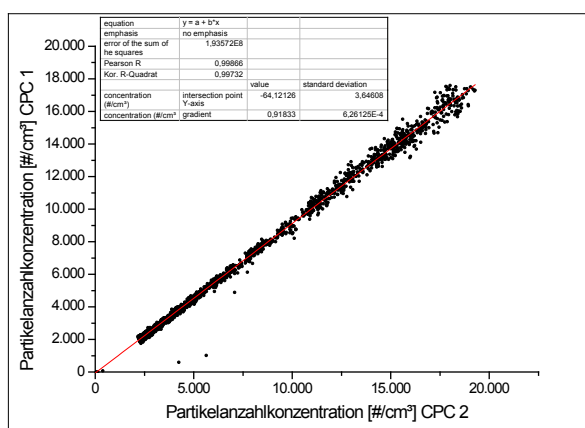


FIGURE 4: COMPARATIVE MEASUREMENTS OF THE CPC 3007 ON-SITE

Both in the laboratory and during the comparative measurements on-site, very good correlations were determined, i.e. the devices work reliably and provide robust and representative measurement results.

6.4 Workplace measurements in the zinc oxide production laboratory

Performance of sampling:

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

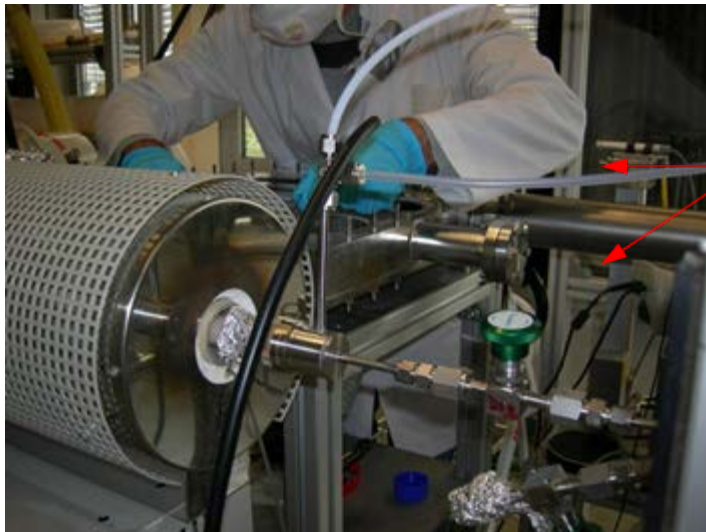
Description of the workplace:

The production of nanomaterials is performed on laboratory scale in the workplace. At the days of the measurement, zinc oxide is produced. Within the enclosure, the heating of the oven, the synthesis itself, the thermophoretic precipitation and the unloading of the material from the collector with subsequent cleaning of the plant is performed. All processes are measured using an expert measurement campaign. The synthesis itself is performed within a closed system, in which the exhaust air is guided to the outside through a cold trap and HEPA filter. After completion of the synthesis and cooling of the plant, the separator / collector is opened and the zinc oxide is taken out. Next, the collector is cleaned using a vacuum cleaner and subsequently with isopropanol.

The permanent exhaust ventilation within the enclosure causes only a slight negative pressure, since the enclosure is not completely closed (segments of the enclosure are missing) respectively the sliding doors also stand open during synthesis.

During the whole synthesis, safety glasses and laboratory coat are worn. Gloves and respiratory protection are only worn during opening of the closed plant (removal of zinc oxide and cleaning) and in case of unintentional release.

The concentrations during the process in the actual working area and in parallel the background concentration outside the enclosure are determined with the CPC 3007 and the SMPS. In this way, one can match the particle number concentrations during the activity with the nanomaterial to the background concentrations. The stationary measurement devices like the SMPS are placed in immediate proximity to the workplaces, i.e. they were operated next to the oven respectively collector (see figure 5). The measurement devices for determining the background concentration are positioned on the window-sill of the laboratory. Additionally, during the synthesis within the enclosure, a MPG II runs in order to determine the gravimetric concentration (mass concentration).



SMPS and CPC 3007

FIGURE 5: SAMPLING DURING ZNO REMOVAL FROM THE COLLECTOR

Room size: Enclosure in the laboratory
Approximately $5 \times 3 \times 3 \text{ m}^3$
Laboratory area approximately $8 \times 5 \times 3 \text{ m}^3$

Ventilation:

- Enclosure - no closed area since segments are missing
- Exhaust ventilation in the front and back area of the enclosure (permanently operating during the measurement)
- Windows and doors of the technical laboratory are closed

Description of the detected substances and preparations:

During the measurement days, nanoscaled zinc oxide was produced and filled.

TABLE 3: SAMPLING PROTOCOL FOR THE WORKPLACE – GENERATION OF ZINC OXIDE

DATE	SAMPLE NUMBER	MEASUREMENT METHOD	MEASUREMENT TASK	VOLUME FLOW l/min	SAMPLING PERIOD		SAMPLING DURATION min	SAMPLING MODE	CLIMATE
					FROM	TO			
07.10.13	AP-2013-10-07-1	SMPS (LDMA)	determination of the particle number concentration inside the enclosure (night measurement to determine the background concentration without activities in the enclosure)	0.3	18:35	09:06	876	stationary	measurement in the outdoor area 15 ... 17 °C, windless In the laboratory: 23 °C, 51 %
07.10.13	AP-2013-10-07-2	SMPS (LDMA)	determination of the particle number concentration in the laboratory, outside the enclosure (night measurement to determine the background concentration without activities in the enclosure)	0.3	18:35	09:06	876	stationary	
07.10.13	AP-2013-10-07-3	Aerosol-spectr. 1.109	determination of the particle number concentration inside the enclosure (night measurement to determine the background concentration without activities in the enclosure)	1.2	18:36	09:06	875	stationary	
07.10.13	AP-2013-10-07-4	Aerosol-spectr. 1.109	determination of the particle number concentration in the laboratory, outside the enclosure (night measurement to determine the background concentration without activities in the enclosure)	1.2	18:36	09:06	875	stationary	
08.10.13	AP-2013-10-08-1	SMPS (LDMA)	determination of the particle number concentration, measurement during production and cleaning inside the enclosure (afterwards night measurement to determine the decay behaviour)	0.3	09:29	08:22 at 09.10.	1,373	stationary	in the measurement area: 15 ... 17°C, windless
08.10.13	AP-2013-10-08-2	SMPS (LDMA)	determination of the particle number concentration, measurement during production and cleaning outside the enclosure (afterwards night measurement to determine the decay behaviour)	0.3	09:29	13:05 at 09.10.	1,653	stationary	in the laboratory: 23 °C, 51 %
08.10.13	AP-2013-10-08-3	Aerosol-spectr. 1.109	determination of the particle number concentration, measurement during production and cleaning inside the enclosure (afterwards night measurement to determine the decay behaviour)	1.2	09:29	13:05 at 09.10.	1,655	stationary	

DATE	SAMPLE NUMBER	MEASUREMENT METHOD	MEASUREMENT TASK	VOLUME FLOW l/min	SAMPLING PERIOD		SAMPLING DURATION min	SAMPLING MODE	CLIMATE
					FROM	TO			
08.10.13	AP-2013-10-08-4	Aerosol-spectr. 1.109	determination of the particle number concentration, measurement during production and cleaning outside the enclosure (afterwards night measurement to determine the decay behaviour)	1.2	09:29	13:03 at 09.10.	1,653	stationary	
08.10.13	AP-2013-10-08-5	CPC 3007	determination of the particle number concentration during production and cleaning inside the enclosure	0.7	09:33	15:00	273	stationary, partly handheld	
08.10.13	AP-2013-10-08-6	CPC 3007	determination of the particle number concentration during production and cleaning outside the enclosure	0.7	10:46	14:41	235	stationary, partly handheld	
08.10.13	AP-2013-10-08-7	NAS	particle sampling for morphological characterisation, measurement inside the enclosure during the synthesis on a Si-wafer	2.5	09:50	13:45	235	stationary	
08.10.13	AP-2013-10-08-8	NAS	particle sampling for morphological characterisation, measurement inside the enclosure during the synthesis on a TEM-net	2.5	09:50	13:45	235	stationary	
08.10.13	AP-2013-10-08-9	NAS	particle sampling for morphological characterisation, measurement inside the enclosure during the synthesis on a TEM-net	2.5	09:50	13:45	235	stationary	
08.10.13	AP-2013-10-08-10	Aerosol-spectr. 1.109	determination of the particle number concentration, measurement during the production and cleaning outside the enclosure	0.3	10:46	14:41	175	stationary	
08.10.13	AP-2013-10-08-11	MPG II	determination of the mass concentration, measurement inside the enclosure during synthesis, removal of nanomaterials and cleaning	46.5	11:25	15:00	215	stationary	
08.10.13	AP-2013-10-08-12	NAS	particle sampling for morphological characterisation, measurement inside the enclosure on a Si-wafer (during ZnO removal and cleaning)	2.5	13:50	14:30	40	stationary	

DATE	SAMPLE NUMBER	MEASUREMENT METHOD	MEASUREMENT TASK	VOLUME FLOW l/min	SAMPLING PERIOD		SAMPLING DURATION min	SAMPLING MODE	CLIMATE
					FROM	TO			
08.10.13	AP-2013-10-08-13	NAS	particle sampling for morphological characterisation, measurement inside the enclosure on a TEM-net (during ZnO removal and cleaning)	2.5	13:50	14:30	40	stationary	
08.10.13	AP-2013-10-08-14	NAS	particle sampling for morphological characterisation, measurement inside the enclosure on a TEM-net (during ZnO removal and cleaning)	2.5	13:50	14:30	40	stationary	
08.10.13	AP-2013-10-08-15	contact sample	particle sampling form morphological characterisation, sampling after cleaning at the flange of the collector						
08.10.13	AP-2013-10-08-16	contact sample	particle sampling form morphological characterisation, sampling after cleaning at the transformer						
08.10.13	AP-2013-10-08-17	material sample	sample of ZnO, produced at the date of measurement						
08.10.13	AP-2013-10-08-18	CPC 3007	determination of the particle number concentration outside the building (outside air measurement)	0.7	15:08	15:18	10	handheld	
09.10.13	AP-2013-10-09-1	SMPS (LDMA)	determination of the particle number concentration, measurement during production and cleaning inside the enclosure	0.3	09:16	13:05	229	stationary	
09.10.13	AP-2013-10-09-2	CPC 3007	determination of the particle number concentration, measurement during weighing and dispersion of ZnO	0.7	08:55	11:12	137	stationary, partly handheld	
09.10.13	AP-2013-10-09-3	CPC 3007	determination of the particle number concentration in the anteroom (seating group), at 10:15 o'clock student group	0.7	09:18	13:03	225	stationary	
09.10.13	AP-2013-10-09-4	NAS	particle sampling for morphological characterisation, measurement in the anteroom (seating group) on a Si-wafer	2.0	09:30	13:03	213	stationary	

DATE	SAMPLE NUMBER	MEASUREMENT METHOD	MEASUREMENT TASK	VOLUME FLOW l/min	SAMPLING PERIOD		SAMPLING DURATION min	SAMPLING MODE	CLIMATE
					FROM	TO			
09.10.13	AP-2013-10-09-5	NAS	particle sampling for morphological characterisation, sampling during weighing and dispersion of ZnO on Si-wafer	2.0	09:58	10:20	22	stationary	
09.10.13	AP-2013-10-09-6	MPG II	determination of the mass concentration, measurement inside the enclosure, removal of nanomaterials and cleaning	46.5	09:20	12:30	190	stationary	
09.10.13	AP-2013-10-09-7	CPC 3007	determination of the particle number concentration outside the building (outside air measurement)	0.7	11:25	11:40	15	handheld	

6.5 Discussion of the measurement results

General:

Product-specific particle number concentrations are influenced by emitters of the outdoor area (e.g. increased traffic volume, particles from power plants and sources of domestic fire), weather influences (among others changing wind directions) and further sources in the interiors (among others smoking, welding, abrasion of electric motors etc.). In the absence of material analysis, the immediate influence of the outdoor conditions (e.g. opened windows, gates) and further background levels in the interiors on the product-specific particle number concentration is generally taken into account.

Currently, no health-based occupational exposure limit value for ultrafine particles / nanomaterials exists, i.e. a correlation to limit values cannot be given yet. Therefore, within research projects the correlation to the outside air concentration and the background concentration in the working area is given.

Production of zinc oxide:

The night measurements (background measurements before the process) showed average particle number concentrations of 8,226 particles/cm³ inside and 9,394 particles/cm³ outside the enclosure.

During the production of zinc oxide, the measurement took place directly next to the oven respectively collector with the SMPS and the aerosol spectrometer (see figures 6 and 7). During this time, a CPC 3007 was also placed inside the enclosure (see figure 8). In order to determine the background concentration, it was measured simultaneously outside the plant with a SMPS and an aerosol spectrometer (see figures 6 and 7). A CPC 3007 was placed in the anteroom to the laboratory during the ZnO synthesis (see figure 8).

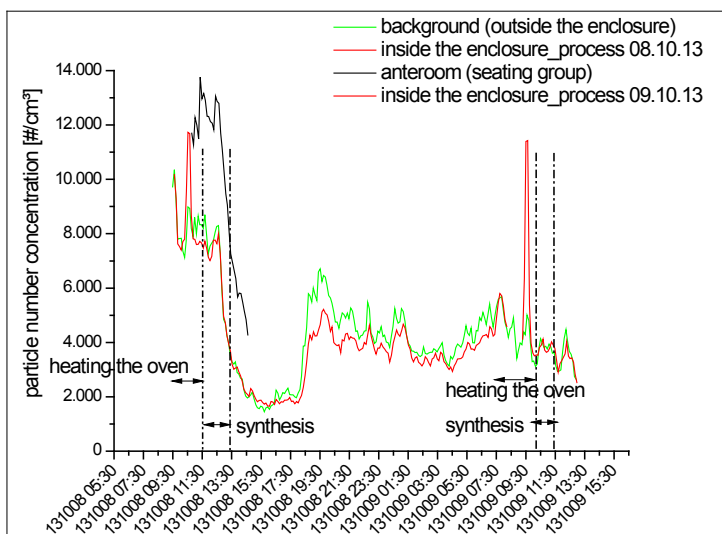


FIGURE 6: TIME COURSE OF THE PARTICLE NUMBER CONCENTRATION INSIDE AND OUTSIDE THE ENCLOSURE FROM 08.10.-09.10.2013, MEASURED WITH THE SMPS

Figures 6, 7 and 8 show that the time course of the particle number concentration in the enclosure during the process resembles the time course of the particle number concentration in the outdoor area, i.e. outside the enclosure. Due to the exhaust ventilation within the enclosure, the particle number concentration depends on the outdoor area if no emissions from the production process occur.

At 08.10., the mean particle number concentration outside the enclosure was 7,157 particles/cm³ during the synthesis and 2,785 particles/cm³ during material sampling. The mean concentrations inside the enclosure were 6,809 particles/cm³ and 2,801 particles/cm³ at or slightly below the same level, which was also confirmed by the night measurements.

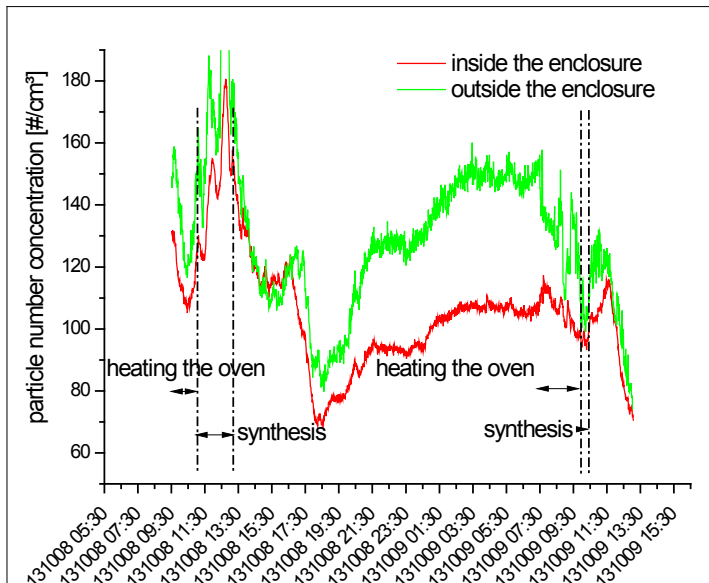


FIGURE 7: TIME COURSE OF THE PARTICLE NUMBER CONCENTRATION INSIDE AND OUTSIDE THE ENCLOSURE FROM 08.10.-09.10.2013, MEASURED WITH THE AEROSOL SPECTROMETER

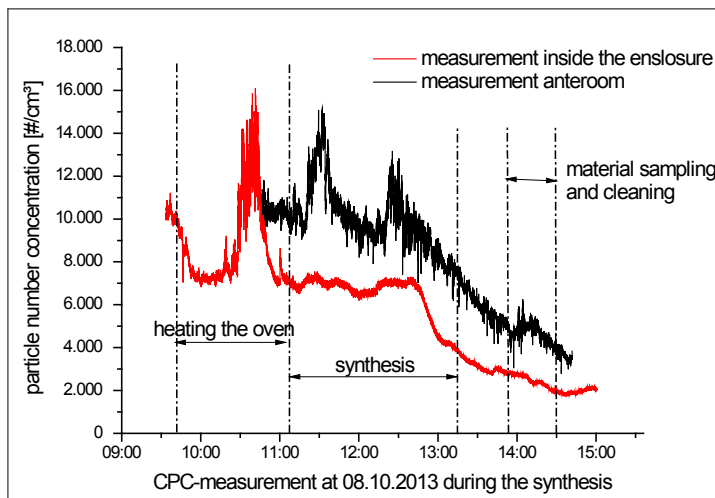


FIGURE 8: TIME COURSE OF THE PARTICLE NUMBER CONCENTRATION INSIDE AND OUTSIDE THE ENCLOSURE AT 08.10., MEASURED WITH THE CPC 3007

A temporary increase of the particle number concentration inside the enclosure was only observed during heating the oven both at the 08. and 09.10. The peaks during this heating phase were registered both with the SMPS and the CPC 3007. However, a significant particle number increase according to the SOP – M – “Expanded measurement” could not be determined. The reason is the relatively short particle number increase, which is in comparison to the time course of the process (heating the oven) rather small.

The heating process of the oven results in ultrafine aerosols. In this process, product particles (nanoscaled zinc oxide particles) are most likely not released, which was confirmed by the morphological examination of the samples.

During the night measurement inside and outside the enclosure the geometric mean of the particle size is about

43 nm (inside) and 42 nm (outside). Thereby, one can assume identical particle sizes. Even when the single process steps (heating the oven, synthesis and sampling / cleaning) are evaluated, no differences of the particle size distribution between enclosure and laboratory are recognizable, as shown in figure 9. Only the particle size distribution during the heating phase of the oven (inside and outside) shows a small increase of the smaller particles (< 30 nm), which can be explained by the emissions of the oven (no product particles).

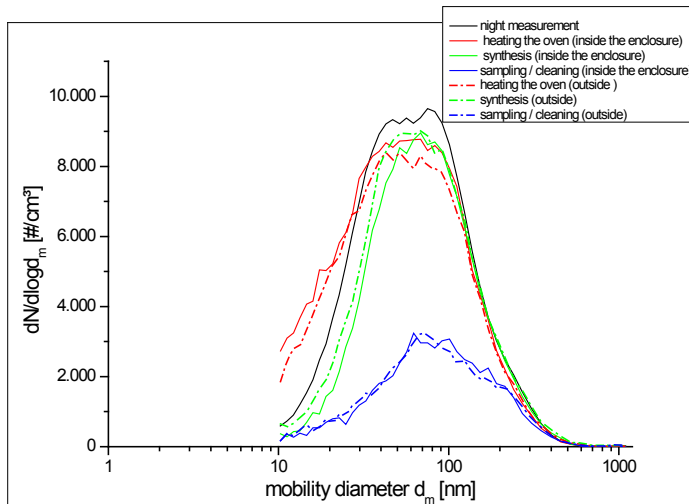


FIGURE 9: MEAN PARTICLE SIZE DISTRIBUTION OF THE BACKGROUND AND DURING THE PRODUCTION PROCESS AT 08.10.2013

In the anteroom (seating group), the particle number concentration was determined at the 08.10. with a SMPS and a CPC 3007 and at 09.10. only with a CPC 3007 (see also figures 6, 8 and 10). The figures show that the particle number concentrations at the measurement days is higher in the anteroom than in the weighing room, laboratory respectively in the enclosure. It can be assumed that the anteroom area is directly influenced by the outside air.

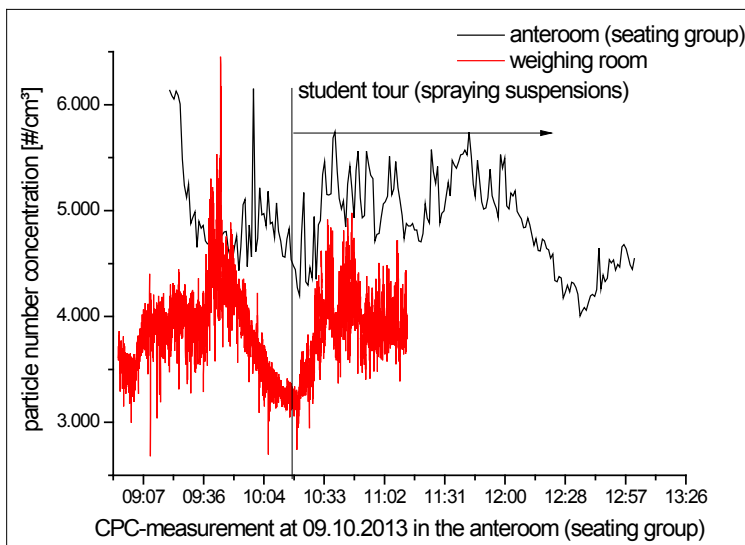


FIGURE 10: TIME COURSE OF THE PARTICLE NUMBER CONCENTRATION IN THE ANTEROOM AND DURING DISPERSION IN THE WEIGHING ROOM

The particle number concentrations in the outside area are higher than in the relevant laboratory rooms. The concentration in front of the building partly increased over 10,000 particles/cm³. These high outside concentrations were caused by the smoking area directly in front of the building as well as by a heavy traffic in immediate vicinity of the laboratory building. In the hallway and staircase, a lower concentration than in the outside area was detected on both days. For this reason, one can assume that the emitters of the detected nanoscaled aerosols are ubiquitous sources.

The essential process steps from the measurements at 08. and 09.10.13 are summarized in table 4.

TABLE 4: PARTICLE NUMBER CONCENTRATION DURING THE PRODUCTION PROCESS (SIGNIFICANT PARTICLE NUMBER INCREASE TOWARDS THE BACKGROUND IS MARKED IN RED, SIGNIFICANT PARTICLE NUMBER INCREASE IF VALUE IN COLUMN 4 > 0)

		SMPS 1 (ENCLOSURE)	SMPS 2 (OUTSIDE ENCLOSURE)	NETTO EXPOSURE	SIGNIFICANCE
		COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4
night measurement (background) 07.10. - 08.10.	average	8,226	9,394	- 1,168	
	standard deviation (3x standard deviation)	2,024	2,577 (7,731)		
	min	4,301	4,563		
	max	14,997	17,205		
heating the oven, 08.10., 9:40 - 11:09 o'clock	average	8,631	8,106	525	- 1,353
	standard deviation (3x standard deviation)	1,525	626 (1,878)		
	min	7,396	7,126		
	max	11,729	9,122		
synthesis, 08.10., 11:10 - 13:15 o'clock	average	6,809	7,157	- 348	- 5,067
	standard deviation (3x standard deviation)	1,318	1,573 (4,719)		
	min	3,944	3,958		
	max	7,999	8,700		
sampling and cleaning, 08.10., 13:50 - 14:30 o'clock	average	2,801	2,785	16	- 1,571
	standard deviation (3x standard deviation)	488	529 (1587)		
	min	2,086	1,957		
	max	3,673	3,530		
heating the oven, 09.10., 7:30 - 9:50 o'clock	average	6,099	4,597	1,502	- 439
	standard deviation (3x standard deviation)	2,450	647 (1941)		
	min	3,965	3,417		
	max	11,428	5,688		

		SMPS 1 (ENCLOSURE)	SMPS 2 (OUTSIDE ENCLOSURE)	NETTO EXPOSURE	SIGNIFICANCE
		COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4
synthesis, 09.10., 9:51 - 10:22 o'clock	average	3,600	3,340	260	- 496
	standard deviation (3x standard deviation)	126	252 (756)		
	min	3,507	3,116		
	max	3,814	3,768		
sampling and cleaning, 09.10., 10:30 - 11:10 o'clock	average	3,839	3,905	- 66	- 450
	standard deviation (3x standard deviation)	182	128 (384)		
	min	3,637	3,762		
	max	4,120	4,137		

Morphological characterisation of the product particles:

During the measurement campaign, several air samples were taken with a NAS in accordance with the different processes and workflows in order to perform subsequent scanning electron microscope analyses. The purpose is to test whether a release of nanomaterials (ZnO) occurs during the analysed processes, since the online measurement devices (SMPS and CPC 3007) can only register the whole particle number concentration without chemical differentiation. At the same time, contact samples were taken from different surfaces in order to verify potential nanomaterial deposits.

NAS samples – heating the oven and synthesis (08.10.2013)

A NAS sample was collected during heating the oven including synthesis (see figures 11 and 12). The evaluation of the digital pictures and the EDX analyses show especially soot particles. These are probably diesel soot particles from the outside area (see figure 11). Hints to emitters from the heating process could not be recognized, i.e. no ZnO particles could be analysed during a representative analysis of the NAS sample.

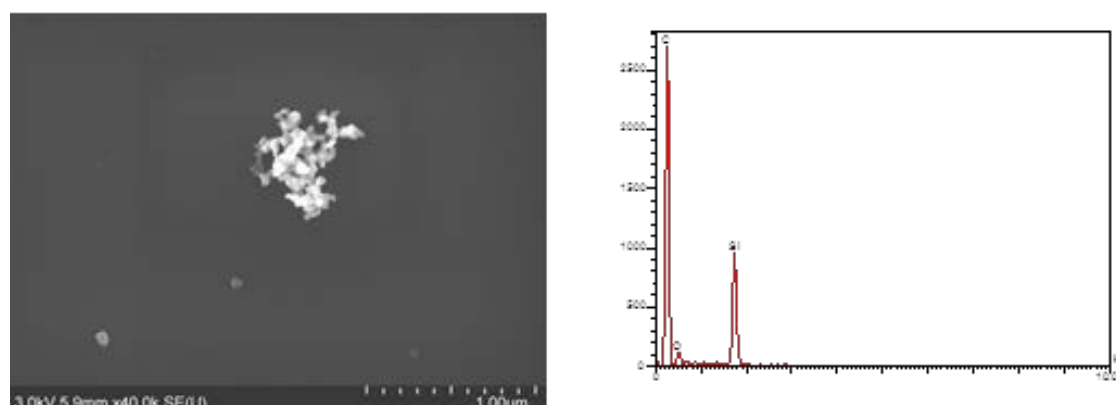


FIGURE 11: SOOT PARTICLES ON THE NAS SAMPLE DURING HEATING THE OVEN AND SYNTHESIS (LEFT SEM PICTURE AND RIGHT EDX ANALYSIS)

Furthermore, respirable, compact particles were visible on the NAS sample, from which the EDX analysis showed no ZnO spectrum (see figure 12).

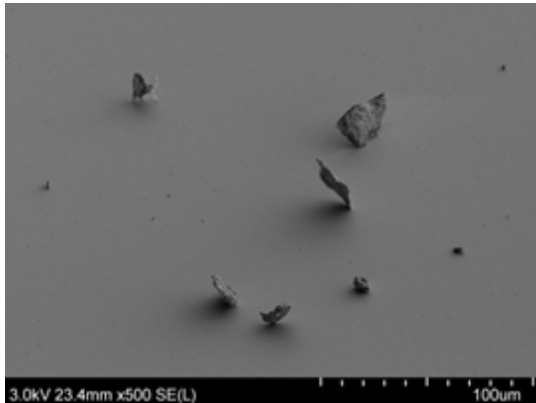


FIGURE 12: COMPACT PARTICLES

NAS samples – sampling product particles (ZnO) and cleaning the plant (08.10.2014):

The NAS specimens, which were collected during the filling process, do not only show soot particles but also ZnO agglomerates, i.e. during these processes single primary particles are released (see figure 13). These particles do not occur as primary particles but as big agglomerates in fine dust range. The sampling device is positioned in close proximity to the oven.

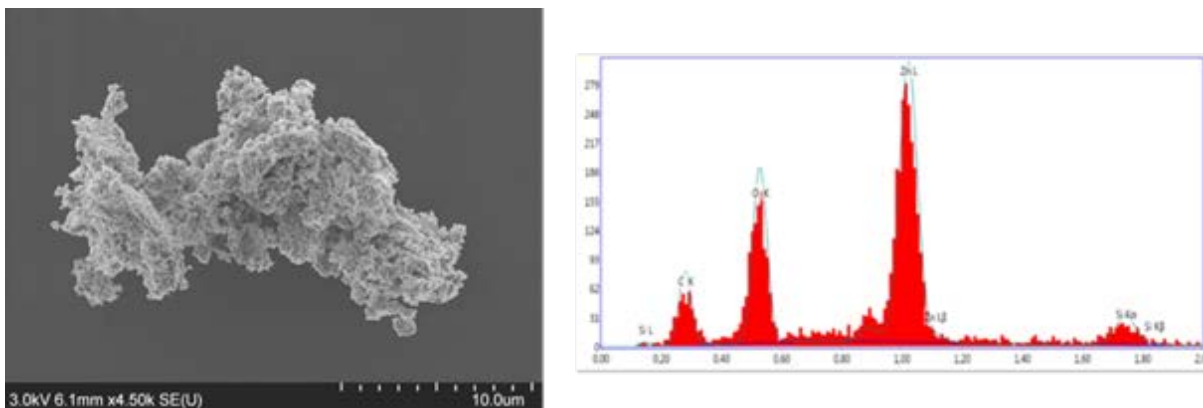


FIGURE 13: ZNO AGGLOMERATE ON THE NAS SAMPLE DURING MATERIAL SAMPLING AND PLANT CLEANING (LEFT SEM PICTURE AND RIGHT EDX ANALYSIS)

Contact samples (08.10.2014):

A contact sample was taken with a spectrotab after sampling and cleaning the plant from the flange of the collector. No ZnO particles or agglomerates could be analysed on the contact sample during the evaluation of a representative area.

NAS sample – anteroom (09.10.2014):

An analysis of especially soot particles and compact respirable particles was possible from the NAS sample collected in the anteroom (see figure 14). ZnO could not be found in the evaluation or a representative sample area.

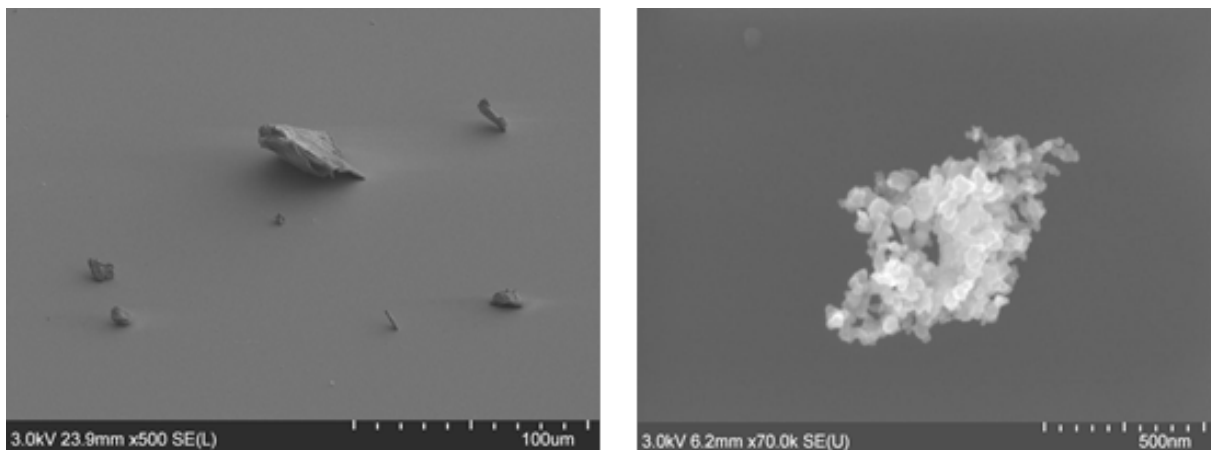


FIGURE 14: NAS SAMPLE OF THE ANTEROOM (LEFT COMPACT PARTICLE, RIGHT SOOT PARTICLE)

Determination of the mass concentration (gravimetric measurement):

In parallel to the determination of the numeric concentrations (particle number concentrations), a gravimetric determination was performed in order to determine the mass concentration. The alveolar dust fraction was determined with the MPG III. The measurements took place inside the enclosure at the 08.10. and at the 09.10. during the whole process. The determined values on both measurement days were below the detection limit of the method.

The detection limit of the method was approximately 0.007 mg/m^3 .

The determination limit of the method was approximately 0.021 mg/m^3 .

6.6 Workplace measurements during the dispersion of zinc oxide

Performance of sampling:

The workplace measurements in the laboratory are made in accordance to the above-mentioned measurement strategy of tier 2 (basic assessment).

Description of the workplace:

After weighing the material, ZnO is added to the suspension in a measuring cup which is subsequently clamped in the dispersion unit. The suspension is treated for approximately 10 min with an ultrasonic disperser. This process was performed with opened door of the noise box at the measurement day in order to detect a potential nanomaterial emission.



FIGURE 15: DISPERSION OF ZINC OXIDE WITH AN ULTRASONIC DISPERSER

The activity is performed in a closed laboratory room with closed windows and doors.

Description of the detected substances and preparations:

At the measurement day, nanoscaled zinc oxide was weighed and dispersed.

TABLE 5: SAMPLING PROTOCOL FOR THE WORKING AREA – ZINC OXIDE DISPERSION

DATE	SAMPLE NUMBER	MEASUREMENT METHOD	MEASUREMENT TASK	VOLUME FLOW l/min	SAMPLING PERIOD		SAMPLING DURATION min	SAMPLING MODE	CLIMATE
					FROM	TO			
09.10.13	AP-2013-10-09-2	CPC 3007	determination of the particle number concentration, measurement during weighing and dispersion of ZnO	0.7	08:55	11:12	137	stationary, partly handheld	measurement in the outdoor area 15 ... 17 °C, windless In the laboratory: 23 °C, 54 %

6.7 Discussion of the measurement results

Generally:

The product-specific particle number concentrations are influenced by emitters in the outdoor area (for instance increased traffic, particles from power plants and domestic fire), weather influences (amongst others changing wind directions) and further sources in the interiors (amongst others smoking, welding, abrasion of electric motors etc.). In case of a missing substance analysis, one has to generally assume the direct influence of the outdoor conditions (for instance opened windows, doors) and further background levels in the interior on the product-specific particle number concentrations have to be determined.

Currently, for ultrafine particles / nanomaterials no health-based occupational exposure limit exists, i.e. a correlation to threshold values cannot be given yet. For this reason, the correlation to the outside air concentration and to the background level in the working area is described in the measurement report in research projects.

Dispersion of zinc oxide:

The time course of the particle number concentration is visualised in figure 16. The background concentrations of potential exposures before and after the process itself are described according to the demands of the screening measurement. In this period, nanomaterials are not handled. These time sections are compared and potential exposures from the process are determined.

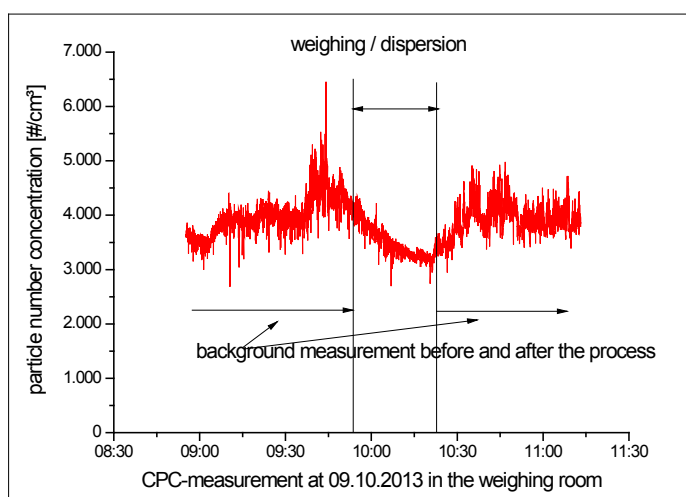


FIGURE 16: MEASUREMENT OF THE PARTICLE NUMBER CONCENTRATION WITH THE CPC 3007 DURING WEIGHING AND THE DISPERSION PROCESS

The mean particle number concentration was approximately 3,866 particles/cm³ before the measurements in the laboratory area and approximately 3,900 particles/cm³ after dispersion. During the activities with nanoscaled ZnO itself (weighing and dispersion), the mean particle number concentrations was approximately 3,430 particles/cm³, i.e. below the background level, which can also be observed from the time course of the particle number concentration (see figure 16).

Therefore, an increased release of nanoscaled zinc oxide particles during weighing and dispersion at the measurement day can be excluded.

Morphological characterisation of the product particles:

Especially soot particles and compact, inhalable particles could be analysed on the NAS sample, which was collected during weighing, filling and dispersion (see figure 17). ZnO could not be found in the evaluation of a representative sample area.

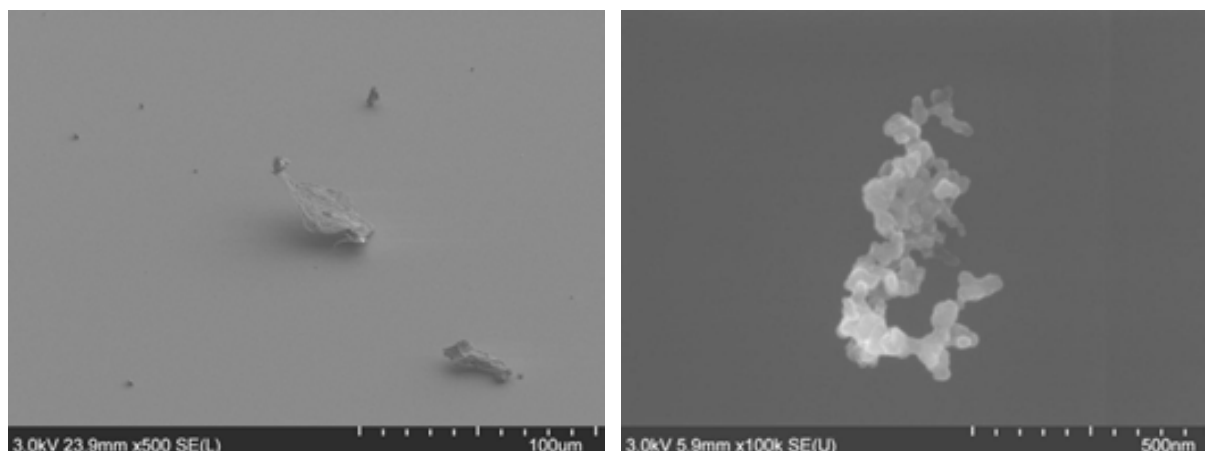


FIGURE 17: NAS SAMPLE DURING WEIGHING / DISPERSION (LEFT COMPACT PARTICLES, RIGHT SOOT PARTICLES)

6.8 Summary of the measurement results

The essential results of the inhalative exposure measurement towards the nanoscaled product particles (ZnO) during the production and processing are summarised as follows:

Synthesis of ZnO

- An increased particle number and mass concentration during the production (synthesis) of ZnO could not be observed. In particular, this relates to both the ultrafine and the total dust range.
- Additionally, no ZnO particles or agglomerates were found in the NAS sample, which was collected during the synthesis. The observed short-time particle release during the heating phase must be emitters from the oven, but these are no product particles.

Sampling and cleaning the plant

- An increased particle number and mass concentration could not be observed either during sampling nor cleaning. This affects both the ultrafine and fine dust range.
- However, the analyses of the NAS samples collected during these processes showed occasionally occurring ZnO agglomerates. It could be shown that occasionally product particles are released during sampling or cleaning. When a relatively high background concentration is present, the occasionally occurring ZnO agglomerates are indeed counted by the online measurement devices, but not registered significantly towards the background level.
- The vacuum cleaner, which is applied during cleaning, is a domestic vacuum cleaner without specific filter (e.g. a HEPA filter). Therefore, it can be assumed that fine dusts including the ZnO agglomerates end up in the working area due to the cleaning with the vacuum cleaner.

Weighing, filling and dispersion of ZnO

- No release of ZnO was detected during weighing, filling and dispersion with the online measurement devices. On the NAS samples, which were directly collected in the working area, also no ZnO particles were analysed.

Anteroom of the laboratory area

- The measurements in the anteroom of the laboratory area (online measurements and NAS sampling) showed that this room was not influenced by the activities in the laboratory on the measurement days. Although the particle number concentrations are higher than in the laboratory area, the ultrafine aerosols probably origin from the outdoor area (road traffic).

Recommendations:

The effectiveness of the protection measures in the laboratory area has to be ensured. Care must be taken to ensure a closed system during the synthesis. The enclosure should also be closed (missing segment). Closed doors of the enclosure should be ensured especially during sampling.

In order to organise a low-emission sampling and cleaning, a proven industrial vacuum cleaner should be applied (see the short description of dust classes at <http://www.ilkdresden.de/index.php?id=983&L=1&cHash=c6f95bf590715047c283668e0a99e7e3>, downloaded on 16.04.2014). Class H vacuum cleaner with a maximum transmittance of ≤ 0.005 % are recommended. Furthermore, it can be considered whether a mobile, trackable exhaust ventilation can be used. The exhaust ventilation should be installed in a way that the exhaust air is directed away from the employee.

If all protection measures are functionally used, a significant increase in particle release during synthesis and handling can be excluded. Such protection measures are: A closed system, exhaust ventilation inside the enclosure and positively tested vacuum cleaner

Based on the exposure measurement data, no immediate further protection measures need to be taken. From the view of these clear exposure data, the protection measures, possibly with additional use of an industrial vacuum cleaner or a mobile exhaust ventilation are regarded as sufficient.

7 Conclusions

7.1 Specific conclusions for the zinc oxide particle production workplaces in a laboratory

It was intended to get a comprehensive view on the safety situation in the visited laboratory. For this reason, measurements and a parallel inspection by a safety expert were combined.

- Immediate measures are not required, but long-term improvements are desirable.
- During the measurement days, a significantly increased concentration of single product particles (ZnO) during the activities was not detected. Hence, no specific protection measures for this substance are necessary beyond those already in operation.
- A low-emission handling and cleaning (to decrease the exposure to dust) should be designed. For this reason, a proven industrial vacuum cleaner should be applied. The missing segment of the enclosure should be closed, especially during sampling.
- A number of organisational measures for the laboratory is recommended, for instance no devices should be positioned near the exhaust ventilation inside the enclosure.

If the existing technical measures are maintained and functionally used and if the organisational measures (general hygiene etc.) are improved, then no further action is required.

7.2 General assessment of the nanoparticle exposure

It seems that the number concentration for spherical nanoparticles, which is substantially more sensitive than a gravimetric measurement, establishes itself. However, one could not detect a general increase of the mean number concentration of produced or handled particles with long-time measurements. On the other hand, short-time peak concentrations were verified with particle number measurement devices. In contrast, an increase of the mass concentration was not detectable at all. Hence, one advantage of the particle number measurements is the identification of short-time peak values. These can be determined especially well with handheld measurement devices, which can describe the dust concentration near the breathing area in real-life situations. It can be advantageous for an enterprise to avoid peak concentrations, for instance during leakages, in order to improve the occupational safety and health situation. The advantage of the mass measurement towards the particle number measurement results from the fact that mainly the mass concentration is regulatory anchored and offers legal certainty. The exposure limit value for respirable dust is listed in the German TRGS 900 exclusively in mg/m^3 (TRGS 900 2014). The Announcement 527 (Announcement 527 2013) refers to this value and gives a benchmark level for nanoparticles of $0.5 \text{ mg}/\text{m}^3$ with a density of $2.5 \text{ g}/\text{cm}^3$.

A significant increase of the particle number concentration compared to the background could not be detected during the NanoValid field measurement and also not during other nanomaterial measurements of BAuA at any of the examined workplaces if nanomaterials were handled properly. However, the layer reference of the TRGS 402 was considered for the measurements (TRGS 402 2014). The examinations of filter- and deposited dust showed that nanomaterials were nevertheless released. In these samples, nanoparticles were detected mainly in form of particle agglomerates.

Short-time particle release can be expected during decanting and filling processes, during dispersing and during deviations of the normal operation (for example cleaning and maintenance). However, these short-time peak concentrations have no influence on potential mean particle number concentrations (possibly time-weighted averages).

8 References

- Announcement 527, 2013. Manufactured nanomaterials, *Gemeinsames Ministerialblatt*, GMBI 2013: 498-511, Available from: <http://www.baua.de/de/Themen-von-A-Z/Gefahrstoffe/TRGS/Bekanntmachung-527.html> [accessed at 30 July 2014].
- Control guidance sheets. Available from: <http://www.baua.de/de/Themen-von-A-Z/Gefahrstoffe/EMKG/Schutzleitfaeden.html> [accessed 10 September 2014].
- TRGS 402, 2014. Technische Regel für Gefahrstoffe 402 (Technical Rule for Hazardous Substances). Ermitteln und Beurteilen der Gefährdungen bei Tätigkeiten mit Gefahrstoffen: Inhalative Exposition (Identification and assessment of the risks from activities involving hazardous substances: inhalation exposure), *Gemeinsames Ministerialblatt*. *GMBI 2014: 254-257*.
- TRGS 900, 2014. Technische Regel für Gefahrstoffe 900 (Technical Rule for Hazardous Substances), Arbeitsplatzgrenzwerte (occupational exposure limit values), *Gemeinsames Ministerialblatt*. *GMBI 2014: 271-274*. Available from: <http://www.baua.de/de/Themen-von-A-Z/Gefahrstoffe/TRGS/TRGS-900.html> [accessed at 30 July 2014].