

**Co-Nanomet**

*Co-ordination of Nanometrology in Europe*

# European Consultation on Metrological Traceability, Standards and Dissemination of Metrology in Industrial Nanotechnology



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# European Consultation on Metrological Traceability, Standards and Dissemination of Metrology in Industrial Nanotechnology

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## Executive Summary

It is widely acknowledged that the industrial exploitation of nanotechnology through innovative products is still lagging, in particular in Europe, despite advances in nanosciences. During 2010, in support of sustainable growth in the nanomanufacturing<sup>1</sup> industry, a CO-NANOMET [EU FP7 CSA-CA 218764] consultation has been made of both the means and content of the dissemination of the particular metrology tools and know-how needed in the nanotechnology workplace. In this consultation, and in this corresponding report, these tools and know-how are covered by the term "nanometrology", which is short for "metrology at the nanoscale" and includes metrological traceability, measurement uncertainty and standardised measurement definitions and methods.

Programmes encouraging industry to innovate by exploiting nanometrology through local networking and through various documentary standards (i.e. written standards, i.e. norms) are found to be promising means of disseminating nanometrology to industry. These are two examples of how a European innovation infrastructure can provide support throughout the innovation process – from initial idea, through design, manufacture, conformity assessment and marketing – through to the finished product. An innovation infrastructure in nanometrology will network and integrate actors in each field – from policy makers to metrologists - so that these can work together to tackle the major challenges.

During the consultation, the five European CO-NANOMET action groups in nanometrology (ENAG): Engineered Nanoparticles; Nanobiotechnology; Thin Films and Structured Surfaces; Critical Dimension and Scanning Probe Techniques; and Modelling and Simulation, have made recommendations of the future needs for A) Documentary standards; B) Measurement methods; and C) Metrological requirements, particularly proposed intercomparisons, as follows:

### A) Documentary standards

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<sup>1</sup> Nanomanufacturing: intentional synthesis, generation or control of nanomaterials, or fabrication steps in the nanoscale, for commercial purposes; ISO/TS 80004-1:2010.

Documentary standards are developed in nanotechnology, as elsewhere, to provide a harmonised and unambiguous framework to enable nanomanufacturing both in the regulatory context, for instance, where there are perceived risks with nanotechnology, but also to ensure general product quality and conformity compliance to facilitate trade, to promote customer satisfaction, and to improve production sustainability. Two main challenges for metrology in standardisation, including nanometrology, to be addressed are:

- Documentary standards sometimes make reference unfortunately to **unrealistic and ambiguous measurement specifications** and unclear requirements.

*Suggested actions:*

- written standards should be checked against a "metrology checklist";
  - written standards describing new measurement procedures should be validated by an interlaboratory comparison before their release.
- Industry and society are placing **increasingly exacting demands** on measurement in terms of complexity and accuracy, including meeting 'grand challenges' such as in energy & the environment, health & safety amongst others, employing nanotechnology.

*Suggested action:*

- There is a need for more **pre-normative R&D** into the metrological aspects of measurement and product norms for nanotechnology. Significant contributions are needed to pre-normative research, in developing the necessary metrological aspects at all steps in product development – from initial product design and specification, through metrological design, procurement and actual measurement, to final product conformity assessment and marketing.

B) Measurement methods

Recommended, standardised measurement methods are needed in support of measurement quality assurance of laboratories making measurements in the workplace. Product quality is very much determined by the quality of the measurements made to test against specifications.

Examples of challenges in developing measurement methods at the nanoscale include:

- The need for new measurement instruments and methods working at the nanoscale;
- New characteristics unique to the nanoscale need to be measured;
- Measurements need to be made in challenging environments, e.g. ultra-high vacuum.

*Suggested action:*

- Continued support for research & innovation activities leading to the **development of new and improved methods for measurement and testing at the nanoscale.**

C) Metrological requirements

Metrological traceability – where possible to the universal measurement references of the SI system – ensures that measurement results made at different times and different locations can be compared objectively and reliably.

Examples of metrological challenges at the nanoscale include:

- Longer chains of metrological traceability;
- The need for new nanoscale reference materials and physical standards.

Meeting these challenges is often more demanding than can be achieved by individual actors, simply because all stages of the innovation process have to be covered at the same time as nanotechnology is rapidly developing.

*Suggested action:*

- A **strengthening** is needed of the **existing network of European measurement facilities** as well as investments in the development and introduction of **new standards and measurement techniques**, as part of establishing the necessary infrastructure to support growth in nanotechnology and nanomanufacturing.

Detailed tables for each area (A), B) and C)) are given in this report, for the different Co-Nanomet action groups (ENAGs).

# European Consultation on Metrological Traceability, Standards and Dissemination of Metrology in Industrial Nanotechnology

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## 1. Background and Task Objectives

One major aim of the CO-NANOMET project has been to formulate recommendations in support of the general ambition of bringing nanotechnology through to successful business by specifically focussing on:

- relevant metrology tools
- suitably skilled human resources able to implement appropriately such tools

Despite advances in nanosciences, it is widely acknowledged that the industrial exploitation of nanotechnology in innovative products is still lagging. CO-NANOMET (via its sub-tasks 4.3.x) aims to identify metrology requirements for the industrial arena:

- *Study of general dissemination of traceable nanometrology to the workplace (4.3.1)*
- *Work on standardisation to be developed in collaboration with the already established CEN technical committee 352 (4.3.2)*
- *Metrological traceability in the form of global equivalence to be addressed (4.3.3)*  
This will involve suggestions for international comparisons to ensure that nanometrology develops into a global and robust discipline to support the coming trade and safety of nanoproducts.
- *Activity to be addressed as sub activity of each ENAG established within Work Package 2 (4.3.4)*

### 1.1 **Metrological infrastructural support for nanotechnological innovation**

In order to sustain the expected considerable growth in the number of nanoproducts, major investment in technological and manufacturing/business infrastructure is needed. This includes metrology and standards which can be used at the nanoscale in support of conformity assessment of nanoproducts of all kinds. Quality-assured measurement in nanometrology – including metrological traceability, measurement uncertainty and standardised definitions and measurement methods – provides an infrastructural support throughout the innovation process – from initial idea, through design, manufacture, conformity assessment and marketing – through to the finished product. This ensures that newly developed products will satisfy the exacting requirements not only of scientific excellence but also of reliability and economy when practically implemented.

The development of infrastructures – that is, strongly integrated resources either at a specific site (e.g. CERN) or in a distributed network (e.g. the European NMIs) – in innovation, education and research are particularly emphasised, both by experts and the general public, in the outcome of a recent public consultation “Towards a Strategic Nanotechnology Action Plan (SNAP) 2010-2015”<sup>2</sup>. The same study emphasised the need for EU policies in the new Action Plan to particularly do more in: (a) developing education & training (b) developing better tools; (c) active communication and (d) international cooperation.

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<sup>2</sup>Report on the European Commission's Public Online Consultation, TOWARDS A STRATEGIC NANOTECHNOLOGY ACTION PLAN (SNAP) 2010-2015, [http://ec.europa.eu/research/consultations/snap/report\\_en.pdf](http://ec.europa.eu/research/consultations/snap/report_en.pdf)

Infrastructures in general lie at the heart of the knowledge triangle – the beneficial combination of research activity, specialised education and innovation that advances our knowledge and understanding across all scientific and societal domains, see figure 1.1.

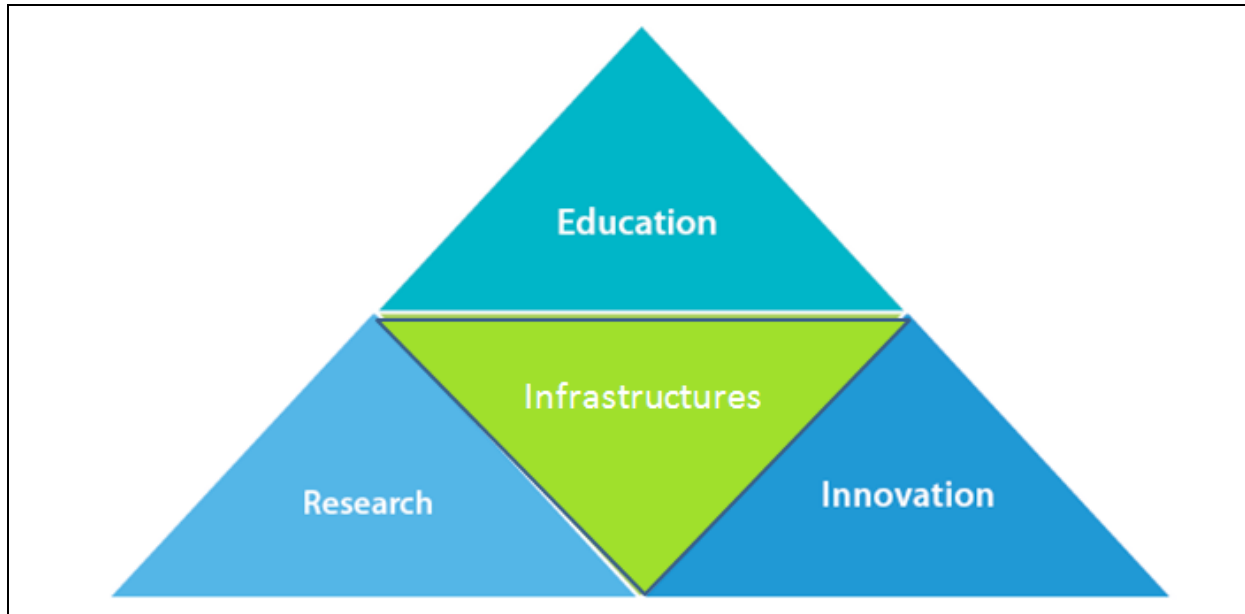


Figure 1.1: Infrastructures positioned within the knowledge triangle (adapted from <sup>3</sup>)

An innovation infrastructural “rectangle” of policy, regulation, standardisation and metrology (Figure 1.2), graphically visualizes the interdependencies between societal needs and challenges, regulation and standardisation and state-of-the-art metrology. An innovation infrastructure in nanometrology will network and integrate actors in each field – from policy makers to metrologists (e.g. EURAMET<sup>4</sup>) so that these can work together to tackle the major challenges.

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<sup>3</sup>A vision for strengthening world-class research infrastructures in the ERA, Report of the Expert Group on Research Infrastructures, ISBN: 978-92-79-14214-7 (2010)

<sup>4</sup>EURAMET European Association of National Metrology Institutes, [www.euramet.org](http://www.euramet.org)

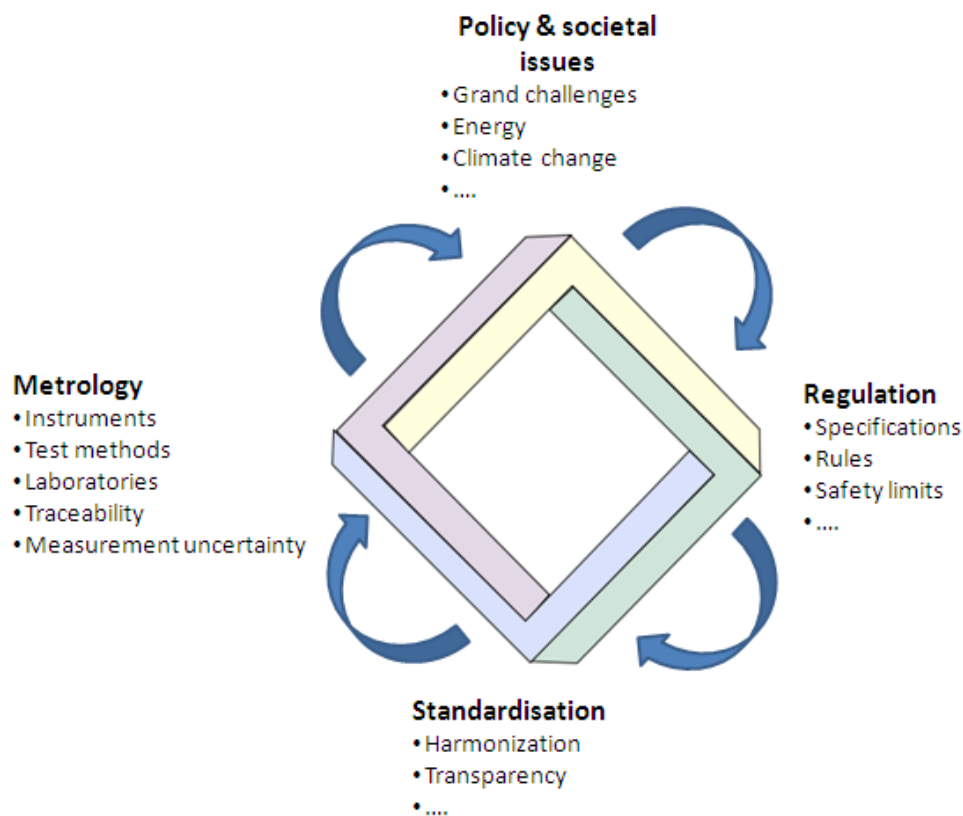


Figure 1.2 Innovation infrastructural 'rectangle': policy, regulation, standardisation and metrology [Pendril 2010]

## 1.2 Challenges for Nanometrology

Developments in nanotechnology place special demands on the required metrology infrastructure: metrology on the nanoscale is demanding, while at the same time, the rate of nanotechnology development continues to increase in both volume and complexity. Demands are more extensive than can be provided by individual actors, simply because all stages of the innovation process have to be covered at the same time as nanotechnology is rapidly developing. A strengthening is needed of the existing network of European measurement facilities as well as investments in the development and introduction of new standards and measurement techniques, as part of the necessary infrastructure to support growth in nanotechnology. Few such standards and techniques exist today which can be used across the nanoscale range (which is currently mainly considered to be from 1 nm to 100 nm) and existing measurement techniques and instrumentation will have to be developed further as whole new ranges of nanomanufactured products will appear.

Following a presentation of the general dissemination of traceable nanometrology to the workplace [Section 2], the main part of this Report contains the results of the CO-NANOMET Consultation on Metrological Traceability, Standards and Metrology in Industrial nanotechnology [Section 3].

## 2. Study of general dissemination of traceable nanometrology to the workplace

In studying the general dissemination of metrological traceability to the nanomanufacturing workplace, we have focussed on two main aspects of presenting metrology in nanotechnology for industry:

- [Contents of dissemination](#)
- [Best practice of dissemination](#)

A relook and strengthening of a European educational infrastructure is needed in support of nanotechnological innovation through better measurements on the nanoscale<sup>5</sup>.

### 2.1 Contents of dissemination

In addition to metrology's contribution to improving scientific understanding, a second equally important benefit of metrology is much more practical, and of particular industrial relevance: metrology is closely linked to the concepts of quality control or conformity assessment, which means making a decision about whether a product, service or other entity conforms to specifications.

Conformity assessment provides confidence for the consumer that requirements on products and services are met, it helps producers and suppliers to ensure product quality, and it is often essential for reasons of public interest (e.g., public health, safety and order, protection of the environment and the consumer), and of fair trade. Conformity assessment is the aspect of metrology that turns science and innovation into economy and prosperity.

With this in mind, one key observation is to place (nano)metrology in the right context, so that when people in the workplace have to choose the relevant metrology tools and human resources, they can relate product requirements – often in terms of specifications for conformity assessment – to the corresponding metrological requirements.

Thus we have emphasised – both in CO-NANOMET deliverables<sup>6</sup> such as the WP1 CO-NANOMET Strategy Paper and the WP3 Introductory Guide to Nanometrology – how metrology is related to product requirements:

- The idea is that – in any field – one firstly (step 1) has to reach a consensus about a common terminology to aid communication, especially in multidisciplinary areas such as nanotechnology. One needs for example to define what is the 'nanoscale', what is a nanoparticle; how does one denote the effective surface area of a nanoparticle; what are relevant material or product properties etc.
- Once the common language is agreed, then the next step (2) is to give a harmonised and unambiguous description of the recommended measurement methods, instruments and laboratory capabilities for making measurement and testing of nanosystems.

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<sup>5</sup>Report on the European Commission's Public Online Consultation, TOWARDS A STRATEGIC NANOTECHNOLOGY ACTION PLAN (SNAP) 2010-2015, [http://ec.europa.eu/research/consultations/snap/report\\_en.pdf](http://ec.europa.eu/research/consultations/snap/report_en.pdf)

<sup>6</sup> <http://www.co-nanomet.eu/>

- Thereafter, with the words and methods to describe and test products, one can then proceed to standardise requirements on nanosystems to promote efficient and fair trade for both producer and consumer, or in view of regulatory limits (step 3, in which standards set the essential requirements).

A final observation about the appropriate contents of any dissemination of nanometrology to the workplace concerns how documentary standards (norms) and what metrological methods and traceability requirements can meet stakeholder needs. This has been dealt with in a consultation of these issues with the CO-NANOMET ENAGs (European Nanometrology Action Groups<sup>7</sup>), as reported in [Section 3](#).

## 2.2 **Best practice of dissemination**

There are several means of disseminating nanometrology to the workplace. For example, new training material – in the form of courses, perhaps on the Internet, and compendia – is being developed – see CO-NANOMET Coordination of Education & Skills<sup>8</sup>.

In making the Consultation of the current CO-NANOMET task (4.3), additionally studies have been made of:

- Programmes using **local networks** aimed at encouraging small to medium sized enterprises to exploit the opportunities offered by for example new micro- and nanotechnologies.
- Development of **written standards (norms) and guidelines** as pedagogical material [[Section 3.1](#)].

### 2.2.1 **Local networking**

One example is the Swedish minST programme:

minST ("Expert competence in micro- and nanotechnology"), is the Swedish Knowledge Foundation's programme for educating small to medium sized enterprises about the opportunities offered by these new micro- and nanotechnologies. Further information about the Knowledge Foundation's motives and objectives is available from their website [www.kks.se](http://www.kks.se).

The aim is to utilize the new opportunities created by the technology to increase companies' profitability and belief in the future. [minST](#)'s operations employ networks and working methods developed within its sister programme [teknIQ](#). This work is led by Mälardalen University together with the research institutes Acreo and Imego and has an initial budget of SEK 20 million (project duration 2005-2011).

Micro- and nanotechnologies have great future potential for Swedish industry; at the same time Swedish universities and colleges are the repositories of great competence in these fields. Components based on nanotechnology have started to become commercially available, but many medium to small sized companies have yet to become aware of the opportunities made available by this technology.

A second programme - [teknIQ](#) ("Expert competence in intelligent products") is an earlier part of the Swedish Knowledge Foundation's programme<sup>9</sup>. Although in a different area, this

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<sup>7</sup>CO-NANOMET 2009 "Nanometrology Discussion Papers", <http://www.co-nanomet.eu/page1198/Training-Resources/Nanometrology-Discussion-Papers>

<sup>8</sup><http://www.co-nanomet.eu/page1014/CoNanomet-Home/Coordination-Of-Education-And-Skills>

<sup>9</sup><http://www.tekniq.se/> [teknIQ](#) Swedish Knowledge Foundation's programme "Expert competence in intelligent products"

programme appears to have set the tone for a number of subsequent programmes, including minST, in providing best practice in the dissemination of new technologies to the SME workplace.

Amongst some of the principal results of the teknIQ study were that it is essential to have in this dissemination:

- **Actively-engaged people** with the skills and capabilities for best knowledge exchange.
- An **active information dissemination**, including homepage, newsletters, articles and papers about successful case studies in industry. An annual competition for the “best product of the Year” was one element with most impact.
- **Division of the programme into regional parts** where the latter – rather than the central programme leadership – have ensured a local anchoring and adaption to local needs and resources.
- **Continued public financing**, since the “motor” of the programme was the search and idea development activities which in teknIQ’s opinion cannot be operated on purely commercial conditions.

Experiences from the teknIQ study which might be applicable also to the future programme recommended by CO-NANOMET in bringing nanotechnology through to successful business include:

- A form of consortium for each product development which included **chosen universities and research institutes** was found to give:
  - a deal of legitimacy in contacts with companies;
  - a long, start-up time but which nevertheless gave a rather complete consensus, even in complex tasks;
  - complementary views of product visions; product development expertise; funding programmes etc;
  - unfortunately an unstable organisation with high rates of personnel change.
- The **programme board** was strengthened by having representatives from both academia as well as large and small companies.
- A relatively **long project time** – six years – was found to be very advantageous in relations with companies.

A working model for **project search activities** included:

- Creating a **broad understanding of the new technology** in the workplace through visionary seminars; publications about successful companies; participation in exhibitions etc;
- Choosing the **‘right’ companies** which have the best technical and business possibilities to appreciate the new technology while not yet having the broader competence in that area;
- **Initial contacts** with an individual, chosen company are made through a joint idea-creation in the form of idea seminars, needs analysis etc, in order to be able to “ask for something one didn’t earlier know one was missing”;
- **Membership contract;**

- The company's pledge to continue in this task is matched by a quotation from the consortium, together with a **'tailor-made' competence package**.

Results of the Swedish teknIQ programme "Expert competence in intelligent products" included:

- 38 product prototypes developed of which 30 were put on the market;
- 23 companies reckon with 100% certainty that their new products will be profitable;
- 23 companies report a cumulative turn-over increase of 25 M€ compared with the initial investment of 6 M€ in the original programme (duration 1999-2005).

### 2.2.2 Norms and guidelines as pedagogical material

The development of written, documentary standards (norms) and guidelines as pedagogical material has been identified in the current Consultation [[Section 3.1](#)]. Amongst recommendations are:

- A **guideline for good experimental practice** as a preparatory stage to standardisation for working with nanoparticles is demanded. Due to the lack of appropriate measurement technology, which is both precise and easy in application, still a large scientific knowledge is required, to achieve reliable measurement data.
- **Entry level standard measurement methods** especially tailored for start-ups and SMEs are required. Otherwise their access to the market will be handicapped by the lack of easy-to-use standards.
- **Guidelines for the calibration of instruments** are very helpful for the users as well as written standard test procedures.
- There is still a rather **large gap between measurement methods** actually applied in practice and currently internationally agreed written standards.

### 3. Consultation on Metrological Traceability, Standards and Metrology in Industrial Nanotechnology

A principal activity of the CO-NANOMET Task 4.3 was the performance of a Consultation on Metrological Traceability, Standards and Metrology in Industrial nanotechnology according to the three main tasks:

- Responsibility for reporting to the relevant standards bodies at an integrated level of requirements emerging. A shortlist of [recommendations in regard to standards](#) will be derived and a presentation to CEN/TC 352 made.
- Identify standardised and validated [measurement methods](#), and the tools enabling the assurance of the quality of measurements.
- Gather [metrological traceability](#) and other metrology requirements for the industrial arena, emerging from all ENAG areas, review for common needs, and where appropriate share developing approaches.

To this end the Task 4.3 leader engaged directly with all CO-NANOMET ENAGs<sup>10</sup> and others (initial e-mail dated 12<sup>th</sup> March 2010, reminder dated 12<sup>th</sup> April, deadline 10<sup>th</sup> May 2010, complementary material added during period May – October 2010).

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<sup>10</sup>CO-NANOMET 2009 “Nanometrology Discussion Papers”, <http://www.co-nanomet.eu/page1198/Training-Resources/Nanometrology-Discussion-Papers>

**3.1 Work on standardisation to be developed in collaboration with the already established CEN technical committee 352 (Task 4.3.2)**

**Standardisation**

Documentary standards are developed in nanotechnology, as elsewhere, to provide a harmonised and unambiguous framework to describe nanomanufacturing both in the regulatory context, for instance, where there are perceived risks with nanotechnology, but also to ensure general product quality and conformity compliance to facilitate trade and promote customer satisfaction and efficient production. Since **product quality** is determined, through conformity assessment, by **measurement quality** in testing products, standardisation is developed not only for the nanoproducts themselves but also the nanometrology used to test them. Quality-assured measurement enters essentially in the development of both **generic standards** and **sector-specific standards**.

From CEN\TC 352<sup>11</sup>:

"Nanotechnology is commonly understood as a technology involving the manipulation and application of material based on its properties at the atomic scale. Nanotechnologies are the design, characterisation, production, and application of structures, devices, and systems by controlling shape and size at the atomic scale. Nanotechnologies are predicted to be the most important driver for economic growth in the 21st century. Applications of nanotechnologies will have an impact on all aspects of life and will enable advances to be realized in areas of communication, health, manufacturing, materials, and knowledge-based technologies. Industrial and consumer applications and uses of nanotechnologies are expected to grow dramatically during the coming years. Given the magnitude of the potential market offered by nanotechnologies, CEN established CEN/TC 352 'Nanotechnologies' at the end of 2005 to develop a set of standards addressing the following aspects of nanotechnologies:

- classification, terminology and nomenclature;
- metrology and instrumentation, including specifications for reference materials;
- test methodologies;
- modelling and simulation;
- science-based health, safety and environmental practices;
- nanotechnology products and processes.

Standards in each of these areas could be specific to a product, process or industry."

Co-Nanomet has reported to both the ISO/TC 229 nanotechnology group as well as CEN/TC 352: The situation is that in standardisation for nanotechnologies, one has the European CEN/TC 352 group which is matched by the international group ISO/TC 229. The work of these two

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<sup>11</sup> <http://www.cen.eu/cen/Sectors/Sectors/Nanotechnologies/Pages/default.aspx>

groups is coordinated following an existing Agreement on technical cooperation between ISO and CEN – the "Vienna Agreement" - where work done in one group is not duplicated by the other. At meetings of ISO/TC 229 (in Maastricht, May 2010 and Malaysia, December 2010) and CEN/TC352 (Brussels, November 2010), CO-NANOMET took this opportunity of reporting to that group, in particular in meetings of the ISO/TC 229/JWG 2 Study Group on Metrology. Referring to the Vienna agreement, these reports to ISO and CEN can be considered as complementary.

### Challenges in standardisation

Two main challenges for metrology in standardisation, including nanometrology, to be addressed are:

- Documentary standards (or norms) are increasingly not only setting basic requirements but also becoming a valuable pedagogical resource in disseminating nanoscale measurement techniques to the workplace. Unfortunately, norms sometimes make reference to **unrealistic and ambiguous measurement specifications** and unclear requirements.

#### *Suggested actions:*

- written standards should be checked against a "metrology checklist"; an example of such metrology check-list has been developed inside the ISO/TC 229/JWG2 (JWG2\_N095), and has been effective in screening submitted new work item proposals. There is a clear similarity with a recent CEN initiative on the consideration of environmental aspects in standards.
  - written standards describing new measurement procedures should be validated by an interlaboratory comparison before their release.
- Industry and society are placing **increasingly exacting demands** on measurement in terms of complexity and accuracy, including meeting 'grand challenges' such as in energy & the environment, health & safety amongst others, employing nanotechnology.

#### *Suggested action:*

- There is a need for more pre-normative R&D in metrological aspects of measurement and product standards for nanotechnology. Significant contributions are needed to **pre-normative research**, in developing the necessary metrological aspects at all steps in product development – from initial product design and specification, through metrological design, procurement and actual measurement, to final product conformity assessment and marketing. One example of a recent action

addressing these challenges is the signing of a Collaboration Agreement between EURAMET (the association of European national metrology institutes) and CEN-CENELEC<sup>12</sup>.

As a result of our CO-NANOMET consultation with the ENAGs<sup>13</sup>, the following recommendations have been developed concerning recommended documentary measurement standards (or measurement norms) in nanotechnology:

### 3.1.1 ENAG Nanoparticles

#### Area 3: Shortlist of recommended standards (norms) in nanotechnology

Methods to assess:

1. the **parameters describing aggregates/agglomerates**, e.g.  $x_{Gyr}$ ,  $N_{agg}$
2. **shape parameters** from morphology data, e.g. sphericity, aspect ratio, fractal dimension for  $x_{Gyr}$
3. the **surface area** of a dispersed phase in a liquid phase (for example via SAXS or via titration experiments )
4. the **concentration** of particles in liquid or solid matrices
5. the **solubility and dissolution kinetics** of engineered nanoparticles (ENP)
6. the **wettability** of ENPs
7. particle **structure** (porosity, fractal dimension)
8. the **composition** of different parts in nanostructured ENPs at the nanoscale (core-shell, hybrid,...)
9. the **density and optical properties** of nanoparticles

### 3.1.2 ENAG Nanobiotechnology

#### Area 3: Shortlist of recommended standards (norms) in nanotechnology?

Since many current and emerging industrial applications in this area incorporate thin films or nanoparticles the needs listed in those ENAGs apply here as well. In addition the following needs have been identified.

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<sup>12</sup> “Metrology and Standardisation in Europe” 2010, <http://www.cenelec.eu/Cenelec/CENELEC+in+action/News+Centre/Press+releases/EURAMET.htm>

<sup>13</sup> CO-NANOMET 2009 “Nanometrology Discussion Papers”, <http://www.co-nanomet.eu/page1198/Training-Resources/Nanometrology-Discussion-Papers>

- biocompatibility; biological effects, including toxicity of particles and surfaces
- surface properties of medical devices (e.g., surface roughness parameters, chemical composition, surface contamination levels)
- certified reference materials and biological formulations for development and benchmarking of new techniques and instrumentation

New standardisation groups addressing normative development (including metrology) have been recently created in CEN and ISO amongst others. Examples of new nanobiotechnology-related standards produced or under development by them are: “Nanotechnologies -- Vocabulary -- Part 5: Bio/nano interface” ([ISO/DTS 80004-5](#)) “Nanotechnologies -- Vocabulary -- Part 7: Healthcare – Therapeutics and Diagnostics” (ISO/DTS 80004-7) and “Nanotechnologies -- Endotoxin test on nanomaterial samples for in vitro systems -- Limulus amoebocyte lysate (LAL) test” (ISO 29701:2010)

Important work on standardization and reference materials to build on is carried out by, for example:

- **ISO/TC 212** – Clinical lab testing and in vitro diagnostic test systems
- **ISO/TC 194** – Biological evaluation of medical devices
- **ISO/TC 201** – Surface chemical analysis
- **EDQM** (Council of Europe) - Harmonisation & Co-ordination of Standardisation, Regulation & Quality Control
- **IRMM and the ERM consortium** – Reference materials for clinical chemistry and biotechnology

### 3.1.3 ENAG Thin Film and Structured Surfaces

#### Area 3: Shortlist of recommended standards (norms) in nanotechnology

*(List mainly refers to ENAG Thin Film and Structured Surfaces, but also reflects impressions voiced by stakeholders of ENAG Nanoparticles & ENAG Critical dimensions and scanning probe techniques)*

- Nanoparticles

A **guideline for good experimental practice** as a preparatory stage to standardisation for working with nanoparticles, is demanded. Due to the lack of appropriate measurement technology, which is both precise and easy in application, still a large scientific knowledge is required to achieve reliable measurement data.

- **Entry level documentary measurement standards** especially tailored for start-ups and SMEs are required. Otherwise their access to the

market will be handicapped by the lack of easy to use standards.

- **Practical support needed** – step-by-step strategy preferred:

1. NMIs and related bodies should focus on the development of new and the improvement of existing instrumentation for nanoscale measurements tailored to the needs and demands of industry and society. In particular for NP measurement a demand for appropriate measurement technology is detected, as many parameters currently cannot be measured or at least not satisfactory.
2. Once the instrumentation is available, its performance can be assessed by round robins.
3. The experience gained in the tests will also ease the process of preparing appropriate standardisation documents: A good and reliable measurement technique tested this way is regarded as the foundation for following successful standardisation.

- **Identified difficulties in present standardization work:**

- **Lack of maturity of methods proposed to become standard methods – time pressure in the development of standards**
- Companies, particularly SMEs, have **difficulties to influence standardisation work**
- **Lack of information/awareness:** A better information policy on documentary standards as well as on transfer standards and metrological support by NMIs, designated institutes and others is recommended.

At the international level, some work is in progress:

- For SIMS, AES, XPS and other surface analytical techniques: in ISO/TC 201 Surface Chemical Analysis: Study Group. Additional New Work Areas: Confocal Laser Scanning Microscopy (CLSM), Ellipsometry (work item under discussion, not yet approved)

### 3.1.4 ENAG Critical dimensions and scanning probe techniques

#### Area 3: Shortlist of recommended standards (norms) in nanotechnology?

- **Guidelines for the calibration of instruments** are very helpful for the users as well as written standards
- There is still a rather **large gap** between measurement methods actually applied in practice and those currently described in internationally agreed written standards. For example, in the field of roughness measurements only the use of tactile instruments for roughness is standardized internationally. Optical methods and scanning probe techniques as well as many other areal measuring methods have not yet been included in international standardization, but are under development. Use of these techniques to validate products still requires an individual bilateral agreement of both partners (measurement laboratory and customer) on the details of the measurement procedure. However, the measurement of a large number of geometrical parameters is already offered as calibration services by NMIs and approved by international comparisons. Here the guideline how to measure and analyse the data is described in the “technical protocols” circulated within the comparisons.

At the international level, some work is in progress by:

- the ISO/TC 201 “Surface Chemical Analysis” Sub-Committee 9 “**SPM**” for the basic calibration of scanning probe microscopes. Much of this work aims to cover SPM standardization over far more than just dimensional aspects. Standardization projects on XRR and TXRF are about to start, based on experiences gained during preceding VAMAS<sup>14</sup> projects
- ISO/TC 213/WG 16 **on surface texture** (ISO 25178) aims to review and update the existing standards for surface texture, and expand them to smaller scales. Furthermore, the existing roughness standards apply to profiles only, while the drafts of new standards are intended to cover areal-measurement methods as well.
- ISO/TC 229 “Nanotechnologies” is working on a long list of techniques to characterise **SWCNT, MWCNT, nanoparticles, nanorods, and other nano-objects by SEM, TEM**, and a large variety of other techniques.
- In cooperation with IEC/TC 113 another document is prepared entitled “Nanotechnologies – **Description, measurement and dimensional quality parameters of artificial gratings**”
- In order to ensure a uniform procedure for **CRM or artefact-based SFM/AFM calibrations**, which agree well to what and how has been certified at the NMIs, guidelines or standards should be adhered to. In the case of SFM/AFM, this is e. g. the VDI/VDE 2656 – Part 1, which is currently being discussed as project 11952 at ISO level to be transformed in an International Standard.

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<sup>14</sup> Versailles Project on Advanced Materials and Standards, [www.vamas.org](http://www.vamas.org)

As an example of national activities, in Germany several guidelines for the application of optical as well as scanning probe microscopes are being drafted for the basic calibration as well as for their use in form and roughness measurements by the respective guideline committees (VDI/VDE GMA, web-site [www.vdi.de](http://www.vdi.de)).

### 3.1.5 ENAG Modelling and Simulation

#### Area 3: Shortlist of recommended standards (norms) in nanotechnology?

##### Terminology & nomenclature

- At the EU level there is currently one directive (Regulation EC/1223/2009 on Cosmetic Products) dealing with cosmetic products that includes a definition of nanomaterials but **allows for a change** in the definition depending on scientific and/or international developments [article 2.3].
- The FDA Nanotechnology<sup>15</sup> Task Force does not recommend attempting to adopt **formal, fixed definitions** of "nanoscale materials," "nanotechnology," or related terms for regulatory purposes at this time.

##### Test methodologies

- A barrier to the development of molecular modelling at the quantum scale is the lack of results of validated methods, and inadequate methods for predicting uncertainties in calculations.
- The identification of a set of test problems in molecular modelling for which answers are already known, or for which good experimental data exist, for use in model validation, is a key requirement<sup>16</sup>.

### 3.1.6 Other areas of nanotechnology – nanomechanical testing

#### Area 3: Shortlist of recommended standards (norms) in nanotechnology?

##### Test methodologies

*Nanomechanical testing*<sup>17</sup>

<sup>15</sup> <http://www.fda.gov/downloads/ScienceResearch/SpecialTopics/Nanotechnology/ucm110856.pdf> , Nanotechnology, Report of U.S. Food and Drug Administration Nanotechnology Task Force. July 25, 2007

<sup>16</sup> <http://www.co-nanomet.eu/content/co-nanomet/demes005.pdf> NPL Report DEM-ES 005 Mathematical Modelling at the Nanoscale, T J Esward and V P Sokhan, 2006

<sup>17</sup> In CO-NANOMET 2009 "Project presentations" <http://www.co-nanomet.eu/page1207/Consortium-Fileshare/Project-Presentations> "European Strategy for Nanometrology", R Leach

- **Nanoindentation** to determine material mechanical properties (hardness, elastic modulus, etc) particularly of coatings and nanocomponents. Widely used technique but many aspects still being developed and standardised – base set of four standards (norms) in ISO/TC 164.
- **AFM** – relatively new technique of determining material mechanical properties, major developments
- **Nanotribology** – to determine friction, wear, degradation of surfaces – is a developing area where agreed test methods have not yet been defined.

### **3.2 Identify standardised and validated methods, and the tools enabling the assurance of the quality of measurements (Task 4.3.1)**

Recommended, standardised measurement methods are needed in support of measurement quality assurance of laboratories making measurements in the workplace. Product quality is very much determined by the quality of the measurements made to test against specifications. Examples of challenges in developing measurement methods at the nanoscale include:

- Need for new measurement instrumentation and test methods working in the nanoscale
- New characteristics unique to the nanoscale need to be measured
- Measurements in challenging environments, e.g. ultra-high vacuum

As a result of our CO-NANOMET consultation with the ENAGs, the following observations have been made concerning the identification of standardised & validated methods, instrumentation & tools enabling nanometrology:

#### **3.2.1 ENAG Nanoparticles**

##### **Area 2: Identify standardised & validated methods, instrumentation & tools enabling nanometrology**

###### *1) standard and validated methods*

Efforts to identify and list standard methods and existing instrumentation for the characterisation of ENPs are made both in CEN/TC 352 (WG 1, EN ISO TR 11808, Nanotechnologies – Guide to nanoparticles measurement methods and their limitations, project leader Alexandre Cuenat, [Alexandre.cuenat@npl.co.uk](mailto:Alexandre.cuenat@npl.co.uk)) and in ISO/TC 229 (WG 3/PG 5, TR 13014, Nanotechnologies – Guidance on physicochemical characterization of engineered nanoscale materials for toxicologic assessment, project leader Dr Richard C. Pleus, [rick@intertox.com](mailto:rick@intertox.com); and WG 4/PG 3, TS 12805, Nanotechnologies - Guidance on specifying nanomaterials, project leader Stuart MacLachlan, [stuart.maclachlan@ceram.com](mailto:stuart.maclachlan@ceram.com)).

*2) (More) on-line/in-line process control instrumentation*

Such instrumentation has to meet the following requirements:

- high temporal resolution, fast and robustness (resistant to fouling, incorrect operation, ...)
- high concentration, harsh environments (pH, temperature, pressure, ...)

In process control, one needs to focus on the characterisation of disperse systems in specific environments (determined by the process conditions); this is an approach which goes beyond the study of individual particles, and has consequences for the validation of instruments and techniques and for the requirements for reference materials. In practice, the traceability issues with these measurements are particularly challenging. Nevertheless, metrological traceability, as a means to achieve comparability and mutual recognition, is an issue of increasing importance, as it is both an advantage for the dissemination of processing techniques between different production plants in globally operating companies, and an advantage when trying to model the process-product-relations.

*3) Methods to assess the structure and the composition of the nanoparticles at the nanoscale*

Real, industrial particles are often different from the pure and spherical particles used to calibrate instruments. Therefore, better methods are needed to assess, at the nanoscale, the complex structures and composition of nanoparticles (and nanoparticle systems).

- *particle structure: porosity, fractal dimension*
- *“composition of the material”: core-shell, hybrid, janus-like, ...*

### 3.2.2 ENAG Nanobiotechnology

#### **Area 2: Identify standardised & validated methods, instrumentation & tools enabling nanometrology**

Measurement needs in this area are addressed with a wide range of microscopy, spectroscopy and molecular biology techniques. The development of new measurement principles, techniques and instrumentation for analysis of biological systems is a rapidly developing area. (see descriptions in ENAG Scoping paper <http://www.co-nanomet.eu/content/Co-nanomet%20protected%20documents/periodic%20reports%20and%20deliverables/D2.1%20Action%20Group%20Meeting%20Reports%202009.pdf>, page 43-63).

### 3.2.3 ENAG Thin Film and Structured Surfaces

#### Area 2: Identify standardised & validated methods, instrumentation & tools enabling nanometrology

- *X-ray technology*: especially Small Angle X-ray Scattering (SAXS) for NP and X-ray reflectometry (XRR) for thin films. Due to the short wavelength, X-ray based methods are inherently well adapted to nanometrology needs; X-ray methods have two main drawbacks: 1. safety due to the harmful nature of the radiation and 2. due to the mapping into the reciprocal space and consequently the requirement of (complex) mathematical modelling of the measurement for the refinement of the data.
- *Ellipsometry*  
Well established in thin film technology, especially in thin film measurement with in-line potential; gains a very high precision; accuracy can be established by transfer standards, which are available by different vendors (NMIs and private/commercial providers).
- *Scatterometry* (in optical region and optionally in extreme Ultraviolet and X-ray regime) A method which has a large potential in the field of structured thin film applications; the instrumentation is quite simple and already available, since the technique is based on ellipsometry technology, but now analyses the diffusely scattered intensity. The main work to establish the technique has to be done in the mathematical modelling of the measurements, since it is an inverse method. Therefore the method needs advanced calculus and high computer power for the data refinement. Currently this technique is developing rapidly, driven by the demand for advanced fast and non destructive analysing technology in applications with critical dimensions.
- *Electron microscopy*, including SEM, TEM, STEM etc: These techniques are very important to provide geometry data for correct modelling of other measurement techniques (like Ellipsometry, Scatterometry, X-ray scattering and reflectometry etc.). TEM is not well suited for in-line measurement due to the large measurement time caused by the intensive preparation process. While TEM can provide direct metrological traceability to the observable crystal lattice constants of, say, silicon, with atomic resolution, it is difficult to provide traceability for images of lesser magnification, between 50 nm and 100 nm. Here the scale of the lattice spacing is no longer visible, and transfer standards with applicable dimensions are rare. Despite the potential to produce good pictures at nanoscale, SEM requires a careful modelling and understanding of the measurement methods in order to analyse and evaluate the obtained images in a metrological way. *(also see comments by ENAG Critical dimensions and scanning probe techniques)*

*Scanning Force Microscopy (SFM):*

- For thin film measurements in the nanometre range, SFMs use step height measurements to determine film thickness. However for those measurements the thin film has to be structured, i.e. partially removed from the substrate by e.g. lithographic techniques. The sample handling itself is more easy, compared to SEM, but tip sample interaction is quite complex, e. g. material contrasts might show up as apparent topography contrast and thereby falsify step height (film thickness) measurements (*also see comments by ENAG Critical dimensions and scanning probe techniques*)
- *Dynamic Light Scattering (DLS), Ultrasonic extinction, Particle counting instruments.* All these techniques have the potential to measure large numbers of NPs to determine the particle distribution function with statistical significance. Nevertheless these methods still have to be improved, to provide sufficient precision and traceability for these instruments.

### 3.2.4 ENAG Critical dimensions and scanning probe techniques

#### Area 2: Identify standardised & validated methods, instrumentation & tools enabling nanometrology

Refer to the ENAG4 scoping paper:

<http://www.co-nanomet.eu/content/co-nanomet/European%20Workshop%20Nov%202009/Nanometrology%20Discussion%20Document%20PDF%20Format.pdf>

### 3.2.5 ENAG Modelling and Simulation

#### Area 2: Identify standardised & validated methods, instrumentation & tools enabling nanometrology

Commonly used methods in modelling: finite-element modelling, Molecular Dynamics, Monte Carlo simulation, Density functional theory, *ab initio* calculations, spin dependent DFT, time-dependent Monte Carlo

Newly-emerged methods:

- Dissipative Particle Dynamics
- Field Theoretic Polymer Simulation
- Electron tomography combined with electrodynamic simulations – a new, rigorous tool for understanding the plasmonic properties of real three-dimensional nano-objects (accurate nanometrological characterization of noble metal nanoparticles)

### 3.2.6 Other areas – Nanoelectronics

#### Area 2: Identify standardised & validated methods, instrumentation & tools enabling nanometrology

##### *Nanoelectronics*<sup>18</sup>

##### *Table MET1 Metrology Difficult Challenges*<sup>19</sup>

##### *Difficult Challenges $\geq 16$ nm*

##### *Summary of Issues*

- Factory level and company wide metrology integration for real-time in situ, integrated, and inline metrology tools; continued development of robust sensors and process controllers; and data management that allows integration of add-on sensors.
- Standards for process controllers and data management must be agreed upon. Conversion of massive quantities of raw data to information useful for enhancing the yield of a semiconductor manufacturing process. Better sensors must be developed for trench etch end point, and ion species/energy/dosage (current).
- Starting materials metrology and manufacturing metrology are impacted by the introduction of new substrates such as SOI. Impurity detection (especially particles) at levels of interest for starting materials and reduced edge exclusion for metrology tools. CD, film thickness, and defect detection are impacted by thin SOI optical properties and charging by electron and ion beams. Existing capabilities will not meet Roadmap specifications. Very small particles must be detected and properly sized. Capability for SOI wafers needs enhancement. Challenges come from the extra optical reflection in SOI and the surface quality.
- Control of new process technology such as Dual Patterning Lithography, complicated 3D structures such as capacitors and contacts for memory, and 3D Interconnect are not ready for their rapid introduction. Overlay measurements for Dual Patterning have tighter control requirements. Overlay defines CD. 3D Interconnect comprises a number of different approaches. New process control needs are not yet established. For example, 3D (CD and depth) measurements will be required for trench structures including capacitors, devices, and contacts.
- Measurement of complex material stacks and interfacial properties including physical and electrical properties. Reference materials and standard measurement methodology for new high- $\kappa$  gate and capacitor dielectrics with engineered thin films and interface layers as well as interconnect barrier and low- $\kappa$  dielectric layers, and other process needs. Optical measurement of gate and capacitor dielectric averages over too large an area and needs to characterize interfacial layers. Carrier mobility characterization will be needed for stacks with strained silicon and SOI substrates, or for measurement of barrier layers. Metal gate work function characterization is another pressing need.
- Measurement test structures and reference materials. The area available for test structures is being reduced especially in the scribe lines.

<sup>18</sup> In CO-NANOMET 2009 “Project presentations” <http://www.co-nanomet.eu/page1207/Consortium-Fileshare/Project-Presentations> “European Strategy for Nanometrology”, R Leach

<sup>19</sup> THE INTERNATIONAL TECHNOLOGY ROADMAP FOR SEMICONDUCTORS: 2009 Edition [http://www.itrs.net/Links/2009ITRS/2009Chapters\\_2009Tables/2009\\_Metrology.pdf](http://www.itrs.net/Links/2009ITRS/2009Chapters_2009Tables/2009_Metrology.pdf)

Measurements on test structures located in scribe lines may not correlate with in-die performance. Overlay and other test structures are sensitive to process variation, and test structure design must be improved to ensure correlation between measurements in the scribe line and on chip properties. Standards institutions need rapid access to state of the art development and manufacturing capability to fabricate relevant reference materials.

*Difficult Challenges < 16 nm*

Nondestructive, production worthy wafer and mask-level microscopy for critical dimension measurement for 3D structures, overlay, defect detection, and analysis. Surface charging and contamination interfere with electron beam imaging. CD measurements must account for sidewall shape. CD for damascene process may require measurement of trench structures. Process control such as focus exposure and etch bias will require greater precision and 3D capability. New strategy for in-die metrology must reflect across chip and across wafer variation. Correlation of test structure variations with in-die properties is becoming more difficult as device shrinks. Sampling plan optimization is key to solve these issues.

Statistical limits of sub-32 nm process control


Controlling processes where the natural stochastic variation limits metrology will be difficult. Examples are low-dose implant, thin-gate dielectrics, and edge roughness of very small structures.


Structural and elemental analysis at device dimensions and measurements for beyond CMOS.


Materials characterization and metrology methods are needed for control of interfacial layers, dopant positions, defects, and atomic concentrations relative to device dimensions. One example is 3D dopant profiling. Measurements for self-assembling processes are also required. Determination of manufacturing metrology when device and interconnect technology remain undefined. The replacement devices for the transistor and structure and materials replacement for copper interconnect are being researched.


<i>Year of Production</i>	2009	2010	2011	2012	2013	2014	2015	2016
<i>Microscopy</i>								
Inline, nondestructive microscopy process resolution (nm) for P/T=0.1	0,18	0,16	0,14	0,13	0,12	0,1	0,09	0,08
Microscopy capable of measurement of patterned wafers having maximum aspect ratio/diameter (nm) (DRAM contacts) [A]	17	>20	>20	>20	>20	>20	>20	>20
	60	50	40	35	30	28	25	23
<i>Materials and Contamination Characterization</i>								
Real particle detection limit (nm) [B]	20	18	16	14	13	11	10	9
Minimum particle size for compositional analysis (dense lines on patterned wafers) (nm)	17	15	13	12	11	9	8	7
Specification limit of total surface contamination for critical GOI surface materials (atoms/cm <sup>2</sup> ) [C]	5,00E+09	5,00E+09	5,00E+09	5,00E+09	5,00E+09	5,00E+09	5,00E+09	5,00E+09
Surface detection limits for individual elements for critical GOI elements (atoms/cm <sup>2</sup> ) with signal-to-noise ratio of 3:1 for each element	5,00E+08	5,00E+08	5,00E+08	5,00E+08	5,00E+08	5,00E+08	5,00E+08	5,00E+08

*Manufacturable solutions exist, and are being optimized* 

*Manufacturable solutions are known* 

*Interim solutions are known* 

*Manufacturable solutions are NOT known* 

### **3.3 Metrological Traceability in the form of global equivalence to be addressed (Task 4.3.3)**

#### **Metrology – Quality-assured Measurement**

Metrological traceability – where possible, to the universal measurement references of the SI system – ensures that different measurement results – those made at different times and different locations, and even different measurement quantities – can be compared objectively. Products and processes assessed for conformity using traceable test results will themselves be comparable and robust.

Measurement uncertainty is a declared level of quality in the measurement result. It is an estimate of the combined effect of all unknown measurement errors. Measurement uncertainty is always needed when judging whether different measured values are equal, or not. It is also essential in assessing the risks of incorrect decisions of compliancy when comparing a test result with a specification limit. The latter is a key concern in nanometrology, since decisions of conformity assessment, for instance in regulatory contexts, are often of concern.

#### **Metrological challenges at the nanoscale**

Each measurement unit of the SI is defined at a level where the actual measurement accuracy is highest. Thus, for example, the unit of mass is defined as the mass of the International prototype kilogram, since weighings at heavier and lighter levels are less accurate – heavier weights are more difficult to handle, while smaller weights are more easily perturbed.

These trends – where accuracy generally falls towards both shorter ranges and longer ranges – are similar for many measurement quantities. Measurements at the nanoscale (1 nm – 100 nm) lie of course at one extreme of the dimension scale. Because of this, it is challenging in nanometrology to establish metrological traceability and to reach target measurement uncertainties.

Examples of nanometrological challenges include:

- Longer chains of metrological traceability
- New nanoscale reference materials and standards
- Need for new measurement instrumentation and test methods working in the nanoscale
- New characteristics unique to the nanoscale need to be measured
- Measurements in challenging environments, e.g. ultra-high vacuum

This part of the Consultation on Metrological Traceability, Standards and Metrology in Industrial Nanotechnology focussed mainly on suggestions **for international comparisons** to ensure that nanometrology develops into a global and robust discipline to support the coming trade and safety of nanoproducts. Such intercomparisons enable the objective demonstration of the mutual equivalence of the metrological traceability systems of the different laboratories participating and can be used to judge the reliability of statements of measurement uncertainty.

We have ensured that CO-NANOMET from the start has a proper coordination with EURAMET, the European association of national metrology institutes<sup>20</sup> since the latter coordinates primary resources for nanometrology in Europe and is also implementing a major European Metrology Research Programme of interest to many CO-NANOMET participants and stakeholders.

As a result of our CO-NANOMET consultation with the ENAGs, the following recommendations have been developed concerning **Requirements for traceability and industrial nanometrology. Proposals for intercomparisons:**

### 3.3.1 ENAG Nanoparticles

#### Area 1: Requirements for metrological traceability and industrial nanometrology? Proposals for intercomparisons?

There is a need to:

1) Specify more accurately the measurands relevant for engineered nanoparticles (ENP) characterisation

Achievement of SI-traceability (for example in electron or scanning force microscopy) is at the expense of important sample preparation steps, which are costly, time-consuming, and, most importantly, which can alter the actual ENP property. In such cases, it may be acceptable to **limit the metrological traceability of the measurement results to a specific procedure** (for example a standard method) or an artefact (for example a commonly available calibrant without a SI-traceable certified property value).

2) Address the relevance of sample preparation and dispersion stability

The state of dispersion is an important property of an ENP system. That means sample preparation should reproduce that state of dispersion, which is relevant for the technical / Environment, Health and Safety / ... problem. Hence, sample preparation determines the significance of a measurement result and affects – sometimes even dominates – its accuracy and uncertainty. For that reason sample preparation procedures

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<sup>20</sup> [www.euramet.org](http://www.euramet.org)

have to be validated, for example in terms of reproducibility, via interlaboratory comparisons.

Related to sample preparation is the issue of dispersion stability. Both for the industrial use of a dispersed material, as well as for the measurement of a test sample of dispersed material, the stability of the dispersion during use or measurement is important. Stability can be defined - and therefore investigated and measured - in many different ways, depending on the parameter that is supposed to keep a stable value.

### 3) Develop and validate standard methods for a number of ENP measurands

The Co-Nanomet ENP ENAG partners, stakeholders and workshop participants put together a list of relevant ENP measurands. These measurands are proposed to be grouped as shown below. **Interlaboratory comparisons are needed** for the development, reproducibility assessment, and the validation of a number of methods, some of which are new, some of which exist, but were not developed or specifically used for the characterisation for ENPs. These methods are highlighted (italic and underlined: need for a new to be developed standard method; italic: method exists, mainly need for interlaboratory comparisons to better assess reproducibility).

- morphology (topology/geometry):
  - characteristic lengths and areas in 2D-projection
  - *parameters describing aggregates/agglomerates, e.g.  $x_{Gyr}$ ,  $N_{agg}$*
  - *shape parameters from morphology data, e.g. sphericity, aspect ratio, fractal dimension for  $x_{Gyr}$*
- size related properties based on hydrodynamics and/or interaction with external fields
  - diffusion coefficient, hydrodynamic diameter (of translation)
  - *settling velocity, Stokes diameter*
  - *aerodynamic diameter*
  - *acoustophoretic mobility*
  - *(partial) scattering or extinction cross section e.g. via SAXS ( $x_{Gyr}$ )*
- surface area of the dispersed phase
  - via adsorption of gases e.g.,  $S_{BET}$
  - *via SAXS*
  - *via titration experiments, with surfactants, polyelectrolytes etc.*

- chemical composition and phase
  - crystallinity (amorphous fraction vs crystalline fraction)
  - phase (fractions of different crystallographic phases)
- concentration of particles in gas, liquid or solid matrices
  - Mass, surface, number concentration (*gas, liquid, solid*)
- interfacial properties (which depend on whether the ENP is in polar and non-polar solvents, or in gas):
  - *surface charge e.g. via zeta-potential*
  - *pristine point of zero charge and iso-electric point (for different charge determining ions)*
- interaction with continuum/solvent
  - *solubility and dissolution kinetics*
  - *wettability*
- basic physical properties of the nanoparticles
  - *density*
  - *optical properties (light absorption/transmission/reflection)*

#### 4) tools enabling nanometrology

One of the findings of the ENP ENAG workshop is the need for an easily accessible and understandable introduction to metrology at the nanoscale. In this respect, the efforts of CO-NANOMET to write an 'Introductory Guide' are very timely.

One class of metrology tools are reference materials. A list of available reference materials (certified and non-certified) can be consulted on the BAM website: [www.nano-refmat.bam.de](http://www.nano-refmat.bam.de). Another kind of metrology tools are the calibration services offered by metrology institutes.

Certified reference materials (CRMs) for nanoparticles which are well characterised by NMIs or other, accredited, CRM producers. Materials and specifications of these nanoparticle CRMs (including materials consisting of particles in a solid or liquid matrix) should be as close as possible to the materials and specifications of the users' nanoparticles, i.e. the primary goal for these CRMs is not a record-breaking small

uncertainty. The design goal should be to keep the additional contribution to the final uncertainty small, allowing for the difference between the user nanoparticles and the CRM nanoparticles.

### 3.3.2 ENAG Nanobiotechnology

#### **Area 1: Requirements for traceability and industrial nanometrology? Proposals for intercomparisons?**

Quality assured measurements, including traceability, are an important requirement for demonstrating the efficacy of products, and not the least to ensure the safety of patients. Measurement quality assurance in this area is to a great extent based on traceability to internal standards, rather than to primary standards. For example, measurements in biology and medicine that are dealing with amount of a specific substance are sometimes using the **International Unit (IU)**, which is based on measured biological activity or effect. The precise definition of one IU differs from substance to substance and is established by international agreement for each substance, and realized in the form of reference preparation of the substance.

Examples of topics suitable for intercomparisons are:

- Surface roughness of medical implants, as measured on different areas and by different methods
- Surface chemical composition, including surface contamination levels, of medical implants
- Amount and activity of biomolecules immobilized on surfaces
- Cytotoxicity of materials and nanoparticles

### 3.3.3 ENAG Thin Film and Structured Surfaces

#### **Area 1: Requirements for traceability and industrial nanometrology? Proposals for intercomparisons?**

##### Metrological traceability and Certified reference materials (CRMs) for thin films

- SI-traceability for thin films is demanded only in exceptional cases, e.g. determination of a fundamental constant with high accuracy like the SiO<sub>2</sub> thickness on a silicon sphere used in the Avogadro project<sup>21</sup>. The user typically needs to select an appropriate CRM depending on his needs which are available from companies and designated institutes such as BAM, VLSI, NIST, IRMM, ... Alternatively, NMIs like PTB calibrate samples from industry on demand providing traceable certified property values obtained with one specific technique or

<sup>21</sup> <http://www.emrponline.eu/selected-JRPs.html> , EURAMET EMRP iMERApus T1.J1.2 NAH Avogadro and molar Planck constants for the redefinition of the kilogram

a combination of techniques.

- Typically instrument manufacturers are interested in making the results of their equipment traceable, since it provides a marketing benefit, but additional expenses for the realization of traceability are not easily accepted.

### 3.3.4 ENAG Critical dimensions and scanning probe techniques

#### Area 1: Requirements for traceability and industrial nanometrology? Proposals for intercomparisons?

Certified reference materials or artefacts, typically calibrated with metrological SFM (model A) or SEM at the primary NMI level<sup>22</sup>, can be used as transfer standards when calibrating industrial SFMs/AFMs and other nanoscale measurement techniques. As in other metrology fields, there may be secondary (accredited) calibration laboratories which act as intermediaries between industrial end-users and primary level NMIs. The customer is advised to enquire carefully how the CRM producer ensures traceability and determines the uncertainties in their CRM certificates; e. g. some companies have had a master set of standards certified at an NMI and then use them to calibrate their instruments which they apply for the calibration of the user standards.

There is no general rule which technique yields the lowest uncertainty of the certified value. The technique of choice mainly depends on the individual properties of the particular artefact to be certified. Furthermore, the instrumentation available at the various NMIs differs. Similarly, no generally valid statement can be given on the calibration costs and order times. Nanoscale CRMs should be carefully selected and it is recommended that customers of NMI calibration services contact NMIs at an early stage to agree on possible certified calibrations: very often the relevant instruments at NMIs are unique, many measurements and their analysis are time-consuming.

Table 8 International comparisons in progress in the field of nanometrology. Working Group of Dimensional Metrology (WGDM) of the Consultative Committee of Length (CCL)

Name	Measurand or Artefact	Status/Results published
<b>Nano 1</b>	Line width	In preparation
<b>Nano 6</b>	SPM Linewidth Standards	In preparation

Future interlaboratory comparisons should focus on the 3D aspect of nanometrology (e.g. measuring shape and form of nano-objects) and

<sup>22</sup> Danzebrink H-U, Koenders L, Wilkening G, Yacoot A and Kunzmann H (2006). Advances in scanning force microscopy for dimensional metrology Annals of CIRP vol 55/2/2006

should be planned for the time after these two NANO comparisons.

Also within EURAMET (the regional metrology organization of Europe), comparisons have been organized (see Table 9), which have the advantage of running faster than international comparisons. In order to ensure intercontinental worldwide linking, normally one NMI from another RMO (i.e. another continent) is included in every EURAMET comparison.

Table 9 Comparisons in progress on dimensional nanometrology in the EURAMET region

Comparison	Measurand	NMI	Status/Report
Euramet L-S15.a (Euromet 925)	Step height, 1D pitch	INRIM, MIKES, <u>PTB</u> , NMC/A*STAR, CMI	Final report published <sup>23</sup> -
<b>Bilateral comparisons</b>			
NMIJ-PTB	1D pitch (25 nm)	<u>NMIJ</u> , PTB	Draft B

### 3.3.5 ENAG Modelling and Simulation

#### Area 1: Requirements for traceability and industrial nanometrology? Proposals for intercomparisons?

Having in mind that the results of measurements depend on the method used, the respective characteristics (size, ...) should clearly carry the information about the method used (example;  $R_{\{AFM\}}$  – THE RADIUS OF A SPHERICAL PARTICLE IS  $R = \dots$  WHEN MEASURED WITH AFM). This is very important when results of simulations are compared with the experimental ones.

<sup>23</sup> [http://www.bipm.org/utils/common/pdf/final\\_reports/L/S15/EUROMET.L-S15.a.pdf](http://www.bipm.org/utils/common/pdf/final_reports/L/S15/EUROMET.L-S15.a.pdf)

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