Standard Operation Procedures
For assessing exposure to nanomaterials, following a tiered approach

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SOP-Tiered Approach

Tiered Approach for the assessment of exposure to airborne nanoobjects in work-places

Date

29th March 2012

Version

1.1 English

Scope

1   Scope

The assessment of exposure to airborne nanoobjects in workplaces requires tailored strategies. This SOP covers the overall strategy following a tiered approach, which contains 3 hierarchical tiers: tier 1: information gathering, tier 2: basic assessment and tier 3: expert assessment. Figure 1 shows the flow chart of the tiered approach. This SOP describes the general procedure, whereas the measurements in tier 2 and tier 3 are described in three main SOPs:

- *SOP-M-Screening* for tier 2
- *SOP-M-Sampling* for sampling of airborne nanoobjects in tier 3 for consecutive offline analysis e.g. of chemical composition
- *SOP-M-Expanded Measurement* for intensive measurements in tier 3

Each of the above main SOPs is accompanied by several sub-SOPs describing the use of instruments, sample preparation and data evaluation.

2   Tier 1 – Data Gathering

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

3   Tier 2 – Basic Assessment

As long as no health based limit values exist for engineered nanomaterials, measured concentrations need to be compared with the background concentration levels to determine a realistic value for the exposure to engineered nanomaterials. The background level can either be measured or assumed from past experience. If tier 2 measurements reveal a concentration level which is significantly increased over the background, a potential exposure exists and has to be assessed in tier 3.

The simplified exposure measurements in tier 2 are conducted using particle size integrating, easy-to-use devices, measuring e. g. the total particle number concentration. Typical instruments are handheld condensation particle counters (CPCs) and diffusion charger based devices (miniDiSC, nanoTracer, Aerotrak 9000). Tier 2

measurements can be conducted in two different ways. On the one hand, permanently installed particle measurement devices can monitor the particle concentration in a workplace and deliver information on potentially increased concentrations (tier 2 b). If permanent monitoring reports a significantly increased concentration, the reasons have to be assessed in a tier 3 measurement. The second possibility of simplified exposure assessment in tier 2 is by screening of a workplace using handheld measurement instruments (tier 2a.1). The screening procedure is described in detail in SOP-M-Screening *Performance of Orientation Measurements ("screening-measurements") for Nano-scale Aerosols.* In tier 2a.1, particle concentrations are measured near potential release locations or in the breathing zone of workers and compared with the background concentration. If these measurements reveal a concentration level significantly higher than the background concentration, the reasons for the increase have to be checked in tier 3. If it is not clear whether an increase is really significant or if the measured increase really stems from the nanomaterial, a temporary monitoring (tier 2a.2) can be conducted. In tier 2a.2, measurements are conducted over a long, but limited time (e. g. 1 week) to record the time series of the particle concentrations. If this monitoring still reveals a significantly increased concentration, the reasons have to be scrutinized in tier 3.

4   Tier 3 – Expert Assessment

Tier 3 measurements are intended to provide clear evidence for the presence or absence of the nanomaterials in the breathing air in a workplace. Tier 3 measurements require an extended set of measurement and sampling equipment for evaluating a possible exposure to engineered nanomaterials in workplaces. Typically used direct-reading measurement instruments include Scanning or Sequential Mobility Particle Sizers (SMPS), Condensation Particle Counters (CPC) and Nanoparticle Surface Area Monitors (NSAM) for submicron and optical or aerodynamic particle sizers for micron particles. These measurements are accompanied by particle sampling systems, collecting airborne particles for consecutive analysis by SEM, TEM, ICP-AES or TXRF. Measurements in tier 3 always include the determination of the particle background in the workplace, either through simultaneous measurement at a repre-

sentative background location or through consecutive measurements at the respective workplace prior to and after the process under investigation. In the latter case, the background can also be determined with the identical process ongoing but prior to and after use of the nanomaterial.

If particle release is determined definitively in tier 3, measures need to be taken for exposure mitigation and the potential exposure needs to be re-assessed according to tier 2.
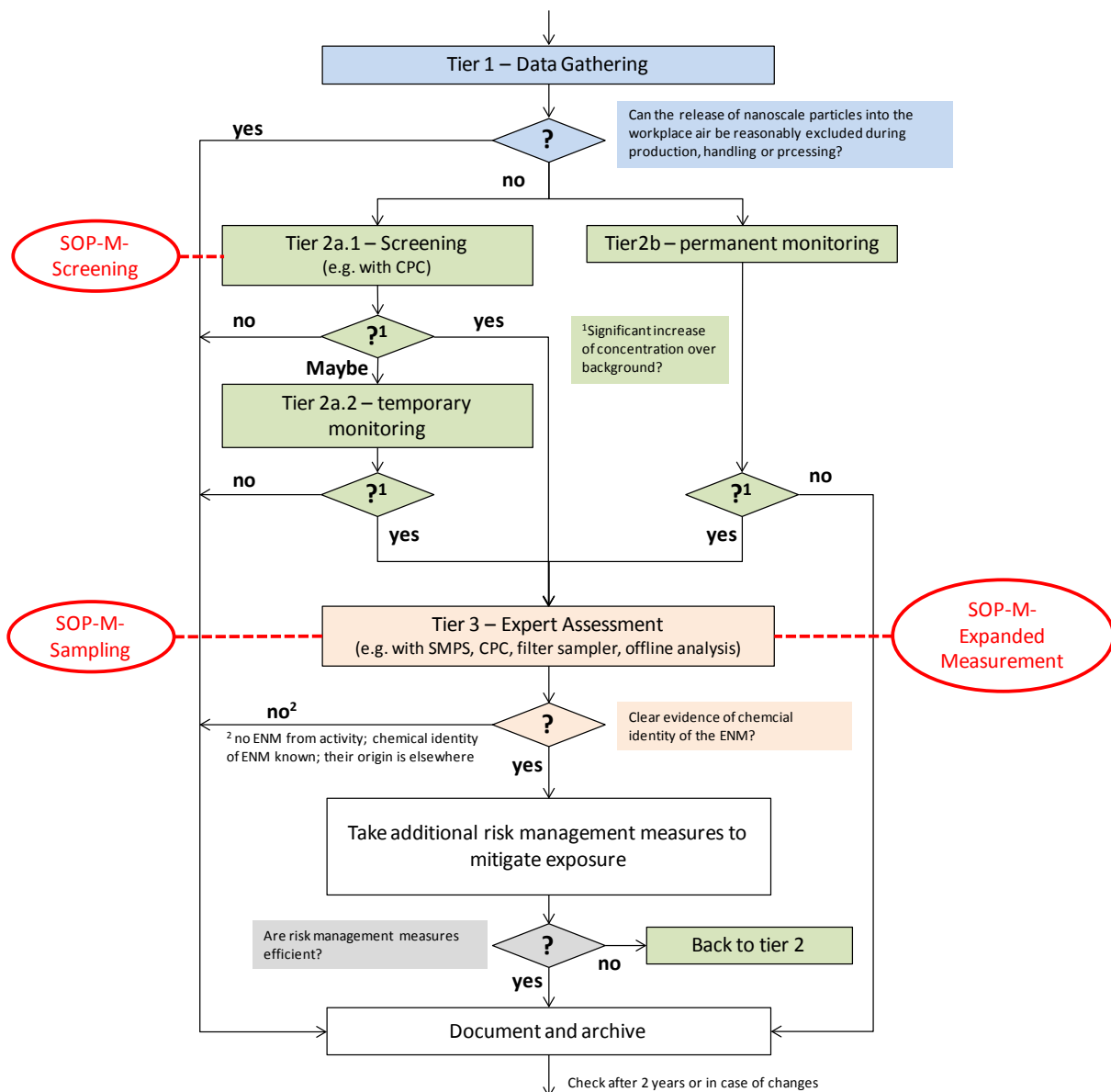

Figure 1: Flow chart of the tiered approach

5 List of Standard Operation Procedures

5.1 Main SOPs

- SOP-M-Screening: *Performance of Orientation Measurements („screening-measurements") for Nano-scale Aerosols* (Tier 2)
- SOP-M-Expanded Measurement: *Measurements of the inhalation exposure to nanoscale product materials and ultrafine aerosols at workplaces including the background concentration* (Tier 3)
- SOP-M-Sampling: *Sampling of Airborne Nanoobjects for Consecutive Microscopic Analysis* (Tier 3)

5.2 Sub-SOPs – Instruments

- SOP-S-SMPS(TSI): *Procedure of particle measurements with the Scanning Mobility Particle Sizer (TSI Model 3936)*
- SOP-S-SMPS(Grimm): *Procedure of particle measurements with the Sequential Mobility Particle Sizer (Grimm 5403)* (thus far only in German)
- SOP-S-FMPS: *Procedure of particle measurements with the Fast Mobility Particle Sizer (TSI Model 3091)*
- SOP-S-NSAM: *Procedure of particle surface determination with the Nanoparticle Surface Area Monitor (TSI Model 3550)*
- SOP-S-handheld CPC: *Procedure of particle measurements with the Condensation Particle Counter Handheld (TSI Model 3007)*
- SOP-S-miniDiSC: *Procedure of particle measurements with the Miniature Diffusion Size Classifier (miniDiSC , FH Nordwestschweiz)*
- SOP-S-nanoTracer: *Procedure of particle measurements with the nanoTracer (Philips Aerasense)* (in preparation)
- SOP-S-nanoCheck: *Procedure of particle measurements with the nanoCheck (Grimm)* (in preparation)
- SOP-S-APS: *Procedure of particle measurements with the Aerodynamic Particle Sizer (TSI Model 3321)*
- SOP-S-Spectrometer: *Procedure of particle measurements with the Aerosol*

Spectrometer (Grimm Model 1.108 and 1.109) (thus far only in German)

- SOP-S-ESP: *Procedure of particle sampling with the Nanometer Aerosol Sampler (TSI Model 3089) or electrostatic precipitator (ESP)*
- SOP-S-TP: *Procedure of particle sampling with the Thermal Precipitator (TP)* (in preparation)

5.3 Sub-SOPs – Other

- SOP-S-Data Analysis: *Procedure for measurement data analysis for the determination of released particles caused by the working process*
- SOP-S-GC Substrates: *Preparation of Glassy Carbon Substrates*
- SOP-S-Substrate Analysis (in preparation)

SOP-M-Screening

Performance of Orientation Measurements ("screening-measurements") for Nano-scale Aerosols

Date
29th March 2012

Version
1.2 English

Content

1 Scope

This document describes a general procedure for the performance of orientation measurements („screening-measurements") for nanoscale aerosols released from engineered nanomaterials in workplace operations. It is meant to answer basic questions about possible workers' exposure as second step in a tiered approach of exposure assessment. It follows a process oriented approach. Wherever applicable it also fulfills the requirements of the German TRGS 402. The particle range of nano-objects (approximately 1 to 100 nm) shall be taken into account. It is desirable to also collect information about the particle range of nanostructured materials, as agglomerates and aggregates in the respirable range according to EN 481 are relevant as well. However, currently the additional application of direct reading measurement devices which record in the range of up to 10 µm is not regarded as practical in the scope of measurements described in this SOP.

2 Reference

In reference to the terminology and definitions, the standard operation procedure refers to

- ISO/TR 27687:2008-08: Nanotechnologies – Terminology and definitions for nano-particles, nanofibre and nanoplate.

- Kuhlbusch, T.A.J. et al: "Nanoparticle exposure at nanotechnology workplaces: A review", *Particle and Fibre Toxicology* 2011, **8**:22 doi:10.1186/1743-8977-8-22

- TRGS 402:Technische Regel für Gefahrstoffe "Ermitteln und Beurteilen der Gefährdungen bei Tätigkeiten mit Gefahrstoffen: Inhalative Exposition", 2010

- VCI 2011: Tiered Approach to an Exposure Measurement and Assessment of Nanoscale Aerosols Released from Engineered Nanomaterials in Workplace Operations (https://www.vci.de/Downloads/Tiered-Approach.pdf)

3 Basics

Before the actual measurements a set of information needs to be gathered and documented. This involves details of the industrial workplaces under investigation, of the measurement

procedure being employed, and about the comparison values for the concentration of air-borne particles intended to be used.

The most important outcome of the measurements described in this document is a decision whether an Expanded Measurement (Tier 3) is necessary or whether emission of nanoscale aerosols released from ENMs into workplace air during production, handling or processing can be reasonably excluded. For this purpose direct reading exposure and emission data will be generated in the course of investigations. These have to be compared to the respective background[1]. It is intended to present and record these data in a way to allow for their storage and use in a respective database.

Under all circumstances all relevant decisions and data used have to be documented according to the requirements of this document.

This SOP contains a data documentation sheet (Annex I) which shall be filled during the investigations to allow for data storage and processing afterwards and to make sure that no important details are left out.

4   Preliminary Data Acquisition and Documentation

Before each measurement a set of information concerning the workplaces investigated and the measurement methods applied has to be acquired and documented. Use the **Annex I** for this purpose.

4.1 Description of the industrial workplaces to be assessed

Document the name and address of the company, where the assessments shall take place and describe in sufficient detail the general processes and materials used in the company, which are possibly giving rise to workers' exposure to nanoscale aerosols.

Describe in sufficient detail the individual workplaces susceptible to nanoscale aerosols exposure during the above mentioned industrial processes including an estimated number of workers involved. Categorize the workplaces into one of the following categories:

- production,
- handling and refinement,
- bagging and shipping,
- processing,
- work processes with nanomaterial production.

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[1] "Background concentration at all workplaces is the concentration at that workplace in a state where the typical industrial environment is running without the nanoparticle process being applied." (analogous to TRGS 402)

Describe the nature (e.g. chemical composition) of the nanomaterials in question, whose presence in workplace air need to be assessed and categorize them into one of the following two categories:

- particles,
- plates, or
- fibers

and

- carbon material,
- organic material,
- metal oxide,
- metals, or
- other

If available add material safety data sheet.

Describe possible background contaminations in the respective workplaces if any and if information is already available.

4.2   Description of the intended measurement instrumentation

Several types of mobile ("handheld") measurement devices are applicable for the screening. Give the *commercial name* of the instrument/s, keeping in mind that some reasonable information on the particle range between 1 nm and 100 nm should be obtained. Describe the *type* of the measurement/sampling device, the *size range*, the *time resolution*, the *metric* (including the equivalent diameter, if applicable).

Indicate, whether a general data set about the measurement characteristics like lower detection limit, cross-sensitivities to be expected, upper limit of measurement range is available to you and document these data.

Give a short description of the quality control measures you have undertaken to ensure validity of the data you generate with this device/procedure.

State the time characteristics of the instrument/s you want to use (averaging time of your sampler/instrument) and use this averaging time throughout the procedure[2]. Keep in mind the requirements as of 5.1. – 5.3.

Possible instrument categories may be (at the current state of knowledge):

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[2] The use of a uniform averaging time throughout the measurements is intended to improve internal and external comparability.

- handheld condensation particle counters (size integrated, time resolved) or

- diffusion charging instruments (size integrated, time resolved).

SOPs for their respective use will be made available in the course of the NanoGEM project.

5   Measurement Strategy - General Remarks

During the investigations, the following questions have to be answered:

- What is the average background concentration based on the measurement characteristics of the measurement procedure involved (e.g. time characteristics) and what is its standard deviation?

- Are defined sources of emissions identifiable/locatable (above background level)? If yes, what are the average emission concentration and its standard deviation?

- Are nanoobjects in the breathing zone of workers (exposure concentrations) identifiable (above background level)? If yes, what are the average exposure concentration and its standard deviation?

- Are the identified exposure or emission concentrations significantly above background level?

Note that in all the cases above, at this stage there is not yet any necessity to record real 8-h shift exposure concentrations. Based on the time characteristics of the measurement procedure and of the respective work process a suitable measurement strategy/averaging time is chosen for the determination of the source concentration as well as the breathing zone concentration AND their respective background concentrations.

5.1   Background Determination and Description

Determine the background concentration at all workplaces intended to be screened (C_{Bl}) in a state where the typical industrial environment is running without the nanoparticle process being applied using the instrument described in 4.2. Specify the conditions of work (possibly with a reference to 4.1) with a short description of why you regard these conditions to be belonging into this clause and to be representative. The background determination measurements have to cover a time period of typically at least **45 min**. During this period several measurements of equal lengths have to be performed (e.g. 9 times 5 minutes or 3 times 15 minutes) The results of these individual measurements (c_{Bkl}) have to be recorded, documented and their arithmetic mean (C_{Bl})

$$C_{BI} = \frac{1}{n}\sum_{k=1}^{n} c_{BkI} \tag{1}$$

as well as standard deviations (s_{DBI})

$$s_{DBI} = \sqrt{\frac{1}{n}\sum_{k=1}^{n}(c_{BkI} - C_{BI})^2}$$

Where:

c_{BkI} = the result of the k-th background determination measurement at the workplace I

C_{BI} = the average background concentration at the workplace I

n = total number of measurements / measurement values

k = running index

have to be calculated and documented.

5.2 Determination of Emission Concentration

If a source of possible nanoobject-emissions could be identified, the concentration near that source has to be determined during application of the relevant nanoobject-process (see 4.1 above) (emission concentration) (C_{EI}). Specify why you regard this possible source of emission as relevant. Repeat these measurements several times making use of the same measurement durations as of 5.1 (i.e: if you used a measurement time of 5 minutes in 5.1, use the same measurement time here as well). Again a total of 45 minutes should be covered. However, if the emission process does not last for such a time period, the complete duration of the process has to be covered as a minimum, possibly still using the measurement time as of 5.1 as frequently as needed. Again, calculate the arithmetic mean of the emission concentrations after recording the required set of individual measurements (c_{EkI}):

$$C_{EI} = \frac{1}{n}\sum_{k=1}^{n} c_{EkI} \tag{2}$$

and their standard deviation (s_{DEI})

$$s_{DEI} = \sqrt{\frac{1}{n}\sum_{k=1}^{n}(c_{EkI} - C_{EI})^2} \tag{3}$$

Where:

c_{EkI} = the result of the k-th emission concentration measurement at the workplace I

C_{EI} = the average emission concentration at the workplace I

n = total number of measurements / measurement values

k = running index

5.3 Determination of Exposure Concentration

Determine the exposure concentration in/near the breathing zones of workers (exposure concentration) (CBRI) applying the relevant nanoobject-process (see 4.1 above).

Repeat these measurements several times making use of the same measurement durations as of 5.1 (i.e: if you used a measurement time of 5 minutes in 5.1, use the same measurement time here as well). Again a total of 45 minutes should be covered. However, if the work process does not last for such a time period, the complete duration of the process has to be covered as a minimum, possibly still using the measurement time as of 5.1 as frequently as needed. Again, calculate the average mean of the exposure concentrations after recording the required set of individual measurements (c_{BRkI})

$$C_{BRI} = \frac{1}{n}\sum_{k=1}^{n} c_{BRkI} \qquad (4)$$

and their standard deviation (s_{DBRI}).

$$s_{DBRI} = \sqrt{\frac{1}{n}\sum_{k=1}^{n}(c_{BRkI} - C_{BRI})^2} \qquad (5)$$

Where:

C_{BRkI} = the result of the k-th exposure concentration measurement at the workplace I

C_{BRI} = the average exposure concentration at the workplace I

n = total number of measurements / measurement values

k = running index

5.4 Determination of Net-exposure and Emission concentrations

Correct the measured concentrations determined above (emission concentration, see 5.2, or exposure concentration, see 5.3, whatever applicable), by the respective background concentration (subtraction) determined above (see 5.1) to receive the net-emission concentration $C_{(net-EI)}$ or the net-exposure concentration $C_{(net-BRI)}$ for the workplace I.

$$C_{(net-EI)} = C_{EI} - C_{BI} \qquad (6)$$
$$C_{(net-BRI)} = C_{BRI} - C_{BI} \qquad (7)$$

5.5 Comparison of Standard Deviations of Background and Emission/Exposure

In order to decide whether the concentration profiles of background concentration and emission concentration/exposure concentration are generally comparable, a comparison of the relative standard deviations of those concentrations has to be performed.

The *relative standard deviations* of the background concentration and the emission/exposure concentrations have to be calculated and documented at this time:

They will be used in 5.7.

5.6 Documentation of Otherwise Significant Sources of Ultrafine Particles

Decide whether otherwise significant emission sources, not related to the nanoobject releasing process investigated, but possibly a source of cross sensitivities, were present during measurements and document these sources, if any. Examples for such significant emission sources could be e.g.: diesel engines or electrical engines used in the vicinity during the measurements, tobacco smoking[3].

5.7 Decision on Significance of Emission/Exposure Concentrations

In this step you need to specify whether the measured emission-concentration/exposure concentration can be regarded as significant ("above background"). This decision needs to be based on the measurement characteristics of the instrument/procedure applied AND the background level recorded in the respective workplace. At this stage an emission concentration/exposure concentration is regarded as significantly above background if

$$C_{(net-EI)} > 3 \text{ x } s_{DBI} \tag{8}$$
$$C_{(net-BRI)} > 3 \text{ x } s_{DBI} \tag{9}$$

If either emission or exposure concentrations are found significantly above background according to equations 6 or 7 an expanded measurement (Tier 3) has to be recommended.

Also, these simplified decision criteria are strictly only valid if the relative standard deviations of background concentration and emission/exposure concentration as determined in 3.2.5 are roughly equal (in the same order of magnitude). If for example the relative standard deviation of the exposure concentration is considerably higher than that of the background con-

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[3] Note: If an exclusion of these cross sensitivity sources BEFORE the measurements is possible, it shall be performed. Thus, smoking e.g. should be prohibited in the presence of the measurements.

centration, this is an indication for a process where significantly higher short term exposure conditions may be present during the process. In such a case an Expert Exposure Assessment (Tier 3) should be recommended even if the criteria of equations 6 or 7 were not fulfilled.

Additionally, a specifically hazardous material may cause the required significance level to be lowered, which may not be achievable with this simplified approach. If you regard this to be the case, give a short description and recommend Expert Exposure Assessment (Tier 3).

5.8 Discussion of the Methodical Approach

The suitability/applicability of the approach has to be assessed if the recommendation for tier 3 measurements was not given[4].

6 Documentation

Write a report containing all necessary documentation as above using the form as in Annex I.

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[4] Examples for conditions, where of such a recommendation has to be made could be that the actual work process was not sufficiently long lasting, that sources of ultrafine particles (cross sensitivities) were causing the simplified methods of this SOP not to be sufficiently precise or an otherwise general lack of analytical power of the method applied here.

1 Annex I: Data collection and report on screening measurements:

1.1 Data pertaining to measurement site:

1. Name of company: _____

2. Location/address of site: _____

3. Description of the technical process/processes investigated (including number of workers involved):

Description:

4. Categorization of workplaces investigated (tick):

   a. production,

   b. handling and refinement,

   c. bagging and shipping,

   d. processing,

   e. work processes with nanomaterial production.

5. Description of nanomaterial involved:

Description:

6. Categorization of the shape of the nanomaterial involved:

   a. particles,

   b. plates, or

   c. fibers

7. Categorization of the chemical composition of the nanomaterial involved:

   a. carbon material,

   b. organic material,

   c. metal oxide,

   d. metals, or

   e. other

8. Material safety data sheet available (yes/no): _____

9. Description of *possible identified* background contaminants :

Description

1.2 Data concerning measurement procedure:

10. Name/type of direct reading measurement device(s) intended to be used:

> Device type

11. Type:
   a. Condensation particle counter
   b. Diffusion charging/electrometer

12. Characteristics
   a. Size range detected:
   b. Time resolution:
   c. Metric:

13. Quality control data set:
   a. Lower detection limit: _____
      i. Not available:
   b. Expected cross sensitivities: _____
      i. Not available:
   c. Upper limit of measurement range: _____
      i. Not available:

14. Short description of quality control measures (e.g.: last calibration maintenance etc.):

> Description

SOP-M-Expanded Measurement

Measurements of the inhalation exposure to nano-scale product materials and ultrafine aerosols at workplaces including the background concentration

<u>Date</u>
07th March 2012

<u>Version</u>
1.1 English

<u>Scope</u>

1   Purpose

The standard work specification must be applied for measurements conducted on the inhalation exposure to nanoscale product materials and ultrafine particles at workplaces taking due account of the supply air and background concentrations. The measurement strategy overall applies to the identification of particle number concentrations and particle size distributions, although for the supply air concentration only the particle number concentrations have to be determined. The background concentration is either determined by measurement of the same process without the use of nano-objects or in the form of spatially separated far-field measurements. The application of the specific measuring instruments is explained in separate Standard Operation Procedures (SOP).

2   References

The measurements to identify the inhalation exposure are conducted on the basis of TRGS 402 "Identification and assessment of the risks from activities involving hazardous substances: inhalation exposure". The terminology and definitions which apply are these of DIN CEN ISO/TS 27687 "Nanotechnologies – terminology and definitions for nano-objects". The SOP emerged as a further development of SOP APM 01 "Procedure for measurements on airborne nano- and ultrafine objects at workplaces within the context of NanoCare" and replaces this.

3   Basis

To verify the release of nanoscale product materials at workplaces the present measurement strategy was developed for online measuring procedures which are to be used in combination with sampling for consecutive analysis. On the basis of this combination it is possible to undertake an estimation of the inhalation exposure to nanoscale product materials at workplaces, and in particular to delimit them in relation to possible background concentrations. To determine larger particles, e.g. possible aggregates and agglomerates of nanomaterials, optical particle counters or other instruments based on the aerodynamic particle diameter are used.

The measurements at the workplace must be representative in accordance with TRGS 402 (including as far as possible in the breathing zone of workers, shift-related or characteristic of the work process, consideration of air flows etc.) and the documentation must be detailed accordingly.

4   Measurement Strategy

During measurement of the inhalation exposure to nanoscale product materials at workplaces the particle number concentrations and the particle size distributions are determined as averages and as time-resolved. After the measurements scanning electron microscope examinations of collected samples are conducted to estimate the contribution and in particular the nature of the nanomaterials.

It must be taken into account that ultrafine particles occur ubiquitously and may influence the measurements of nanoscale product materials. On the one hand this may occur through interferences in the working area itself which are recorded with the background concentration and, on the other hand, by the supply air (including domestic heating). For this reason the supply air concentrations are always determined simultaneously and in parallel to the workplace measurements and background measurements.

Examples of interferences which may influence the concentration of nanoscale product materials:

- o diesel engines emission (forklifts, trucks, heavy goods vehicles)
- o electric motors
- o two-stroke engines exhaust gas (lawnmowers)
- o open flames (fireplaces, furnaces, gas-fired ovens)
- o fumes in general (welding, tobacco smoke)
- o hot, greased metal parts (extruders)
- o emissions from hot metals (melts, cooker rings, heating radiators)
- o grinding processes (abrasive cutting)
- o liquid aerosols (spray, oil mist for example thermal oil, kitchens)
- o cross-sensitivities (solvent vapours)

5   Instruments

Examples for online measurement techniques:

- SMPS or FMPS:Scanning Mobility Particle Sizer or Fast Mobility Particle Sizer (particle size distributions in overall particle size range 1 to 1,000 nm)
- optical particle counter (particle size distributions in typical particle size range 250 nm to > 32 μm) or aerodynamic particle sizer (particle size distribution, size range 0.7 to 20 μm)
- Condensation particle counter (particle number concentration in typical particle size range ≤10 to 1,000 nm) or diffusion charger with charge detection principle (particle number concentration in typical particle size range 25 nm - 350 nm)
- as an option Surface Area Monitors for nanoparticles (typical particle size range 10 nm to 300 nm)
- Combination of methods for example to extend the size ranges

Examples for sampling devices (see SOP-M-Sampling):

- electrostatic precipitator
- thermal precipitator
- samplers with suitable substrates

Accessories:

- control computer
- climate measuring instrument
- flow meter or electronic bubble meter

6 Measurement

6.1 Performance of Sampling

o An inspection of the measuring location according to Annex I must be conducted in the run-up to the measurements in order to fix the parameters (measuring period, workplaces and measuring locations, nanomaterials used, measurement strategies and measuring times, other emission sources in the area, working sequences, accessibilities, information on ventilation system, responsibilities, areas that can be sealed off, office for radiation protection)

o The sampling should preferably be performed by personal sampling. If only stationary measuring instruments are available, these must be sampling at breathing level and in the immediate proximity of the worker.

o The sequence of work processes must be recorded in order to identify those work processes where it is not possible to exclude a possible release of nanoscale product materials (including sampling at reactors, maintenance work, filling process, chaff cutter etc.), and these must be measured as a priority.

o Before every measurement campaign, all instruments with identical measurement ranges must be intercompared. The concentrations must be compared against one another over at least 30 minutes. The cycle times and all internal clocks (including notebook) must be synchronized here.

o At the same time volumetric flow rates must be checked and all instruments zeroed.

6.2 Instrument settings and on-site preparation of measurements

o The instruments are operated following the relevant standard operation procedures.

o Volumetric flow rates and the zero point calibration need to be checked for all instruments.

o Identical instruments are regularly (before and after each measuring campaign) compared for 15 minutes at a suitable location with expected homogenous distribution of particle concentration in order to detect possible strong

deviations. If the deviation of an instrument is more than 30% at a particle concentration > 10.000 P/cm³ the respective measurement result must be rejected, the instrument maintained or sent in for servicing. For concentrations < 10,000 P/cm³, deviations of up to 50% are acceptable.

6.3 Performance of measurements

Measurement of the background concentration

In order to delimit the fraction of the nanoscale product materials to be determined against other interfering variables, the background concentration is identified before commencement of the activities involving nanomaterials. For this purpose two alternative measurement strategies are possible:

1) Background determination by means of identical activities without the use of nanomaterials.

Ideally, a measurement is conducted during which the same activities are being performed as during the actual measurement but without the use of nano-objects. This measurement can then be performed as described in the section "Measurement of workplace concentration". This method of determining the background concentration should be preferred since it is then possible to make a direct comparison of the measured concentrations.

2) Background determination by means of "far-field measurement" during the activity

In this case the background is determined at a location which is far away from the possible emission source. At this location, the boundary conditions should be roughly the same as at the actual measurement location, however no influence from the direct process is to be expected.

Measurement of supply air concentration

The particle number concentration in the supply air must at least be measured in parallel to the determination of the background and workplace concentrations.

- o The measurements must normally be conducted outdoors in an upwind location using a suitable instrument for determining particle number concentrations. If the measurement location is a room or building with forced ventilation, the supply air concentration is to be determined close to the suction point of the ventilation system. If the supply air is filtered, measurement directly at the air outlet of the forced ventilation system is preferred.

- o The beginning and end of the measurement are identical with those of the background and workplace measurements.

Measurement of the workplace concentration

- o The actual measurements of the workplace concentrations are conducted during regular operation, i.e. during normal activities involving nanomaterials.
- o The particle number concentrations and the particle size distributions are determined with suitable measuring instruments (e.g. SMPS, FMPS, diffusion chargers).
- o The particle number concentrations and the particle size distributions in the µm range are determined using suitable measuring instruments (OPC or APS). With NAS or TP particle samples are collected at the workplace for a subsequent electron microscopic analysis (see SOP Sampling of Airborne Nanoobjects for Consecutive Microscopic Analysis").
- o If necessary material and settled dust samples from representative surfaces are to be taken.

6.4 Termination of measurement

o The measurements must be terminated in accordance with the corresponding SOPs for the measurement instruments. The measurement results should preferably be stored redundantly. Potential product contaminations on the instrument surfaces must be wiped off before packaging, for example using moist cloths.

7 Data Evaluation / Reporting

Measurement preparation and implementation as well as the data evaluation of the measurements must be documented in a test report (see TRGS 402).

7.1 Analysis of the particle number concentrations

o The measured results are exported from the instrument software to the analysis software (Origin, Excel etc.) for further processing.
o For each workplace the average, maximum and minimum readings must be calculated for the entire particle spectrum for the background, workplace and corresponding supply air measurements. The same data (except for the supply air measurements) shall be collected for the particle size ranges lower size limit (LSL) – 100 nm, 100 – 400 nm, 400 nm – 1 µm, 1 – 10 µm (only applicable to the size ranges that have been determined).
o If different measurement principles have been used, the equivalent particle diameters determined in each case must be taken into account. In any case, representation of these data must include a clear indication as to which equivalent diameter was used.
o The time series for the particle number concentration and the geometric mean of the particle size distribution at the workplace must be presented and every relevant event interpreted. The same data must be collected for the particle range LSL – 100 nm, 100 – 400 nm, 400 nm – 1 µm, 1 – 10 µm (only applicable to the size ranges that have been determined).

- o The concentration ratio CR is calculated and evaluated as follows tor the entire size range, as well as for the ranges LSL – 100 nm, 100 – 400 nm, 400 nm – 1 µm, 1 – 10 µm,:

$$CR = \text{workplace concentration/background concentration}$$

- A significant increase of the respective particle fraction, caused by the process has to be assumed if CR is greater **3**[*]. If the background concentration has not been measured simultaneously, the time series of the supply air concentration shall be scrutinized.
  - o If further disturbances during the measurement of the background concentration cannot be excluded and if the average concentrations are above the supply air concentrations, the time series of the workplace concentrations must be critically evaluated in relation to the technical working sequences. In this case, particularly the EM images must be analysed in view of presence of nanoscale product materials.

7.2 Electron microscopic analysis

The electron microscopic analysis of the NAS- or TP samples and the samples on gold coated filters are carried out according to the corresponding SOPs.

8 Quality control measures

- o Comparison and (if necessary) adjustment of the instruments in the laboratory before each measurement campaign
- o Quality point measures according to 6 before and during each measurement (instrument-specific deviations, on-site calibration etc.)
- o Servicing of the instruments following the intervals specified/recommended by the manufacturer.

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[*] Due to experience gained from error calculations from workplace measurement (IUTA e.V. …), for simplification, the factor 3 is adopted.

8.1 Potential error sources when conducting measurements

o Further emission sources must be taken into account and interpreted.

o In particular aerosols with liquid droplets (including fine oil mist) must be taken into account during the measurements

o If, for example, a thermo denuder or hoses are used, possible particle losses (SMPS, CPC, diffusion chargers) must be calculated and taken into account for data analysis.

o Air flow at the workplaces must be identified and appropriate measurement locations selected such that the measurements are influenced as little as possible. If necessary, the determined flows have to be taken into account for the interpretation of the measured results.

o The instruments must be regularly observed during the measurement in order to immediately eliminate possible instrument failures (cleaning of impactors, refill of butanol or isopropyl alcohol reservoir, etc.)

o Weather influences must be taken into account. Under very wet weather conditions, voltage fluctuations may cause error messages (e.g. after a thunderstorm). At ambient temperatures above 30°C, requirements for the internal temperatures of the SMPS cannot be kept, and measurements will then no longer be possible. At ambient temperatures below 10°C instruments should be hosted inside an actively heated container.

o In any case a detailed record of measurements must be kept in which all possible disturbances are noted with time stamps.

8.2 Occupational safety

Local safety instructions have to be followed. Furthermore the measurement staff can decide independently whether additional personal protective equipment is necessary and whether the measurement needs to be aborted due to irregularities or hazardous incidents.

SOP-M-Sampling

Sampling of Airborne Nanoobjects for Consecutive Microscopic Analysis

<u>Date</u>
21st March 2012

<u>Version</u>
1.1 English

<u>Scope</u>

1   Scope

This standard operation procedure covers the sampling of airborne nanoobjects (definition according to DIN CEN ISO/TS 27687) onto substrates for further microscopic analysis. Sampling on filters and subsequent chemical analysis are not covered by this SOP. Also sampling by applying passive samplers (based on diffusion), cyclones or impactors are not covered by this SOP.

This SOP covers the overall setup for particle sampling. The use and maintenance of specific instruments for sampling and the analysis of the substrates is addressed in the following sub-SOPs:

- SOP-S-ESP: Procedure of particle sampling with the Nanometer Aerosol Sampler (TSI Model 3089) or electrostatic precipitator (ESP)
- -SOP-S-TP: Procedure of particle sampling with the thermal precipitator
- SOP-S-SEM: Investigation of nanoobjects applying electron microscopic methods (still to be written)
- SOP-S-GCS: Preparation of glassy carbon substrates (still to be written)

2   Introduction

Besides the online analysis of airborne nanoobject number concentrations and/or size distributions using spectrometers, it is often necessary to sample particles for further offline analysis to determine e.g. morphological features like state of agglomeration and/or aggregation or chemical composition of the objects. This type of analysis therefore allows for the clear identification of the nanoobjects and their agglomerates under investigation. It is therefore necessary to take representative samples of the aerosol onto suitable substrates.

3   Instruments and Substrates

Different instruments are available for the sampling of airborne nanoobjects. These instruments are based either on electrostatic precipitation (e.g. NAS, TSI Model 3089, ESP, NANODEVICE development) or thermal precipitation (e.g. BAuA prototype TP). In case of electrostatic precipitation, a suitable charger may optionally be applied to enhance sampling efficiency. Other kinds of samplers are beyond the scope of this SOP.

Different kinds of substrates can be used for sampling, depending on the sampler applied and the instrument used for analysis:

- TEM grids for analysis by TEM
- Silicon substrates for analysis by SEM
- Glassy carbon for analysis by TXRF

The substrates have to be particle free. To avoid cross-sensitivities, the substrate should be made from a material not commonly found in the aerosol.

4 Sampling

Sampling can be divided into setup and preparation of the measurement and the actual conductance of sampling.

4.1 Preparation

- Preparation of instruments

The instruments have to be cleaned and properly maintained before sampling. The instrument specific flow rate is to be checked (where applicable), to allow for a (semi-) quantitative analysis. The inlet of the sampler should be placed close to the position of the inlets of other instruments used to sample the same aerosol as e.g. spectrometers. If required, connect a sample tube to the aerosol inlet. Conductive tubing is then to be used to minimize particle losses within the tubing.

- Preparation of substrates

    - TEM-Grids: TEM-Grids are specifically used for subsequent TEM - analysis. They are usually singly packed in dedicated containments. No special treatment before sampling is necessary, but care must be taken to use the correct side of the grids for sampling. There is no general appearance of the collection side, but typically it is darker than the other side. The grid must be properly attached to the substrate holder (e.g. magnetically or via clamps or double sided conductive tape).

    - Silicon substrates (applicable also to other semiconductor substrates): Usually, silicon substrates are delivered with a protection layer on the polished surface side. This protection layer has to be removed (rinsing and wiping in acetone bath followed by isopropyl alcohol bath, removal of liquid using a particle free air blast) and the surface has to be inspected optically by a light microscope (if possible dark field mode) to be particle free as far as possible before use of the substrates. In some cases silicon substrates are delivered pre-

cleaned in single containers. In the latter case, no further treatment is necessary. Silicon substrates are used with the polished side facing up.

- Glassy carbon substrates: These substrates are specifically used for TXRF analysis (dimensions: 30 mm diameter and a thickness of 3 mm). Before use, these substrates have to be cleaned according to SOP-S-GC Substrates and the blind values have to be evaluated by a TXRF measurement. Glassy carbon substrates are used with the polished side facing up.

4.2 **Performance of Sampling**

- Set up samplers for sampling according to applicable instrument SUB-SOP and/or instrument manual.
- Document position of sampling device with respect to other instruments and the working process.
- Check substrates optically (naked eyes) for cleanliness before insertion into the sampling device.
- Sampling times should be estimated according to the measured or expected particle concentration, sampling efficiency (where possible) and the process under investigation (see device specific SOP for estimated sampling times). If concentration is unknown take samples with different sampling times. Where necessary stick to preset sampling times. Document sampling times.
- Take a sample with high efficiency (e.g. HEPA) filter attached to inlet of sampling train to identify contaminations stemming from instrument used (if possible).
- Take sample during no (specific) activity to derive corresponding information for typical background particles.
- After sampling: deposit substrates in clean, sealed containments for later analysis.

5 **Data Evaluation / Reporting**

The samples are analysed, e. g. using Scanning Electron Microscopy (SEM) or Transmission Electron Microscopy (TEM). In special cases (e.g. fluorescent particles) also optical microscopy might be applied. Evaluation of substrates is described in SOP-S-Substrate analysis.

The report, if not included within the general report for the measurement campaign, should include the following items:

- Short description of purpose of measurement campaign
- Short description of sampler used and setup for sampling (sketch and/or photo)
- Representative EM images; (if possible data medium or reference to complete image set)
- Results of EM-Analysis (qualitative or quantitative)

- Conclusions with regard to purpose of campaign and sampled objects

6   Quality control

The proper operation of samplers is to be checked periodically according to the applicable SUB-SOPs and/or manuals of the instruments used.

SOP-S-SMPS(TSI)

Procedure of particle measurements with the Scanning Mobility Particle Sizer (TSI Model 3936)

<u>Date</u>
07th March 2012

<u>Version</u>
1.0 English

<u>Scope</u>

1   Scope

The scope of this standard operation procedure is the procedure of the data collection and logging as well as the quality control of the determined and logged data from the SMPS (TSI Model 3936) including the routine instrumentation maintenance. The scope of this standard operation procedure does not include the establishment of a sampling station.

2   Notes

This standard operation procedure corresponds to ISO 15900 *Determination of Particle Size Distribution - Differential Electrical Mobility Analysis for Aerosol Particles* and is used along with SOP-M-Expanded Measurement.

3   Basics

The SMPS classifies the aerosol particles based on their size and counts the classified particles. A bipolar charger achieves a defined charge distribution of the particles prior to the classification in the DMA (Differential Mobility Analyzer). The particles are fractionated based on their electrical mobility by scanning the voltage of the inner cylinder of the DMA. The particle size distribution is then calculated using the particle count per mobility class and the known particle charge distribution. Depending on the configuration (DMA, CPC), the SMPS can cover a size range between approximately 3 nm and 1000 nm with a resolution up to 64 channels per decade.

4   Instrumentation

The main components of the SMPS spectrometer model 3936 are:
- Aerosol inlet with impactor for pre-separation of larger particles
- SMPS Classifier Model 3080 with neutralizer model 3077 (Krypton-85) and DMA (Differential Mobility Analyzer) model 3081 or NanoDMA model 3085
- CPC (Condensation Particle Counter) e. g. Model 3786 or Model 3010
- Flow equalizer assembly to adjust the sample flow, depending on the CPC used
- PC or laptop to data collecting and logging

5   Preparation for sampling

5.1 Preface

Connect the SMPS spectrometer according to the manufacturers' instructions with tubes and data cables. Install the impactor with the desired orifice (cut off) and grease the impactor plate slightly, and then connect the impactor with the aerosol inlet. Fill in the CPC Model 3786 according manufacturers' instructions with distilled water, or the CPC Model 3010 with butyl alcohol. For the measurement data logging, connect the CPC via Universal Serial Bus (Model 3786) or RS-232 (Model 3010) and computer cable with the PC or laptop. Switch on

all devices (Classifier, CPC, and PC) after connection to the power supply. The CPC Model 3786 warm-up period is approximately 15 minutes. After CPC warm-up the status screen should display following temperatures (in °C):

- Optc   75.0   (Optics)
- GT   75.0   (Growth Tube)
- SAT   12.0   (Saturator)

To check the status of these temperatures on the CPC display during the warm-up, select the **Status Screen** with the display button on the front panel. Once warm-up is complete, the CPC display shows the **Primary Concentration Screen**.

5.2 Hardware adjustments

- On the classifier, the voltage control should be set to **Analog Ctrl** to allow the DMA voltage to be controlled by the CPC. To do so, rotate the black control knob until the **Ctrl-Pane** in the Classifier LCD Display is highlighted, and then press the knob to change from **Panel Ctrl** to **Analog Ctrl**.
- The volume flows have to be set depending on the particle size range used. According to the manufacturers' instructions, the ratio of the sheath air to aerosol flow rates is normally set to 10:1. For example, the covered particle size range is 13.5 to 750 nm mobility particle diameter for the settings of sheath flow 3.0 lpm and aerosol sample flow 0.3 lpm.
  Sheath Flow adjustment
  o   Rotate the black control knob until the **Sheath Flow** pane in the Classifier LCD is highlighted.
  o   Click the control knob by pushing in.
  o   Scroll the control knob until the correct sheath flow is indicated.
  o   Click the control knob by pushing in. The sheath flow will then be updated with the actual flow.
  o   The **Sheath Flow LED** lights up when the sheath flow is stabilized at set flow.
  Sample Flow adjustment
  o   Connect a suitable flow meter to the aerosol inlet
  o   Install the flow equalizer assembly according to the manufacturers' instructions between DMA and CPC. For CPC Model 3786: If sample flow is set to 0.6 lpm, the flow equalizer assembly is unnecessary and sheath flow should be set to 6.0 lpm.
  o   Turn on the CPC pump by pushing the **Pump** button
  o   Adjust the filter valve until the correct aerosol flow is indicated on the flow meter.

5.3 Software adjustments

The TSI software **Aerosol Instrument Manager** (Release version 8.1.0.0) is used for measurement data logging. After starting the software, open a new file with **File – New**, data type **SMPS Data file (*.S80)** and select a filename. The desktop opens in **4-Pane Layout** (prede-

termined auto-fit) with the windows **Size Data Graph**, **Size Data Table**, **SMPS-Sample List,** and **Statistics Table**. With the **Window** menu and **2-Pane Layout** only the windows Size Data Graph and SMPS-Sample List are displayed. A user-defined layout of the windows is possible, too. With **File – Properties**, **Run – Properties** or mouse button right after clicking **New Sample** in window **SMPS-Sample List** and selecting properties open the dialog box **SMPS Properties**.

- **Hardware Setting**
    - o   Classifier Model: 3080
    - o   DMA: 3081 or 3085
    - o   Impactor Type: depending on use
    - o   CPC: 3786 (depending on CPC model)
    - o   DMA Flow Rate: Enter the Sheath and Aerosol Flow
    - o   td: Use the calculated value from the hardware settings by using 10 inch tubing. (td is the time taken by the aerosol to flow through the classifier and the connection tubing between the DMA and the CPC, which is assumed to be 10 inches (25.4 cm) long.)
    - o   Size Range Bounds: Enter the minimum and maximum size range to be sampled using the **Lower** and **Upper Diameter** pull-down lists or select the button **Set to Max Range** to the maximum range based on current DMA and flow settings.
    - o   Scan Time: The scan **Up** range is 30-300 s, **Retrace** range is 10-300 s

- **Scheduling**
    - o   Sample: **Scans per Sample** and **Number of Samples,** if desired
    - o   Scheduled: Select **Only Once** to collect one set of samples. For continuous monitoring, select the **Repeat Every** and enter interval starting time.
    - o   Start At Time: If desired, select the check box and enter the clock time at which the sampling should begin.

- **Physical Properties**
    - o   Gas Properties: Enter the Gas Viscosity and Mean Free Path (Default settings for Air at 293.15 K and 101.3 kPa)
    - o   Particle Density: Enter the density, if known
    - o   Correction Flags and Values:
        - ▪   Multiple Charge Correction: For the correction of multiple charged particles
        - ▪   Diffusion Correction: For the correction of particle losses caused by diffusion only within the SMPS. This does not account for the particle losses in sample tubes!
        - ▪   Nanoparticle Aggregate Mobility Analysis: For the correction from spheres to aggregates.

        These corrections are mathematically based on the identified raw counts and can be switched on or off retrospectively, too, i. e. after sampling.

By pressing the **OK** button the program retains the current settings.

6 Sampling

- If required, connect a sample tube to the aerosol inlet (impactor). (Particle losses caused by diffusion occur because of the use of a sampling tube. These particle losses have to be corrected for during further data interpretation).

- Before sampling start, the CPC should be drained manually to reduce measurement data losses by draining the reservoir (pump will be turned off during draining). To do so, press the **Drain/Prime** button for one second to select the drain mode and press the **Drain/Prime** key again for 2 seconds to start draining, duration 1 minute.

- If the check box by **Properties – Scheduling – Start at Time** is marked and a clock time is entered, the sampling starts at the entered start time.

- Otherwise select **Run – Start Data Collection** to start the sampling immediately.

- Select **Run – Finish Current Sample** to stop the continuous monitoring after the current sample.

- Select **Run – Abort Current Sample** to stop the current sampling immediately and the data for the current sample is discarded.

7 Interpretation

- Simple data analysis with the **4-Pane-Layout**:
  - o Select the sample in the **SMPS-Sample List** with mouse click
  - o The window **Size Data Graph** displays the particle size distribution of the selected sample
    - ▪ The lower and upper size limit can be changed with the mouse pointer and pressing left mouse button (pointer becomes a hand).
    - ▪ Position the pointer on a bar (depending on type of graph that is active) and the pointer becomes a hand. By clicking the left mouse button the values diameter and concentration are displayed.
    - ▪ The displayed size distribution can be zoomed in by placing the pointer at one point of the area to be enlarged by pressing the left mouse button and dragging the mouse to the opposite point of the data. Release the left mouse button and the selected area is enlarged. To zoom out, select **Format – Undo Zoom** and the enlarged area is returned to normal view.
  - o The window **Size Data Table** displays the collected measurement data for each size class in table form.
  - o The window **Statistics Table** displays the different diameters, deviations, and the total concentrations.
- For further data interpretation:
  - o Select the samples, which should be exported in the **SMPS-Sample List**. With **File – Export** the samples can be exported in a file. In the dialog box **Export Parameters**, select the data types. After selecting a filename, the data can be exported as a text file, and then imported into a spreadsheet program.

8   Maintenance

- Filling of the water source bottle with distilled water and draining of the drain bottle, depending on consumption and demand.
- Cleaning of the impaction plate and impactor orifice depending on use and demand.
- Cleaning of the mobility analyzer center rod and outer electrode, depending on use and demand, for continuous operation every 6 months, see Electrostatic Classifier Instruction Manual
- Replacement of the Sheath Flow HEPA cartridges, for continuous operation annually, see Electrostatic Classifier Instruction Manual
- Cleaning of the dracon screen (sheath flow laminator), for continuous operation annually, see Electrostatic Classifier Instruction Manual
- Replacement of the CPC cartridges, for continuous operation annually, see CPC Operation und Service Manual
- Replacement of CPC wick on sample inlet, for continuous operation every 6 months, see CPC Operation und Service Manual
- Checking of the calibration with PSL particles every 6 months or depending on demand.

9   Quality assurance

Measures for quality assurance:
- Zero tests:
    o Periodical checking of adjusted volume flows (sheath and aerosol flow) with a suitable flow meter. By adjusting the voltage to zero V at the collector rod, the airstream flowing out of the monodisperse aerosol connector should be particle free and the CPC should not detect particles.
    o Periodical testing for leaks and sampling with filtered air (HEPA filter); the CPC should not detect particles.
- Routine checking of the calibration with particles of certified aerodynamic diameters.
- Realization and reporting of the maintenance
Reporting of anomalies during sampling or maintenance

Procedure of particle measurements with the
Scanning Mobility Particle Sizer (TSI Model 3936)

SOP – S- SMPS(GRIMM)
Vorgehensweise bei Partikelmessungen mit dem Sequential Mobility Particle Sizer (GRIMM Modell 5403)

Datum
16.03.2012

Version
1.0 Deutsch

Inhalt

Vorgehensweise bei Partikelmessungen mit dem Scanning Mobility Particle Sizer (GRIMM Model 5403)

1 Zweck

Zweck dieser Standardarbeitsanweisung ist die Datenerfassung und –sicherung sowie Qualitätskontrolle der mit dem SMPS (GRIMM Modell 5403) ermittelten und aufgezeichneten Messdaten zur Erfassung der inhalativen Exposition gegenüber nanoskaligen Produktmaterialien und ultrafeinen Aerosolen an Arbeitsplätzen. Dies umfasst auch die routinemäßig anfallende Gerätewartung.

2 Hinweise

Die vorliegende SOP – S- SMPS(GRIMM)- vertieft die *SOP-M-Expanded Measurement -* „Measurements of the inhalation exposure to nanoscale product materials and ultrafine aerosols at workplaces including the background concentration" und bezieht sich auf die ISO 15900 *Determination of Particle Size Distribution - Differential Electrical Mobility Analysis for Aerosol Particles".*

3 Grundlagen

Der Sequential Mobility Particle Sizer (auch Scanning Mobility Particle Sizer) ist ein stationäres, zeitauflösendes Messgerät zur Bestimmung der größenklassierten Anzahlkonzentrationen von Nanopartikeln. Das System besteht aus einem DMA zur Klassierung der Partikel, einem Kondensationspartikelzähler (CPC) als Erfassungssystem, sowie der Software. Die Messdatenabspeicherung erfolgt über einen von der Software abgelegten Messfile auf dem verwendeten Computer (PC, Notebook, Netbook). Dabei ist die Möglichkeit einer online Überwachung jederzeit über eine RS232 Schnittstelle verfügbar. Zusätzlich können die Daten zur späteren Auswertung auf einer Datenspeicherkarte hinterlegt werden.

Während der Messung werden die Partikel in einen definierten Ladungszustand gebracht und anhand ihrer elektrischen Mobilität in einem elektrischen Feld fraktioniert. Durch eine kontinuierliche Veränderung der angelegten Spannung im elektrischen Feld kann, in Abhängigkeit der verwendeten Hardware (M-DMA, L-DMA), der Partikelgrößenbereich von 5 nm bis 1000 nm mit einer Auflösung von bis zu 44 Kanälen (Softwareversion 1.35) beziehungsweise bis zu 89 vorgegebenen Kanälen (Software 1.2.1) vermessen werden. Bei der Software 1.2.1 ist z.B. zur Messung von hochauflösenden monodispersen Aerosolen auch eine Einstellung bis zu 255 Kanälen möglich.

Aufgrund des im DMA installierten Neutralisierers (Alpha-Strahlungsquelle) sind die Strahlenschutzanweisung sowie die Umgangsgenehmigung bei Tätigkeiten mit dem Messgerät oder beim Transport zu beachten. Das Gerät darf nur nach Unterweisung von einem Strahlenschutzverantwortlichen betrieben werden.

4 Geräte

Das GRIMM-SMPS enthält folgende Gerätekomponenten:

- Elektromobilitätsklassier „Vienna U-Type" (Differential Mobility Analyzer, DMA), alternativ L(ong) oder M(iddle),
  Messbereich Softwareversion 1.35: 11,1 – 1083,3 nm oder 5,5 – 350,4 nm mit angeschraubtem Neutralisator AM-241 l
  Messbereich Softwareversion 1.2.1: 10,33 – 1091,3 nm oder 5,15 – 351,04 nm
- Kondensationskernzähler, Typ 5.403 (Condensation Particle Counter, CPC) mit Butanol-Vorratsflasche und Kondensatflasche
- Laptop mit Grimm-Software 5.477, Steuerung und Datenerfassung inkl. Datenkabel USB – Seriell
- Reparatur- und Ersatzteilset mit Vakuumfett, Dichtungen, Filter und Werkzeug, Dichtigkeitsprüfer
- Handbuch, aktuelle Strahlenschutzanweisung inkl. Umgangsgenehmigung

Momentan sind zwei Versionen der GRIMM Software 5.477 aktuell (Version 1.35 und 1.2.1). Vergleichsmessungen zeigen, dass die Version 1.2.1 eine sehr gute Vergleichbarkeit mit anderen artgleichen Messgeräten liefert (Veröffentlichung in Vorbereitung). Alte Messdaten können mit der neuen Software eingelesen werden.

5. Messung

5.1. Transport

- Bei Messungen außerhalb des Standortes muss u.U. der jeweilige Betrieb und die atomrechtliche Behörde informiert werden.
- Die Transporthinweise von radioaktiven Quellen sind zu beachten
- Auf einen möglichst waagerechten Gerätetransport ist zu achten. Kann dies nicht sichergestellt werden, muss eine vorherige Trocknung des Saturators erfolgen (Einstellung *Dryer Mode* für mindestens 12 h). Netzschalter betätigen (aus dem *Charge Mode* heraus wird *Standby und Status* gedrückt), vorher die Kondensatflasche leeren.
- Während des Transports ist zur Sicherung des Batteriebetriebes die Sicherung gezogen (alte Systeme 5A Kfz-Sicherung, neue Systeme 6,3A Sicherungsfach)

5.2. Messvorbereitungen

- Die DMA (M oder L) entsprechend der Messaufgabe wählen. Bei DMA-Wechsel auf Sauberkeit der Elektrode achten (bei Bedarf Reinigung mit Isopropanol)
- Dichtigkeitsprüfung nach Umbau oder Reinigung der DMA durchführen (siehe Handbuch)
- Überprüfung des eingesetzten Impaktors (entsprechend der DMA wird der entsprechende Impaktor gewählt, Kontrolle auf Sauberkeit – durch Zusetzen der Düsen kann es zu Messausfall kommen, Abscheideplatte des Impaktors reinigen und mit Vakuumfett dünn bestreichen. Impaktorwechsel entsprechend Handbuch).
- Bei Messung sehr hoher Konzentrationen ist über die Verwendung eines Vorimpaktors bzw. eines Verdünnungssystems nachzudenken.

- Erfolgt die Messung nach Lagerung des Gerätes in kalten Räumen bzw. nach Transport bei kalten Umgebungstemperaturen (< 10°C) muss eine Akklimatisierung des Gerätes erfolgen
- Wird die Messung nach dem Transport mit trockenem Saturator begonnen, sollte 1 h das Gerät ohne Datenaufzeichnung erfolgen (gleichmäßige Durchfeuchtung des Saturators).

5.3. Geräte- und Softwareeinstellungen

- CPC und DMA auf der mitgeführten Metallplatte anordnen und ggf. befestigen
- Sicherung im hinteren Bereich des CPC stecken. Ohne Sicherung kann es zu falschen Fehlermeldungen kommen.
- **Leere** Kondensatflasche an *Condensate Outlet* anschließen.
- 1-Buthanol vor den Messungen auffüllen. Grüne Füllstandanzeige auf der Geräterückseite beachten. Bei angeschlossener Butanolflasche muss diese offen sein.
- Schlauchverbindung DMA – CPC herstellen.

DMA	**CPC**
Sample Outlet (kurze Verbindung mit Spezialschlauch) ➔	Sample Inlet
Sheath Air Inlet (gelber Schlauch oben) ➔	Sheath Air Outlet
Excess Air Outlet (schwarzer Schlauch unten) ➔	Excess Air Inlet

- Steckverbindung DMA – CPC
- Messwerterfassungsrechner starten, einloggen, Rechner mit CPC verbinden und dabei auf die intern festgelegten COM-Stellen achten
- SMPS starten dazu CPC am Frontpanel einschalten. Auf LCD-Anzeige die Abfrage „Warm Up?" durch Drücken der „+"-Taste mit Ja bestätigen.
- Volumenstrom prüfen
- Nullmessung mit dem Nulltestfilter

5.4. Messung

- Grimm-Software starten und weiter entsprechend der Software verfahren (Einstellung von Datum/Uhrzeit, Scheduling entsprechend der Software)
- Messung über die Software starten, Übertragung Softwareeinstellungen und Warm up beginnt und kann bis zu 15 min dauern
- Vor jeder Messung führen alle SMPS+C Systeme einen Selbsttest durch. Der Selbsttest beinhaltet einen Dichtheitstest, eine Überprüfung des angeschlossenen DMAs, eine Überprüfung des DMAs auf Kriechströme und die Überwachung des Kondensationsprozesses.

- Möglichst direkt das Aerosol messen, d.h. ohne Schlauch oder Messlanze. Falls eine Anpassung nötig ist, dann nur antistatischen Probenahmeschlauch verwenden, am Aerosol Einlass (Impaktor) anschließen und entstehende Diffusionsverluste bei der Auswertung berücksichtigen.
- Insbesondere bei Messungen in kleinen Räumen sollten Kohlefilter zum Abscheiden des Butanols gesteckt werden (Anschluss *Sample Qutlet*, auf die max. Einsatzdauer achten, dann Trocknung). Das Stecken eines Schlauchanschlusses mit Verbindung zur Außenluft ist ebenfalls möglich.

Tabelle: Fehlermeldungen oder Störungen im Messablauf und Hilfestellung:

Fehler / Störung	Mögliche Ursache	Behebung
Keine Verbindung zu CPC, CPC reagiert nicht	• CPC nicht eingeschaltet • USB-Kabel war beim Start des Rechners nicht eingesteckt • bei Betrieb mit USB-Hub falschen Port benutzt oder falsche COM eingestellt. • Verwendung des falschen Verbindungskabels	• CPC einschalten, Grimm-Software neu starten • Rechner neu starten richtigen COM-Port wählen • Verwendung eines geeigneten Verbindungskabels (Grimm 1.141A)
Beim Gerätetest zu Beginn einer Messung wird in angemessener Zeit keine Null-Zählrate erreicht	• System undicht • DMA verschmutzt • Laminator verschmutzt	• Dichtigkeitsprüfung durchführen – wenn OK weiter wie beschrieben, wenn nicht, Undichtigkeit lokalisieren, Schläuche und ggf. Dichtungen tauschen • Impaktor ausbauen und komplett reinigen • DMA demontieren und mit Isopropanol reinigen, Kanäle mit sauberer Pressluft ausblasen • Neutralisator demontieren und mit Pressluft (pmax 0,5 bar) vorsichtig ausblasen • Filter tauschen • Laminator reinigen • Wenn die beschriebenen Maßnahmen erfolglos sind, dann sind Messungen mit dem DMA nicht möglich. DMA tauschen. Nach Beendigung der Messungen Gerät zur Wartung zum Hersteller schicken

Fehler / Störung	Mögliche Ursache	Behebung
Flow Error – Messung wird abgebrochen	- falscher Impaktor - Impaktor verstopft - Verbindungsschläuche falsch angeschlossen - Adsorptionsfilter gesättigt - falscher Auslassfilter	- Impaktor tauschen - Impaktor komplett demontieren und reinigen - Verschlauchung überprüfen - Austauschen / entfernen Adsorptionsfilter - Originalfilter (Aktivkohle) einsetzen
Warm-Up wird nicht beendet	Gerätesicherung auf der Rückseite nicht gesteckt oder defekt	Sicherung stecken bzw. tauschen
Warm Up wird nicht beendet, Liquid Level Led bleibt rot	- Zu wenig Butanol im Liquidtank - Luftblase im Schlauch zwischen Liquidtank und Saturator	- Butanolvorratsflasche anstecken - Butanolvorratsflasche anstecken um Druck zu erhöhen
Warm Up wird nicht beendet, Temperatur-LED bleibt gelb/rot	- Umgebungstemp. >30 °C - Heizung/Kühlung defekt - Wärmetransport nicht möglich durch Kühlflüssigkeitsmangel - Wärmetransport nicht möglich durch defekte Membranpumpe	- Messung nicht möglich - beim Hersteller reparieren - Nachfüllen der Kühlflüssigkeit - bei defekter Membranpumpe Gerät beim Hersteller reparieren
Messung läuft nicht konstant	Gerätesicherung auf der Rückseite nicht gesteckt oder defekt	Sicherung stecken bzw. tauschen

5.5. Beendigung der Messung

- Die Messung wird über die Software beendet.
- Speicherung der Daten auf den Messwerterfassungsrechner (als Rohdaten, Excelfile der Messdaten, Excelfile der Statistikdaten)
- Ggf. Reinigung des Gerätes mit Alkoholtüchern
- Kondensatflasche leeren

6. Auswertung

Erste Messergebnisse sind über die Software am Rechner ersichtlich (aktuelle Scan der Partikelanzahl, geometrischer Mittelwert der Partikelgröße). Bei der Softwareversion 1.35 sind jeweils der letzte und der aktuelle Scan ersichtlich und bei der Softwareversion 1.2.1 können alle Scans angezeigt werden.

Die Auswertung der Messdaten erfolgt nach den Vorgaben der SOP-M-Expanded Measurement „Measurements of the inhalation exposure to nanoscale product materials and ultrafine aerosols at workplaces including the background concentration" bzw. SOP-S-Data Analysis „Procedure for measurement data analysis for the determination of released particles caused by the working process".

7. Wartung

- Eine regelmäßige Wartung und Kalibrierung der Messgeräte bei der Herstellerfirma (GRIMM Aerosoltechnik) ist durchzuführen (möglichst in einem jährlichen Rhythmus)
- Regelmäßige Prüfung der „Nullkonzentration" mit dem Nulltestfilter
- Reinigung der Prallplatte und Düse des Vorabscheiders (Impaktor) je nach Anwendung und Bedarf
- Reinigung der DMA-Innen- und Außenelektrode je nach Anwendung und Bedarf, bei Dauerbetrieb mindestens halbjährlich, siehe Handbuch

8. Qualitätssicherung

- Durchführung und Protokollierung der Gerätewartungen
- Protokollierung von Auffälligkeiten bei der Probenahme und Gerätewartung. Wenn möglich, regelmäßige, interne Vergleichsmessungen mit geeigneten Aerosolmessgeräten

SOP-S-FMPS

Procedure of particle measurements with the Fast Mobility Particle Sizer (TSI Model 3091)

Date

07th March 2012

Version

1.0 English

Content

Procedure of particle measurements with the
Fast Mobility Particle Sizer (TSI Model 3091)

1   Scope

The scope of this standard operation procedure is the procedure of the data collection and logging as well as the quality control of the determined and logged data from the FMPS (TSI Model 3091) including the routine instrumentation maintenance. The scope of this standard operation procedure is does not include the establishment of a sampling station.

2   Notes

This standard operation procedure is used along with the standard operation procedure SOP-M-Expanded Measurement.

3   Basics

The Fast Mobility Particle Sizer spectrometer measures submicrometer aerosol particles in the size range from 5.6 nm to 560 nm with a resolution of 16 channels per decade. Due to its design, the FMPS spectrometer is capable of making particle size distribution measurements with one-second resolution. An electrical diffusion charger is used to charge the aerosol particles. While the charged particles stream through the electric field of a DMA with constant high voltage, they are repelled from the high voltage electrode because of their electrical mobility and travel towards the 22 sensing electrodes, which are arranged around the DMA. Thus the aerosol size distribution is determined simultaneously over the whole particle size range. The generated current is amplified by the electrometers, digitized, and read by a microcontroller. The data are processed in real time to obtain one particle size distribution per second.

4   Instrumentation

The main components of the FMPS Spectrometer Model 3091 are:
- Aerosol inlet with cyclone to pre-separation of larger particles
- FMPS Platform Model 3091
- HEPA filter to zero the electrometers
- PC or laptop to data collecting and logging

5   Preparation for sampling

5.1 Preface

During transport, the electrometer column has to be secured with the belt supplied with the instrument. The cyclone is always used and should only be removed when transporting or servicing the instrument. It will remove large particles and fibers that can cause excessive noise on one or more electrometer channels. The cyclone will be more effective in removing large fibers if the inside surfaces are lightly coated with a light oil.
Set up the FMPS according to the manufacturers' instructions and install the cyclone at the

| Procedure of particle measurements with the Fast Mobility Particle Sizer (TSI Model 3091)

aerosol inlet. For the measurement data logging, connect the FMPS via RS-232 and computer cable with the PC or laptop. Turn on the FMPS and the PC after connection to the power supply. The instrument requires at least 10 minutes to warm up (depending on conditions, this may take up to one hour) and the LCD illuminates this **Warming Up** status (yellow) with the warming time. When the warm up is finished the status (green) will change to **Normal**.

5.2   Electrometer offset

After the warm up, the offset of the electrometer should be checked. For this, install the HEPA filter at the aerosol inlet to provide the FMPS with particle-free air. As the instrument becomes dirty, the noise level on all channels may gradually drift up. This can be seen when there is a considerable signal above the **RMS lower noise limit** (yellow line) even when sampling filtered air. This can be corrected with the **Zero Electrometer** function. Rotate the black control knob until the **Menu** is marked in the LCD. Press the knob and the menu is displayed. With rotating and pressing the knob, select the **User Settings** from which **Zero Electrometer** is selected. After confirmation, the zeroing of the electrometer starts and requires 45 seconds. Normally, the zero function should remove the baseline noise.

5.3   Software adjustment

The TSI software **fmps** (Release version 2.1.0.0 or 3.1.0.0) is used for measurement data logging. After starting the software, open a new file with **File – New**, and selecting a filename. The desktop opens in **5-Pane Layout** (predetermined auto-fit) with the windows **FMPS Run View**, **Particle Table**, **Histogram**, **Total Concentration,** and **3D Particle Concentration**. It is possible to select the view with 4, 3, or 2 windows (**x-Pane Layout**) with the buttons at the toolbar or with the **Window** menu, depending on application and overview. A user-defined layout of the windows is possible too.

6   Sampling

- If required, connect a sampling tube to the aerosol inlet (cyclone). (Particle losses caused by diffusion occur by using a sampling tube. The FMPS operates with a sample flow of 10 lpm and particle losses by diffusion are low by use of short tubing.)
- In the fmps software select **Run – Start Data Collection**, click the red button (Record) on the toolbar, or press **<F10>**. Then the dialog box **Properties – New Run** opens on the desktop.
- The parameter of the **Properties – New Run**:
  - Title
  - Run Length
  - Start at Time
  - Enable External Trigger: only necessary if the sampling is remote controlled
  - Run Only Once or Run Continuous with delay between the runs
  - Data Type: Concentration

- After pressing the **OK Button** the sampling starts if no start time is entered, otherwise the sampling starts at the entered start time. Sampling with a specified start time is preferred so that all other measurement devices can also be started at the same time.
- The fmps software displays the measured data online in the opened windows.
- When sampling time ends the data are saved and the measurement stops. Selecting **Run – Stop Data Collection** or pressing the black button (Stop) on the toolbar stops sampling immediately.

7   Interpretation

- Simple data analysis with the **5-Pane-Layout**:
  - o The data can be viewed at different time resolutions by selecting an average interval (from 1 second to 60 minutes) in the drop-down selector on the toolbar, depending on the length of the run. The displayed concentration range can be changed by selecting a maximum concentration value from the concentration scale drop-down selector, also the scale between log and linear mode by pressing the log/lin button or the display of the absolute values (dN) or normalized values (dN/dlogD$_p$).
  - o The window **FMPS Run View** displays the particle size distribution against the time (contour graph). The color scale indicates blue for low particle concentration and red for high concentration. When the mouse pointer is clicked at a point in the graph, an annotation shows the selected time as time since the start of the run. The cursor corresponds to the particle histogram shown in the window **Concentration or dN/dlogDp Histogram**.
  - o The window **Concentration or dN/dlogDp Histogram** displays the selected particle size distribution. Position the mouse pointer on a bar (depending on type of graph that is active) and the pointer becomes a hand. By clicking the left mouse button the values diameter and concentration are displayed.
  - o The window **Particle Table** displays the collected measurement data for each size class in table form.
  - o The window **Total Concentration** shows the concentration run for the sampling time. The selected time point in the window **FMPS Run View** is marked here with time and concentration value.
  - o The window **3D Particle Concentration** displays a 3D graph of the particle size distribution against the sample time. The prior selected time point is highlighted in a different color.
- For further data interpretation:
  - o With **File – Export** the measurement data can be exported in a file. In the dialog box **Export Data options**, select the data types, time range and time resolution, and the output file type (Excel or text). After selecting a filename with the **Save as** button, the data can be exported.

| Page 4 of 5 | Procedure of particle measurements with the Fast Mobility Particle Sizer (TSI Model 3091) | |

8   Maintenance

- Cleaning the cyclone: Remove the cyclone cover and clean interior surfaces, especially the wall opposite the inlet nozzle every 100 hours of operation or as needed.

- Checking or/and cleaning of the charger electrodes every 100 hours of operation, see FMPS Operation and Service Manual.

- Cleaning of the column and outer electrode, the high voltage column and sensing electrodes every 500 hours of operation, see FMPS Operation and Service Manual.

- Replacement of the manifold filter cartridges (sheath flow HEPA filter), depending on use, for continuous operation annually, see FMPS Operation and Service Manual.

- Replacement of the pump filter cartridges, depending on use, for continuous operation annually, see FMPS Operation and Service Manual.

- Checking of the calibration suitable particles every 6 months or depending on demand.

9   Quality assurance

Measures for quality assurance:
- Periodical leak tests of the FMPS: Sampling with filtered air (HEPA filter), the FMPS signal should be below the lower noise limit
- Periodical check of the volume flows and adjustment if necessary
- Periodical check of the instrument calibration
- Realization and reporting of the maintenance
- Reporting of anomalies during sampling or maintenance

SOP-S-NSAM

Procedure of particle surface determination with the Nanoparticle Surface Area Monitor (TSI Model 3550)

Date
07th March 2012

Version
1.0 English

Content

1   Scope

The scope of this standard operation procedure is the procedure of the data collection and logging as well as the quality control of the determined and logged data from the NSAM (TSI Model 3550) including the routine instrumentation maintenance. The scope of this standard operation procedure does not extend to the establishment of a sampling station.

2   Notes

This standard operation procedure is used along with the standard operation procedures SOP-M-Screening and SOP-M-Expanded Measurement.

3   Basics

The operating principle of the Nanoparticle Surface Area Monitor Model 3550 is based on diffusion charging of sampled particles, followed by detection of the aerosol using an electrometer. The charged particles are passed through an ion trap to remove excess ions and desired amount of small particles. The aerosol then moves on to an aerosol electrometer for charge measurement. In the electrometer, current is passed from the particles to a conductive filter and measured by a very sensitive amplifier. The measured signal is converted via calibration curves to human lung-deposited surface area of particles corresponding to tracheobronchial (TB) und alveolar (A) regions of the lung of a reference worker.

4   Instrumentation

The main components of the NSAM Model 3550 are:

- Aerosol inlet with cyclone to pre-separation of larger particles
- NSAM Model 3550
- PC or laptop to data collecting and logging

5   Preparation for sampling

5.1 Preface

The cyclone is always used and should only be removed when transporting or servicing the instrument. It will remove large particles and fibers, which can clog the inlet orifice. The cyclone will be more effective in removing large fibers if the inside surfaces are lightly coated with a light oil.

Set up the NSAM according to the manufacturers' instructions and install the cyclone at the aerosol inlet. For the measurement data logging, connect the NSAM via RS-232 and com-

puter cable with the PC or laptop. Turn on the NSAM and the PC after connection to the power supply. The instrument requires 10 minutes to warm up.

5.2 Software adjustment

The TSI software **nsam** (Release version 2.3.1.0) is used to log the measurement data. After starting the software, a new nsam data file is created by selecting **File – New** and selecting a filename. After pressing the **Open** button and the connection to the instrument is complete, the software shows the **4-Pane Layout** with the windows **Sample List**, **Sample Statistics**, **Sample Graph,** and **Sample Table**. Depending on application and clearness the windows on the desktop can be arranged with the buttons on the toolbar or via **Window** on the menu bar.

The properties for the measurement are set with **Run – Properties** or mouse button right on **Sample 1** in the window **Sample List.** A new popup window **Sample Properties** appears with:

- **Instrument Response**
    - o Instrument Response: Alveolar Deposition (200 V), Tracheobronchial Deposition (100 V), Custom, Trap Off
    - o Lung Mass (kg): 1 kg (reference worker)
    - o Lung Surface Area (m^2): 80 m^2 (reference worker)
    - o Calibration Coefficient (dependent on the NSAM serial number): e. g. 0,5667 for A and 0,1233 for TB (NSAM S/N 70552200) or selectable for custom settings
- **Settings**
    - o Title
    - o Sample Length (hh:mm), maximum 24 h
    - o Averaging Interval (sec)
    - o Start At Time
    - o Run Only Once or Run Continuous
    - o Auto-Export Data marked if desired
    - o Comment
- **Communications**
    - o Available Connections: Select and test of COM-Ports

Return with **OK**.

| Procedure of particle surface determination with the Nanoparticle Surface Area Monitor (TSI Model 3550)

6   Sampling

- If required, connect the sampling tube to the cyclone of the aerosol inlet.

- If the check box by **Properties – Setting – Start at Time** is marked and a clock time is entered, the sampling starts at the entered start time.

- Otherwise select **Run – Start Data Collection**, press the red button (Record), or press **<F10>** to start the sampling immediately.

- The nsam software displays the measured data online in the opened windows.

- When sampling time ends the data are saved and the measurement stops. Selecting **Run – Stop Data Collection** or pressing the black button (Stop) on the toolbar stops the sampling immediately.

7   Interpretation

Simple data analysis with the **4-Pane-Layout**

- Select the sample in the window **Sample List** with a mouse click

- The statistical data of the selected sample are displayed in the windows **Statistics**

- The window **Sample Graph** displays the deposited surface area run against the sampling time. It shows the curve of the average log internal values (set in the properties) and the calculated 8-hr Time-Weighted Average (TWA).

- The window **Sample Table** displays the collected measurement data for log interval in table form.

- For further data interpretation select **File – Export** to export the measurement data in a file. In the appeared dialog box **Export Data options**, select the data types, and the output file type (Excel or text). After selecting a filename with the **Save as** button, the data can be exported.

8   Maintenance

- Cleaning the cyclone: Remove the cyclone cover and clean interior surfaces, depending of use every 100-500 hours of operation

- Cleaning of the inlet orifice, depending of use every 500-1000 hours, see NSAM Operation and Service Manual

- Cleaning of the charger orifice and needle annually, see NSAM Instruction Manual

- Replacement of the activated carbon cartridge, depending of use every 500-1000

hours, see NSAM Operation and Service Manual

- Replacement of the charger filter, depending of use every 1000-4000 hours, see NSAM Operation and Service Manual

- Replacement of the pump exhaust filter, depending of use every 4000-8000 hours, see NSAM Operation and Service Manual

- Replacement of the electrometer filter, depending of use every 1000-4000 hours, see NSAM Operation and Service Manual

9   Quality assurance

Measures for quality assurance:

- Periodical testing for leaks of the NSAM

- Periodical check of the volume flow

- Periodical check and adjustment of the electrometer offset

- Realization and reporting of the maintenance

Reporting of anomalies during sampling or maintenance

SOP-S-handheld CPC

Procedure of particle measurements with the Condensation Particle Counter Handheld (TSI Model 3007)

<u>Date</u>
07th March 2012

<u>Version</u>
1.0 English

<u>Scope</u>

1   Scope

The scope of this standard operation procedure is the procedure of the data logging and backup as well as the quality control of the determined and logged data from the CPC Handheld (TSI Model 3007) including the routine instrumentation maintenance. The scope of this standard operation procedure does not include the establishment of a sampling station.

2   Notes

This standard operation procedure is used along with SOP-M-Screening and SOP-M-Expanded Measurement.

3   Basics

In operation, the CPC 3007 draws an air sample through an ambiance that is saturated with isopropyl alcohol. In the following cooling section, particles present in the air sample serve as condensation nuclei. Once condensation begins, particles that are larger than a threshold diameter grow into larger droplets and pass through an optical detector where they are counted easily. The CPC 3007 detects the particle number in the size range of 10-1000 nm and concentration range up to 10^5 particles/cm^3.

4   Instrumentation

The CPC has the following components
- CPC Model 3007
- HEPA zero filter
- PC or laptop with computer cable for logged data reading

5   Measurements

5.1 Setting up

- For the use of the CPC as a mobile measurement device:
  Install six individual AA batteries into the battery pack, and then install the pack into the battery compartment at the bottom of the CPC
- For the use of the CPC as a locally fixed measurement device:
  Install the AC adapter in the socket and connect it with the power supply
- Twist the alcohol cartridge out of the alcohol fill capsule and fill the capsule with isopropyl alcohol until the scribed fill-line.
- Insert the alcohol cartridge into the alcohol fill capsule and wait a few minutes while the wick inside the cartridge soaks up the alcohol.
- Twist off the black storage cap from the CPC and insert the cartridge into the cartridge cavity on the CPC.
- Twist on the black storage cap on the alcohol fill capsule.

- Turn on the CPC by pressing the ON/OFF switch. The instrument immediately begins a warm-up countdown sequence which takes 600 seconds to fully warm-up the instrument.

5.2 Zero check

Before beginning to sample with the CPC, it is important to verify that the instrument is operating normally. This daily zero check should be performed at least once a day or before each measurement if the CPC is not used every day.

- After the CPC warm-up, attach the zero filter assembly to the inlet screen assembly.
- The particle concentration should go to zero in approximately 5-10 seconds. Leave the zero filter attached to the instrument for 30 seconds, to make sure the zero reading is stable.
- Remove the zero filter. The instrument is now ready for operation.

5.3 Sampling

The CPC has two main modes of operation:
Survey mode:

- If required, connect a sample tube to the CPC aerosol inlet.
- The CPC displays the real-time particle concentration in pt/cc (particles per cubic centimeter). The instrument will update the displayed concentration once each second.
- When **ABS PRESSURE** is selected with the arrow key and the **Return Key (↵)** is pressed, the CPC displays the particle concentration in pt/cc and the absolute pressure of the aerosol inlet in units of mbar.

Data log mode:

- If required, connect a sample tube to the CPC aerosol inlet.
- When **SETUP** is selected with the arrow key and the **Return Key (↵)** is pressed, the program opens the setup menu. With the arrow and Return keys, select **LOG INTERVAL**.
- The current logging interval of **LOG MODE 1** is displayed and can be adjusted to a different value with the arrow keys. (**Log Mode 2** and **3** may be programmed for more sophisticated data logging modes, using the Aerosol Instrument Manager software.) When the **Return Key (↵)** is pressed, the program retains the current setting and returns to the Setup menu.
- The logging interval for **LOG MODE 1** must be adjusted from the Setup menu before beginning the logging session. To begin a data logging session, select **LOG MODE 1** and press the **Return Key (↵)**. The average particle concentration is logged after each adjusted log interval.
- The CPC screen displays the current particle concentration, the minimum and maximum particle concentration with the respective times, and the remaining memory capacity in percentage.

- By pressing the **Return key (↵)** the data logging is stopped.

6 Data assurance and interpretation

- When **SETUP** is selected with the arrow key and the **Return Key (↵)** is pressed, the program opens the setup menu. With the arrow and Return keys, select **STATISTICS**.
- The CPC screen displays the **Logged Test Statistics**:
  TestNumber, START and STOP with time and date, MIN and MAX particle concentration with respective times, and the average particle concentration during the measuring.
- Via **Return key (↵)** the Setup Menu is displayed again which can be closed via **EXIT**.

For data backup and interpretation, the data are saved by means of the computer cable and the TSI Software (Aerosol Instrument Manager) to a PC or laptop.

- Connect the CPC and PC via computer cable and start the CPC.
- Start the AIM Software at the PC. Open a new file with **File – New**, data type **CPC 3007 Data file (*.C07)** and select a filename.
- The desktop opens in **4-Pane Layout** (predetermined auto-fit) with the windows **Data Graph**, **Data Table**, **CPC-Sample List**, and **Statistics Table**. With the **Window** menu and **2-Pane Layout** only the windows Data Graph and CPC-Sample List are displayed.
- Select **Run – Connect to Instrument** to verify the connection to the CPC
- Select **Run – Receive Logged Data** and the dialog box **Receive Samples from Instrument** appears. The dialog box displays all logged CPC data with Sample ID, Date and Time.
- Select one sample at a time by highlighting the sample or select several samples at a time by highlighting one sample and then holding down the Ctrl key and select other samples, or click the **Select All** button to highlight all samples.
- By clicking the **Receive-Button** the samples are downloaded to the PC.
- In the window **CPC-Sample List** select the sample by mouse clicking.
- The window **Data Graph** displays the particle concentration run of the selected sample. The average particle concentration of each logging interval is displayed in the **Data Table** and the statistical data in the **Statistics Table**.
- With **File – Export** the measurement data can be exported for further interpretation. In the Export Data Option box, select the data types. After selecting a filename, the data can be exported as a text file or a spreadsheet file.

7 Maintenance

- Realization of daily zero checks or before each use
- Daily recharge of the alcohol wick or before each use
- Change of the alcohol wick as needed, see CPC Operation and Service Manual.
- Return to factory for cleaning and calibration, annually

8   Quality assurance

 Measures for quality assurance:

- Zero checks before the measurements

- Routine volume flow check

- Realization and reporting of the maintenance

Reporting of anomalies during sampling or maintenance

SOP-S-miniDiSC

Procedure of particle measurements with the Miniature Diffusion Size Classifier (miniDiSC, FH Nordwestschweiz)

<u>Date</u>
14th March 2012

<u>Version</u>
1.0 English

<u>Content</u>

1   Scope

The scope of this standard operation procedure is the procedure of the data collection and logging as well as the quality control of the determined and logged data from the miniDiSC (FH Nordwestschweiz) including the routine instrumentation maintenance. The scope of this standard operation procedure does not extend to the establishment of a sampling station.

2   Notes

This standard operation procedure is used along with the standard operation procedures SOP-M-Screening and SOP-M- Expanded Measurement.

3   Basics

The operating principle of the Miniature Diffusion Size Classifier (miniDiSC) is based on the deposition of charged particles in two consecutive stages and subsequent current measurement from both stages using Faraday cup electrometers. In the miniDiSC, particles get charged in a unipolar diffusion charger, before they are passed on to a dual stage particle deposition system. The first stage contains a diffusion screen where particles are deposited with a size-dependent efficiency. The second stage contains a high efficiency filter, on which all particles that penetrated the first stage are captured. Small particles have a larger diffusivity, and therefore are more likely to be collected in the diffusion stage, while larger particles are more likely to end up in the filter stage. Both stages are connected to electrometers that continuously measure the current, induced by the deposited particles. The average particle size is determined by comparing the currents in the diffusion and the filter stage. The total current and the particle size are then combined to determine the number concentration.

4   Instrumentation

The main components of the miniDiSC are:
*   miniDiSC instrument
*   Pre-separator (6 hole impactor)
*   SD-Card for data collection and logging
*   Charger/power supply unit

5   Measurements

5.1   Setting up

Set up the miniDiSC according to the manufacturer's instructions.
*   For long term measurements (e. g. monitoring) at a fixed location, connect the miniDiSC with the AC/DC power adapter and then plug in the power adapter to a 230 V power outlet.
*   To use the instrument as a mobile measurement device, the miniDiSC is also equipped

with rechargeable batteries (lifetime about 8 hours).

- For data logging, insert the SD card in the card slot on the left side of the instrument.
- Turn on the miniDiSC by pressing the **Power Button** for 2 seconds. The instrument immediately begins a warm-up following a 300 s countdown sequence. The manufacturer suggests further 10 minutes waiting time to fully warm-up before starting the measurements.
- After warm-up the miniDiSC display shows the main screen containing the particle concentration (**N XXXX pt**) and average particle diameter (**Size XXX nm**) on the left, the control signals depending on the status of the miniDiSC: high voltage (**lightning bolt**), Flow (**Φ**), Heating (**H**), and Recording (**blinking circle** or number **1** for not recording) top right, and the remaining battery power (**XX%**) bottom right.
- Before start with recording measurements, set the internal clock of the miniDiSC: Press the menu button (middle button) for 3 seconds to move into advanced mode with the auxiliary screens. Press the menu button again to flip through the auxiliary screens. When the date/time screen appears, the year will be blinking for a few seconds. During this time the year can be changed by pressing the left or right arrows. After a couple of seconds without action the month starts blinking and can changed with the arrow keys. This procedure continues until every value is set. Then the Set Clock? screen appears. By pressing the right arrow key located below the YES you will save the adjusted date and time.

5.2 **Zero check**

Before beginning to sample with the miniDiSC, it is important to verify that the instrument is operating normally. This zero check should be performed at least before you start the measurement, and also after you finish:

- After the miniDiSC warm-up, attach a particle filter (HEPA) to the aerosol inlet.
- The particle concentration should go **N < 100 pt** in a few seconds. The average particle diameter should show **Size --- nm**.
- By pressing the right arrow button (►) the display shows the raw data screen with the two electrometer currents (upper value diffusion stage, lower value filter stage). The stage signals should indeed very close to zero fA.
- Remove the particle filter and press the left arrow button (◄) to go back to the main screen. The instrument is now ready for operation.

5.3 **Sampling**

- If required, connect a sampling tube to the aerosol inlet.
- The main screen shows the number concentration und mean particle size.
- By pressing the left arrow button (◄) the display shows the surface area screen with a quantity that can be described as "alveolar lung-deposited surface area, A-LDSA" (**SA [µm2/cm3]**).

- To save the measurements to the SD card, start recording by pressing the red record button. Recording is indicated by a blinking closed circle in the top right corner of the display in the main screen.
- By pressing the red record button again for 2 seconds the recording stops and a beep sound will acknowledge the stop.

5.4 **Measurement data**

The recorded measurement data are saved as text files on the SD card. With a card reader the tab-delimited text files can easily be imported into all common data processing programs. The use of the **miniDiSC data conversion tool** (version 1.18) is recommended. With this little tool it is easy to load and analyze raw miniDiSC data files, view the data, and export it for further use in other programs.

6 **Maintenance**

- Clean the impaction surface before use (unscrew the impactor cap, and wipe the flat surface below the thread). Make sure to screw the impactor cap firmly into the impactor to ensure proper functioning of the impactor. Clean the impactor orifices regularly in an ultrasonic bath; place the impactor with the solid side down and the thread facing up in-to a beaker and fill the beaker with an alcoholic cleaning fluid up to the level of the orifices; make sure not to cover the internal thread of the impactor to avoid degreasing. Place the beaker in an ultrasonic bath and start the cleaning process.
- The instrument has to be serviced and calibrated once per year. Alternatively, the miniDiSC reading should regularly be cross-checked against a CPC in regular intervals. Remember: the miniDiSC is not a high precision instrument. Deviations of up to ±30% compared to a CPC are tolerable.

7 **Quality assurance**

Measures for quality assurance:
- Periodical testing for leaks of the miniDiSC
- Periodical check of the volumetric flow rate (Aerosol sample flow 1 lpm)
- At high humidity, the electrometer zero offsets can drift. The instrument is verified for up to 80% relative humidity at 20°C. Up to this point, drifts are small (at most a few fA). At higher humidity, proper operation of the instrument is not guaranteed. Please check the stability of the zero offsets when measuring at high humidity, and if possible, dry the aerosol upstream of the miniDiSC.
- Periodically check the electrometer zero offsets.
- Report anomalies during sampling or maintenance

SOP-S-APS(TSI)

Procedure of particle measurements with the Aerodynamic Particle Sizer (TSI Model 3321)

Date

13th March 2012

Version

1.0 English

Content

1   Scope

The scope of this standard operation procedure is the procedure of the data collection and logging as well as the quality control of the determined and logged data from the APS (TSI Model 3321) including the routine instrumentation maintenance. The scope of this standard operation procedure does not include the establishment of a sampling station.

2   Notes

This standard operation procedure is used along with the standard operation procedures SOP-M-Screening and SOP-M- Expanded Measurement.

3   Basics

The operating principle of the Aerodynamic Particle Sizer (Model 3321) is based on the acceleration of aerosol particles in response to the accelerated flow of the sample aerosol through a nozzle. The aerodynamic size of a particle determines its rate of acceleration, with larger particles accelerating more slowly due to increased inertia. As particles exit the nozzle, the time of flight between two laser beams is recorded and converted to aerodynamic diameter using a calibration curve.

4   Instrumentation

The main components of the APS Model 3321 are:

- APS Model 3321
- PC or laptop to data collecting and logging

5   Preparation for sampling

5.1   Preface

Set up the APS according to the manufacturers' instructions. For the measurement data logging, connect the APS via RS-232 and computer cable with the PC or laptop. Turn on the APS and the PC. The APS does not require time to warm up.

5.2   Software adjustment

The TSI software **Aerosol Instrument Manager** (Release version 8.1.0.0 with APS module version 5.0) is used for measurement data logging. After starting the software, open a new file with **File – New**, data type **APS 3321 Data file (*.A21)** and select a filename. The desktop opens with 10 different windows. Press button **4-Pane Layout** (or select from the menu **Window - 4-Pane Layout)** to arrange the windows **Aerodynamic Diameter Graph**, **Aerodynamic Diameter Table**, **Sample List,** and **Statistics Table**. With the **Window** menu and **2-Pane Layout** only the windows **Aerodynamic Diameter Graph** and **Sample List** are displayed. User-defined layouts of the windows are also possible. With **File – Properties**, **Run**

Procedure of particle measurements with the
Aerodynamic Particle Sizer (TSI Model 3321)

– Properties or right click on **New Sample** in window **Sample List** and selecting properties open the dialog box **APS 3321 Properties**. A new popup window appears with:

- **Data Settings**
  - o Dilution/Efficiency File (only useful in combination with TSI Aerosol Diluter Model 3302)
  - o Particle Density (g/cc)
  - o Apply Stokes Correction
  - o Phantom Count Correction
- **Scheduling**
  - o Sample length (Sec)
  - o Number of samples
  - o Scheduled: Only Once or Repeat Every hh:mm
  - o Start At Time hh:mm
- **Data Types**
  - o Aerodynamic Diameter with Channel data and Raw data
  - o Side Scatter with Channel data and Raw data
  - o Sample Mode with Summing or Correlated

Return with **OK**.

6 Sampling

- If required, connect the sampling tube to the aerosol inlet.
- If the check box by **Properties – Scheduling – Start at Time** is marked and a clock time is entered, the sampling starts at the entered start time.
- Otherwise select **Run – Start Data Collection**, press the red button (Record), or press **<F10>** to start the sampling immediately.
- The AIM software displays the measured data online in the opened windows.
- When sampling time ends the data are saved and the measurement stops. If the check box by **Properties – Scheduling – Repeat Every** is marked and a time is entered, the next measurement sample starts after the desired recurrence interval.
- By selecting **Run – Abort current sample** or pressing the black button on the toolbar the sampling stops immediately without saving the sample data; by selecting **Run – Finish current sample** the measurement stops after finishing the current sample with saving the sample data and stopping the measurement repeats.

7 Interpretation

Simple data analysis with the **4-Pane-Layout**

- Select the sample in the window **Sample List** with a left click
- The statistical data of the selected sample are displayed in the windows **Statistics**
- The window **Aerodynamic Diameter Graph** displays the particle size distribution of the selected sample.

- For further data interpretation select **File – Export** to export the measurement data to a text file. When the dialog box **Export Parameters** shows up, select the data types, the units and weightings, the delimiter and the orientation. After pressing the OK button and selecting a filename in the **Export As** dialog, the data can be exported.

Coincidence: Particle coincidence means that more than one particle is present in the detection volume of the particle counter, thus creating a superimposed signal that causes the counter to incorrectly classify the particles as a single, wrongly sized particle. In the case of the APS 3321 the double-crested signal processing technique allows the processor to determine when a signal is caused by a single low scattering particle and when it is caused by coincidence. This means that the particle size distribution during coincidence can still be accurately measured. Coincident particles can be detected as events 3s (see from menu **View – Event Data** or **Strg V)**, but cannot be sized. Therefore they are not included in the size distribution, but are recorded for possible concentration corrections.

8   Maintenance

- Cleaning the inner nozzle: depending on use, usually after 750 hours of operation, see APS instruction manual
- Cleaning the outer nozzle: depending on use, usually every 2500 hours, see APS instruction manual
- Replacement of air filters every 5000 hours, see APS instruction manual
- Check and update calibration every 5000 hours, see APS instruction manual or send APS to TSI

9   Quality assurance

Measures for quality assurance:
- Periodical leak tests of the APS
- Periodical check of the volumetric flow rates (aerosol sample flow 1 lpm, sheath flow 4 lpm)
- Realization and reporting of the maintenance
Reporting of anomalies during sampling or maintenance

SOP – S – Spectrometer (GRIMM)
Procedure for particle measurement with the aerosol spectrometer
(GRIMM portable model 1.108/1.109)

<u>Date</u>
2012-05-10

<u>Version:</u>
1.0 English

<u>Contents</u>

1 Purpose

The purpose of this Standard Operating Procedure is to support the collection, protection and quality assurance of data measured and recorded by the aerosol spectrometer (GRIMM model 1.108/1.109) to determine inhalation exposure to fine particulates from product materials and other aerosols in the workplace. It also encompasses routine maintenance of the device.

2 Note

The present SOP – S – Spectrometer (GRIMM) is an addition to SOP-M-Expanded Measurement: "Measurements of the inhalation exposure to nanoscale product materials and ultrafine aerosols at workplaces including the background concentration."

3 Basics

The portable aerosol spectrometer model 1.109 measures airborne particles from 0.25 µm to 32 µm in 31 size channels in real time and supplies the readings as particle counts and dust mass fractions. The basic model 1.108 detects particles from 0.3 µm to 20 µm in 15 size channels. All measured particles are collected on a removable 47 mm PTFE filter inside the unit (Dual Technology) and are thus available for further chemical, microscopic or gravimetric analysis. The data is stored on a removable data storage card and accessible online at all times via an RS-232 interface.

A laser diode serves as the light source in all Grimm Laser Aerosol Spectrometers. The measuring cell comprises an optical detection system. The scattered light is detected directly and simultaneously by a wide angle optical system with reflector at a scattering angle of 90°. This minimizes the dependency of the refraction index on the measured signal, and the size of individual particles is determined by the intensity of their scattered light.

It must be kept in mind that spectrometers 1.108 and 1.109 have internally set mass calibration factors of 1.48 and 1.0, respectively. If mass concentrations are to be generated, this factor must be adapted using the secondary gravimetric measurement.

4   Equipment

The following components are required for workplace measurements:
- Dust monitor with data storage card and rechargeable battery
- Radial-symmetric sampling head
- Battery charger with mains cable
- Filter for baseline measurement
- PTFE filter, 47 mm diameter, 0.2 µm pore size
- Laptop with Grimm Spectrometer Software for control and data recording (this SOP applies to Spectrometer Software versions 3.20 and 2.1.4 / 2.2.3)
- Suitable cable for serial - USB
- Flow meter

5. Measurement

5.1. Preparation

- The unit should never be operated without the PTFE filter. Check if the filter is inserted inside the unit and insert one if it is not.
- Attach the radial-symmetric sampling head to the unit (sample inlet).
- Connect the unit to the computer.
- Switch on the unit, observe the LCD display, wait for it to go from self-test to the "Change Filter" prompt, and then respond yes or no by pressing the "+" or "-" button (hold down the button until you hear the acoustic signal). The unit then begins a measurement cycle.
- With version 3.20 of the software, the date and time are set directly on the unit.
- Put the unit in standby mode by pressing the "Standby" button.
- Start the spectrometer software (versions 3.20 or 2.1.4 / 2.2.3).
- Check the standard settings in accordance with the software (license, otherwise no connection is made to the unit; settings e.g. date/time, measurement interval).
- Unit test: Baseline measurement (place filter for baseline measurement in the sample inlet, perform measurement (duration: 5 min.). All channels must be at zero after one minute at most. If all the channels do not return to a baseline of zero, the unit and possibly the lines must be cleaned and the baseline measurement repeated.

5.2. Equipment and software settings

Depending on the software, all data are shown numerically and/or graphically in the following formats:

- Number distribution: Particle number concentration in all channels expressed as particles/liter
- Mass fractions: Occupational (inhalable, thoracic, alveolic) in µg/m³, in accordance with DIN EN 481
- Emission (PM10, PM2.5, PM1)
- Service data: Pump current, battery capacity, error codes, etc.

Keep in mind that the readings (particle counts) are converted using a unit-specific factor, which makes it possible to specify mass concentrations. These may differ from the actual mass concentrations depending on the aerosol measured. For this reason, it is necessary to perform gravimetric analysis of the PTFE filter and subsequent calibration, and then to convert the measured values into mass concentrations (see Section 6). If this should not be possible under certain circumstances, the density of the material to be analyzed can be considered as a calibration factor and adapted, taking into account other accompanying aerosols.

The software supports online data acquisition, display of the measured values and the current unit functions. The readings are stored on 6 MB of memory in the unit. However, the data is overwritten once storage space is full.

5.3. Measurement

- Start the Grimm spectrometer software and continue as prompted by the software (input date/time, settings, etc.).
- Start measurement via the software.

Table: Potential sources of error

Error / Failure	Possible cause	Corrective action
CHECK FILTER	Motor current <20% or >70% • Filter forgotten or clogged	Insert or change filter
FLOW ERROR	Pump regulator outside normal range • Internal filter clogged • Hoses inside the unit defective • Other problems in the gas line	Open the unit, check filter and hoses, change if necessary • Have unit repaired by manufacturer
PUMP CURRENT TOO HIGH	Motor current >100% • Filter or incoming lines	Change filter and/or clean incoming lines

Error / Failure	Possible cause	Corrective action
	clogged • Electrostatic charge • Other problems in the gas line	 • Ground the unit • Have unit repaired by manufacturer
Unit does not respond either to commands via the keypad or from the PC. LCD display is frozen, no data transmission to PC	Undefined status	Unplug charger, remove battery • If the unit starts up after reinstalling the battery or connecting the charger, the measurement can be restarted. • Have unit repaired by manufacturer

5.4. Ending measurement

- End measurement from the software program.
- Save data on the computer for storing measured values (software versions 3.20: data export as Excel file; software version 2.1.4 / 2.2.3: data stored in three ASCII files (C.dat - Particle number concentration, M.dat - Mass concentration and L.dat – Service file), which can be edited e.g. in Excel).
- Clean the unit if necessary with alcohol wipes.
- After the measurement, open the filter chamber, remove the filter and place it in a suitable, sealable container. Insert a new filter.
- Gravimetric analysis of the PTFE filter makes it possible to calibrate the measurement results (see Section 6).

6. Analysis

The measurement data is analyzed in accordance with the instructions in the SOP "Measurements of the inhalation exposure to nanoscale product materials and ultrafine aerosols at workplaces including the background concentration."

For gravimetric conversion to mass concentration:
- Weigh the PTFE filter
- Software versions 3.20: In the program under Extras and Gravimetry, calculate the current C factor and apply that to the measurement data.
- Software versions 2.1.4 / 2.2.3: The C factor is changed directly via the control panel on the unit (Factor C button). If the C factor is to be adopted for later measurements, then the change is made via Settings and Factor C. The current C factor is applied to the current measurement later on, for example in Excel).

7. Maintenance

- The measurement equipment must be routinely serviced and calibrated by the manufacturer (GRIMM Aerosoltechnik), ideally once a year.
- Regularly check the "baseline concentration" using the baseline test filter.
- Regularly change the PTFE filter

8. Quality assurance

- Service the unit and document the process
- Document any unusual occurrences during sampling and servicing, and report them if necessary to the responsible person.

SOP-S-ESP

Procedure of particle sampling with the Nanometer Aerosol Sampler (TSI Model 3089) or electrostatic precipitator (ESP)

Date
07th March 2012

Version
1.0 english

Scope

Procedure of particle sampling with the Nanometer Aerosol Sampler (TSI Model 3089) or electrostatic precipitator (ESP)

1   Scope

The scope of this standard operation procedure is the procedure of the particle sampling with the Nanometer Aerosol Sampler (TSI Model 3089) or an electrostatic precipitator including the routine instrumentation maintenance. The scope of this standard operation procedure does not include the establishment of a sampling station.

2   Notes

The Nanometer Aerosol Sampler is a commercial sampler with integrated high voltage supply; the electrostatic precipitator ESP is a self-made sampler with external high voltage supply. This SOP covers only the NAS.

This standard operation procedure is used along with the standard operation procedure SOP-M-Sampling.

3   Basics

The Nanometer Aerosol Sampler is an electrostatic precipitator which was developed to sample charged nanometer particles. The sampling procedure is based on the unipolar charging of the particles with subsequent deposition on a substrate or sample carrier due to the applied electric field. By use of a pre-charger with unipolar charging of the particles, the NAS samples particles up to 5 µm. By operating the NAS without a pre-charger, particles up to 200 nm are sampled.

4   Instrumentation

The main components of the NAS Model 3089 are:

- NAS Model 3089 with different electrodes
- Optional: Point to plate pre-charger
- Optional: High voltage supply for the pre-charger

5   Sampling

5.1   Preparation

- Open the NAS cover and install an electrode (9.5 mm or 25 mm)
- Mount a sample substrate (e. g. glassy carbon or TEM grid) onto the electrode
- Close the NAS cover
- Install the particle pre-charger at the inlet of the cover
- Connect the pre-charger to the high voltage supply with a high voltage cable
- Connect the NAS and the high voltage supply with the power supply and turn on all devices

- If required, connect a sample tube to the aerosol inlet of the pre-charger

5.2 Sample collection

- Adjust the pump with the **Flow (LPM)** rotameter to the desired flow (flow range 0.2-2.5 lpm)
- Adjust the voltage for the electric field inside the NAS with the **Voltage (KV)** controller to the maximum value of 10 kV (voltage range 0-10 kV)
- Adjust the voltage for the particle pre-charger with the voltage controller of the high voltage supply to 4.5 kV (or higher but avoid sparkovers).

5.3 Post-processing

- When sampling is finished, turn off both high voltage supplies and the pump.
- Note the sampling time
- Open the NAS cover and remove the sample substrate
- Place the substrate in a suitable substrate container for further analysis by microscopy, SEM, or TEM

6 Maintenance

- Cleaning of the interior surfaces of the sampling chamber, depending on use every 50-100 hours.
- Checking and/or cleaning of the pre-charger electrode, depending on use every 50-100 hours.
- Replace the pump filter cartridges, depending on use every 1,000-2,000 hours, see NAS Instruction Manual.

7 Quality assurance

Measures for quality assurance:
- Periodical testing for leaks
- Periodical check of the volume flow
- Realization and reporting of the maintenance
- Reporting of anomalies during sampling or maintenance

SOP-S-Data Analysis

Procedure for measurement data analysis for the determination of released particles caused by the working process

Date
07th March 2012

Version
1.0 English

Content

Page 1 of 5   Procedure for measurement data analysis for the
                 determination of released particles caused by the
                 working process

1   Scope

The scope of this standard operation procedure is the description of the analysis of the measured data from the particle measurements at work place and the detection of released product nanoparticles.

2   Analysis method

Absolute values (e.g. particle number concentrations) are not relevant during work activities but the values measured in periods without work activities or in periods with work activities but without nano particle supplement are set in relation to the infiltrating particle concentrations from outside of the process or working area. It is assumed that particles from the outside area or the comparison station are transported to the working area and influence the measurement results. The influence of the particles from outside on measurements depends on factors such as environmental impacts, other working activities (welding, cleaning, etc.) or emissions from other vehicles (gas or diesel working forklifts, lorries, etc.). A general assumption is that the comparison site is representative for the determination of the background particle concentration. The assumption that the basic conditions during the measurement periods without work activities and the measurement periods with work activities are identical needs to be checked carefully (plausibility check). Measurement data which can ascribe to special events close to the comparison site and influence data interpretation therefore have to be neglected for data interpretation, i.e. all data from those periods (work place and comparison site) were neglected.

2.1   Procedure of analysis

- According to the SOP of the measurement devices, the collected measurement data are exported to a spreadsheet program.
- For all the devices (e. g. SMPS, FMPS, NSAM, CPC) the measurement data are fitted to a uniform average interval.
- Particle losses on surfaces caused by diffusion due to measurements with tubes and measuring rods connected to measurement devices with a small sample volume flow and low aerosol velocity (e. g. SMPS) have to be corrected. These particle losses have to be calculated (e.g. according to *Hinds: Aerosol technology: properties, behavior, and measurement of airborne particles, 2nd Edition, New York, Wiley-Interscience, 1999*) and considered for further interpretation. The particle losses within the SMPS are corrected by means of the measurement device software as well as the consideration of multiply charged particles.
- All collected data from the measurement devices are displayed and analyzed to identify special events. If the times of special events are noted, all the data from all the meas-

urement devices have to be neglected so that the same measurement periods are always compared.

- For the overlapping particle size ranges of the measurement devices from indoor site (work place) and outdoor site(comparison side) and the corresponding time periods (measurement without and with work place activity and without nano particle supplement and measurement with work place activity with nanoparticle supplement respectively), the average particle number concentrations of each size class from inside and outside area are set in relation to one another. The particle size ranges of the particular size class have to be identical or adapted for both measurements (work place and comparison site).

$$R_{with\ work\ place\ activity} = \frac{Inside_{with\ work\ place\ activity}}{Outside_{with\ work\ place\ activity}}$$

$$R_{without\ work\ place\ activity} = \frac{Inside_{without\ work\ place\ activity}}{Outside_{without\ work\ place\ activity}}$$

- The ratio calculation for the period without work place activity is of importance here. The ratios $R_{with\ work\ place\ activity}$ and $R_{without\ work\ place\ activity}$ should be equal assuming there is no particle release caused by the work or production process. This assumption allows the calculation of theoretical background particle concentrations for the work place, which are due to transported particles, based on measured outside concentrations. The outside particle concentrations are measured at the comparison sites. This theoretical particle concentration called *Setpoint value$_{Inside}$* is given by the following equation.

$$Setpoint\ value_{Inside} = \frac{Inside_{without\ work\ place\ activity}}{Outside_{without\ work\ place\ activity}} \cdot Outside_{with\ work\ place\ activity}$$

- The ratio of the measured particle concentrations at the work place during activity to the calculated *Setpoint value$_{Inside}$* is called *ActiveRatio*

$$ActiveRatio = \frac{Inside_{without\ work\ place\ activity}}{Setpoint\ value_{Inside}} =$$

$$= Inside_{without\ work\ place\ activity} \cdot \frac{Outside_{without\ work\ place\ activity}}{Inside_{without\ work\ place\ activity} \cdot Outside_{with\ work\ place\ activity}}$$

- The calculated *ActiveRatio* values of the different particle size classes are
  - o larger than unity if particles are released,
  - o unity if no particles are released, and
  - o below unity if
    - ▪ particle deposition/removal is enhanced during work activity or
    - ▪ if a process and hence a particle emission was active during the period without work place activity and inactive during the actual measurements

during work place activity. (The latter should certainly be avoided but can never be absolutely excluded, e.g. change of ventilation)

- value significantly < 1 means representativeness of the comparison measurements was not given ➔ assessment of the consequences

- Furthermore, the absolute value of particle concentration of potential particle release is computed by calculating the difference between the effective measured particle concentration at the work place with activity and the *Setpoint value$_{Inside}$*. This value is called *ActiveAbsolute*. In section 2.2 the uncertainties of this calculation are considered seperately.

$$ActiveAbsolute = Inside_{with\ work\ place\ activity} - Setpoint\ value_{Inside}$$

$$= Inside_{with\ work\ place\ activity} - \frac{Inside_{without\ work\ place\ activity} \cdot Outside_{with\ work\ place\ activity}}{Outside_{without\ work\ place\ activity}}$$

- The concentration of nanoparticles released is calculated by integrating the *ActiveAbsolute* values up to 100 nm and 450 nm, respectively. The lower particle size limit is always specified!

2.2 Data uncertainty estimate

- Uncertainty of the measurement devices
  Before and after the measurement campaign the measurement devices should be operated simultaneously at a comparison site to ensure comparability of the devices. The results of the comparison measurements can be displayed in summary. Hence the uncertainties *u(measurement device)* of the ratios can be calculated for the size classes of the measurement devices.

- Uncertainty of measurements inside-outside
  Parts of the measuring equipment are moved to the work place from outside. Because of this change of location, a constant uncertainty of 50 % is assumed in the comparison of the measurements from inside and outside .

The overall uncertainty is a combination of the uncertainty from changing the measurement site and the uncertainty from the deviation of measurement devices. The overall uncertainty *u(overall)* is calculated as:

$$u_{upper}\left(overall\right) = \frac{u_{upper}\left(measurement\ inside/outside\right)}{u_{lower}\left(measurement\ inside/outside\right)} \cdot u_{upper}\left(measurement\ devices\right)$$

$$u_{lower}\left(overall\right) = \frac{u_{lower}\left(measurement\ inside/outside\right)}{u_{upper}\left(measurement\ inside/outside\right)} \cdot u_{lower}\left(measurement\ devices\right)$$

With the uncertainty from the measurement devices determined by the comparison measurement and the uncertainty from changing the measurement location an upper and lower

particle size dependent uncertainty limit is calculated. Only ratios outside these uncertainty limits are viewed as significant.

Procedure for measurement data analysis for the determination of released particles caused by the working process

SOP-S-GC Substrates
Preparation of Glassy Carbon Substrates

Date

07th March 2012

Version

1.0 English

Scope

1   Scope

This standard operation procedure describes the preparation of glassy carbon substrates to be used for sampling of airborne nanoobjects (def. of objects according to DIN CEN ISO/TS 27687).

This SUB-SOP is intended to be used in conjunction with SOP-M-Sampling (Main Document).

2   Introduction

Glassy carbon substrates are specifically used for a total reflection x-ray fluorescence (TXRF) analysis (e.g. using a Bruker PicoFox x-ray spectrometer) of airborne nanoobjects. For the commonly used instruments they have a diameter of 30 mm and a thickness of 3 mm with one side polished.

3   Procedure for cleaning glassy carbon substrates

The glassy carbon substrates have to be cleaned before use. The substrates can be re-used. Cleaning has to be carried out in a chemical hood. The procedure for cleaning is as follows:

- If the substrates are visibly dirty they have to be wiped using isopropyl alcohol and a lint-free paper (e.g. Kimwipes)
- Teflon-holder and substrates are boiled in distilled water for 15 minutes. Afterwards they have to be cooled down to approximately 35°C
- Teflon-holder and substrates are taken out of the water bath and dried with lint-free paper
- Teflon-holder and substrates are boiled in concentrated HNO_3 for one hour (if necessary refill of HNO_3). Afterwards they have to be cooled down to approximately 35°C
- Teflon-holder and substrates are then moved into fresh distilled water and heated up to 50 °C
- Teflon-holder and substrates are removed from the water bath, rinsed again with fresh distilled water and put into a dry, clean glass beaker covered by a watch glass.
- The glass beaker is transferred to an oven for drying the substrates at ca. 80°C.
- The thickness of each substrate has to be checked to be strictly 3 mm or below (min. 2.95 mm) in order not to destroy the spectrometer.

- Substrates are finally stored in suitable containments protecting them from contamination.

General care has to be taken that only clean vessels and pure chemicals are used during the cleaning procedure

4   Quality control

The cleaned substrates have to be measured by TXRF before use to quantify possible residues from the cleaning procedure. If no elemental peaks (besides artifacts like the argon peak) are clearly developing during a short scan of e.g. 100 seconds the substrate should be clean enough for usage. Depending on the necessary detection limit (due to e.g. only little amount of airborne particles present, short sampling times) clear "zero counts" might be necessary; if the substrates fail to fulfill this quality control the cleaning procedure should be repeated.

In case blank values are measurable but acceptably low they may be subtracted from the actual measurement results.

Nanostrukturierte Materialien – Gesundheit, Exposition und Materialeigenschaften

Glossary

For standard operation procedures for assessment of exposure to engineered nano-materials

<u>Date</u>

21st March 2012

<u>Version</u>

1.0 English

Aerodynamic diameter d_{ae}

The aerodynamic diameter d_{ae} of a particle is the diameter of a unit density sphere of 1 g/cm³ that has the same settling velocity as the particle in question.

ANT

Aerasense Nano Tracer, handheld diffusion charging instrument, measures particle number concentration and mean particle size of particles between 10 and 300 nm

APS

Aerodynamic Particle Sizer, measures particle number size distributions based on aerodynamic diameter between 700 and 20,000 nm

Arithmetic mean

The arithmetic mean A is the central tendency of a collection of measured values a_i and equals the sum of all measured values divided by the number n of measured values.

$$A = \frac{1}{n}\sum_{i=1}^{n} a_i$$

Background concentration

The background concentration at all workplaces is the concentration in that workplace in a state where the typical industrial environment is running without the product nanomaterials process being applied (analogous to TRGS 402).

Background contamination

The background contamination is the particle concentration in the air that would be present at the workplace during measurements if the work activities with hazardous materials were not ongoing.
(Source: TRGS 402: "Ermitteln und Beurteilen der Gefährdungen bei Tätigkeiten mit Gefahrstoffen: Inhalative Exposition", Ausgabe Juni 2008)

Background level
The background level is the average background concentration that has to be investigated for a representative period.

CPC
Condensation Particle Counter, measures particle number concentrations of particles larger than 2.5-10 nm (dependent on model)

DiSCmini
Miniature diffusion size classifier, identical with miniDiSC, measures particle number concentration and mean particle size of particles between 20 and 400 nm

DMA
Differential Mobility Analyzer; fractionates submicron particles based on electrical mobility, size range dependent on model

EM
Electron Microscopy

Events
Events are incidents that have a direct influence on the measurements. Events that occur due to activities inducing release of nanoparticles (e. g. bag damages) during the process run have to be differentiated from events that occur due to activities not related to the work or process activities and induce ultra fine particles (e. g. emissions of forklifts, heatings or weldings).

Far-field measurements
Measurement of the background concentration in a sufficient distance to the emission source of product nanomaterials.

FMPS
Fast Mobility Particle Sizer, measures particle number size distributions based on mobility/Stokes diameter between 5.6 and 560 nm

miniDiSC
Miniature diffusion size classifier, identical with DiSCmini; measures particle number concentration and mean particle size of particles between 20 and 400 nm

Mobility diameter ≙ Stokes diameter d_{st}
The Stokes diameter d_{st} of a particle is the diameter of a spherical particle with the same density and settling velocity as the particle in question.

NAS
Nanometer Aerosol Sampler

NSAM
Nanoparticle Surface Area Monitor, measures lung deposited surface area concentrations between 10 and 1,000 nm, identical with Aerotrak 9000

OPC
Optical particle counter, measures particle number size distributions, based on the optical equivalent diameter, typically in a size range from 250 to 30,000 nm

Product nanoobjects
Product nanoobjects are particles of a single product with at least one dimension <100 nm.

Product nanomaterials
Product nanomaterials are nanoobjects of a single product including agglomerates which were produced industrially or for research.

SEM
Scanning Electron Microscopy

Significance
A result is called statistically significant if it is unlikely to have occurred by chance.

SMPS
Scanning Mobility Particle Sizer, measures particle number size distributions based on mobility/Stokes diameter between 2.5 and 1,000 nm (depending on setting)

Spectro-Tabs
Object slide for the analysis for example from wipe samples using Scanning Electron Microscopy

Standard deviation
The standard deviation σ is a statistical value that describes how much dispersion the normal-distributed measured values a_i show around the mean A, n is the total number of measured values.

$$\sigma = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(a_i - A)^2}$$

Supply air concentration
Particle concentration of the air flowing into the work places area from outside (including via doors and windows).

TEM
Transmission Electron Microscopy

TEM-Grids
Object slide for Transmission Electron Microscopy analysis.

TP
Thermal precipitator