VAMAS

LNE [1] IRSN [2] lisa [3]

Le progrès, une passion à partager

PRESTANDARDIZATION STUDY ON THE CHARACTERIZATION OF AIRBORNE NANOPARTICLES SIZE:

Size characterization of airborne SiO_2 nanoparticles with on-line and off-line measurement techniques: validation with an interlaboratory comparison

C. Motzkus[1]*, F. Gaie Levrel[1], T. Macé[1], S. Vaslin-Reimann[1], A. Delvallee[1], S. Ducourtieux[1], N. Michielsen[2], F. Gensdarmes[2], S. Bondiguel[2],

P. Ausset[3] and M. Maillé[3]

MESURES & RÉFÉRENCES
Clés de la COMPÉTITIVITÉ et d'un MONDE PLUS SÛR

Laboratoire national de métrologie et d'essais

Context

- Production and use of manufactured nanoparticles, nano-objects, nanostructured powders and nanomaterials (ISO/TS 80004-1:2010) in ≠ forms (TiO_2, SiO_2, NTC, Ag, Al_2O_3,…) by industry and research laboratories

  ≠ Applications : environnement, energie, electronics, cosmetics, car industry construction, medicine, bio-technology, food…

SiO_2

SiO_2 for food

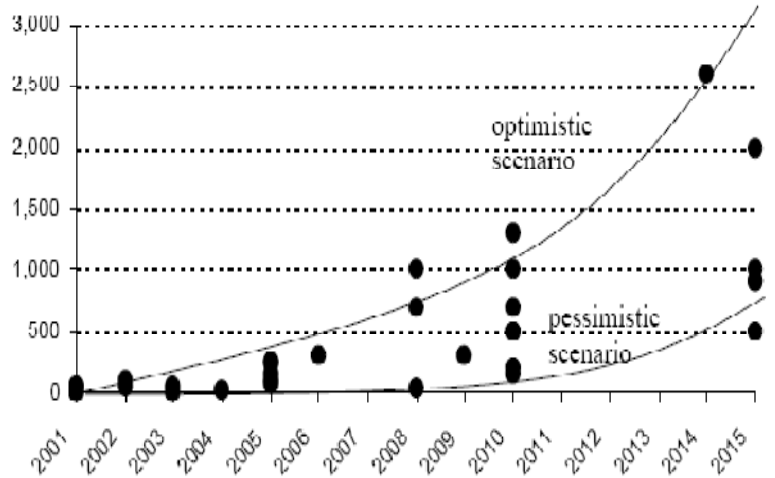
SiO2 for rubber

SiO2 for plastic

TiO_2

CNT

World growing market for nanotechnology (billion US $)



Nano-scale **1nm** ≤ d_p ≤ **100nm**

➡ Nano-object (nanofiber, nanoparticle, nanoplate)

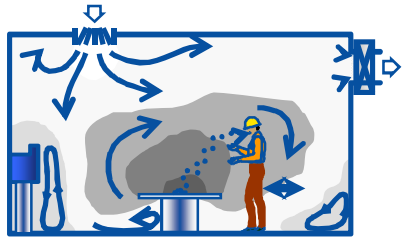
ISO TS/27687: 2008

Context

- **Potential Risks: General population, Environment and product**

Human protection

Atmospheric measurement



Process and workers

- **Need to have some airborne NP characterization metrological standard procedures**

→ **To curb to reliable toxicology studies and ecotoxicology, quality control in industry, the monitoring, the reglementation which begin to arrive now in France** *(Décret 2012-232 du 17 février 2012 et arrêté du 6 août 2012 relatifs à la déclaration annuelle des substances à l'état nanoparticulaire)*

→ **Project VAMAS**

Objectives of VAMAS project

VAMAS : Versailles Project on Advanced Materials and Standards (1985)

- **An international collaborative organization on prestandardization research projects and specifications for advanced materials**

Objectives

- **To develop size characterization methods for airborne nanoparticles that include the entire measurement chain (sampling, analysis, data process) which are traceable and accurate including metrological traceability, calibration, and evaluation of the measurement uncertainty.**

- **Validated the developed protocols by an interlaboratory comparison based on metrological approaches**

Organisation

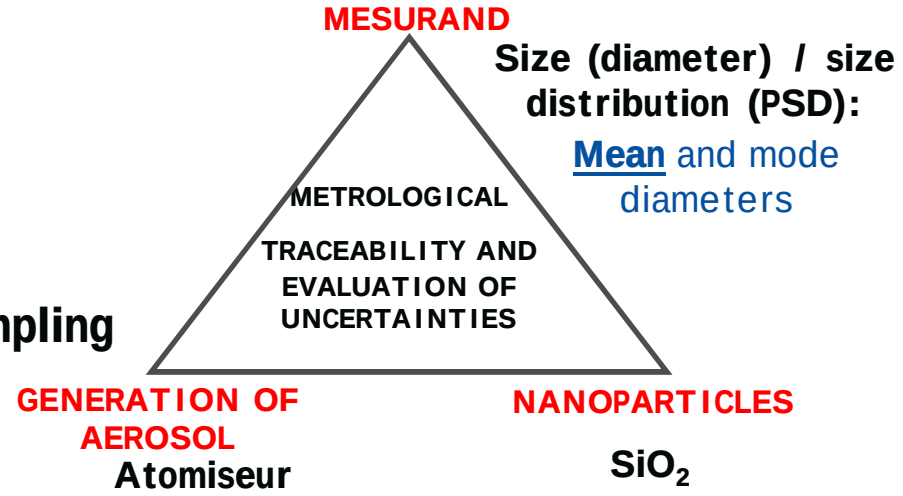
- The study performed within the framework of the **Technical Working Area (TWA) 34 – "Properties of Nanoparticle Populations"** of the VAMAS in the **project n°3 "Techniques for characterizing size distribution of airborne nanoparticles"**
- Mai 2009 - septembre 2012
- Participants :
  - LNE : leader du projet
  - 12 national Metrology Institutes : BAM (Germany), CENAM (Mexico), DFM (Denmark), NMIA (Australia), NMISA (South Africa), INPL (Israel), KRISS (South Korea), LNE (France), NIST (USA), NPL (UK), NMIJ-AIST (Japan) and NPLI (India)
  - 6 laboratories involved in nanoparticle metrology : LPMA (France), LISA (France), ILAQH - SEF (Australia), UNC (Israel) and UNIGE (Italy)

Work plan: *project in 3 phases*

➢ Phase 1: Mai 2009 – June 2011

- **Identification :**

-> **Mesurand**,
-> **Particules of interest**,
-> **Generation system of aerosol**,
-> **Techniques of measurements and of sampling**



- **Developpement of protocols**
(generation, sampling and characterisation)

➢ Phase 2: Mai 2011 – April 2012

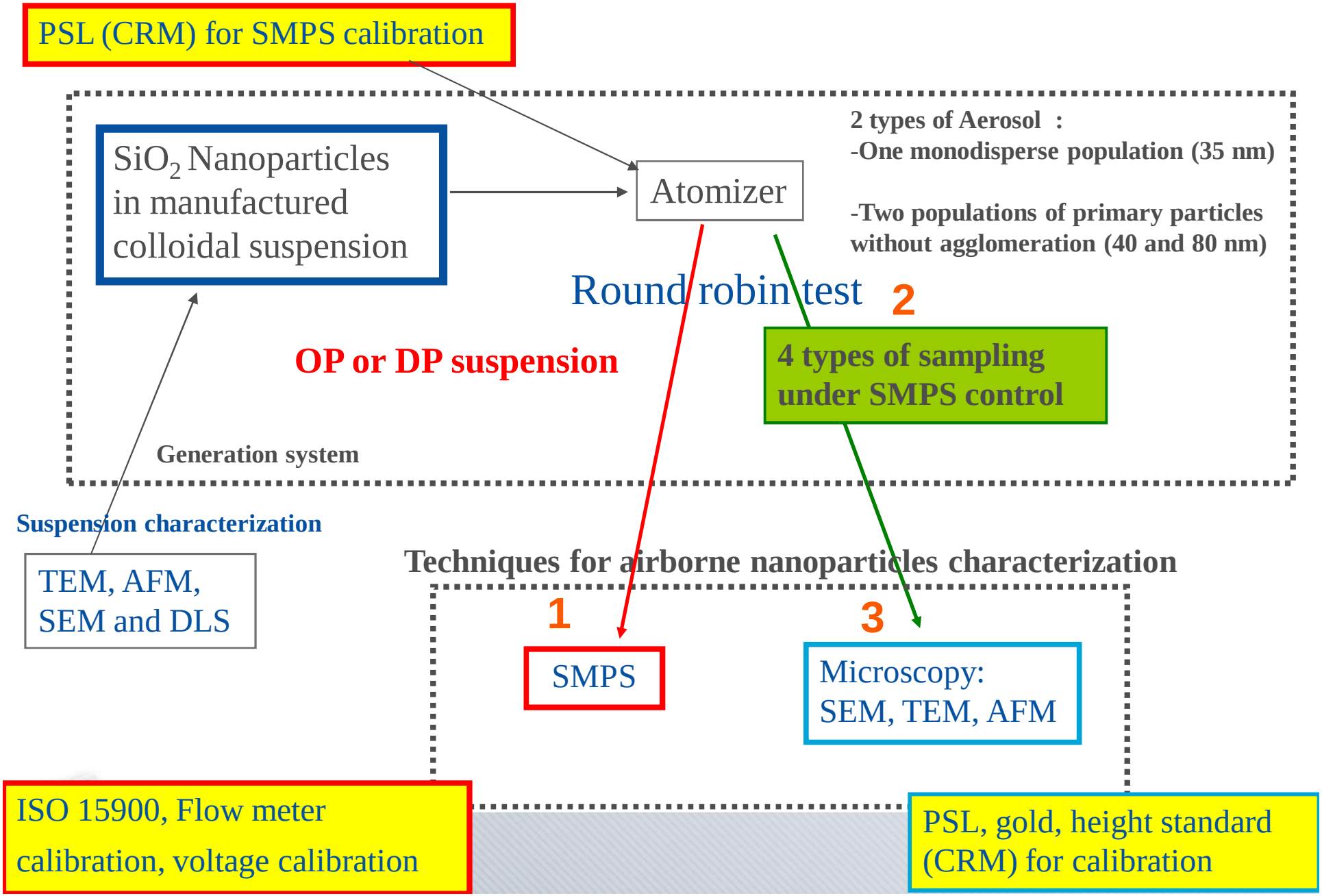
- Evaluation of protocols developped

Interlaboratory comparison with on-line (SMPS) and off-line (AFM, MEB et TEM) measurement techniques

➢ Phase 3: Mai 2011 – September 2012

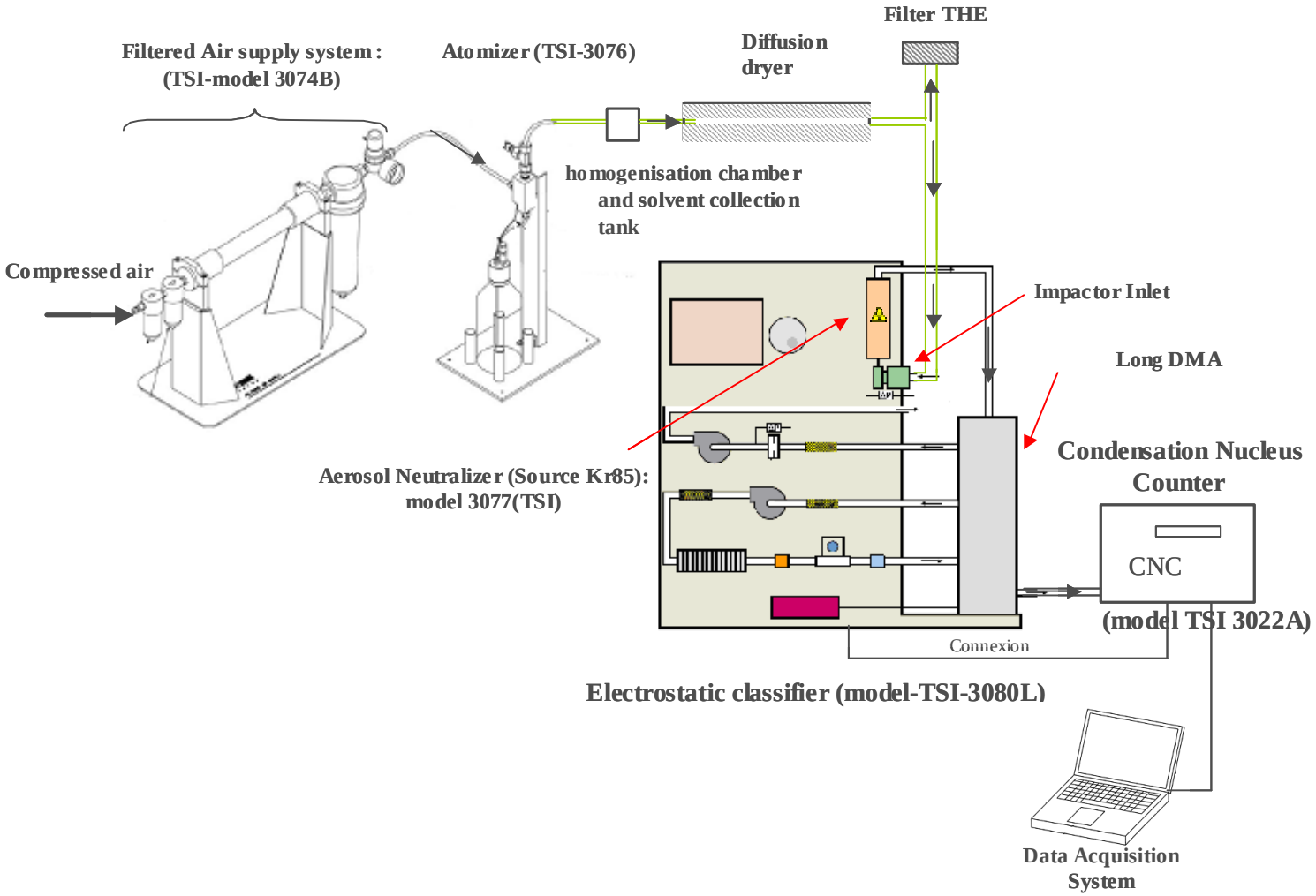
- Analyse of results and validation of protocols

Project description



Generation of nanoaerosols + On-line Measurement (1/2)

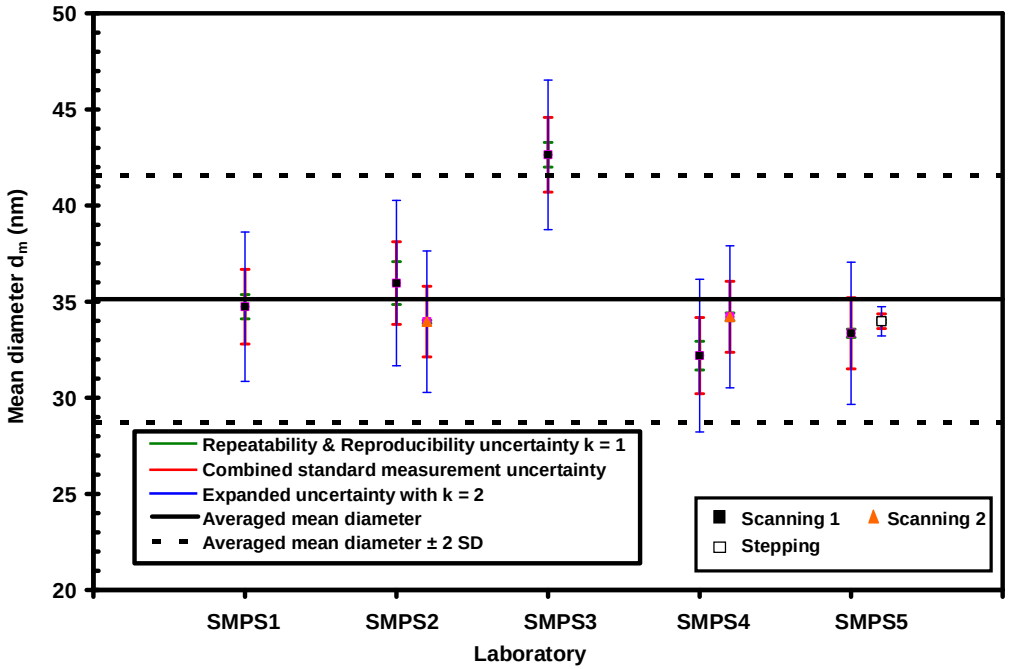
Using of Scanning Mobility Particle Sizer (SMPS)

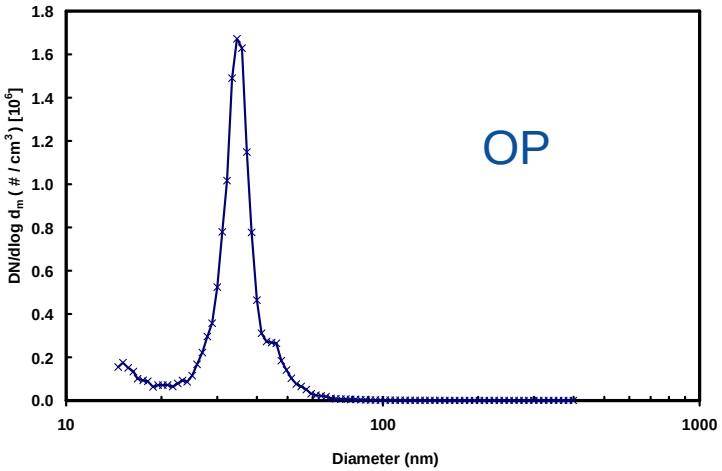


Generation of nanoaerosols + On-line measurement (1/2)

- Preparation of colloïdales suspensions :
  - 2 manufactured colloïdales suspensions diluted with Milli-Q water in order to obtain 2 types of non-agglomerated nano-aerosols (1) a monodisperse population called “Aerosol One Population” (aerosol OP). (2) two nanoparticle populations (a bimodal PSD) called “Aerosol Double Population” (aerosol DP) of isolated (no-agglomerated) airborne particles
- Generation :
  - Cleaning procedure
  - Analyse of background
  - P = 2.4 bar with atomiser
- Measurement : SMPS
  - Scanning mode (Commercial software AIM)
  - Stepping mode (DMA moment method) with same DMA (3080, TSI)
- Traceability :
  - Calibration of DMA with PSL (CRMs) certified by TEM : 46 nm ± 2 nm, 81 nm ± 3 nm et 100.82 nm ± 0.66 nm (conpliant to the standard ISO 15900 “Determination of particle size distribution – Differential electrical mobility analysis for aerosol particles“)
- Results treatement :
  - **Using differents laws :** gaussian (normal), asymmetric gaussian, and log-normal
  - **Uncertainty evaluation :** ISO 5725-2 (repeatability and reproducibility) et sources (≠ generators, DMA flow conditions, diffusion and charge corrections)

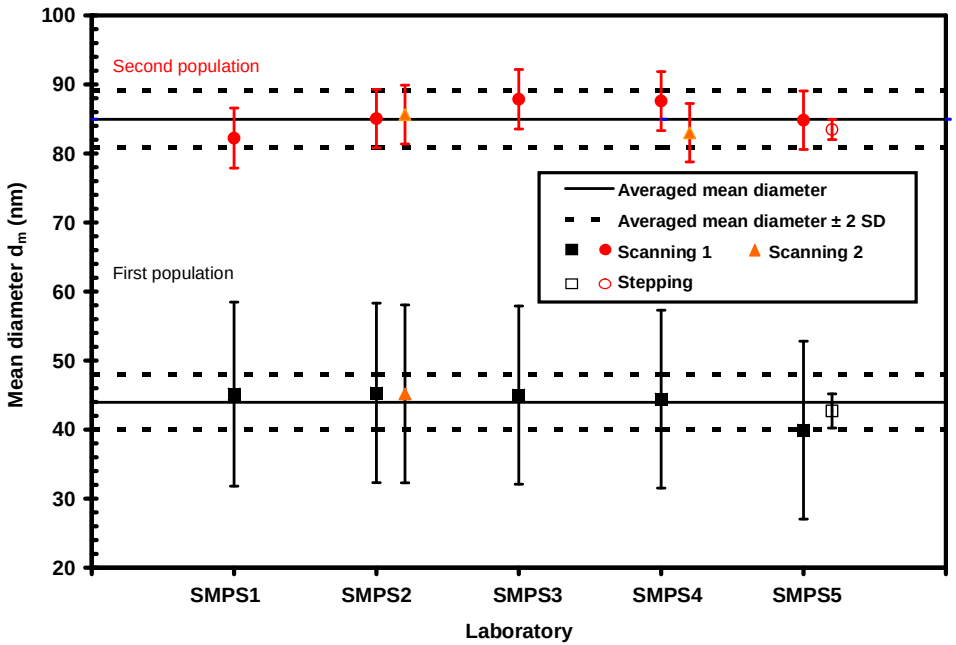
On-line measurement (SMPS): Results

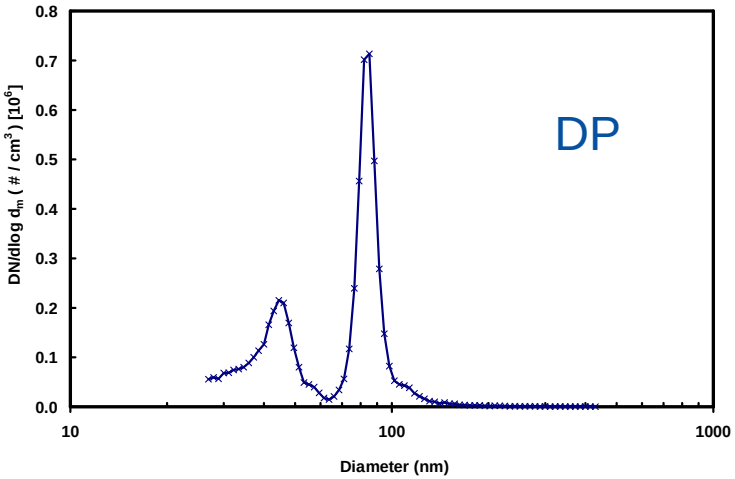




- 32 nm < dp mean < 36 nm, except SMPS3 (43 nm)
- SD repro ≤ 1 nm / U(k=2) ≤ 4 nm
- **Influence of range used to determine the mean diameter** (≠ of 2 nm for atomiseur and ≠ of 0,6 nm for electrospray)
- **Incertainty stepping ≤ scanning**

On-line measurement (SMPS): Results





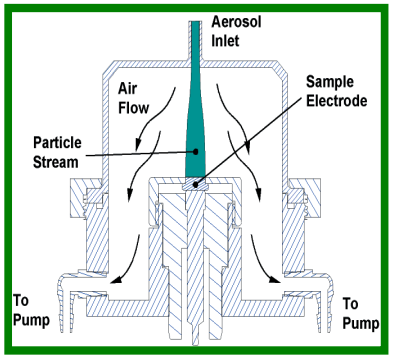
- 1er population : 39 nm < dp1 mean < 46 nm
  2nd population : 82 nm < dp2 mean < 88 nm
- 1er population : SD repro ≤ 2 nm / U(k=2) ≤ 13 nm
  2ème population : SD repro ≤ 0,5 nm / U(k=2) ≤ 4 nm
- **Influence of range used** to determine the mean diameter (≠ max of 5 nm)
- **Ratios in number concentration** between the 2 populations: peak et area

Off-line measurement: Sampling

2 types of sampling methods + 3 supports types

1 - Filtration (Diffusion-impaction-interception) → - Polycarbonate membrane filter (PMF)
- Grilles TEM deposited on PMF

2 - Electrostatic precipitation (NAS) → MICA and TEM Grids



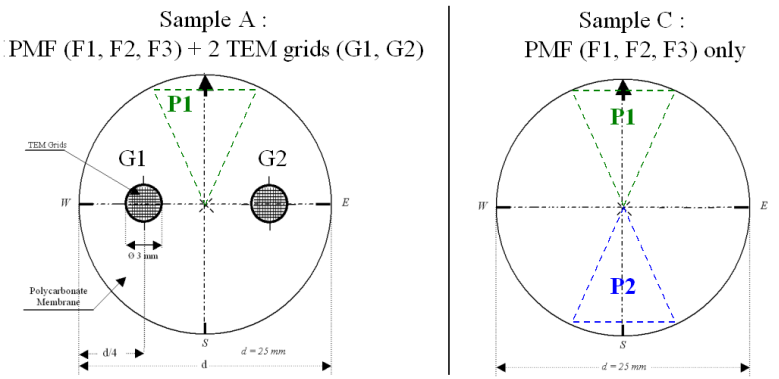
- Sampling performed by 4 laboratories :

  4 types of samples :
  - Sample A (filtration + 2 TEM grids« G »)
  - Sample B (NAS + Grids « N1, N2, N3 et N4 »)
  - Sample C (filtration + PC alone « F1,F2 et F2 »)
  - Sample D (NAS + MICA « M1, M2 et M3 »)

- Protocols of sampling
  (scientific literature + consensus)

  (Q, diameter of the filters and the pores, sampling time,…)

- Protocols for storage conditions and sample transport

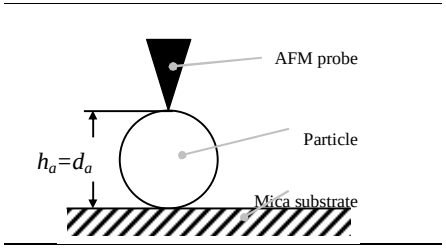


Part P_1 : for transfer on TEM grids (g1, g2)
Part P_2 : used for SEM

Off-line measurement: Protocols AFM, SEM and TEM

Samples preparation :

Examples :
- SEM with high-voltage : Coating
- MET : Transfer of particles from PMF to TEM grids

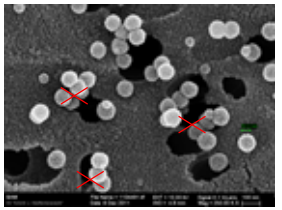


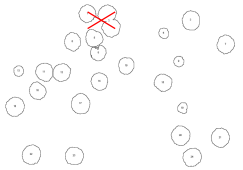
Protocole de mesures :

Mesurand / Conditions of measurement / Materials / Traceability (CRM) / Number of measured particles :

Example for AFM: maximum particle height (Apex) / 2 CRM for the metrologic comparability *(calibrated step height of 41.2 ± 0.7 nm and PSL with a mean calibrated diameter of 46 ± 2 nm certified by TEM)* / scan range = 2 x 2 µm / image size: 512 x 512 pixels /Tapping or intermittent mode / Supersharp tips / Recommandation of a minimum of 400 measured particles per sampleper sample in order to allow a reasonable statistical evaluation of the PSD …

Results treatement : Images treatement



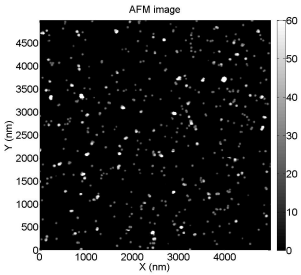


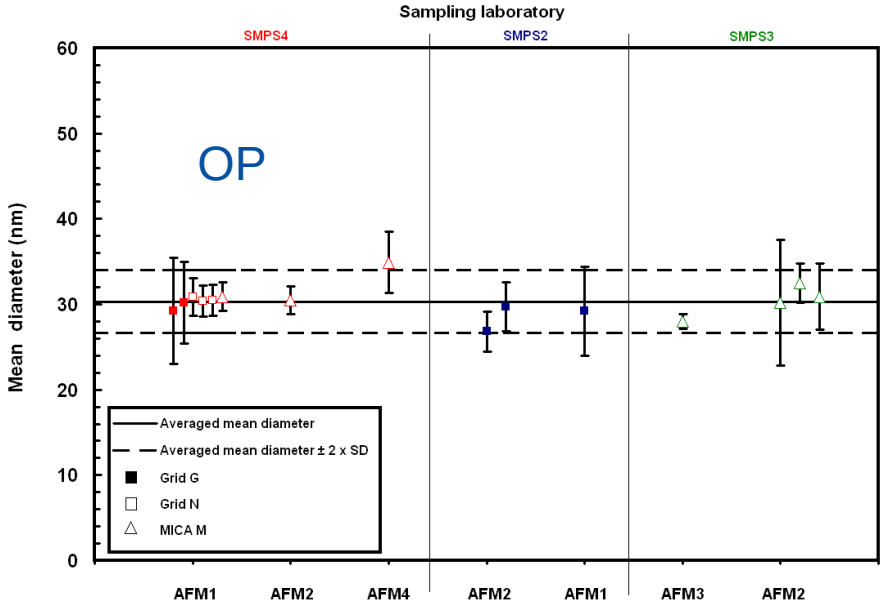
Measurement uncertainty evaluation :

Estimation by each participants in function of their measurement methods, data treatement and of their instrumentation : contribution of severeal sources

Example for SEM and TEM: correction or taken into account of the coating thickness, calibration of the magnification, threshold in the greyscale images.

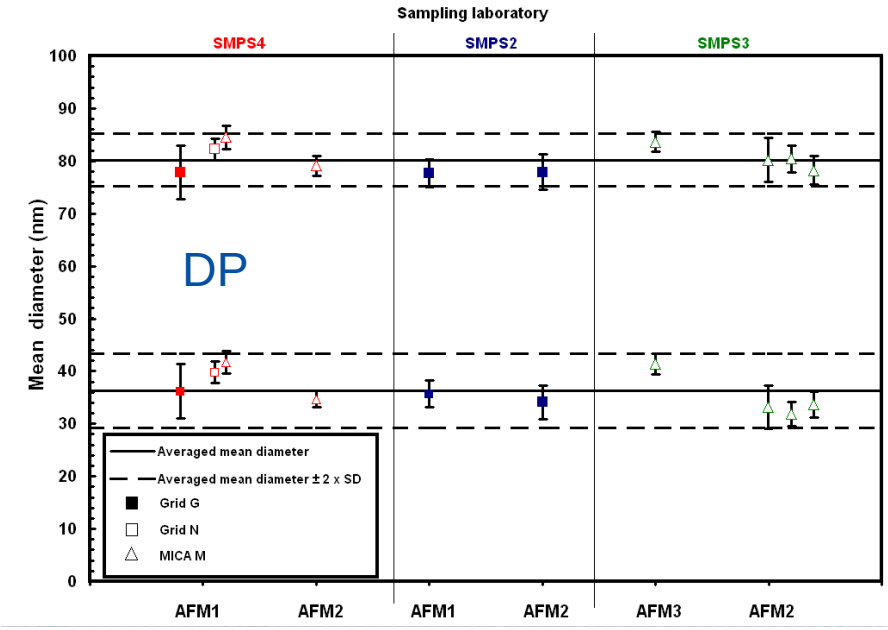
Off-line measurement: AFM Results





4 laboratories involved

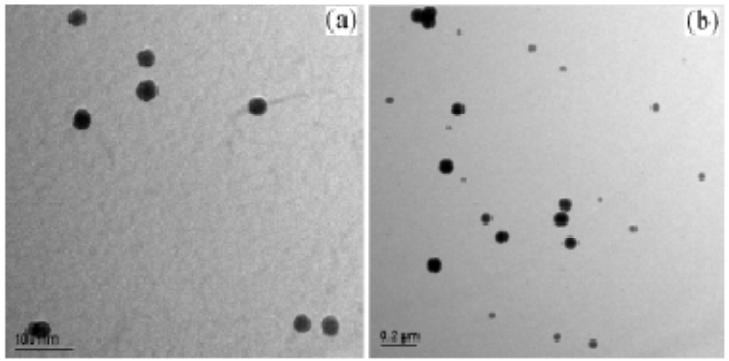
- Good agreement between the results of different participants
- 27 nm < dp mean < 33 nm, except AFM4 (35 nm)
- U (k=2) ≤ 7 nm / total mean average = 30.3 ± 3.7 nm
- No significant difference between the ≠ samples types (Samples A, B et D)
- **The Lowest uncertainty obtained with MICA**

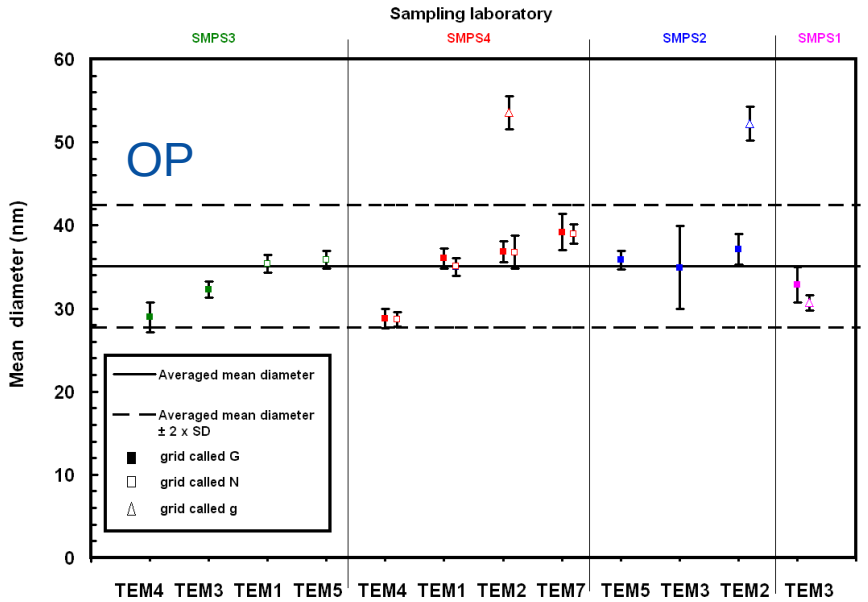


- Good agreement between the results of different participants
- 1er population : 32 nm < dp1 mean < 42 nm
  2nd population : 78 nm < dp2 mean < 85 nm
- U (k=2) ≤ 5 nm for 1er population and 2nd population
- Total mean averages = 36.2 ± 7.1 nm / 80.2± 5.0 nm
- **Ratios in number concentration between the 2 populations: peak et area**

Off-line measurement: TEM Results

7 laboratories involved



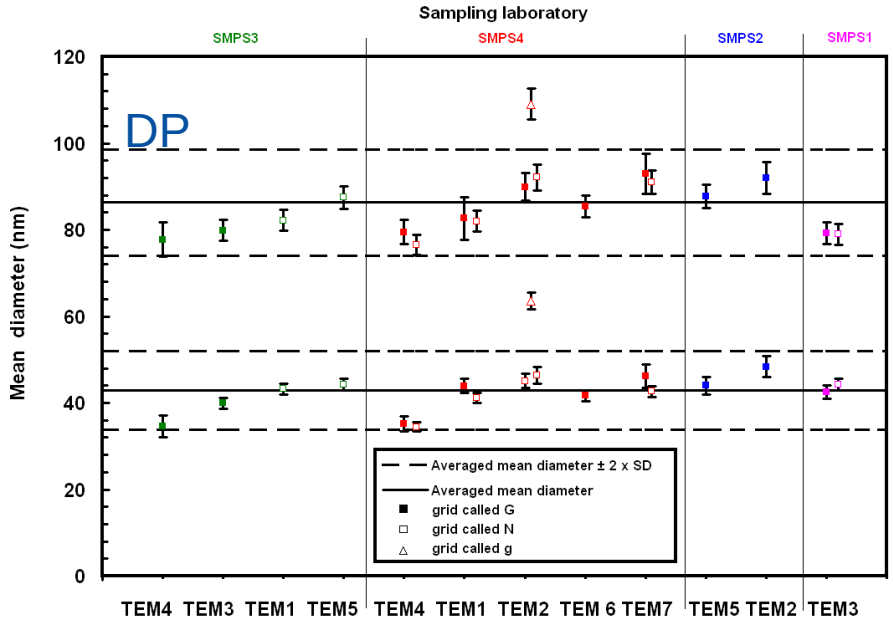


- 29 nm < dp mean < 39 nm, **except for the g grids (transfer)**
- U (k=2) ≤ 5 nm / Total mean average = 35.1 ± 7.4 nm
- **High difference** between the grids G and g (17 nm): **influence of transfer**

For TEM, avoid to use the transfer of particles from filter to TEM and choose to use the direct deposition on grids: High impact on PSD

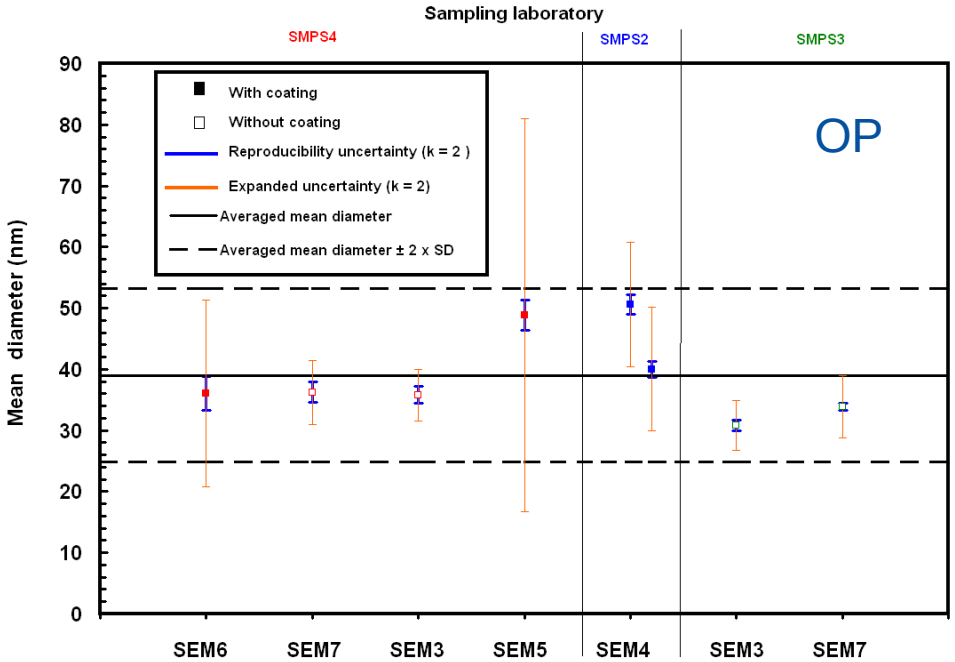
Off-line measurement: TEM Results

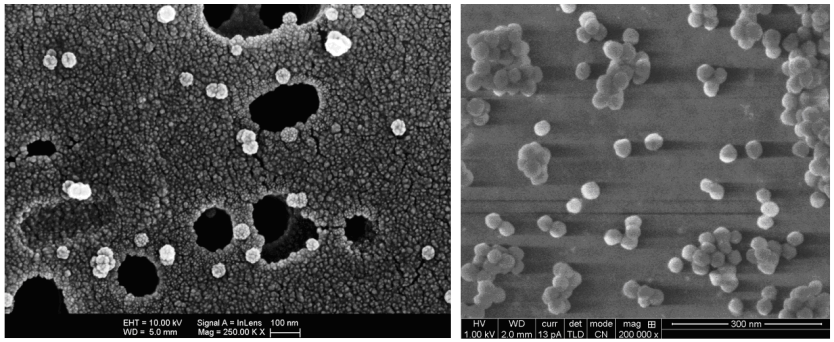
7 laboratories involved



- 1er population : 35 nm < dp1 mean < 49 nm
  2nd population : 77 nm < dp2 mean < 92 nm **except for the g grids (transfer)**
- U ≤ 5 nm for 1er population and 2nd population
- Total mean average = 42.9 ± 9.0 nm / 86.3 ± 12.3 nm
- **Ratios in number concentration between the 2 populations: peak et area**

Off-line measurement: SEM Results





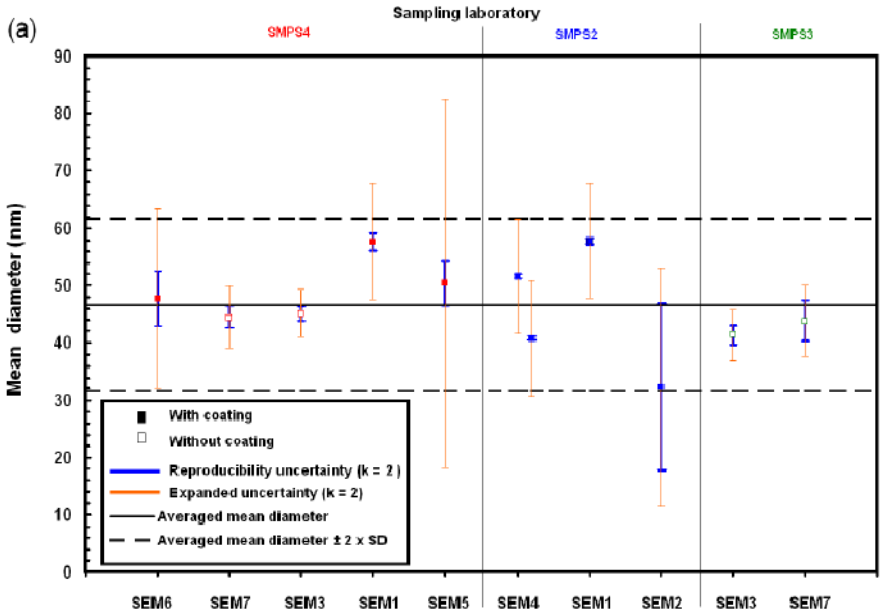
7 laboratories involved

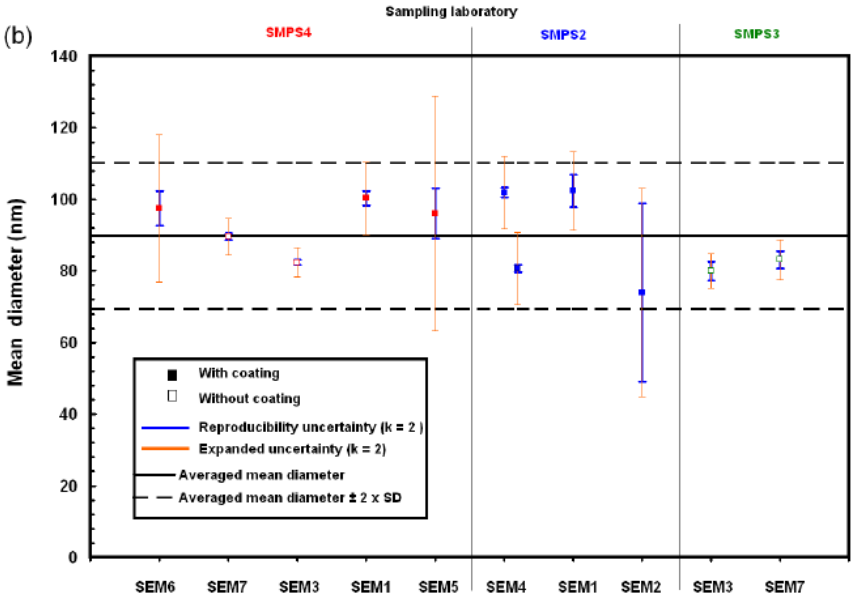
- 30 nm < dp mean < 51 nm
- **High dispersion of results : SD interlabo for SEM >> AFM and TEM**
- SD repro ≤ 3 nm
- U (k=2) ≤ 5 nm **without coating**
  U (k=2) ≤ 32 nm **with coating**
- Total mean average = 39.0 ± 14.2 nm
- **The Lowest uncertainties** were obtained for the low-voltage SEM (without coating)

Off-line measurement: SEM Results

DP

7 laboratories involved





- 1er population : 32 nm < dp1 mean < 58 nm
  2nd population : 74 nm < dp2 mean < 102 nm
- SD repro ≤ 7 nm for 1er population and 2nd population except SEM2
- U (k=2) ≤ 5 nm **without coating**
  U (k=2) ≤ 32 nm **with coating**

For SEM , don't use coating : high impact on PSD and strong increase of measurement uncertainty

- Total mean averages = 46.6 ± 15.1 nm / 89.8 ± 20.4 nm
- **Ratios in number concentration between the 2 populations: peak et area**

Summary of results

OP

	Averaged mean diameter d_p (nm)	2* SD (nm)	Averaged mode diameter d_p (nm)	2* SD (nm)
SMPS	35.1	6.4	35.4	2.0
TEM	35.1	7.4	35.6	7.6
SEM	39.0	14.2	38.3	14.1
AFM	30.3	3.7	30.4	5.1

DP

	First population				Second population			
	Averaged mean diameter d_p (nm)	2* SD (nm)	Averaged mode diameter d_p (nm)	2* SD (nm)	Averaged mean diameter d_p (nm)	2* SD (nm)	Averaged mode diameter d_p (nm)	2* SD (nm)
SMPS	44.0	4.0	44.2	5.3	85.0	4.1	83.1	3.4
TEM	42.9	9.0	43.7	11.9	86.3	12.3	88.1	12.0
SEM	46.6	15.1	47.0	13.8	89.8	20.1	91.1	19.8
AFM	36.2	7.1	39.2	6.8	80.2	5.0	81.0	5.3

➡ Comparable results by techniques: validation of PSD characterization protocols

➡ Comparable results between techniques :

⚠ implementation of different techniques : ≠ diameters types (mobility, height, …)

Spherical particles (equivalence of diameters)

Conclusions

- Developement and validation of generation protocols of 2 nano-aerosols types : OP and DP isolated ariborne nanoparticles (non-agglomerated)

- Developement of sampling protocols for off-line measurements by 2 methods (filtration and et electrostatic precipitation) on appropriate supports (grids, filters and MICA plates)

- Developement and validation of procedures for the size distribution characterization of SiO_2 airborne nanoparticles by on-line (SMPS) and off-line (MEB, MET et AFM) techniques: mean and mode diameters

- Interlaboratory comparison with metrological approaches (metrological traceability, calibration, and evaluation of the measurement uncertainty)

- Recommendations

IMPACT of the VAMAS project

- To provide measurements protocols accurate, reliable and robust and to give recommendations (scientific community, industry, legislative and regulatory authorities, etc.).

- To answer some needs
  - ➡ To perform reliable toxicology studies,
  - ➡ Quality control in industry and monitoring

- To provide Internationally harmonized measurement procedures for spherical airborne nanoparticles characterization for organizations in charge of standardization (CEN, ISO) in order to disseminate consensual and applicable standards for the size characterization of airborne nanoparticles

➡ Transfer of this work in standardization committees (AFNOR, ISO):

Submission by AFNOR of a New Work Item Proposal for a project of International Standard (IS) « On-line/off-line techniques for characterizing size distribution of airborne nanoparticle population »

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RESEARCH PAPER

Size characterization of airborne SiO_2 nanoparticles with on-line and off-line measurement techniques: an interlaboratory comparison study

C. Motzkus · T. Macé · F. Gaie-Levrel · S. Ducourtieux · A. Delvallee · K. Dirscherl · V.-D. Hodoroaba · I. Popov · O. Popov · I. Kuselman · K. Takahata · K. Ehara · P. Ausset · M. Maillé · N. Michielsen · S. Bondiguel · F. Gensdarmes · L. Morawska · G. R. Johnson · E. M. Faghihi · C. S. Kim · Y. H. Kim · M. C. Chu · J. A. Guardado · A. Salas · G. Capannelli · C. Costa · T. Bostrom · Å. K. Jämting · M. A. Lawn · L. Adlem · S. Vaslin-Reimann

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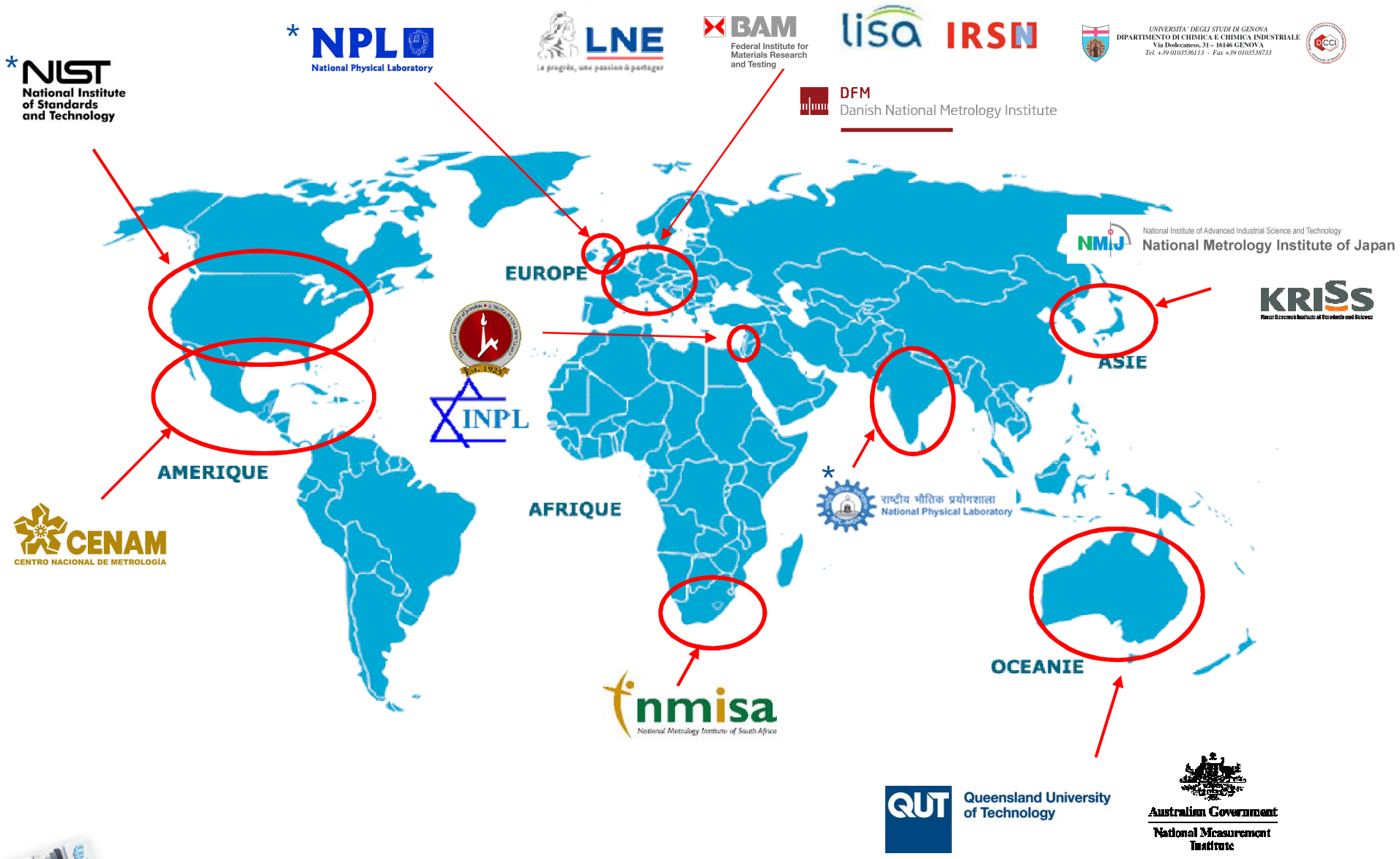
Abstract Results of an interlaboratory comparison on size characterization of SiO_2 airborne nanoparticles using on-line and off-line measurement techniques are discussed. This study was performed in the framework of Technical Working Area (TWA) 34—"Properties of Nanoparticle Populations" of the Versailles Project on Advanced Materials and Standards (VAMAS) in the project no. 3 "Techniques for characterizing size distribution of airborne nanoparticles". Two types of nano-aerosols, consisting of (1) one population of nanoparticles with a mean diameter between 30.3 and 39.0 nm and (2) two populations of non-agglomerated nanoparticles with mean diameters between, respectively, 36.2–46.6 nm and 80.2–89.8 nm, were generated for characterization measurements. Scanning mobility particle size spectrometers (SMPS) were used for on-line measurements of size distributions of the produced nano-aerosols. Transmission electron microscopy, scanning electron microscopy, and atomic force microscopy were used as off-line measurement

Internationally harmonized measurement procedures for airborne SiO_2 nanoparticles characterization



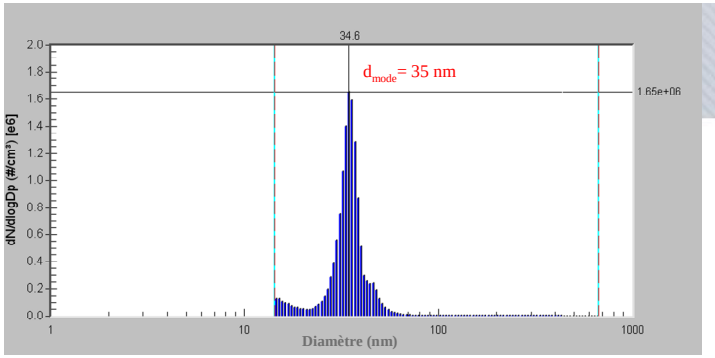
* NPLI, NPL and NIST were involved in this project but they didn't participate in the round robin test.

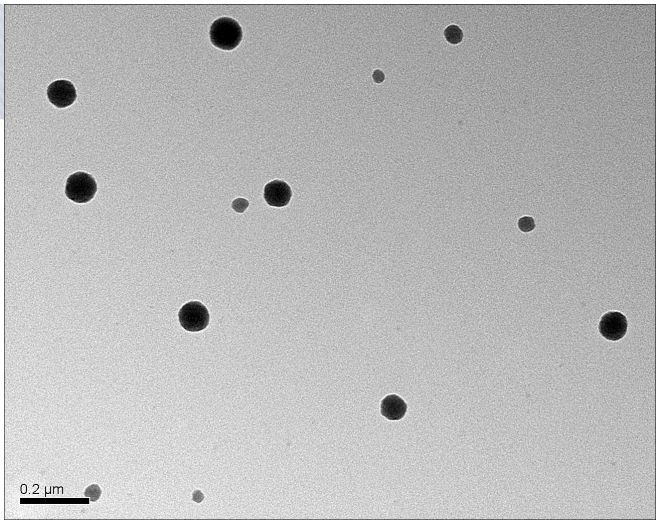
Perspectives

- By our knowledge, it would be interesting **to work on more complex particles** (CNT,…)

- **To work on the development of procedures** internationally harmonized with metrological approach to the **other relevant parameters** identified by the ISO TC 229 "Nanotechnology" and the OECD (Organisation for Economic Co-operation and Development)

  Surface area, shape, surface charge, aggregation/agglomeration state, chemical composition (crystallinity, purity/impurity, global chemical composition), surface chemistry solubility/dispersibility





Thank you for your attention