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1. Purpose

The objective of Task 2 in Work Package 2 (WP2) of the NanoStreeM project is to identify state-of-the-measurement standards, for their ability to measure correctly in clean rooms.

The incertitude and lack of information about NOAA\(^1\) toxicity avoids currently defining exposure regulation. Discussions are even still ongoing on the more relevant metric to use. For some years, several approaches have been proposed in order to assess a potential exposure of workers, based on the exposure assessment state-of-the-art.

2. Methodology

The following steps associated with Task 2.2, were defined in the project work plan to develop the inventory:

1. Compile initial list of methodologies in nano-aerosol measurement, as:
   - Identified by scientific literature review,
   - Used by partners.
2. Present each of the methods listed,
3. Circulate draft lists to consortium members for comments and input,
4. Agree on final list.

An excel template (see Appendix 1) was developed to house the nano-aerosol equipment, devices and protocols information. A first worksheet was dedicated for equipment and devices. A second one was also proposed for methodologies, as requested in the task 2.2.

A description was asked to be filled in:

- Reference:
  - Title
  - Publication references
- Origin of the methodology
- Already used in the labs or fabs
- Appliance to clean room environment

\(^1\)engineered Nano-objects (<100nm) and their agglomerates and aggregates (including structures that are > 100nm), OECD approach
The template entitled ‘Nanostreem Task 2.1 & 2.2 – Air sampling and monitoring.xls’ has circulated by email and all partners with experience in semiconductor manufacturing and field and lab measurement, environmental and monitoring, were invited to populate with related information. This compilation has been the first step necessary, before allowing the identification of suitable protocols to use in clean rooms. These results will feed remaining tasks of WP2, but also others WP of the project. Several types of documents were analyses: methodologies, approaches, standards. To easy the reading, the term “protocol” will be used in a generic way in this deliverable to cover all types of documents.

3. Results

Four partners submitted information on protocols: CEA, TNO, IMEC & VITO. A total of 11 different documents were submitted. A majority are dedicated to the assessment of potential exposure to nanoaerosols. The others deal with specific aspects. After examination of the documents listed in the spreadsheet, most of methodologies are based on a tiered approach, combining real-time measurement and sample analyses.

For a better understanding, a description of each method is presented below.

3.1. Recommendations for Characterizing potential Emissions and exposure to aerosols released from nanomaterials in workplace operations

**Published:** 2012 (HST n°226, p41-55)

**Authors:** Olivier WITSCHGER (INRS), Olivier LE BIHAN (INERIS), Martine REYNIER (INRS), Catherine DURAND (CEA-PNS), Alain MARCHETTO (CEA-PNS), Eric ZIMMERMANN (CEA-PNS), Dominique CHARPENTIER (INERIS)

**Description:**
This paper describes a suggested tiered approach to characterising emissions and exposures to aerosols where nanomaterials are processed or used during workplace operations. The proposed approach follows a 5-stage procedure. Three levels should be successively passed before a measurement campaign to be considered, and the last of them includes the possibility of particle release tests are performed under laboratory conditions. The measurement strategy in itself is based on two levels of intervention: level 1 is intended primarily for industrial hygiene practitioners, while level 2 is intended primarily for researchers with experience in (nano)aerosol measurement in the workplaces.

**Application fields**
This methodology was proposed to answer questions about potential worker exposure to nanoaerosols in labs but also in Industry. It was developed in order to be applicable in most of exposure situations, mainly using a constant background level measurement and an association of samplers and real-time instruments.
Instrumentation used
Devices used depend on the measurement strategy. A complete study, named level 2, includes
- 2 Condensation Particles Counters (CPC), one for the workplace and one for the background
- Particles sizers covering a range from some nanometres to several µm in order to get aggregates and agglomerates of nanoparticles
- At least one sampler in order to perform chemical and/or electronical microscopy characterizations

Experience/feedback
A similar methodology was used by CEA since 2009, before using this harmonized approach from 2012. More than 300 studies were performed, mainly in industry including semi-conductor facilities.

Application in clean rooms
This methodology was used more than 10 times in clean rooms. Advantages and drawbacks are on the overall the same as in other workplaces. The preparation time has to be noticed. Hence, all equipment has to be cleaned before entering the clean room. This method can’t provide particle size data for brief and low-concentrated emissions except with sample analyses by electronic microscopy.

3.2. Tiered approach to an exposure measurement and assessment of nanoscale aerosols released from engineered nanomaterials in workplace operations

Published: August 2011

Authors: IUTA, BAuA, BG RCI, VCI, IFA, TUD

Description:
This document was built by an association of several German Institutes. It describes a suggested three-tiered approach to characterising emissions and exposures to aerosols. The first tier is dedicated to information gathering. If an exposure cannot be excluded at this first step, a basic exposure assessment is performed in tier 2. The last tier is called “expert measurement assessment” and has to be realized if a potential emission was detected in tier 2.

Application fields
This methodology seems to be applicable in any situation involving airborne nanoparticles.

Instrumentation used
Devices used depend on the measurement strategy. A complete study can includes
- Condensation Particles Counters (CPC)
- Particles sizers, for example scanning mobility particle sizer (SMPS)
- Samplers in order to perform chemical and/or electronical microscopy characterizations
Experience/feedback
Partners didn’t report the use of this approach. Nevertheless, it can be assumed that experience and feedback gathered with other tiered approach protocols are on the overall transposable.

Application in clean rooms
This methodology seems to be fully applicable in clean rooms. As for others tiered approaches, the application will be mainly driven by instruments and substances features.

3.3. Harmonized tiered approach to measure and assess the potential exposure to airborne emissions of engineered nano-objects and their agglomerates and aggregates at workplaces

Published: 2015 (OECD, Series on the Safety of Manufactured Nanomaterials No. 55)

Authors: OECD, workgroup led by the Business and Industry Advisory Committee to the OECD especially: Michele Ostraat (Aramco Research Center, Boston); Stefan Engel (BASF SE); Keith A. Swain (DuPont); Thomas A. J. Kuhlbusch and Christof Asbach (IUTA).

Description:
This approach is a synthesis of existing methodologies for the exposure assessment to NOAA. Authors concluded at a three-tiered approach after the analysis of 14 references. The first tier is dedicated to information gathering in order to assess if an exposition can be excluded or not. The second tier is a first measurement performed with a “straightforward approach”. The last tier is a complete study with a large set of equipment.

Application fields
OECD approach can be used in any filed where potential exposure to NOAA can’t be excluded.

Instrumentation used
OECD approach provides a compilation of most used technics for exposure characterization with some key points for each one.

Experience/feedback
This approach had never been used by partners. Nevertheless, it can be assumed that experience and feedback gathered with other tiered approach protocols are on the overall transposable to OECD approach. Hence; it is based on a tiered approach using commercial equipment for the measurement.

Application in clean rooms
This methodology seems to be fully applicable in clean rooms. As for others tiered approaches, the application will be mainly driven by instruments and substances features.
Figure 1: flow chart of the OECD approach
3.4. Field Application of the Nanoparticle Emission Assessment Technique (NEAT): Task-Based Air Monitoring During the Processing of Engineered Nanomaterials (ENM) at Four Facilities

Published: 20 July 2012 (Journal of Occupational and Environmental Hygiene, 9: 543–555)

Authors: M. Methner, C. Beaucham, C. Crawford, L. Hodson, and C. Geraci

Description:
This method was proposed by the American National Institute for Occupational Safety and Health (NIOSH) to assess the concentration of airborne Engineered NanoMaterials (ENMs). This method is based on data gathering in order to assess a potential release of nanoparticles. On-site study is conducted thanks to real time measurements and samplings.

Application fields
This methodology seems to be applicable in any situation involving airborne nanoparticles. It point out the specificities of some ENMs’ measurements, like tubes or fibres. It was applied in 4 sites where nanoparticles were produced, handled or used.

Instrumentation used
This methodology combines real time instruments and sampling analyses. The concentration in nanosize range was obtained by subtracting results of two devices (OPC and CPC). Samples were analysed by electronic microscopy.

Experience/feedback
NEAT publication includes examples, with their critical analysis. Studies are deeply described. They showed the presence of airborne nanoparticles, including Carbone nanotubes.

Application in clean rooms
This protocol is developed to be generically used in workplace where NOAA are used, so there is no reason to believe that it is not applicable to clean rooms.
3.5. CEN WI137053 Workplace exposure — Assessment of inhalation exposure to nanoobjects and their agglomerates and aggregates

Draft: 2016

Authors: CEN TC 137 WG3

Description:
This European standard provides guidelines to assess inhalation exposure to Nano-objects and their agglomerates and aggregates (NOAA) at different levels, as well as to evaluate the results of the assessment either as stand-alone assessment or embedded in a tiered approach framework. While the focus of the Standard is on the assessment of nano-objects, the approach is also applicable for exposure to the associated agglomerates and aggregates, i.e. NOAA, and particles released from nano composites and nano-enabled products.

Application fields
This European standard can be used in any field where potential exposure to NOAA can’t be excluded.

Instrumentation used
This CEN approach provides a compilation of most used technics for exposure characterization.

Experience/feedback
This standard is still being developed and has not yet been used.

Application in clean rooms
This standard is developed to be generically used in workplace where NOAA are used, so there is no reason to believe that it is not applicable to clean rooms.
3.6. **CEN W100137056** Metrics to be used for the measurements of exposure to inhaled nanoparticles (nano-objects and nanostructured materials) such as mass concentration, number concentration and surface area concentration

Draft: 2016

**Authors:** CEN TC 137 WG3

**Description:**
This European standard provides a guideline on the implications of choice of particle metric to express the exposure to nanoaerosols and present the principles of operation, advantages and disadvantages of various techniques that measure these aerosol metrics. The standard specifies which metrics shall be measured during a basic assessment and a comprehensive assessment, respectively, as described in WI 00137053. Potential problems and limitations are described and need to be addressed when occupational exposure limit values might be adopted in the future and compliance measurements will be carried out.

Specific information is mainly given for the following metrics/measurement techniques:
- Number/Condensation Particle Counters;
- Number size distribution by electrical mobility;
- Surface area (electrical charge on available surface);
- Mass/chemical analyses (e.g. Inductively Coupled Plasma atomic Mass Spectrometry (ICP-MS), X-Ray Fluorescence (XRF)) on size-selective samples (e.g. by impaction or diffusion);
- Size distribution of the primary particles of agglomerates

**Application fields**
This European standard can be used in any field where potential exposure to NOAA can't be excluded.

**Instrumentation used**
This CEN approach provides a compilation of most used technics for exposure characterization for different metrics.

**Experience/feedback**
This standard is still being developed and has not yet been used.

**Application in clean rooms**
This standard is developed to be generically used in workplace where NOAA are used, so there is no reason to believe that it is not applicable to clean rooms.
3.7. CEN WI137057 Workplace exposure — Measurement of dustiness of bulk nanomaterials (Parts 1 - 5)

Draft: 2016

Authors: CEN TC 137 WG3

Description:
This European standard provides the methodology for measuring and characterising the dustiness of a bulk material that has the propensity to release nano-objects and respirable and inhalable particles. In addition, it specifies the environmental conditions, the sample handling procedure and the method of calculating and presenting the results. Reasons are given for the need for more than one method and advice is given on the choice of method to be used.
The methodology described in this European Standard enables:
   a) the quantification of dustiness in terms of health-related index mass fractions;
   b) the quantification of dustiness in terms of an index number and an emission rate.
   c) the characterisation of the aerosol from its particle size distribution and the morphology and chemical composition of its particles

Application fields
This European standard is applicable to testing powders for all dustiness methods and to granules or pellets containing nanoparticles for all dustiness methods except the vortex shaker. This standard is relevant to bulk material containing nano-objects including those made of particles with a nominal diameter greater than 100nm as the main component. The methods specified in this European Standard have not yet been evaluated for nanofibres and nanoplates. This European standard does not provide methods for assessing the release during handling or mechanical reduction of machining (e.g. crushing, cutting, sanding, sawing, etc...) of solid nanomaterials (e.g. nanocomposites).

Instrumentation used
This CEN approach provides a compilation of most used technics for characterization of dustiness of nanomaterials.

Experience/feedback
This standard is still being developed and has not yet been used.

Application in clean rooms
This standard is developed to be generically used for measuring and characterising the dustiness of a bulk material that has the propensity to release nano-objects, so there is no reason to believe that it is not applicable to clean rooms.
3.8. Occupational Exposure to Carbon Nanotubes and Nanofibers

Published: Current Intelligence Bulletin 65, April 2013

Authors: NIOSH

Description:
This document deals with risks linked to exposure to Carbone Nano Tubes (CNT) or Cabone Nano Fibres (CNF). Main part of the study is dedicated to toxicological aspects. Nevertheless, a paragraph describes the use of elemental carbon (EC) determination to estimate the mass concentration of CNT and CNF. The referenced method for EC measurement is “NIOSH Method 5040”. This method can be applied in the framework of a tiered approach.

Application fields
This method is applicable for mass-based airborne concentration measurement of CNT or CNF. Other sources of EC have to be identified. Hence, diesel soot, carbon lack can interfere with CNT/CNF detection.

Instrumentation used
This method is based on Thermo-optic analysis. The sampling on quartz filter media is described as common.

Experience/feedback
Thermo optic devices are well known for EC determination. Nevertheless, their use stay limited to experienced persons. For the specific case of CNT/CNF, NIOSH publication mentions a reference as example with a brief description and analysis.

Application in clean rooms
This protocol is developed to be generically used for measuring and characterising the dustiness of a bulk material that has the propensity to release nano-objects, so there is no reason to believe that it is not applicable to clean rooms.
4. Conclusion

The purpose of this document is to identify and analyse existing standards, for their applicability to measure ultrafine and nanoparticle emission in semiconductor processing and to identify gaps in methodologies if present. For this purpose 11 different protocols are collected and eight have been analysed. The majority of them are generic. Some were dedicated to specific situations or NPs that cannot be assessed with classical methods.

Analysis of the protocols demonstrate that they share some common principles. Most of the authors agree upon following a tiered approach in the potential exposure assessment. Differences can be identified in the number of tiers or their organisation but the followed process is in general common. The principle is to progress step by step, seeking if an exposure to NOAA can be excluded. If it is not the case, the standard leads to the next step. The analysis depth increase at each step: Firstly, a documental step that will enable to identify potential exposure ways, process emissivity etc; Secondly, a simple exposure assessment and finally an extensive field measurement campaign in the most complicated situations.

It is noteworthy that generic protocols propose a logical progression to reach a conclusion on potential exposure. Standards propose also instruments, but generally more as a list of possible techniques or devices. The correspondence between the process and suitable equipment depends a lot on instrument availability and the user experience in doing measurements. Thus, cost of equipment and experience in its use (e.g. for potential exposure assessment) remain limitations for the wider spread of these methodologies outside nanosafety expert community. This point is also identified in Deliverable 2.1, "List of air sampling equipment and list of environmental and individual monitoring devices". Hence, only R&D institutions provided information showing that nanoaerosol measurement remains essentially limited to research organizations. Even if a certain standard is applied, the sampling and analysis techniques employed still require dedicated equipment and knowledge when the particles of interest have uncommon properties like nanotubes or nanowires.

In principle semiconductor industry can try out the tiered approaches studied in this document. The absence of background is a major advantage that facilitates and enhances the measurement sensibility. Devices will have to be selected to benefit from this environment (see Deliverable 2.1). If a gap has to be pointed out, it is more in the training of safety personnel in facilities. We can conclude that what was initially assumed in the NanoStreeM project proposal and led to proposing WP4 (Internal Communication, Information and Training of Employees) and especially Task 4.3 (Training of Employees) remains valid.
Appendix 1 – Nanomaterial Inventory Excel Spreadsheet template

### Instructions:
Each Nanostream Partner is invited to list every air sampling and assessments standard known, if applicable to clean room environment. Knowledge can come from bibliography, published information, corporate procedure, ...

<table>
<thead>
<tr>
<th>STANDARD 1</th>
<th>STANDARD 2</th>
<th>STANDARD 3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PARTNER</strong></td>
<td><strong>PARTNER</strong></td>
<td><strong>PARTNER</strong></td>
</tr>
<tr>
<td>Reference of the methodology (name, publication reference, ...)</td>
<td>Reference of the methodology (name, publication reference, ...)</td>
<td>Reference of the methodology (name, publication reference, ...)</td>
</tr>
<tr>
<td>Origin of the methodology</td>
<td>Origin of the methodology</td>
<td>Origin of the methodology</td>
</tr>
<tr>
<td>Already used in my proper site / fab?</td>
<td>Already used in my proper site / fab?</td>
<td>Already used in my proper site / fab?</td>
</tr>
<tr>
<td>State of the methodology (experimental, published, ...)</td>
<td>State of the methodology (experimental, published, ...)</td>
<td>State of the methodology (experimental, published, ...)</td>
</tr>
<tr>
<td>Short description</td>
<td>Short description</td>
<td>Short description</td>
</tr>
<tr>
<td>Appliance to clean room environment (according to partner)</td>
<td>Appliance to clean room environment (according to partner)</td>
<td>Appliance to clean room environment (according to partner)</td>
</tr>
<tr>
<td>Additional comments (if needed)</td>
<td>Additional comments (if needed)</td>
<td>Additional comments (if needed)</td>
</tr>
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</table>