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*Methods for the use of simulation approaches*

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4	2014/10/23	1 <sup>st</sup> submission to MC
5	2015/01/12	Corrections and additions from INRS and NRCWE
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## 1 Description of task

Accordingly to the Document of Work, the overall goal of the WP3 is to characterize real exposures (intensity and frequency) to humans (workers and consumers) and the environment through NM life cycle in order to provide companies and legislators with a set of tools for risk assessment and decision making for the short to medium-term, by gathering data and performing pilot risk assessment, including exposure monitoring and control, for a selected number of manufactured nanomaterials (MNMs) used in products; and to develop, for the long-term, new testing strategies adapted to a high number of MNMs for many factors susceptible to affect their environmental and health impact.

Regarding specifically task 3.2, a number of subtasks are envisaged:

- a. Comparison of existing dustiness testing methods and development of a generic ranking approach/model.
- b. Development of simulation approaches for key exposure scenarios (e.g. spraying, cleaning, abrasion, or weathering) and use of these to collect relevant data.
- c. Simplify or develop the following pre-screening exposure procedures:
  - Aquatic/environmental exposure procedure (Standard procedure to determine, solubility, stability, aggregation (specifically for ecotox, whether water column - or benthic organisms should be given priority)) = exposure pre-screening test. The applicability of this kind of approach with respect to environmental cases has already been validated (von der Kammer F. et al. 2010, Ottofuelling S. et al., 2011). ). The most relevant parameters can be used to establish a decision tree to categorize MNM and residues as entry point for (eco)toxicity assessment.
  - Development and Implementation of resistance/aging tests for materials incorporating nanoparticles (outdoor paint resistance tests, polymer crash test ...) = Life cycle stages (including end of life/disposal)

The aim of this deliverable is to provide a compendium of protocols to perform simulation approaches for key exposure scenarios (e.g. spraying, cleaning, abrasion, or weathering) and use of these to collect relevant data. Once relevant products or processes will be chosen, tests will be performed following those procedures through Task 3.3 to generate data on occupational exposure, consumer exposure and environmental exposure. The generated data will be described in the corresponding chapter of Deliverable 3.7 entitled "Improved data on specific scenario" which is due for M34. Results concerning the procedures to generate controlled aerosol using the shaker method and dustiness testing using small rotating drum and vortex shaker methods will be reported in the Deliverable 3.2 entitled "Comparison of existing dustiness testing methods".

## 2 Description of work & main achievements

### 2.1 Summary

Among the partners involved in NanoReg task 3.2 and 3.3, BAuA, NRCWE, CNRS CEREGE, LEITAT, INRS and CEA provided their standard operating procedures to:

- simulate the use of products (i.e. textiles washing ; polymer aging in water ; paints, coating and nanocomposites sanding; paints and coating environmental aging) => simulation approaches for consumer exposure and to evaluate the nanoparticle release to the various relevant environmental compartments (air, water and soil)
- to evaluate nanoparticle release rates for processes placed under fume cupboards and hoods => simulation approaches for occupational exposure
- to generate controlled aerosol from nanomaterials using the shaker method (fibrous nanomaterials such as CNT and CNF ; granular bio-persistent particles) => generic method to evaluate dustiness and to simulate emission to indoor air
- to evaluate dustiness indexes of nanomaterial powders

Those protocols will be used to generate data on occupational exposure, consumer exposure and environmental exposure once WP3 partners will agree on products such as packaging materials, concrete, automotive lubricants, nano-enabled medical devices and paints. The protocol from BAuA, NRCWE and INRS will be used in the dustiness sub-task.

### 2.2 Background of the task

WP3 is developing methods and approaches to measure and characterize nanomaterials within realistic exposure situations to humans (workers and consumers) and the environment throughout the different stages of the life cycle of nanomaterials. The aim of the tasks 3.2 and 3.3 is to address the following key questions from a regulatory perspective:

No	Key question from a regulatory perspective
11	<b>Exposure:</b> What are the main determinants for occupational and consumer exposure to MNM and what are the duration and type of exposure?
12	<b>Exposure:</b> How should human and environmental exposure be assessed in practice (determining exposure scenario, quantify input parameters for models, assumptions and use of proxy indicators, background and uncertainty estimation)? Consider both measuring and specific modelling for nanomaterials and evaluate the needs for standardization and validation.
13	<b>Exposure and life cycle analysis:</b> Which scenarios could denote potential exposure and what information do we have on them? Can we develop standardized and efficient testing procedures for estimating release of nanoparticles from powders and nanoparticles in matrices? What are situations in which MNM exposure is expected to be negligible / high? Are the amount and the nature of releases of MNM similar to regular chemicals, when common recycling and end-of-pipe techniques are used?  How to minimize and structure LCA to avoid ending up with a '1:1 model of the world'?  In other words: what is the exposure probability throughout the different life cycle stages

	<p>of the MNM: production process of the NM itself, releases during the production process of products in which MNM are used, waste treatment, consumer articles, wearing, abrasion, etc.? Do waste treatment / recycling processes lead to exposure to NMs that can be hazardous to health and environment? If so, are additional risk management measures required? Do the recycled product / residues lose some value / usefulness due to undesired characteristics?</p>
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## 2.3 Description of the work carried out.

### 2.3.1 Method for the evaluation of nanoparticle release from textiles to the water compartment during washing cycles

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#### **Aim(s) or Objective(s) of SOP**

This SOP describes the implementation of a method for the evaluation of nanoparticle release from textiles to the water compartment during washing cycles.

**Version 1.0 Date: 17:07:2014; first draft by Elisabet Fernandez, LEITAT, Spain**

**Version 1.1 Date: 22:10:2014; revision by Elisabet Fernandez, LEITAT, Spain**

#### 2.3.1.1 Scope and required operating conditions

The scope of those protocols is to simulate the use phase of commercially available textiles containing nanomaterials. Particularly to evaluate the release rates of nanoparticles from textile during washing cycles following the ISO 105-C06:1994 and ISO 6330:2012.

#### 2.3.1.2 Materials and equipment needed

The textile used will have the following composition: PES/Ly, mixture of polyester (90%, PES 167/144 BIELTEX) and elastane (10%, 40 DN CREORA). The nanoparticles are incorporated in the fabrics to provide bactericidal and odorless properties. Here, three types of coatings containing nanoparticles will be applied to the described textile:

- Impregnation with a mixture of TiO<sub>2</sub> nanoparticles and AgCl,
- Impregnation with two different sized Ag nanoparticles.

It should be mentioned that other additives (surfactants, binders...) are included in the impregnation solutions. Nanoparticles are applied following a padding process. Briefly, first the samples are dipped into a tank containing the aqueous nanoparticle dispersions, and then the samples are drained in a foulard to a pressure of 4 kg/m<sup>2</sup>. Finally, the fabric is dried and cured at temperatures ranging from 140-160 °C.

Regarding raw nanomaterial, both morphology and size will be characterized by means of transmission electron microscopy (TEM). The nanoparticles will be also analyzed by UV-vis spectroscopy, dynamic light scattering (DLS) and FT-IR.

#### 2.3.1.3 Setup of experiments

The sportswear textiles will be washed to investigate and characterize the release of nanomaterials into the water compartment, according to the following procedures.



## Textiles:

Ti and Ag concentration will be determined by ICP-MS before and after the washing cycles. An acid digestion of the fabric will be applied to prepare the samples for the measurement. The morphology and size of the textile fibers will be evaluated by scanning electron microscopy (SEM). SEM-EDX observations will be performed in order to identify the chemical composition of individual/aggregated nanoparticles on the fibers. In addition, the fabric will be characterized by TGA and FT-IR. Apart from that, the functionality of the fabric will be tested by investigating its antimicrobial activity (*S. aureus*) following the norm UNE-EN ISO 20743.

## Collected waters:

Individual / aggregated nanoparticles will be identified and its chemical composition will be defined by TEM-EDX, when possible. The concentration of Ag and Ti in collected solutions will be determined directly by ICP-MS. Analysis will be also performed on centrifuged samples / supernatant solutions to differentiate ionized / non-ionized fractions. When possible and appropriate, Ag<sup>+</sup> concentrations will be determined by using a Ag<sup>+</sup> selective electrode.

When possible, Field flow fractionation (FFF) coupled to a multi angle light scattering detector (MALS) and to an inductively coupled plasma-mass spectrometer (ICPMS) will be used (Partner 41 - VN) to characterize the size distribution and the concentration of the Ag and TiO<sub>2</sub> nanoparticles.

### 2.3.1.3.1 Procedure 1:

Experiments will be performed in a lab-washing machine, based on the international standard ISO 105-C06:1994 for determining color fastness in commercial and industrial laundering followed by a rinsing cycle (GyroWash, from James Heal). This method aims at studying the transference of color from the fabric to an adjacent fabric. In our case, we will not include a reference textile because the goal is to evaluate the release of nanomaterials to the water compartment. The standard describes a series of possible tests, and initial conditions will be established according to the literature (e.g. 40°C for 30 min). The experiments are commonly conducted in stainless steel bottles in which approximately 8 g of fabric are introduced together with 120 mL of detergent solution (ECE Color Fastness Test Detergent, 4 g/L) prepared in distilled water type II (electrical conductivity  $\leq 1 \mu\text{S}/\text{cm}$  @ 25°C). In this test, 10 stainless steel balls are as well included. In proof of concept tests it has been confirmed by ICP-MS that no release of Ti and Ag from both the containers and the balls occur during the experiments.

Different washing cycles will be applied to the textiles and the presence and concentration of released nanoparticles into the washing solution will be determined, and compare to that fraction remaining on the surface of the fabrics.

From this data, the source term of the process releasing nanoparticles is made available, which is essential for exposure modelling among others.



Figure 1: GyroWash machine used to perform the lab-washing experiments in procedure 1.

### 2.3.1.3.2 Procedure 2:

Depending on the results obtained following the procedure 1, a second protocol will be applied. In this case, the ISO 6330:2012 for domestic washing will be also followed to evaluate possible nanomaterial migration to both adjacent fabric and water environment. This simulation is performed in a conventional washing machine, and accordingly, the weight of sample, the temperature and duration of the test as well as the detergent employed must be adapted. Waste water will be collected for further analyses through the evacuation tube of the washing machine (see figure 2).



Figure 2: Conventional washing machines (left) used for the lab-washing experiments in procedure 2 and disposition of the evacuation tube to collect the laundering waters (right).

### 2.3.1.3.3 Procedure 3:

Apart from the washing experiments, the sportswear textiles will be exposed to artificial sweat solutions of either pH 5.5 or pH 8.0, adapting the standard ISO 105-E04:2008 to evaluate migration of nanomaterials to perspiration solutions.

Each litre of the alkaline sweat solution is composed by: 0.5 g of L-histidine monohydrochloride monohydrate ( $C_6H_9O_2N_3 \cdot HCl \cdot H_2O$ ), 5g of sodium chloride (NaCl) and 5g of disodium hydrogen orthophosphate dodecahydrate ( $Na_2HPO_4 \cdot 12H_2O$ ). For one litre of the acidic solution the latter component is substituted by 2.2g of sodium dihydrogen orthophosphate dihydrate ( $NaH_2PO_4 \cdot 2H_2O$ ). In both cases, pH is adjusted by adding NaOH 0.1 M.

### 2.3.2 Method for the evaluation of nanoparticle release from polymers to the water compartment during accelerated aging

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<b>Aim(s) or Objective(s) of SOP</b>
This SOP describes the implementation of a method for the evaluation of nanoparticle release from polymers to the water compartment during accelerated aging.

**Version 1.0** Date: 30:09:2014; first draft by **Astrid Avellan, CEREGE, France**  
**Version 1.1** Date: 15:10:2014; revision by **Armand Masion, CEREGE, France**

### 2.3.2.1 Scope and required operating conditions

The scope of this protocol is to simulate the aging of polymers in water. Particularly to evaluate the release of nanoparticles from polymers debris when they are in the environment (water compartment).

### 2.3.2.2 Materials and equipment needed

In this study we used different polymers. PolyPropylene (PP) is a semi crystalline thermoplastic resin. PolyAmide (PA) is containing amide functions; and PolyUrethane (PU) is a chain of organic units jointed by carbonate (urethane) links. This three kind of polymers will be studied pures, or dopped with nanoparticle : nano-silica (-SiO<sub>2</sub>) or nano-clays –Montmorillonite- (-MMT). The following tables give an overview of these components.

Tableau 1: description of nanoparticles used in polymers.

Nanofiler	Polymer			Origin
	Polypropylene	Polyamide	Polyurethane	
Nano Silica (SiO <sub>2</sub> )	Aerosil 974 Hydrophobic : surface modified with dimethyl dichlorosilane	Aerosil 200 Hydrophilic		Industrial - DEGUSSA
Layered Silicates (MMT)	Dellite 72T Ditallowdimethyl amonium ion	Dellite 43B Tallowbenzildimethyl amonium ion		Industrial - LAVIOSA

#### ➤ Preparation of starting materials: mechanical abrasion of macro-size samples (i.e. production of small size fractions to simulate use of products due to abrasion)

Mechanical erosion of the polymers will be performed to simulate ageing during use of products due to abrasion and then generate new type of dust. Polymer plaques (several centimeter long and large) will be used as starting materials. Usure of polymer is simulated by grating nine grams of each polymer with a metallic grate of 200 mm size producing. Mechanical procedure tested is implemented manually to avoid increase of temperature during abrasion. Mortar grinding in ceramic bawl for half an hour will also be performed after grating procedure. Mortar grinding will be used with a large gap between the rotating agate part and the fixed container. 2mm gap is selected. The aim is not to crush the samples, but to gently separate particles that are interlinked or interconnected (“Jackstraws” effect).

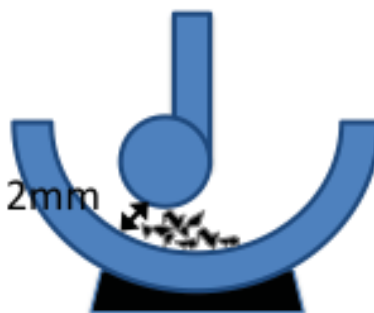


Figure 3: Diagram of the mortar set-up to separate particles of polymer that are interlinked or interconnected

All apparatus are treated with alcohol to decrease at maximum the bacterial contamination. The fraction smaller than 20 µm produced by abrasion is generally low. The objective is to produce a minimum of 200 mg of dust <20 µm for each sample.

Polymer shavings will be suspended in ethanol, and sieved with a sieve of 20µm mesh. The size distribution of fine particles (<20µm) will be measured in ethanol to prevent aggregation and using laser diffraction (static light scattering SLS). The structure of the fine particles before and after ageing experiments will be characterized by means of X-ray Diffraction (XRD) and Fourier Transform InfraRed spectroscopy (FTIR, ATR mode).

The following schema is a summary of the procedure to prepare the actual starting material of the aging procedure:

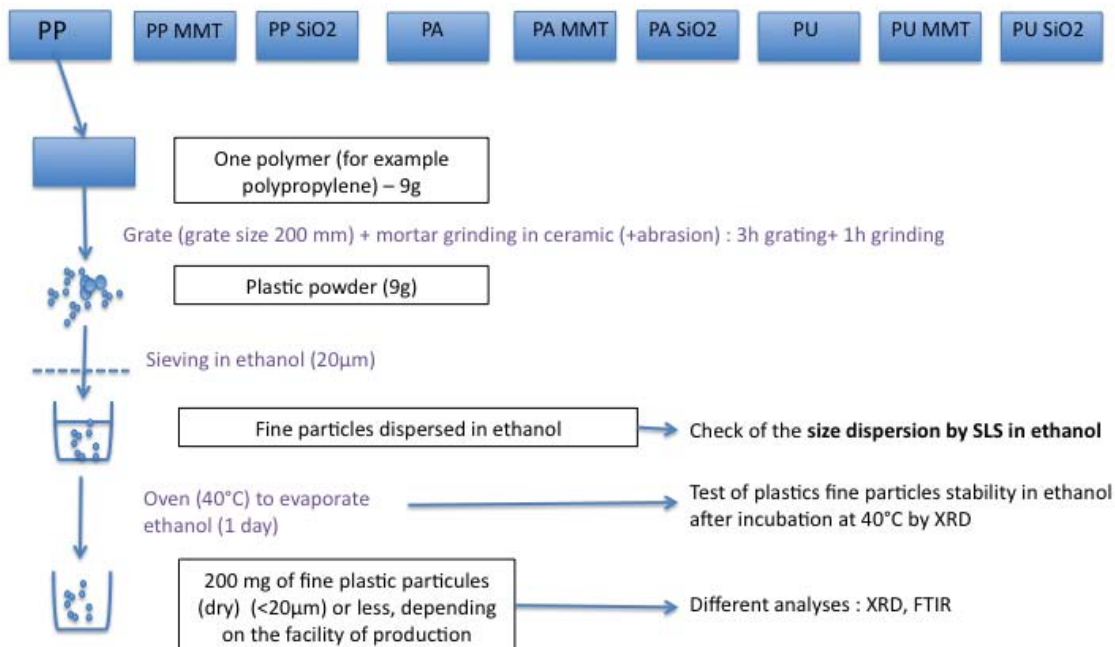


Figure 4: Process for obtaining particles below 20 µm from selected composites and nanocomposites samples

### 2.3.2.3 Setup of experiments

The 200 mg of fine particles of polymer will be divided in 10 lots of 20mg (5 lots aged under UV and 5 lots aged in the dark). The aging of the polymer fine particles will be studied by introducing 20 mg of the fine particles powder into a large mouth 1L PTFE beaker containing 200 mL of ultrapure/sterile water. Then NaCl will be added to reach a concentration of  $10^{-2}$  mol/l.

Aging is simulated by submitting these mixtures (100 mg/l  $\pm$  3 mg/l of fine particles) to magnetic stirring at 400 rpm. Natural sunlight is simulated using a sodium discharged 400W lamp, located 30 cm from the open reactor, and continuously cooled via a connection to air extraction. The temperature is maintained at 24 ( $\pm$ 4 °C). Water loss from the sample due to evaporation will be compensated for by adding appropriate amounts of sterile water (NaCl  $10^{-2}$  Mol/l) to the reactor on a daily basis. The experiments will be performed over a whole week (seven days). To study the aging of fine particles of each polymer samples in the absence of light, the reactor will be covered and capped with aluminum foil. These samples will be subjected to the same procedure under the same time and temperature conditions except that LDPE bottles will be used instead of PTFE under light. During all aging experiments, the solution pH and conductivity will not be modified and will be checked every day in one bottle of each condition to avoid particle lose in other 4 bottles.

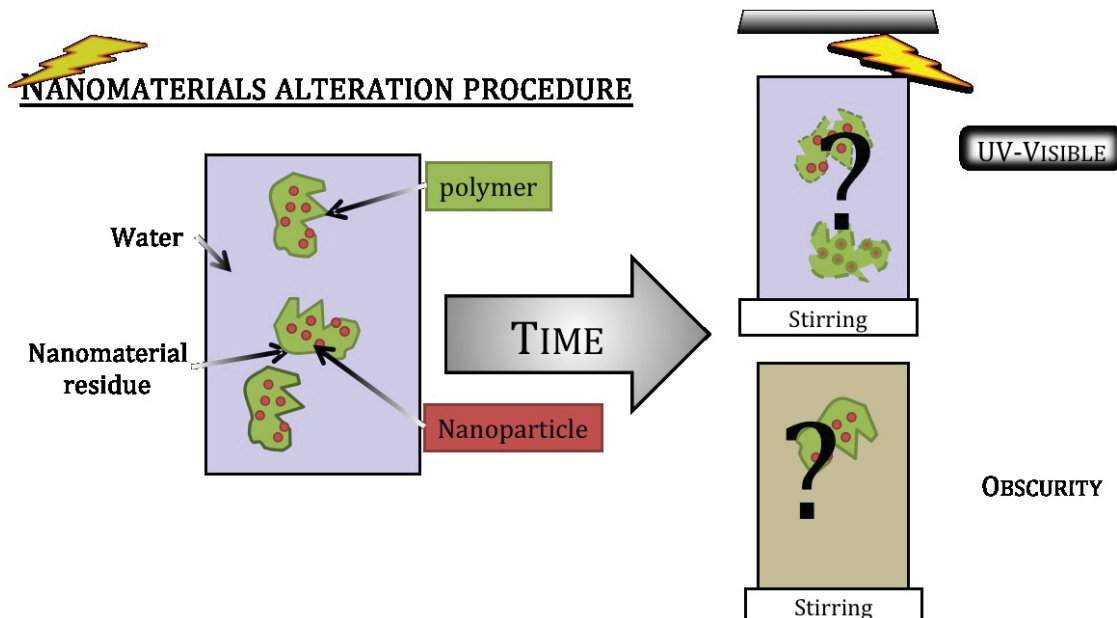


Figure 5: Alteration procedure

Each aging experiment will be conducted using 5 samples under light and five samples in dark conditions. At the end of the alteration, solutions will be transferred in LDPE bottles.

In the fifth bottle the stability of the suspension after 5 days in ambient temperature will be checked with static light scattering measurements and particles counter. Then this bottle will be stored at 5°C in the dark and its stability (in term of pH, conductivity and size distribution) will be controlled each 10 days.

The following schema is a summary of the procedure:

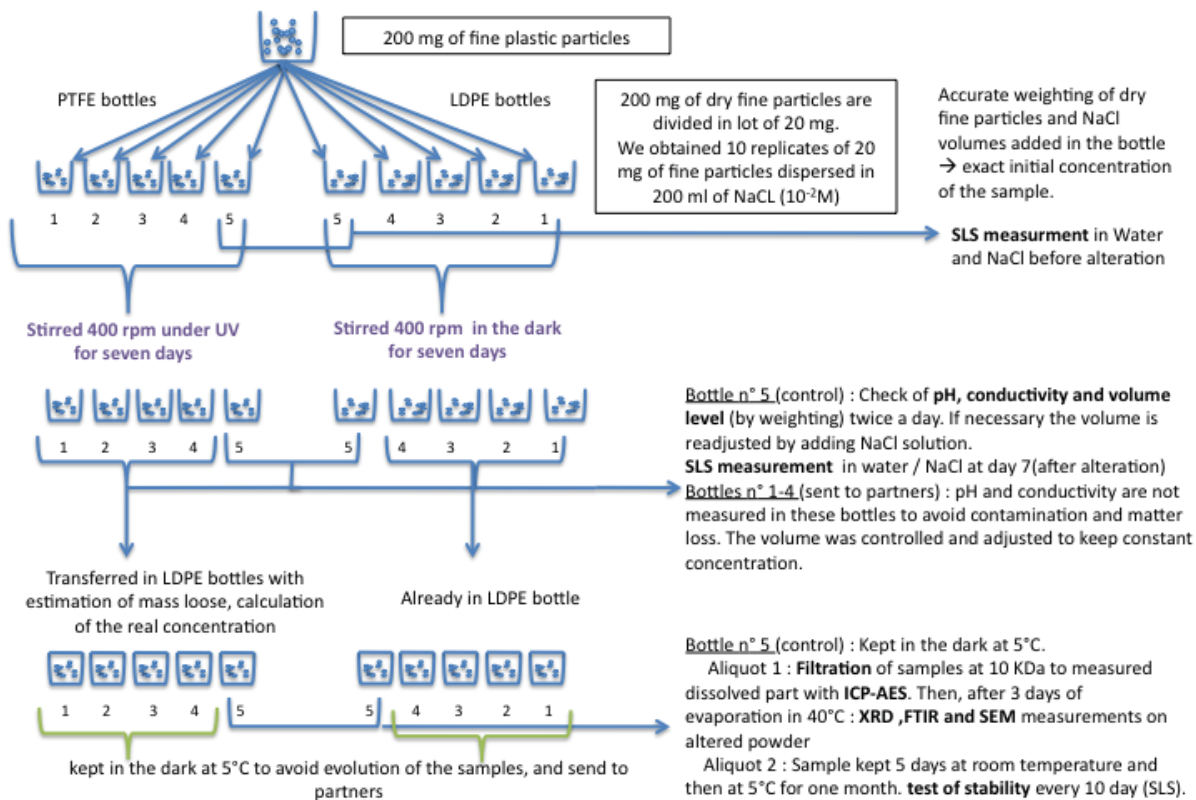


Figure 6: Protocol for the accelerated ageing of the particles below 20  $\mu m$

### 2.3.3 Method for the evaluation of nanoparticle release during sanding processes

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#### **Aim(s) or Objective(s) of SOP**

This SOP describes the implementation of a method for the evaluation of nanoparticle release during sanding processes.

**Version 1.0** Date: 24:03:2014; first draft by **Delphine Boutry, CEA, France**  
**Version 1.1** Date: 14:10:2014; revision by **Simon Clavaguera, CEA, France**

#### 2.3.3.1 Scope and required operating conditions

This procedure describes a method to determine the potential emission level of nanoparticles from different commercial composite products. This procedure could also be used to determine personal exposure level of practitioner when performing abrasion tests on different composite products. The aim of this SOP is also the development and implementation of “resistance” tests for materials incorporating nanoparticles. Thanks to the Taber Abrader, it is possible to deduce the effect of the aging on the resistance material. Weight mass loss deduced by the difference of specimen weight before and after abrasion is one of the possible evaluations with the Taber device. Another possible measurement is the Taber Wear Index. It indicates the rate of wear and calculates by measuring the loss in weight (in milligrams) per thousand cycles of abrasion. The lower the wear index is, the better the abrasion resistance is.

##### ➤ **Nano-enabled paints and coatings**

To perform accelerated wear testing for paint samples, the TABER® Rotary Platform Abrasion Tester (Model 5135 or 5155) is commonly used. The Taber Abraser (Abrader) rapidly became the world standard for evaluating abrasion resistance. This precision built instrument is capable of providing reliable data in a matter of minutes compared to the years that may be required by in-use testing. International Standard ISO 7784-1 specifies the conditions of paints abrasion with a Taber.

Taber tests involve mounting a flat specimen of about 100 mm<sup>2</sup> of surface or a round specimen of about 10 cm of diameter to a turntable platform that rotates on a vertical axis at a fixed speed. The standard material thickness that can be evaluated with the Taber Rotary Abraser is 6.35 mm (materials greater than 6.35 mm but less than 40 mm can be tested with optional accessories). Two genuine Taber abrasive wheels, on which a specific pressure is applied, are lowered onto the specimen surface.

##### ➤ **Nanocomposites**

For nanocomposites materials like tyres, specific International Standard was published with the number ISO 5470-1. This standard is entitled Rubber or plastic coated fabrics – Determination of abrasion resistance – Part 1: Taber abrader specifies the abrasion conditions with a Taber. Another possibility is to use a home-made apparatus for the abrasion. This apparatus is composed of a weighing scale, an abrasive paper stuck with a double-face scotch tape, a circular support connected to an electric drill on which the sample is stuck with a double-face scotch tape. With this experimental apparatus, it is possible to control parameters like rotation speed, pressure on the sample to reproduce different abrasion conditions. In the case of nanocomposites, the sample will be abraded keeping a relative speed between paper and sample of 0.5 m/s or 1.8 m/s. Then, the sampler suck up the aerosol and the particles are analyzed by CPC, FMPS and ELPI. Particles are

also collected on a TEM grid thanks to a specific device. ELPI membranes might be advantageously studied by SEM/EDX.

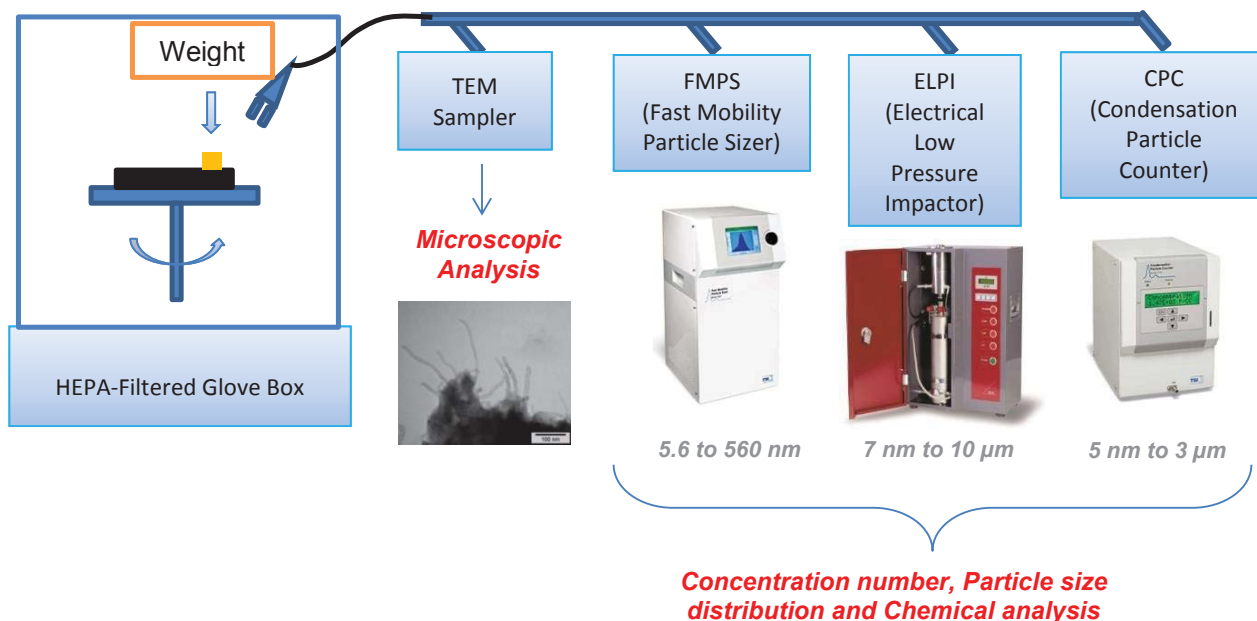


Figure 7: Diagram of a typical sanding experiment on nanocomposites

### 2.3.3.2 Materials and equipment needed

#### ➤ Nano-enabled paints and coatings

In the case of paint materials, in order to represent commercial product, nanoparticles of interest could be TiO<sub>2</sub>, ZnO or SiO<sub>2</sub> for example.

For paints, the coating needs to be applied on test panels. It is really important to achieve a uniform coating to perform these tests. Different panels are available. In function of the formulation, specific type of panel has to be selected:

- Steel (S-16) - Uniformly blanked from 20-gage auto body sheet steel and dull finished for good adhesion of the coating to the metal. 100 mm square with rounded corners and a 6.35 mm center hole.
- Wood (S-17) - Manufactured from grade A1, 6.35 mm (0.25 inches) birch plywood which has been sanded on both sides. 100 mm square with a 6.35 mm center hole.
- Aluminum (S-18) - Produced out of #19 gauges 5052 aluminum. 100 mm square with rounded corners and a 6.35 mm center hole.
- Glass (S-31) - Quality plate glass, approximately 3.15 mm thick. 100 mm square with a 6.35 mm center hole.

Size of samples: 10 cm x 10 cm with a thickness around 0.5 cm.

#### ➤ Nanocomposites

In the case of nanocomposite materials, carbon nanotubes (CNT) based products might be studied since CNT are often used to improve mechanical properties of polymer material. It has been decided to study discs of 1 cm thick and 11 cm in diameter for practical reasons. For each material, experiments will be repeated four times and as a consequence, 4 samples at least will be needed.

#### ➤ Equipments



To perform sanding experiments on paints or nanocomposites, the following material will be used within a glove box having a low nanoparticle background:

<i>Paints and coatings</i>	<i>Nanocomposites</i>
<ul style="list-style-type: none"> <li>- TABER® Rotary Platform Abrasion Tester (Model 5135 or 5155)</li> <li>- S42 Taber abrasive paper</li> </ul>	<ul style="list-style-type: none"> <li>- Abrasive paper (32 mm diameter paper with a 80 to 320 grit size)</li> <li>- Double-sided adhesive tape</li> <li>- Electric drill that will be set at a specific rotation corresponding to a relative speed between the abrasive paper and the material being studied of 0.5 m/sec and 1.8 m/sec.</li> <li>- 1kg weight to ensure contact between the sample and the abrasive</li> <li>- Laboratory jacks</li> </ul>

The glove box is sealed and equipped with transparent organic glass walls (charge dissipative material). The volume of the cubic chamber is 0.2 m<sup>3</sup>. Ventilation hoods are installed and 2 levels of ventilation rates are available. Two small holes were drilled on the wall: one for the sampler and another for the electric drill. A HEPA filter H14 is used in order to limit the initial presence of particles in the atmosphere and the air is sucked up at 10 cm/s of speed. The drill is placed outside the glove box in order to prevent false positive measurements coming from the motor of the drill.

To characterize the released particles during the abrasion of paints or nanocomposites, the following devices will be used:

- ELPI (Dekati ELPI "Classic): the Electrical Low Pressure Impactor sucked-up the particles released by a sampling line at a rate of 10 L/min. This instrument is used to measure the number size distribution in the range between 7 nm and 10 µm but gives no information on the chemistry of the particles. It is capable of achieving real-time measurements and displays concentration changes for each size class. The ELPI allows also depositing released particles on filters after putting them on impaction plates. These filters (hydrophilic polycarbonate membrane) are then analyzed by Scanning Electron Microscopy (SEM) to observe the morphology and size of the collected particles. In this way, the released nanoparticles are studied in order to determine their shape/aggregated state: nanoparticles in agglomerated or free form or even nanoparticles embedded in the paint matrix. EDX analysis can also be performed to determine the elemental composition.
- FMPS (TSI Model 3091): the Fast Mobility Particle Sizer spectrometer measures particle sizes in the range between 5.6 and 560 nm, offering a total of 32 channels of resolution (16 channels per decade). This produces particle-size-distribution measurements with one-second resolution, providing the ability to visualize particle events and changes in particle size distribution in real time. It operates at a high flow rate (10 L/min) to minimize diffusion losses of ultrafine and nanoparticles. It operates at ambient pressure to prevent evaporation of volatile particles and it requires no consumables.
- CPC (TSI Model 3785): the Condensation Particle Counter is a compact, rugged and full-featured instrument that detects airborne particles down to 10 nm at an aerosol flow rate of 1.0 L/min, over a concentration range between 0 and 10<sup>7</sup> particles/cm<sup>3</sup>. Thanks to this device, particles concentration number can be determined.
- Sampler for SEM and/or TEM analysis: another way to collect nanoparticles with a sampler for characterization purpose is to suck up air in a particular device in which is placed a Transmission Electron Microscopy (TEM) grid. The released particles are collected on TEM grids via air filtration sampling to determine if abrasion-released nanoparticles are in free or agglomerated form and to identify their elemental composition by energy dispersive X-ray spectroscopy (EDS). Thus, it is possible to measure the size distribution, the morphology of particles and to perform chemical characterization of the collected particles.

### 2.3.3.3 Setup of experiments

The setup combines a mechanical solicitation tool with a sampling line where several counters, granulometers and samplers will be connected. The sampling line will be located at the closest point where the abrasion occurs between the sample and the tool (usually 5 cm). The sampling line will allow a complete characterization of the aerosol (particle size distribution, particle number evolution with time, physical-chemical characterization of the collected particles...). HEPA Filtered Gloves Box is used to provide a leak-tight physical barrier to protect operator from hazardous airborne particulates and powders but also to protect analysis from a potential pollution. The volume of the cubic chamber is 0.2 m<sup>3</sup>. Ventilation hoods are installed and 2 levels of ventilation rates are available. Two small holes were drilled on the wall for the collection of particles by the sampler. A HEPA filter H14 is used in order to limit the initial presence of particles in the atmosphere and the air is sucked up at 10 cm/s of speed.

Figure 7 represents an experimental setup to perform the abrasion tests where the abrasion is achieved by an electric driller for nanocomposite materials.

#### ➤ Nano-enabled paints and coatings

In the case of paints and coatings, a Taber Abraser will be preferred and will be placed in the glove box (Figure 8). In the case of the use of the Taber abrader, a specific rotation speed and an abrasive paper which are consistent with the ISO standard is applied. The sampler suck up the aerosol and the particles are analyzed with CPC, FMPS and ELPI. ELPI membranes might be additionally studied by SEM/EDX for morphologic and chemical analysis. Each sample has to be tested several times (at least two times).



Figure 8 : Taber abrader

#### ➤ Nanocomposites

Figure 9 shows a nanocomposite sample placed between the rotating plate connected to an electric driller placed out of the glove box (below) and the sanding paper with a weight (above).



Figure 9: Experimental apparatus for sanding experiments

➤ **Generic procedure for an experiment:**

- Put on protective equipment (gloves, glasses and laboratory coat).
- Clean the glove box and check the filter.
- Ensure that the ventilation of the gloves box is turned on at the correct rate.
- Fix the sample on the Taber abrader or on the circular support accordingly to the description above.
- Fix the abrasive paper on the wheels of the Taber or on the specific support accordingly to the description above.
- Close the door of the glove box.
- Turn on the ELPI and the pump. The equipment has to be clean with a pure air flow during 15 min (before each test, all the filters of the column of the ELPI have to be changed).
- Turn on the CPC. This device must warm up for 10 min so that the detector is operational.
- Turn on the FMPS. This device must warm up for 10 min.
- Make the baseline of the ELPI.
- Stop the cleaning of the equipment and connect the ELPI to the aspiration system.
- Synchronize the starting time of all tools and start data acquisition.
- Reduce the ventilation flow to 30 L/min.
- Start the abrasion process. Note down the starting time point. This process lasts approximately 4 minutes.

➤ **Cleaning procedure:**

- Turn on high level ventilation.
- Use the special vacuum cleaner equipped with an HEPA filter to clean the box.
- Remove the abraded sample.

### 2.3.4 Method for the evaluation of nanoparticle release during environmental aging

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#### **Aim(s) or Objective(s) of SOP**

This SOP describes the implementation of a method for the evaluation of nanoparticle release during environmental aging.

**Version 1.0** Date: 24:03:2014; first draft by **Delphine Boutry, CEA, France**  
**Version 1.1** Date: 14:10:2014; revision by **Simon Clavaguera, CEA, France**

#### 2.3.4.1 Scope and required operating conditions

Coatings from paints, varnishes and similar materials are often used outdoors or in indoor locations where they are exposed to solar radiation or to solar radiation behind glass for long periods. It is therefore very important to determine the effects of solar radiation, heat, moisture and other climatic stresses on the colour and other properties of polymers.

Therefore, it can be interesting and time-saving to perform artificial accelerated weathering or artificial accelerated irradiation exposures that use specific laboratory light sources in order to assess the effects of light, heat and moisture on the physical, chemical and optical properties of coatings.

The aim of this SOP is the development and implementation of aging / weathering tests for paints and coatings incorporating nanoparticles. To that purpose we will use the following instruments that are complying with ISO 11507 / ISO16474 and ISO 4892 respectively:

- Accelerated weathering tester (Q-UV from Q-LAB) that allows UV irradiation, heat and water spray. The irradiance spectrum is increased in the UV region to provide accelerated degradation of the samples.
- Xenon test chamber (Q-SUN from Q-LAB) that allows light irradiation, heat, moisture and water spray. The irradiance is close to the solar spectrum with enhanced energy.

Both instruments will also be used for artificial weathering of other products containing nanoparticles such as nanocomposites and the procedure will be adapted accordingly.

#### 2.3.4.2 Materials and equipment needed

##### ➤ **Materials**

In the case of paint materials, in order to represent commercial product, nanoparticles of interest could be TiO<sub>2</sub>, ZnO or SiO<sub>2</sub> for example.

For paints, the coating needs to be applied on test panels. It is really important to achieve a uniform coating to perform these tests. Different panels are available. Depending on the formulation, specific type of panel has to be selected:

- Steel (S-16) - Uniformly blanked from 20-gage auto body sheet steel and dull finished for good adhesion of the coating to the metal. 100 mm square with rounded corners and a 6.35 mm center hole.
- Wood (S-17) - Manufactured from grade A1, 6.35 mm (0.25 inches) birch plywood which has been sanded on both sides. 100 mm square with a 6.35 mm center hole.
- Aluminum (S-18) - Produced out of #19 gauges 5052 aluminum. 100 mm square with rounded corners and a 6.35 mm center hole.
- Glass (S-31) - Quality plate glass, approximately 3.15 mm thick. 100 mm square with a 6.35 mm center hole.

Size of samples: 10 cm x 10 cm with a thickness around 0.5 cm.

### ➤ Equipments

To perform aging / weathering experiments on paints or nanocomposites, the following material will be used:

- Accelerated weathering tester (Model Q-UV/Spray from Q-LAB)
- Xenon test chamber (Q-SUN, Model Xe-3)



Figure 10: Q-UV from Q-LAB, Accelerated weathering tester



Figure 11: Q-SUN from Q-LAB, Xenon test chamber

To study the effect of the surface modification induced by the two climatic testers, several types of characterizations can be performed using the following instruments to focus on the chemical modifications of the surface:

- X-ray Photoelectron Spectroscopy (XPS)
- Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR)
- Scanning Electron Microscopy with Energy Dispersive Spectrometer (SEM-EDS).

To study the leaching and to evaluate the subsequent emission to the environmental compartment, the waste water from the experiment will be analyzed using the following instruments:

- Dynamic light scattering (DLS, Zetasizer Nano ZSP+ from Malvern) will be used to characterize the hydrodynamic diameter distribution and the zeta potential.
- Field flow fractionation (FFF) coupled to a multi angle light scattering detector (MALS) and to an inductively coupled plasma-mass spectrometer (ICPMS) will be used to characterize the size distribution, the chemical composition and the concentration of the nanoparticles.

- Transmission electron microscopy (TEM Osiris) will also be used with or without a cryogenic mode to corroborate the information regarding the size distribution and the chemical composition of the particles and their state (primary particles, aggregates or agglomerates, particle bounded to chunks of matrix ...).

#### 2.3.4.3 Setup of experiments

The tests for paints and coating samples will follow the exposure cycles from NF EN ISO 16474-3, particularly Method C, cycle n°5:

- A first exposure in the Q-UV instrument of the samples to a dry atmosphere and to an irradiance of  $0.71 \text{ W/m}^2$  at 310 nm using the UVB-313 lamp at 50°C for 5 hours,
- A second exposure under water spray with the UV lamps off at 25°C for 1 hour
- Those two cycles are repeated one after the other over a total of 500h

#### ➤ Procedure for an experiment using the Q-SUN or Q-UV apparatuses:

- Put on protective equipment (gloves, glasses and laboratory coat)
- Clean the plate where samples will settle using wipes and deionized water
- Start a cleaning procedure (see below) and empty the drain water collector
- Fix the sample on the main plate and check if the correct side is oriented towards the lamps
- Close the door of the apparatus
- Turn on the equipment and program the weathering cycles to be applied (temperature, moisture, irradiance, water spray, time ...)
- Start the program
- Once the program ended, take the samples out and collect the drain water if needed
- Start a cleaning procedure (see below)
- Turn off the apparatus

#### ➤ Cleaning procedure:

- Check the irradiation chamber is empty
- Start the cleaning program (water spray for 24h, lamps off, room temperature)
- empty the drain water collector

The sanding procedure could be applied to artificially aged material in order to evaluate the influence of the aging / weathering on the release of nanoparticles from paints, coatings or composites.

### 2.3.5 Method for the evaluation of nanoparticle release rates for processes placed under fume cupboards and hoods

<b>Authors</b> (Authors who actively wrote the report)	<b>Emmanuel Belut, emmanuel.belut@inrs.fr</b>
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#### **Aim(s) or Objective(s) of SOP**

This SOP describes the implementation of a method for the evaluation of time-resolved nanoparticle release rate by operations placed under fume cupboards.

**Version 1.0** Date: 17:07:2014; first draft by **Emmanuel Belut, INRS, France**  
**Version 1.1** Date: 16:10:2014; revision by **Emmanuel Belut, INRS, France**

#### 2.3.5.1 Scope and required operating conditions

This procedure describes a method to collect the data necessary to measure indirectly the release rate of nanoaerosols generated by a polluting process placed in a fume cupboard (or in a similar ventilated enclosure). From these data, the source term of the polluting process is made available, which is essential for exposure modeling among others.

The underlying source estimation method relies on the construction of a transfer function between the source term and the concentration signal measured in the exhaust duct of the fume cupboard. In a first step, this transfer function is calibrated experimentally by using a controlled nanoparticle source (NaCl solution nebulizer) and measuring simultaneously the concentration signal in the exhaust duct. In a second step, the concentration signal obtained when the polluting process of interest operates is recorded. Starting from this concentration signal, the transfer function is inverted so as to reconstruct the source term of the process.

The underlying hypothesis is that the concentration signal convolves linearly with the emission rate of the process, which is only verified if the velocity field of the carrier flow remains stable throughout the experiment<sup>1</sup>, a corollary being that the studied process must little affect the airflows with respect to the calibration situation. This is facilitated by the strong mixing occurring naturally in the fume cupboard (turbulence and distribution plenum), assisted by a small mixing fan: the effect of the process on the global airflow becomes insignificant. Note that the transfer function must be recalibrated at each significant modification of the airflow in the fume cupboard, before trying to estimate the release rate of a polluting process.

The method provides time-resolved data. Note that if the flow rate of the fume cupboard is simultaneously recorded, an estimation of the amount of aerosol deposited on the surfaces of the fume cupboard is possible.

##### 2.3.5.1.1 Operating field

The method applies to processes placed in fume cupboards (or equivalent) emitting ultrafine or nano-sized particles (Chemical vapor deposition reactors, flame spray pyrolysis, weathering processes, lab grinders, spray drying, weighing or transferring of powders, cleaning...).

<sup>1</sup> And if the aerosol coagulation is negligible, which is verified in practice given the fast occurring dilution

An access to the exhaust duct of the fume cupboard is mandatory. It is also necessary to place several devices in the fume cupboard together with the existing process. The compatibility of these requirements with the process has to be considered beforehand.

An example of suitable process and of the required access to the exhaust duct are depicted in Figure 12 and Figure 13.

#### 2.3.5.1.2 *Operating conditions*

The fume cupboard must be operated with the same flow-rate all along the process, which means that a constant height of the sash aperture must be maintained and that the pressure drop<sup>2</sup> of the fume cupboard must be monitored during the whole procedure.

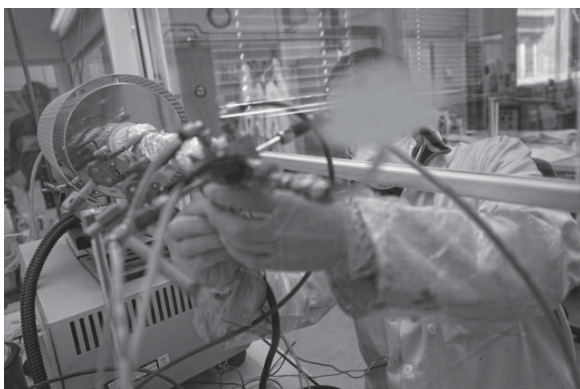


Figure 12: Example of suitable case study: CVD reactor in a fume cupboard



Figure 13: Required accesses to the exhaust duct

#### 2.3.5.2 *Material and Equipment needed*

##### 2.3.5.2.1 *Reference nanoparticle source*

The reference nanoparticle source consists of several parts:

- An aerosol generator based on solution nebulisation : PALAS AGF 10.0 or PALAS AGK 2000 (Figure 14);
- A reservoir filled with a solution of NaCl (0.1% mass) in demineralised, de-ionised water ;
- A filtered and oil free supply of dry compressed air (Figure 15);
- A mass flow controller for the supplied air (Figure 16):
  - o Range 0-50  $\text{NL}\cdot\text{min}^{-1}$  , accuracy 0.6% or lower;
  - o PC-controlled with programmable set-point;

<sup>2</sup> Or any other measurement highlighting the constancy of the airflow



- An ejector with a side sampling junction to measure the properties of the emitted aerosol (Figure 18). It consists of a metal pipe (inner diameter 17mm, length 10cm) onto which a sampling junction is welded (inner diameter 5.5mm);

The source is associated with a small mixing fan (Figure 17: PC fan, 7 blades, 9cm in diameter, operated at 1900rpm)



Figure 14: PALAS AGF 10 nebuliser and NaCl solution

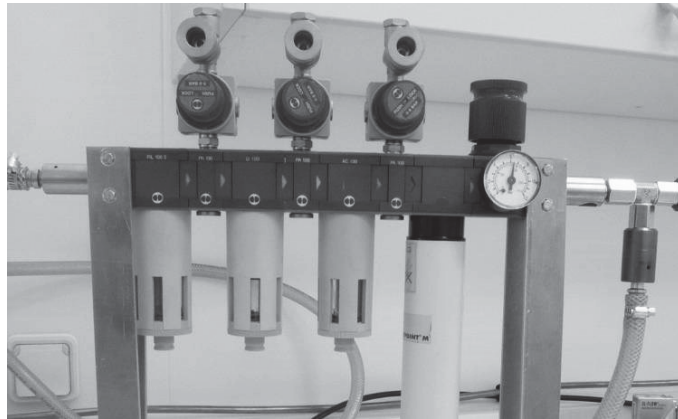


Figure 15: Dry filtered pressurized air supply

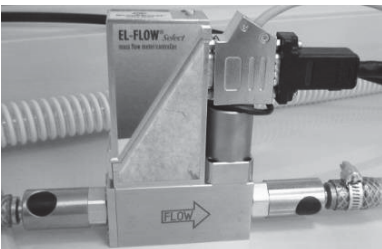


Figure 16: Mass flow regulator



Figure 17: small mixing fan



Figure 18: Ejector with side sampling junction

### 2.3.5.2.2 Aerosol characterization devices

Aerosol measurements are performed using a Condensation Particle Counter - CPC (GRIMM 5403). It detects airborne particles down to 4.5 nm at a flow rate of  $0.3 \text{ l}\cdot\text{min}^{-1}$ , over a concentration range between 1 and  $10^7$  particles/ $\text{cm}^3$ . It provides measurements at a frequency of 1Hz with a response time of 3.9s. The particle concentration accuracy is of 5% if the particle concentration is below  $1.4 \times 10^4 \text{ cm}^{-3}$  (single particle counting mode).

The CPC is associated with an aerosol diluter PALAS VKL 100 which allows diluting the samples before measuring their concentration.

Samples are realized through conductive sampling pipes so as to avoid deposition in sampling lines. A 3 way ball valve (conductive metal) is used to switch between the sampling points. It presents no constriction in diameter with respect to sampling pipes to prevent deposition. The inner diameter of sampling lines is of 5.5mm, the residence time of aerosols in sampling lines is then of 4.8s per meter of pipe, for CPC measurements.

### **2.3.5.2.3 Ventilation characterization devices**

The pressure drop of the fume cupboard is monitored using a micromanometer TSI DPCALC 8710. Any other micromanometer presenting a repeatability lower than 1Pa could be used. The micromanometer must offer data logging capabilities with a logging interval set to 10s or lower.

#### **2.3.5.2.3.1 Optional: air flow rate measurements**

Optionally, the air flow rate of the fume cupboard can be measured using either a pressure differential device such as described in ISO 5167 standard, or using tracing gas dilution (standard NF X 10-141), or any other reference method offering an accuracy below or equal to 5%.

### **2.3.5.2.4 Other equipment required**

- 3 antistatic aerosol sampling pipes (inner diameter 5.5 mm or lower) of suitable length;
- Thermometer and barometer to report ambient conditions;
- Aluminum tape for ventilation ducts sealing.

### **2.3.5.3 Setup of experiments**

The experimental setup to perform the source estimation is depicted on Figure 19.

#### **2.3.5.3.1 Position of probes and devices**

- The static pressure probe to monitor the pressure drop of the fume cupboard should be placed at least one duct diameter downstream of the junction between the exhaust pipe and the fume cupboard;
- an aerosol sampling pipe is placed in the exhaust duct of the fume cupboard. It should be placed as much downstream as possible to ensure proper mixing. Its tip should be placed in the middle of the exhaust pipe section;
- the nebulizer is placed in the fume cupboard so as not to prevent the studied process from operating;
- the ejector is adjusted to the tip of the nebulizer;
- the mixing fan is placed in the fume cupboard so as to blow sideways towards the nebulizer (rotation axis parallel to the sash plane). It is located so that its rotation axis is aligned with the tip of the ejector. The distance from the fan to the tip of the ejector is 20cm;

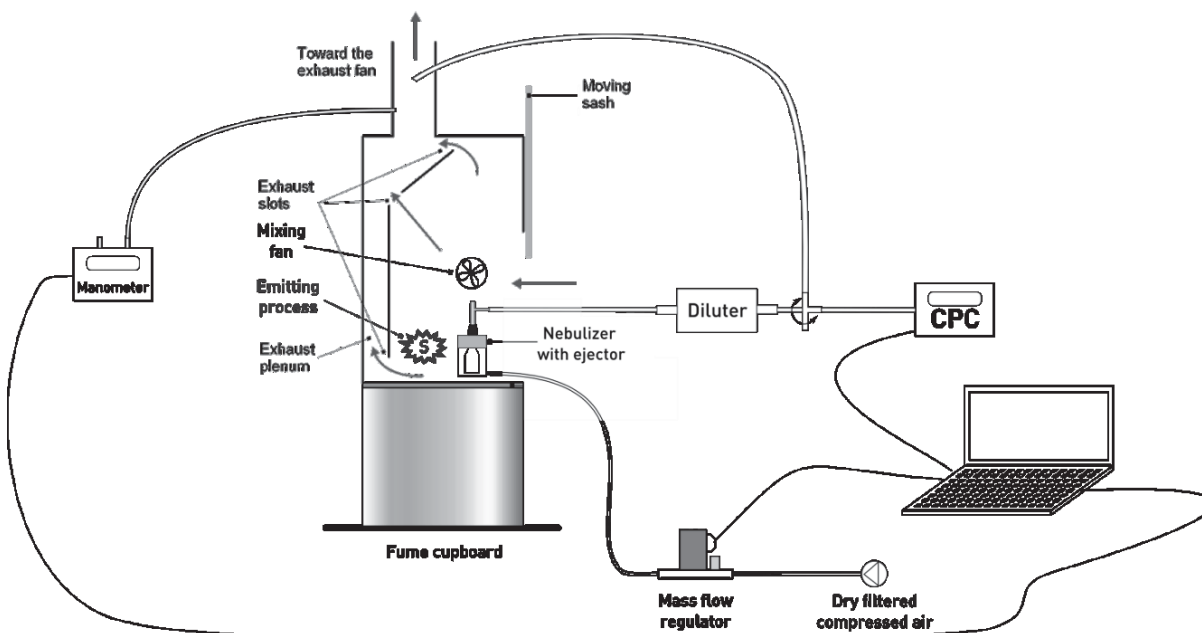


Figure 19: Diagram of the experimental setup

### 2.3.5.3.2 Setup

- Note the sash aperture used when the studied process is operating normally;
- Place the nebulizer, the ejector and the mixing fan in the fume cupboard as stated previously. Plug the mixing fan to a power supply;
- Plug the mass flow regulator to the feeding compressed air source and to the nebulizer. Open the tap of the nebulizer at its maximum so that it is controlled by the mass-flow regulator;
- Access the exhaust duct of the fume cupboard:
  - o plug the tip of a pressure probing pipe in the duct (make a hole if necessary). Connect its other end to the manometer;
  - o plug a first (antistatic) aerosol sampling pipe in the exhaust duct as described above (make a hole if necessary). Connect the other end to the 3-ways ball valve.
- Plug a second aerosol sampling pipe to the sampling junction of the ejector, connect the other end to the diluter, then connect the diluter outlet to the 3-ways ball valve;
- Connect the last branch of the 3-ways ball valve to the CPC;
- Connect the control cables of the CPC, of the mass-flow regulator and of the manometer to a laptop computer.

### 2.3.5.3.3 Procedure for an experiment

#### ➤ Step 1: startup

- If it is turned off, switch on the ventilation of the fume cupboard;
- Place the sash aperture at its working position, as stated previously;
- Make sure that the process of interest is warmed up and ready to start on demand;
- Start the mixing fan;
- Start monitoring the pressure drop of the fume cupboard and wait 10min or until it stabilizes within 5% of its mean value;
- Let the CPC and other devices warm up meanwhile;
- Start the diluter;
- Note ambient temperature and atmospheric pressure.

➤ **Step 2: reference source calibration**

The second step consists in calibrating the reference source:

- Switch the 3-ways ball valve so as to sample at the exhaust of the reference source directly (sampling junction of the ejector);
- From the laptop, schedule a gate signal for the mass-flow regulator: the period should be of 180s, the amplitude of the gates of  $40\text{NI}\cdot\text{min}^{-1}$  (air), the duration of the gates of 120s, and the time lapse between gates of 60s. The signal should begin with one of these 60s time lapse.
- Start recording the concentration at the reference source with the CPC (at 1Hz);
- Simultaneously start sending the gate signal to the mass-flow regulator (record the response);
- Record the concentration with the CPC for 5 gate periods (900s – 15min).
- Check the reproducibility of the concentration plateau from one gate to another.

➤ **Step 3: establishing the source/response relationship**

- Switch the 3-ways ball valve so as to sample the fume cupboard exhaust;
- Make sure the mixing fan is still in operation;
- From the laptop, schedule a gate signal for the mass-flow regulator: the period should be of 240s, the amplitude of the gates of  $40\text{NI}\cdot\text{min}^{-1}$  (air), the duration of the gates of 120s, and the time lapse between gates of 120s. The signal should begin with one of these 120s time lapse.
- Start recording the concentration at the fume cupboard exhaust with the CPC (at 1Hz);
- Simultaneously start sending the gate signal to the mass-flow regulator and record the response;
- Record the concentration with the CPC (at 1Hz) for 10 gate periods (2400s – 40min).
- Check and report the stability of the fume cupboard pressure drop meanwhile.

➤ **Step 4: recording the response of the process of interest**

- Start recording the concentration at the fume cupboard exhaust with the CPC (at 1Hz);
- Start the process of interest in the fume cupboard, making sure that the mixing fan is still in operation;
- Keep recording the concentration at the fume cupboard exhaust until 120s after the process is finished;
- Check and report the stability of the fume cupboard pressure drop during the whole process.

➤ **Optional step 4: measuring the air volume flow rate of the fume cupboard**

Measure the volume flow rate of the fume cupboard for the sash aperture and pressure drop used for the experiment:

- Periodically during the whole experiment if possible (if using for instance a pressure differential device as flow meter);
- Once before step 2 and after step 3 otherwise (if using for instance tracing techniques).

#### 2.3.5.3.4 *Uninstalling after the experiment*

- Seal the holes made in the duct properly using aluminum tape.

#### 2.3.5.3.5 *Reporting*

The following data must be reported after the experiment:

- Ambient temperature and atmospheric pressure;
- Height of the sash aperture in working conditions;
- Reference source calibration data obtained in step 2:
  - o Time variation of the mass flow regulator set point;
  - o Corresponding concentration signal measured at the reference source by the CPC;
- Source/response data obtained in step 3:
  - o Time variation of the mass flow regulator set point;
  - o Corresponding concentration signal measured at the fume cupboard exhaust by the CPC;
- Concentration data of the studied process obtained in step 4:
  - o concentration signal measured at the fume cupboard exhaust by the CPC when the process is operating;
- Documented pressure drop of the fume cupboard throughout the experiment;
- If performed, measurement of air flow rates of the fume cupboard.

Note that concentration and mass-flow regulator data must be given with their time abscissa, in ascii or excel format.

### 2.3.6 Method to generate controlled aerosol from nanomaterials using the shaker method

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#### **Aim(s) or Objective(s) of SOP**

This SOP describes a method to generate controlled aerosol from nanomaterials (carbon nanotubes and fibers) using the Shaker-Method.

**Version 1.0 Date: 25:08:2014; first draft by Volker Bachmann, BAuA, Germany**

#### 2.3.6.1 Purpose and scope of application

The controlled aerosol generation from dry/powder nanomaterials (NM) using the Shaker Method is used to characterize nanomaterials (in particular CNT/CNF – carbon nano tubes and fibers) in a test chamber for their materials properties (dustiness behavior) or to compare measurement instruments. The method is to be set up as closed System. This Standard Operating Procedure (SOP) is not valid for granular biopersistant particle (GBP).

#### 2.3.6.2 Jurisdiction

The SOP “Controlled Aerosol generation from Nanomaterials using the Shaker-Method“ applies to the Dust and Nano Laboratory at the BAuA location Berlin. The laboratory working instructions have to be followed.

#### 2.3.6.3 Process description

##### ➤ Short description of the method

As vibrating system the TIRA-Shaker (100 N) is used (Fig. 1). The Shaker is controlled by a function generator and a power amplifier. A sample holder is stiffly connected to the Shaker. It is made of anodized aluminum and contains a glass frit on which the nanomaterial is placed for testing. With the constant unidirectional oscillation of the Shakers and the transport of air through the glass frit nanomaterials and their agglomerates are being transported with the air stream to reach the testing chamber. Within the testing chamber measurement systems like the Thermal Precipitator (TP), SMPS (Scanning Mobility Particle Sizer), CPC (Condensation Particle Counter) or the sampling head for sampling on gold metalized filters can be mounted.

Using Hepa-Filters ubiquitous occurring ultrafine aerosol are kept from the sample holder as they would interfere with the experimental setup.

A schematic drawing of the swing bed aerosol generator with the testing chamber is shown in Figure 20 and an example for an experimental setup is shown in Figure 21.

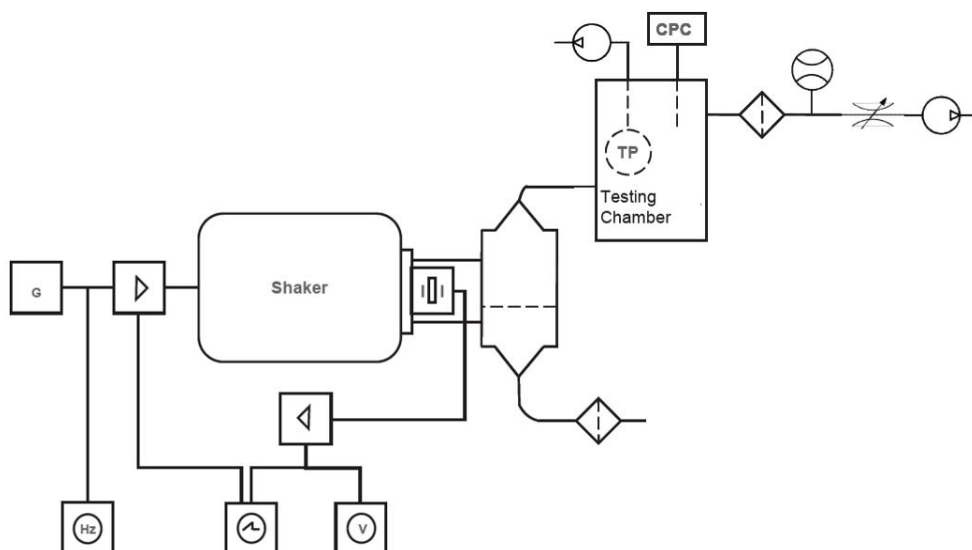







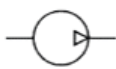




Figure 20: Schematic drawing of the swing bed aerosol generator with the testing chamber



Figure 21: Experimental setup

➤ **Hardware and auxiliaries**

	Oscilloscope		Accelerometer
	Voltmeter		Flow meter
	Frequency counter		Generator
	Hepa filter		Pump
	Flow controller		Amplifier

➤ **Chemicals**

Nanomaterials according to the design of experiments.

➤ **Experiment preparation**

The experimental setup is taking place according to Fig. 1 and 2. The experimental setup has to be assembled as a closed system. Especially the leak tightness of the system has to be assured and the cleaning of the outgoing air with a Hepa filter for the setup as well as for the measurement instruments.

According to the design of experiment the Shaker-parameter are to be set and surveyed with the system integrated measurement instruments.

▪ **Dosing of the sample material (NM) in the glove box**

- The storage of experiment relevant nanomaterials as well as the glass frits for the different NM has to be done in the glove box.
- The necessary amount of nano scaled sample material is weight in inside the glove box and carefully transferred to the glass frit.
- For this the glass frit is already positioned inside the open sample carrier which itself is mounted in a clamping system.
- The sample carrier is closed and tightened carefully and the on top opening is firmly closed with a plug. At the bottom opening of the sample carrier a Hepa filter is permanently installed. It stays fixed to the sample carrier all through the running experiment.
- The firmly closed sample carrier is removed from the glove box using the loadlock.

▪ **Mounting the measurement instruments within the testing chamber**

The controlled release of dust is amongst others used to characterize nanomaterials or to validate measurement instruments with NM. Different types of measurement systems can be applied.



- The SMPS or CPC are placed as close as possible to the testing chamber to allow for a short as possible connection to the measurement system.
- The sample inlet of SMPS and CPC are connected to the sample drawing lance – positioned in the top lid of the testing chamber – using anti-static piping (keep connection as short as possible).
- The thermal precipitator-head or the FAP-Filter head are mounted inside the testing chamber the respective aspirators in close proximity outside the chamber. The connection through the chamber lid is realized through the sample drawing lance.
- After all built-in components are in place the chamber lid is tightly closed (either with adequate tape or with screws).

- **Leakage test of the sample holder and installment in the experimental setup**

- The leakage test is conducted inside the chemical fume hood. The bottom opening is sealed with a plug and a defined overpressure controlled with a pressure meter is applied (100 mm Hg = 133 mbar). For a time of 5 minutes the pressure has to be held in order to pass the leakage test.
- Using a pipe clamp the sample holder is fixed at the Shaker. The permanent installed Hepa filter stays at the bottom opening of the sample holder. After loosening the upper plug the top sample holder opening is instantly connected to the test chamber. The connection is tested for their durability.

- **Leakage test of the entire experimental setup**

- The leakage test is conducted after the installment of the sample holder and with the test chamber duly closed.
- The leakage test of the entire experimental setup is conducted using a condensation particle counter (CPC 3007) inside the test chamber (zero measurement).
- Using an auxiliary pump the remaining aerosol in the experimental setup is evacuated. The CPC shows the particle number concentration. The setup is considered leak-proof once the zero concentration inside the test chamber is hold for a time of 5 minutes.
- Afterwards measurements in the closed system can be started.

- **Conducting the experiments**

- According to the experimental design the measurements using the Shaker method are conducted.

- **End of experiment and disposal of the sample material**

- After finishing the measurements the Shaker and the measurement instruments are turned off. The connection between sample holder and test chamber is discontinued. The sample holder is closed tightly using a plug. At the entrance of the test chamber as Hepa filter is installed.
- The TP-Head and other measurement instruments connected to the setup via the probe lances are disconnected from the aspirator. The probe lances are firmly seal with a plug. Afterwards the auxiliary pump is turned on to clean the setup for at least 20 minute with an volume rate of about 0,7 l/min. Afterwards the setup should be free of NM.
- The test chamber can now be opened. Additionally to the personal safety equipment mentioned in chapter 3.7 a P3 level respirator mask has to be worn while doing this task. After opening the test chamber it is cleaned immediately using a K1 vacuum cleaner (Nilfisk) which is provided in the laboratory.

- Now the sampling devices inside the test chamber (TP-Head or FAP-System) can be removed. The inside of the test chamber and upon removal of the probes from the sampling devices the devices themselves are cleaned using wet alcohol soaked cloths which are disposed in a designated container for NM contaminated waste.
- The firmly closed sample holder is removed from the Shaker and stored in a holding clamp inside the glove box.
- The residual material is removed from the glass frit into an intermediate waste container inside the glove box. The final disposal is regulated in the laboratory working instructions.
- Used glass frits are marked with the NM used and stored inside the glove box. It can be reused once the respective NM is used in future experiments.

#### ➤ **Personal Safety Equipment**

- During the handling of NM chemical safety gloves made of nitrile rubber (thickness  $\geq 0,35$  mm) following DIN EN 374-3 have to be used. After contamination professional disposal in waste containers for NM has to occur.
- As eye protection safety goggles with integrated lateral protection have to be used.
- The laboratory coat serves general hygiene measures and has to be changed immediately following contamination.
- While opening the test chamber after the end of an experiment the wearing of a P3 level respirator mask is mandatory.
- The behaviour in the event of malfunction is regulated in the laboratory working instructions. Additional personal safety equipment (FFP 2, protective clothing for one-time use) has to be worn.

#### ➤ **Quality assurance**

- The leakage test of the experimental setup is conducted prior to each measurement.
- The Shaker parameters are monitored and documented while the experiment is running.
- The calibration and setup of the measurement instruments are described in the respective instrument SOP.

#### **2.3.6.4 Documentation**

- The documentation of the experimental parameters has to be done in the laboratory journal. To be documented are the Shaker parameters and additionally the room humidity and temperature as well as unexpected incidents.
- The sample signature has to follow the procedure "Exposure assessment for epidemiological studies"
- The measurement protocols are to be documented and filed in the respective project folder.

#### **2.3.6.5 Further applicable documents**

- SOP "Measurement of number concentrations of nanoparticle using a SMPS"
- Operating Procedure "Measurement of number and mass concentration using an aerosol spectrometer"
- Operating Procedure "Workplace measurement using the PGP-FAP"
- Operating Instructions "Controlled dust packing of nanomaterials"
- Hazard analysis for the work at the Dust and Nano laboratory
- Procedure "Exposure assessment for epidemiological studies"
- User manual of the used measurement and control devices (Shaker, Amplifier, Frequency generator etc.)

### 2.3.7 Method to generate controlled aerosol from nanomaterials using the shaker method

<b>Authors</b> (Authors who actively wrote the report)	<b>Volker Bachmann, bachmann.volker@baua.bund.de</b> <b>Asmus Meyer-Plath, Meyer-Plath.Asmus@baua.bund.de</b>
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#### **Aim(s) or Objective(s) of SOP**

This SOP describes a method to generate controlled aerosol from nanomaterials (granular biopersistent particles) using the Shaker-Method.

**Version 1.0 Date: 25:08:2014; first draft by Volker Bachmann, BAuA, Germany**

#### 2.3.7.1 Purpose and scope of application

The controlled aerosol generation from dry/powder nanomaterials (NM) using the Shaker Method is used to characterize nanomaterials (in the sense of GBP – granular biopersistent particles) in a test chamber for their materials properties (dustiness behavior) or to compare measurement instruments. The method is to be set up as closed System. This Standard Operating Procedure (SOP) is not valid for fibrous nanomaterials.

#### 2.3.7.2 Jurisdiction

The SOP “Controlled Aerosol generation from Nanomaterials (esp. GBP) using the Shaker-Method“ applies to the Dust and Nano Laboratory at the BAuA location

#### 2.3.7.3 Process description

##### ➤ Short description of the method

As vibrating system the TIRA-Shaker (100 N) is used (Fig. 1). The Shaker is controlled by a function generator and a power amplifier.

A sample holder is stiffly connected to the Shaker. It is made of anodized aluminum and contains a glass frit on which the nanomaterial is placed for testing. With the constant unidirectional oscillation of the Shakers and the transport of air through the glass frit nanomaterials and their agglomerates are being transported with the air stream to reach the testing chamber. Within the testing chamber measurement systems like the Thermal Precipitator (TP), SMPS (Scanning Mobility Particle Sizer), CPC (Condensation Particle Counter) or the sampling head for sampling on gold metalized filters can be mounted.

Using Hepa Filters ubiquitous occurring ultrafine aerosol are kept from the sample holder as they would interfere with the experimental setup.

A schematic drawing of the swing bed aerosol generator with the testing chamber is shown in Figure 22 and an example for an experimental setup is shown in Figure 23.

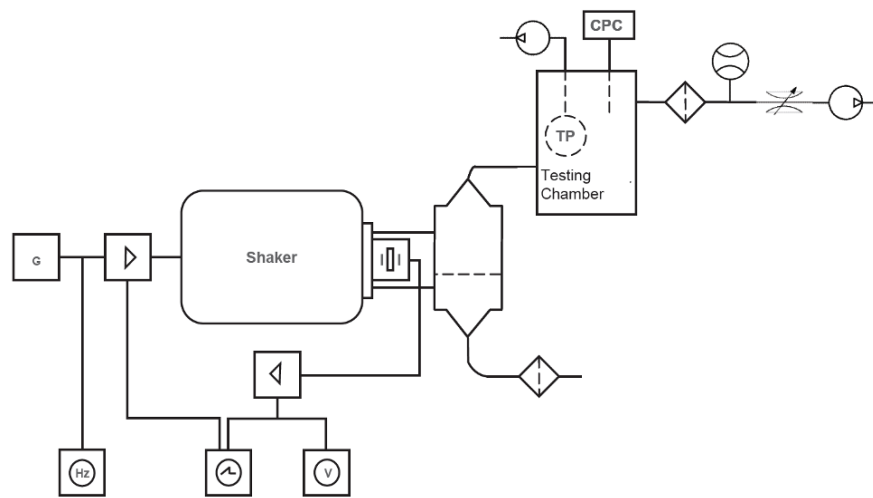












Figure 22: Schematic drawing of the swing bed aerosol generator with the testing chamber



Figure 23: Experimental setup

➤ **Hardware and auxillaries**

	Oscilloscope		Accelerometer
	Voltmeter		Flow meter
	Frequency counter		Generator
	Hepa filter		Pump
	Flow controller		Amplifier

➤ **Chemicals**

Nanomaterials according to the design of experiments.

➤ **Experiment preparation**

The experimental setup is taking place according to Fig. 1 and 2. The experimental setup has to be assembled as a closed system. Especially the leak tightness of the system has to be assured and the cleaning of the outgoing air with a Hepa filter for the setup as well as for the measurement instruments.

According to the design of experiment the Shaker-parameter are to be set and surveyed with the system integrated measurement instruments.

▪ **Dosing of the sample material (NM) in the glove box**

- The storage of experiment relevant nanomaterials as well as the glass frits for the different NM has to be done in the chemicals fume hood.
- The necessary amount of nano scaled sample material is weight in inside the chemical fume hood and carefully transferred to the glass frit.
- For this the glass frit is already positioned inside the open sample carrier which itself is mounted in a clamping system.
- The sample carrier is closed and tightened carefully and the on top opening is firmly closed with a plug. At the bottom opening of the sample carrier a Hepa filter is permanently installed. It stays fixed to the sample carrier all through the running experiment.

▪ **Mounting the measurement instruments within the testing chamber**

The controlled release of dust is amongst others used to characterize nanomaterials or to validate measurement instruments with NM. Different types of measurement systems can be applied.

- The SMPS or CPC are placed as close as possible to the testing chamber to allow for a short as possible connection to the measurement system.

- The sample inlet of SMPS and CPC are connected to the sample drawing lance – positioned in the top lid of the testing chamber – using anti-static piping (keep connection as short as possible).
- The thermal precipitator-head or the FAP-Filter head are mounted inside the testing chamber the respective aspirators in close proximity outside the chamber. The connection through the chamber lid is realized through the sample drawing lance.
- After all built-in components are in place the chamber lid is tightly closed (either with adequate tape or with screws).

- **Leakage test of the sample holder and installment in the experimental setup**

- The leakage test is conducted inside the chemical fume hood. The bottom opening is sealed with a plug and a defined overpressure controlled with a pressure meter is applied (100 mm Hg = 133 mbar). For a time of 5 minutes the pressure has to be held in order to pass the leakage test.
- Using a pipe clamp the sample holder is fixed at the Shaker. The permanent installed Hepa filter stays at the bottom opening of the sample holder. After loosening the upper plug the top sample holder opening is instantly connected to the test chamber. The connection is tested for their durability.

- **Leakage test of the entire experimental setup**

- The leakage test is conducted after the installment of the sample holder and with the test chamber duly closed.
- The leakage test of the entire experimental setup is conducted using a condensation particle counter (CPC 3007) inside the test chamber (zero measurement).
- Using an auxiliary pump the remaining aerosol in the experimental setup is evacuated. The CPC shows the particle number concentration. The setup is considered leak-proof once the zero concentration inside the test chamber is hold for a time of 5 minutes.
- Afterwards measurements in the closed system can be started.

- **Conducting the experiments**

- According to the experimental design the measurements using the Shaker method are conducted.

- **End of experiment and disposal of the sample material**

- After finishing the measurements the Shaker and the measurement instruments are turned off. The connection between sample holder and test chamber is discontinued. The sample holder is closed tightly using a plug. At the entrance of the test chamber as Hepa filter is installed.
- The TP-Head and other measurement instruments connected to the setup via the probe lances are disconnected from the aspirator. The probe lances are firmly seal with a plug. Afterwards the auxiliary pump is turned on to clean the setup for at least 20 minute with an volume rate of about 0,7 l/min. Afterwards the setup should be free of NM.
- The test chamber can now be opened. Additionally to the personal safety equipment mentioned in chapter 3.7 a P3 level respirator mask has to be worn while doing this task. After opening the test chamber it is cleaned immediately using a K1 vacuum cleaner (Nilfisk) which is provided in the laboratory.
- Now the sampling devices inside the test chamber (TP-Head or FAP-System) can be removed. The inside of the test chamber and upon removal of the probes from the sampling devices the devices themselves are cleaned using wet alcohol soaked cloths which are disposed in a designated container for NM contaminated waste.

- The firmly closed sample holder is removed from the Shaker and stored in a holding clamp inside the chemical fume hood.
- The residual material is removed from the glass frit into an intermediate waste container. The latter is stored inside the chemicals cabinet. The final disposal is regulated in the laboratory working instructions.
- Used glass frits are marked with the NM used and stored inside the chemical fume hood. It can be reused once the respective NM is used in future experiments.

#### ➤ **Personal Safety Equipment**

- During the handling of NM chemical safety gloves made of nitrile rubber (thickness  $\geq 0,35$  mm) following DIN EN 374-3 have to be used. After contamination professional disposal in waste containers for NM has to occur.
- As eye protection safety goggles with integrated lateral protection have to be used.
- The laboratory coat serves general hygiene measures and has to be changed immediately following contamination.
- While opening the test chamber after the end of an experiment the wearing of a P3 level respirator mask is mandatory.
- The behaviour in the event of malfunction is regulated in the laboratory working instructions. Additional personal safety equipment (FFP 2, protective clothing for one-time use) has to be worn.

#### ➤ **Quality assurance**

- The leakage test of the experimental setup is conducted prior to each measurement.
- The Shaker parameters are monitored and documented while the experiment is running.
- The calibration and setup of the measurement instruments are described in the respective instrument SOP.
- For the testing of fibrous nanomaterials, e.g. CNT/CNF the SOP "Controlled Aerosol generation from Nanomaterials using the Shaker-Method" is to be used.

#### **2.3.7.4 Documentation**

- The documentation of the experimental parameters has to be done in the laboratory journal. To be documented are the Shaker parameters and additionally the room humidity and temperature as well as unexpected incidents.
- The sample signature has to follow the procedure "Exposure assessment for epidemiological studies"
- The measurement protocols are to be documented and filed in the respective project folder.

#### **2.3.7.5 Further applicable documents**

- SOP "Measurement of number concentrations of nanoparticle using a SMPS"
- Operating Procedure "Measurement of number and mass concentration using an aerosol spectrometer"
- Operating Procedure "Workplace measurement using the PGP-FAP"
- Operating Instructions "Controlled dust packing of nanomaterials"
- Hazard analysis for the work at the Dust and Nano laboratory
- Procedure "Exposure assessment for epidemiological studies"
- User manual of the used measurement and control devices (Shaker, Amplifier, Frequency generator etc.)
- SOP "Controlled Aerosol generation from Nanomaterials using the Shaker-Method"

### 2.3.8 Small rotating drum (SD) method

<b>Authors</b> (Authors who actively wrote the report)	<b>Marcus Levin</b> <b>Ismo K Koponen</b> <b>Keld Alstrup Jensen, kaj@arbejdsmiljoforskning.dk</b>
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#### Aim(s) or Objective(s) of SOP

This SOP describes an agitation method to test dustiness: small rotating drum (SD) method.

**Version 1.0 Date: 12:01:2015; first draft by Keld Astrup Jensen, NRCWE, Denmark**

#### 2.3.8.1 Purpose and scope of application

The small rotating drum method described below is used to characterize nanomaterial powders in order to determine their dustiness indexes. The small rotating drum (Figure 24) was designed as a downscaled version of the EN 15051 rotating drum while maintaining important test parameters. This enabled testing of smaller material amounts (~6g).

#### 2.3.8.2 Description of the method

The drum consists of a cylindrical part [internal diameter (i.d.) 16.3 cm, length 23.0 cm, volume 4.80 l] with a truncated cone at each end (half angle 45°, length 6.3 cm, volume 1.13 l). The total volume of the drum is 5.93 l. The drum was made of stainless steel and all inside surfaces were polished to  $450 \pm 50$  gloss units to minimize surface adhesion and to facilitate cleaning. The drum was electrically grounded as prescribed by EN 15051. The drum contains three lifter vanes (2 x 22.5 cm). In EN 15051, a 1-min rotation at 4 rpm and eight lifter vanes are prescribed. Therefore, the present drum was operated at 11 rpm to obtain the same number of powder parcels falling per minute as in the EN 15051 test (Schneider and Jensen, 2008). The inlet air to the drum was controlled at 50 % RH and HEPA-filtered to ensure no particle background.



Figure 24: Photograph showing the high-gloss polished inside of the dustiness drum. Also note the three lifter vanes marked a, b, and c at each 120° in the drum.

In the applied set-up, respirable dust is collected by a GK2.69 respirable dust sampler at 4.2 lpm (BGI, UK) and dust particle size-distributions are measured using the Fast Mobility Particle Sizer (FMPS 3091, TSI), with a range of 5.6 to 560 nm, and the Aerodynamic Particle Sizer (APS 3321, TSI) with a range of 0.5 to 20  $\mu\text{m}$  (Figure 25). It is important to note that these two instruments provide a size distribution which is expressed for the FMPS in electric mobility equivalent diameter,



whereas for the APS, it is the equivalent aerodynamic diameter that is obtained. A GRIMM CPC may also be connected for simultaneous number-concentration measurements.

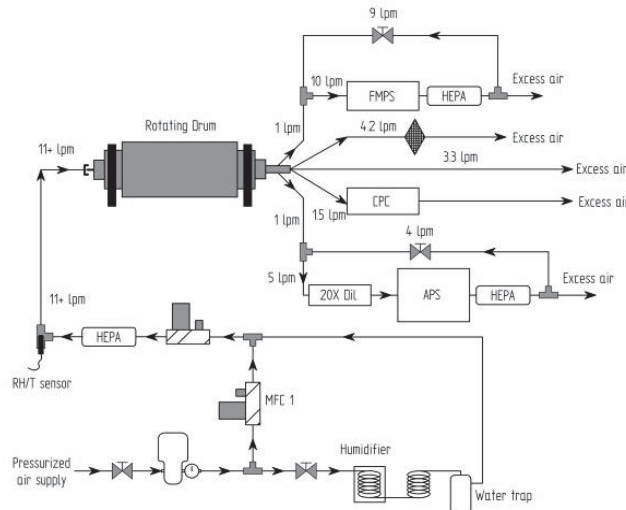


Figure 25: Small rotating drum setup at NRCWE in the standard set-up for sampling respirable dust contemporaneously with online size-distribution analyses by FMPS, APS and number concentration by CPC.

The dustiness test is conducted in triplicates for each powder preceded by a so-called saturation run completed to coat all inner surfaces of the system with dust. The saturation test is performed using 2 grams of powder and rotation for 60 seconds. Then, the actual triplicate tests are completed using 6 grams of test material per run. After each run the drum is emptied by pouring out the residual powder and gently tapping the drum three times with a rubber hammer. When loading the powder in the drum, it is carefully placed centrally in the drum on the upwards moving side of three inner lifter vanes placed at bottom position. Then the drum is sealed followed by 60 seconds of background measurements to ensure a particle free test atmosphere. The experiment is then initiated by rotating the drum for 60 seconds during which particles are emitted and led through the airflow to the sampling train. After the drum is stopped, measurements and sampling are continued for additional 120 sec to catch the remaining airborne particles in the dust cloud. Thus, the total time during which the measurement is made is 180 s. This then completed the rotational test. The drum and sampling lines are thoroughly cleaned between each powder type using a HEPA-filter vacuum cleaner designed for asbestos cleaning and wet-wiping. Then the drum is let to air-dry before the next powder could be tested.

The mass of collected respirable dust is determined after conditioning the filters and controls in NRCWE weighing room (22°C; 50 %RH) using a Sartorius microbalance (Type R162 P; Sartorius GmbH, Göttingen, Germany). The mass is used to categorize the dustiness levels of the powders according to EN15051. Calculations of Dustiness Indexes,  $DI_{mass}$ , are done according to:

$$DI_{mass} = \frac{Q_{drum} \cdot m_{filter}}{Q_{cyclone} \cdot m_{drum}} \quad \text{Eq. 1}$$

where  $Q_{drum}$  and  $Q_{cyclone}$  is the flows through the drum and cyclone respectively,  $m_{filter}$  is the blind-filter corrected filter mass in mg and  $m_{drum}$  is the powder mass loaded into the drum in kg.

In addition to the mass-based dustiness index, indexes for the total number of generated particles per mg of material during the 60 seconds of rotation and the 120 second directly follow are calculated as:

$$DI_{Number} = \frac{Q_{drum}}{m_{drum}} \cdot \sum_{t=0}^{180s} N_t^{cpc} \quad \text{Eq. 2}$$

where  $Q_{drum}$  is the flow through the drum in  $\text{cm}^3/\text{s}$ ,  $m_{drum}$  is the powder mass loaded into the drum in mg and  $N^{cpc}$  is the CPC count in particles/ $\text{cm}^3$ . Number size distributions are calculated as the summed up numbers over the 180 sec as measured by FMPS and APS.

### 2.3.9 Vortex Shaker(VS) method

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#### Aim(s) or Objective(s) of SOP

This SOP describes an agitation method to test dustiness: vortex shaker (VS) method.

**Version 1.0 Date: 12:01:2015; first draft by Olivier Witschger, INRS, France**

#### 2.3.9.1 Purpose and scope of application

The vortex shaker method described below is used to characterize nanomaterial powders in order to determine their dustiness indexes.

#### 2.3.9.2 Process description

The vortex shaker method (VS) consists of a centrifuge stainless tube agitated by a vortex in which the test powdered material is placed together with 100 µm diameter bronze beads. These are used to help the de-agglomeration of powders. HEPA filtered air, controlled at 50% RH, pass through the tube in order to transfer the released aerosol to the sampling and measurement section. The protocol developed for the experiments performed within this project used two different versions of the sampling and measurement section.

Tests are conducted with VS method using approximately 0.5 ml powder, which is placed in the sample vial together with 5 g bronze beads (100 µm), used to agitate and de-agglomerate the powder. The sample is allowed conditioning in the 50% RH before the shaker for a powder agitation period of 3600 s (60 min).

The first version (Figure 26) is devoted for real-time measurement using ELPI™ Classic (10 Lpm, Dekati) for size distributions according to the equivalent aerodynamic diameter and CPC (Model 3786 UWPCP, TSI) for number concentrations. This version is also devoted for collecting airborne particles for subsequent electron microscopy (EM) observations (see Figure 31). The dustiness test is conducted in triplicates for each nanomaterial sample.

The results of the tests performed with this first version of the VS method leads to the determination of:

- Dustiness indices expressed as the total number of particles emitted (based on data from CPC).
- Particle size-distribution of the aerosol (based on data from ELPI™ Classic in its standard configuration).

The CPC used is the Model 3785 Water-based Condensation Particle Counter (TSI, USA). This CPC detects particles from 5 to >3000 nm. It provides a wide, dynamic, particle-concentration range, an essential characteristic for the tests considered. Featuring a single-particle-counting mode with continuous, live-time coincidence correction and a photometric mode, the CPC measures particle number concentrations up to 10<sup>7</sup> particles/cm<sup>3</sup> with high accuracy.

ELPI™ (Electrical Low Pressure Impactor) is an instrument to measure airborne particle size distribution and concentration in real-time. It operates in the size range of 7 nm – 10 µm in its standard configuration. Because of its wide particle size range and rapid response (< 5 s), the ELPI™ has been considered an ideal measurement instrument for the analysis of the unstable concentrations and size distributions, or the evolution of size distributions that could be observed in

these tests. In order to prevent particle bounce and charge transfer during the tests, all collection substrates used (PVC GELMAN GLA-5000 5µm / 25 mm) are greased.

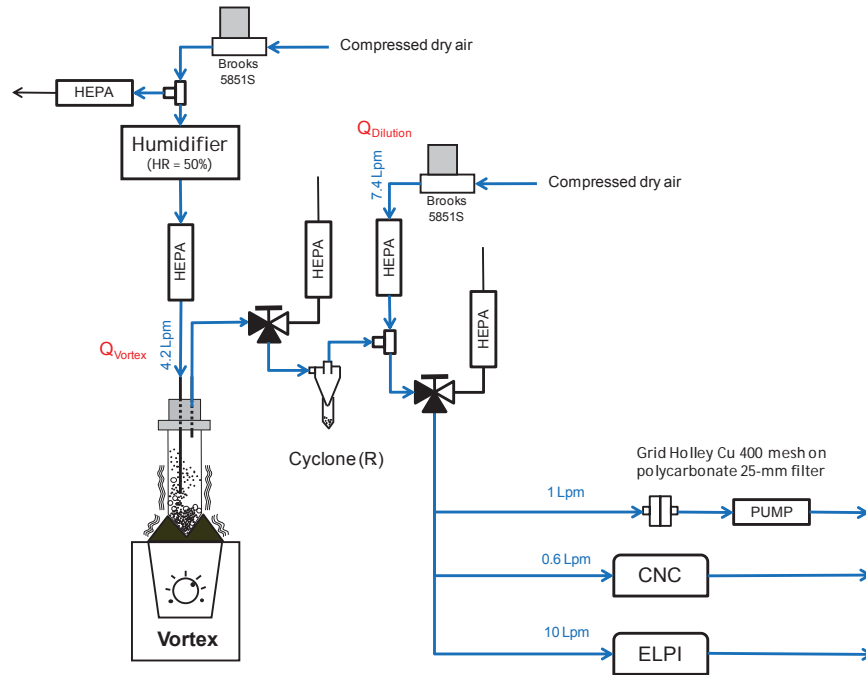


Figure 26: Experimental set-up of the vortex shaker method for measuring number concentrations and particle-size distributions, and for collecting airborne particles for subsequent EM observations.

In the ELPI the measured current signals are converted to (aerodynamic) size distribution using particle size dependent relations describing the properties of the charger, the impactor stages, and the effective density of the particles. The particle effective density provides a relationship between mobility and aerodynamics sizes. Effective density is a parameter which is complex to measure (Olferta et al., 2007), and values for samples used in the project are not available in the literature. Therefore, the following assumption has been made for the data from the ELPI: spherical particle with a density equal to the density of the condensed phase of the material constituting the NM. Densities used are: 3.84 g/cm<sup>3</sup> for NM100, 101, 102 and 4.26 g/cm<sup>3</sup> for NM103, 104, 105 based on Teleki et al. (2008); 2.2 g/cm<sup>3</sup> for all NM20x; 1.75 g/cm<sup>3</sup> for all NM40x based on Kim et al. (2009). If this assumption is questionable, there is no robust method that can be applied to polydispersed aerosols over a wide size range, such as those used in the project. However, to assess the effect of this parameter on the results, the number size distributions were also calculated for a density of 1 g/cm<sup>3</sup>.

The total number of generated particles from the Vortex tube,  $S_{Vortex}^{Number(CNC)}$ , was calculated as:

$$S_{Vortex}^{Number(CNC)} = [Q_{Vortex} + Q_{Dilution}] \cdot \Delta t \cdot \sum_{i=0}^{T/\Delta t} C_{CNC}(t_0 + i \cdot \Delta t) \quad (-) \quad \text{Eq. 3}$$

Where:

- T is the time over which the total number of particles is calculated. This time is between 5 and 3600 s, the latter is the test duration in the original protocol of the VS method.
- $\Delta t$  is the step time of the CNC (for all tests it was set as 5 s)
- $C_{CNC}(t_0 + i \cdot \Delta t)$  is the number concentration measured during the  $i$ th time interval

- $Q_{Vortex}$  is the total air flow rate passing through the vortex tube (4.2 lpm)
- $Q_{Dilution}$  is the flow rate of dilution air (7.4 lpm).

The dustiness index in number of particles per gram,  $DI_{Number(CNC)}$ , is calculated as the total number of generated particles divided by the total mass of the test NM sample in milligrams:

$$DI_{Number(CNC)} = \frac{S_{Vortex}^{Number(CNC)}}{m_{NM}} \quad DI_{Number(CNC)} = \frac{S_{Vortex}^{Number(CNC)}}{m_{NM}} \quad (1/mg) \quad \text{Eq. 4}$$

To get information on particle morphology of the emitted aerosol, a simple but specific sampling set-up has been designed (see Figure 31). Transmission electron microscope (TEM) copper grids are taped onto 25 mm diameter polycarbonate membrane filters (0.4 or 0.8 $\mu$ m). Fiber backing filters are used to support the polycarbonate filters. Air flow is driven by a personal sampling pump at a flow rate of 1 L/min. The duration of the sampling is set to 1 hour. The sampling period is set equal to the duration of a test (1 hour). For some test, the sample might be accumulated over two trials in order to have enough particles to observe. Different TEM copper grids having different carbon are used (Carbon film, Quantifoil Holey Carbon Films or Holey Carbon Support Film).

It is important to note that the duration of the test is to be considered as the process is dynamic. In the original INRS protocol developed, the duration of a test was set equal to 3600 s. But in the first version of the set-up (cf. Figure 26), as the instruments measure in real time, it is possible to perform the calculation for different durations between 0 and 3600 s. In this report, the calculations based on the CNC data are performed for two durations: 180 s and 3600 s. The first duration (180 s) is chosen to be consistent with the method SD. For the second version of the setup, the duration of the test is set to 3600 s, which corresponds to the original protocol of the Vs method.

The second version of the setup (Figure 27) is used for collecting respirable mass fraction of the emitted aerosol. The respirable mass fraction is obtained by sampling with a GK2.69 cyclone (BGI, UK). The filters are pre-weighed and post-weighed following the recommendations of the ISO 15767:2009 on the same analytical balance.

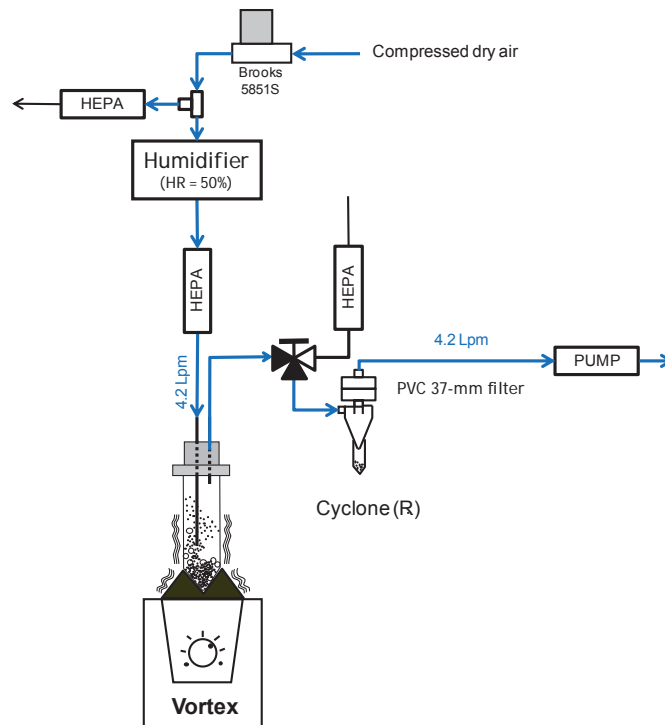


Figure 27: Experimental set-up of the vortex shaker method for collecting respirable mass fraction of the emitted aerosol.

The dustiness index in respirable mass (mg) of particles per kilogram,  $DI_{Mass (GK2.69)}$ , is calculated as the respirable mass of generated particles in milligrams divided by the total mass of the test NM sample in kilograms:

$$DI_{Mass (GK2.69)} = S_{Vortex}^{Mass (GK2.69)} / m_{NM} \quad (\text{mg/kg}) \quad \text{Eq. 5}$$

The recommendations of the standard ISO 15767:2009 are followed to determine the LOD of the weighing procedure for the filters used for sampling respirable mass of particles during this project. The LOD for the PVC GELMAN GLA-5000 (5 µm/37 mm) filters is equal to 20 ng. This value is used to determine the LOD expressed in dustiness index.

The figure below shows the flow diagram of the experimental protocol used for the NGT project.

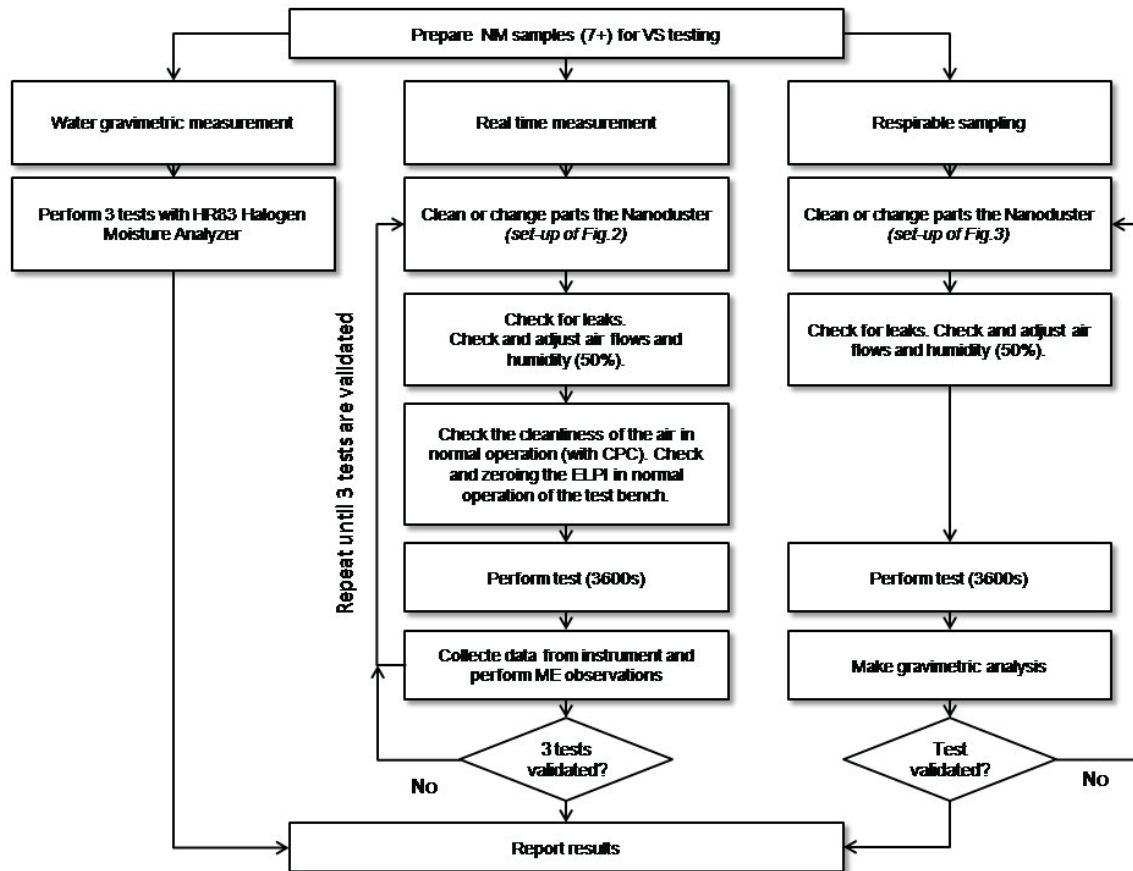


Figure 28: Flow diagram describing the different stages of the cycle of a test conducted according to the VS method for a powder sample NM.

The preparation of NM samples for VS testing include: 1) to take a series of several samples of 0.5 cm<sup>3</sup> of the vial containing the nanomaterial received, 2) to accurately weigh the samples. Microcentrifuge graduated tubes with secure seals and caps have been chosen to keep the 0.5 cm<sup>3</sup> samples.



Figure 29: Microcentrifuge tube filled with a NM sample of  $0.5 \text{ cm}^3$  for a dustiness test according to the VS method.

The gravimetric water content is performed using a HR83 Halogen Moisture Analyzer (Mettler Toledo) and following a drying program defined specifically for small quantities of used NM (Temperature =  $160^\circ\text{C}$ ; duration = 170 s).

The weighing of the NM samples is performed with a XP205 analytical balance ( $10 \mu\text{g}$  readability, Mettler Toledo) while the weighing of the 37-mm filters from the respirable sampler is performed with a MX5 microbalance ( $1 \mu\text{g}$  readability, Mettler Toledo).

Particular attention is given to the experimental device cleaning between successive tests. All pipes and other connections are systematically cleaned with water and/or ethanol and dried in an oven, or eventually changed. The checking of the airflows is performed using a primary flow bubble calibrator (Gillian<sup>®</sup> Gillibrator 2). Prior to each test, the cleanliness of the air is assessed on the basis of measurements made using the CNC. In the case of a non-compliant result, everything is taken from the beginning.

The validation of a test depends on several factors such as: 1) the stability of the parameters during the test, 2) a good reproducibility of measured number concentrations, 3) a good sequence of steps for the respirable aerosol sampling etc.

The entire set-up is located inside a variable volume fume hood to prevent exposure of the operator (see Figure 30 and Figure 31). Similarly, all operations like weighing, water content measurement and sample preparation are carried out in a specific containment system that has a unique turbulent-free, low flow design which allows our sensitive balance to operate without fluctuation and protects the operator from exposure to airborne particles that could be released when handling and weighing NM samples (see Figure 32).



Figure 30 : Overview of the vortex shaker set-up positioned in the variable flow fume hood at INRS.



Figure 31 : View of the set-up designed to collect emitted particles on grids for EM observations.





Figure 32 : Operator during NM sample preparation (weighing and water content measurement) in the powder handling enclosure at INRS.

Dustiness tests performed with carbon nanotubes samples requires that the operator wears a respirator mask as shown on the Figure 33 to further limit potential exposure.



Figure 33: Operator introducing a NM sample into the Vortex Shaker positioned in the variable volume fume hood used at INRS.

### 3 Results

As indicated in the “Deviation from the work plan” section, it has been decided to split the protocols from the results. Hence Deliverable 3.3 will be a compendium of SOPs while Deliverable 3.7 entitled “Improved data on specific scenario” will contain among others results regarding the procedures tested on the chosen relevant products (consumer exposure). Results concerning the procedures to generate controlled aerosol using the shaker method and dustiness testing using small rotating drum and vortex shaker methods will be reported in the Deliverable 3.2 entitled “Comparison of existing dustiness testing methods”.

### 4 Deviations from the work plan

Accordingly to the Document of Work, IOM (9) was the original lead beneficiary for this deliverable. It has been decided to switch the responsibility of this deliverable to CEA (23) since IOM was not involved in the corresponding sub-task.

In the Document of Work it is indicated that the Deliverable 3.3 corresponds to the following subtask “Development of simulation approaches for key exposure scenarios (e.g. spraying, cleaning, abrasion, or weathering) and use of these to collect relevant data”. However, for practical reasons since at the due date of the deliverable 3.3 relevant products were not chosen, it has been decided to split the protocols from the results. Hence Deliverable 3.3 will be a compendium of SOPs while Deliverable 3.7 entitled “Improved data on specific scenario” will contain among others results regarding the procedures tested on the chosen relevant products (consumer exposure). Results concerning the procedures to generate controlled aerosol using the shaker method and dustiness testing using small rotating drum and vortex shaker methods will be reported in the Deliverable 3.2 entitled “Comparison of existing dustiness testing methods”.

### 5 References / Selected sources of information

EN ISO 105-C06	Textiles - Tests for colour fastness - Part C06 : colour fastness to domestic and commercial laundering
EN ISO 6330	Textiles - Domestic washing and drying procedures for textile testing
EN ISO 20743	Textiles - Determination of antibacterial activity of textile products
EN ISO 105-E04	Textiles - Tests for colour fastness - Part E04 : colour fastness to perspiration
EN ISO 7784-1	Paints and varnishes - Determination of resistance to abrasion - Part 1 : rotating abrasive-paper-covered wheel method
EN ISO 5470-1	Rubber- or plastics-coated fabrics. Determination of abrasion resistance. Part 1 : Taber abrader.
EN ISO 11507	Paints and varnishes - Exposure of coatings to artificial weathering - Exposure to fluorescent UV and water
EN ISO 16474	Paints and varnishes - Methods of exposure to laboratory light sources
ISO 4892	Plastics - Methods of exposure to laboratory light sources
NF X 10-141	Measurement of gas flow in conduits. Tracer methods. Part 1 general.

## 6 List of abbreviations

ATR	Attenuated total reflectance
CNT	Carbon nanotubes
CNF	Carbon nanofibers
CPC	Condensation particle counter
CVD	Chemical vapor deposition
DLS	Dynamic light scattering
EDS	Energy dispersive X-ray spectroscopy
ELPI	Electrical low pressure impactor
FTIR	Fourier transform infrared spectroscopy
FFF	Field flow fractionation
FMPS	Fast mobility particle sizer
GBP	Granular biopersistent particle
ICP-MS	Inductively coupled plasma-mass spectrometry
LDPE	Low density polyethylene
NM	Nanomaterial
MALS	Multi angle light scattering
MNM	Manufactured nanomaterial
PTFE	Polytetrafluoroethylene
SEM	Scanning electron microscopy
SOP	Standard operating procedure
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
TP	Thermal precipitator
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction