JRC
EUROPEAN COMMISSION

Co-Nanomet
Co-ordination of Nanometrology in Europe

Institute for Reference Materials and Measurements

Application of documentary standards in the characterisation of manufactured nanoparticles

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- **Introduction**
  - JRC-IRMM - Co-Nanomet ENAG Nanoparticles - definitions
  - Relevant nanoparticle characteristics
- **Why use a *standard* nanoparticle characterisation method?**
- **Where to find the appropriate standard?**
  - ISO/TC 24/SC 4 Particle Characterisation
  - ISO/TC 229 Nanotechnologies
  - …
- **How to apply the standard method?**
  - Quality Control
- **How can Co-Nanomet help?**
  - Workshop announcements
- **Conclusions**

- **EC - DG JRC**

  = European Commission Directorate-General Joint Research Centre

  'Robust science for policy making'

- **IRMM**

  = Institute for Reference Materials and Measurements

  'Confidence in measurements'

  Geel, Belgium, since 1960.

IRMM – Reference Materials Unit

Mycotoxins
Vitamins
PCBs
Proximates
Veterinary drugs
Prions
TSE QCMs
Food CRMs
Clinical CRMs
Enzymes
Hormones
Microorganisms
Proteins
PAHs
Microbiol. CRMs
GMO CRMs

Hydrocarbons
DNA
Dioxins
Soil/ Sediment CRMs
Engng Matl. CRMs
Size
Water CRMs
Elements
Isotopes
Ions
Metal species
Impact toughness

~ 70 people, > 650 reference materials

- **The ERM initiative**

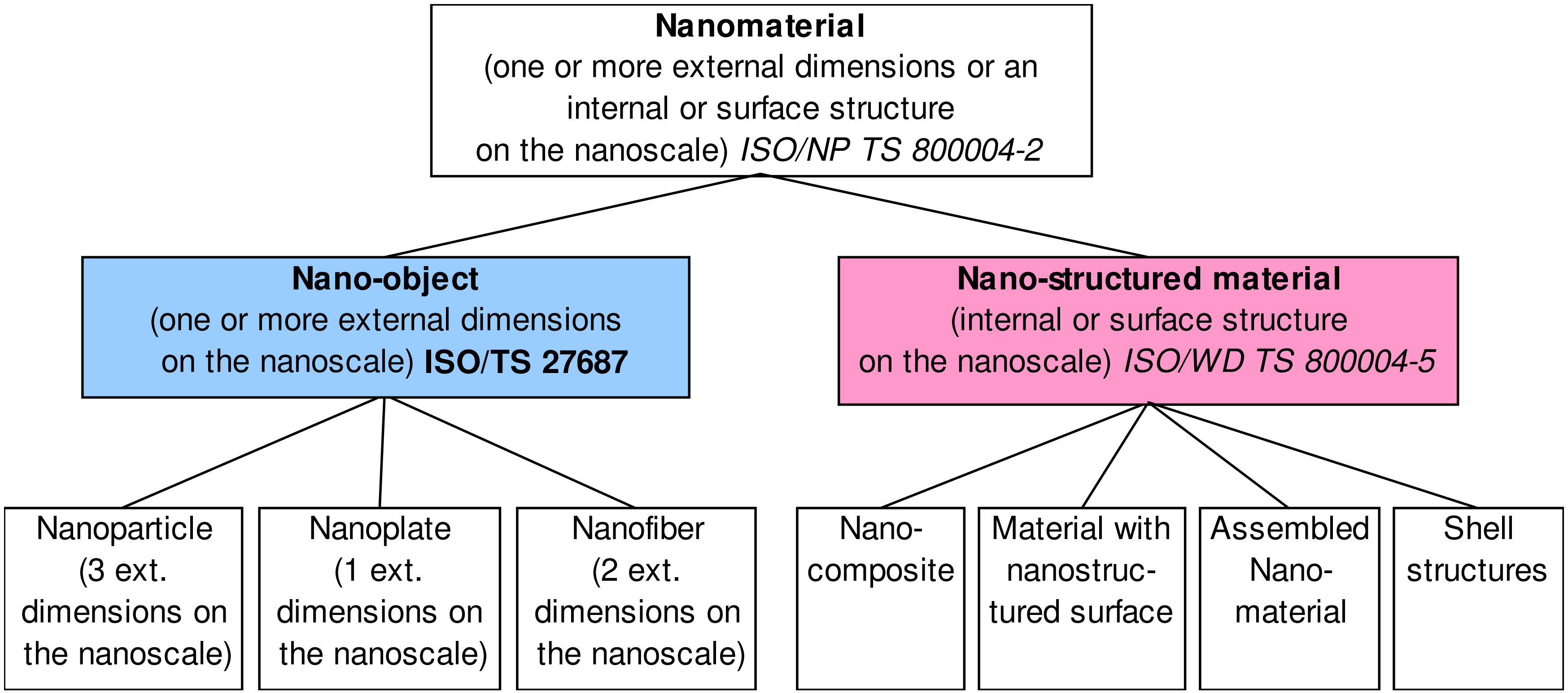
- **Founding partners:**
  IRMM (EU), BAM (DE), LGC (UK)

European Reference Materials

- **Principles:**
  - transparent quality criteria for ERM®s & membership conditions for joining the partnership (www.erm-crm.org)
  - mutually agreed technical ERM® guidelines in accordance with ISO Guides 34 and 35
  - CRMs undergo additional peer-review & shelf-life audits
  - ERM® certificates & reports carry transparent information on uncertainty and traceability of the certified values
  - each institution keeps ownership & responsibility for its ERM®s

- **Co-Nanomet 'Co-ordination of nanometrology in Europe'**
  - Substructure: ENAGs = European Nanometrology Action Groups
- **Action Group 'Manufactured Nanoparticles'**
  - Lead partner T.U. Dresden
  - Definition nanoparticle (CEN ISO/TS 27687:2008):
    - Nanoparticle = nano-object with all 3 external dimensions at the nanoscale
    - Nano-object = material with 1, 2 or 3 external dimensions at the nanoscale
    - Nanoscale = size range from approximately 1 nm to 100 nm
  - Definition manufactured nanoparticle?
    - Manufactured = intentionally produced (also 'engineered')
    - Contrasts with naturally occurring or accidentally produced nanoparticles

Nanomaterials classification (ISO/TC 229 Nanotechnologies, draft)



Why try to characterise nanoparticles?

- To enable process design and modeling
  - Polke et al., Chem. Engng Sc. 57 (2002) 4295-4299
  - …
- To understand, compare and predict particle (product) properties
  - ISO/TC 229/WG 3/PG 5: particle phys/chem properties relevant for toxicological studies
  - …
- To enable classification, identification, correct communication
  - Nomenclature for trade (business-to-business) or for end-user information

Groups of nanoparticle characteristics

- What are the particles made of?
  - bulk composition, surface composition (coating, …), impurities, …
- What do the particles look like?
  - size, shape, aggregation, …
- How do the particles interact with their environment?
  - Surface charge, agglomeration state, …
  - Dynamic characteristics (easily modified during life-cycle!)
- Additional consideration, common for all groups:
  - '… the physical properties of a disperse material depend not only on its median value but also on its spread of sizes…' (Leschonski, Part. Charact., 1 (1984) 7-13)

Metrology or Standardisation?

System 1: **Standardisation**

"harmonized methods"

ISO cen

Prescribed procedures to enable comparability '*within-method*'

System 2: **Metrology**

"ultimate" analysis

- metrol. traceability
- measurement uncertainty

ΜΕΤΡΩ ΧΡΩ

Comité international des poids et mesures

Bureau international des poids et mesures

Organisation intergouvernementale de la Convention du Mètre

Prescribed performance characteristics to enable comparability *'beyond-method'*

Metrology and standardisation: 2 systems, 1 common aim: improved comparability of measurement results

Why use a documentary measurement *standard*?

To enable metrological traceability for a method-defined property!

- **'Verification of traceability = verification of absence of significant bias'**
  - *Eurolab Technical Report 1/2007, Measurement uncertainty revisited*

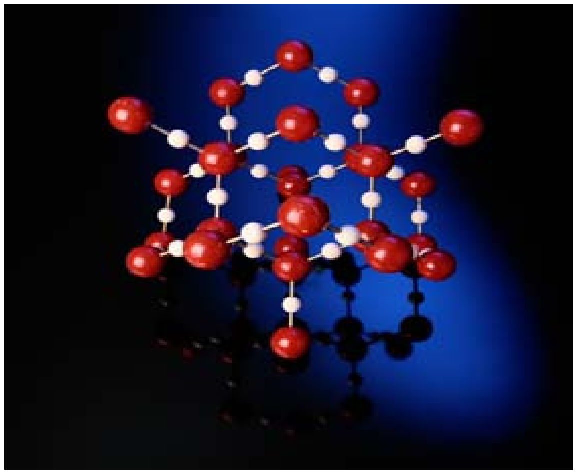
- **To verify absence of bias, one needs to understand and specify what exactly is measured:**
  - identity of the kind of quantity (measurand)
    - Cannot be described without making reference to the method in the case of a method-defined property
  - identity of the analyte (measurement object):
    - Can depend on the sample preparation defined in the method
  - *ERM 'Policy for the statement of metrological traceability on certificates of ERM® Certified Reference Materials', H. Emons, May 2008, on www.erm-crm.org.*

- **Conclusion: to enable meaningful comparison of measurement results of a method-defined property, one needs to use standard methods.**

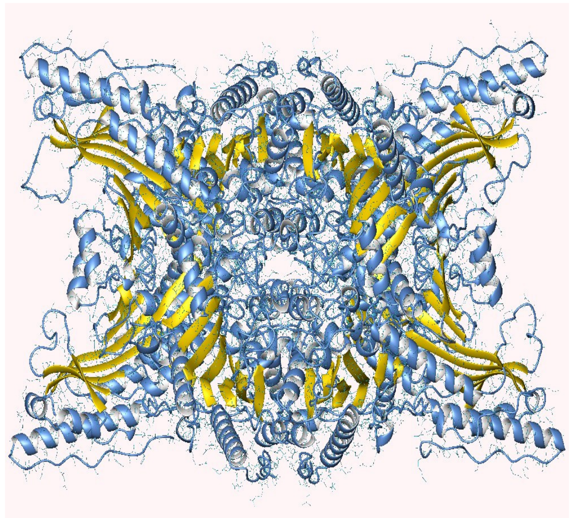
Nanoparticle-specific characterisation issues: examples

– General nano-issue: what is the measurement object?

"trivial" for:
atoms, small molecules, pure crystalline materials



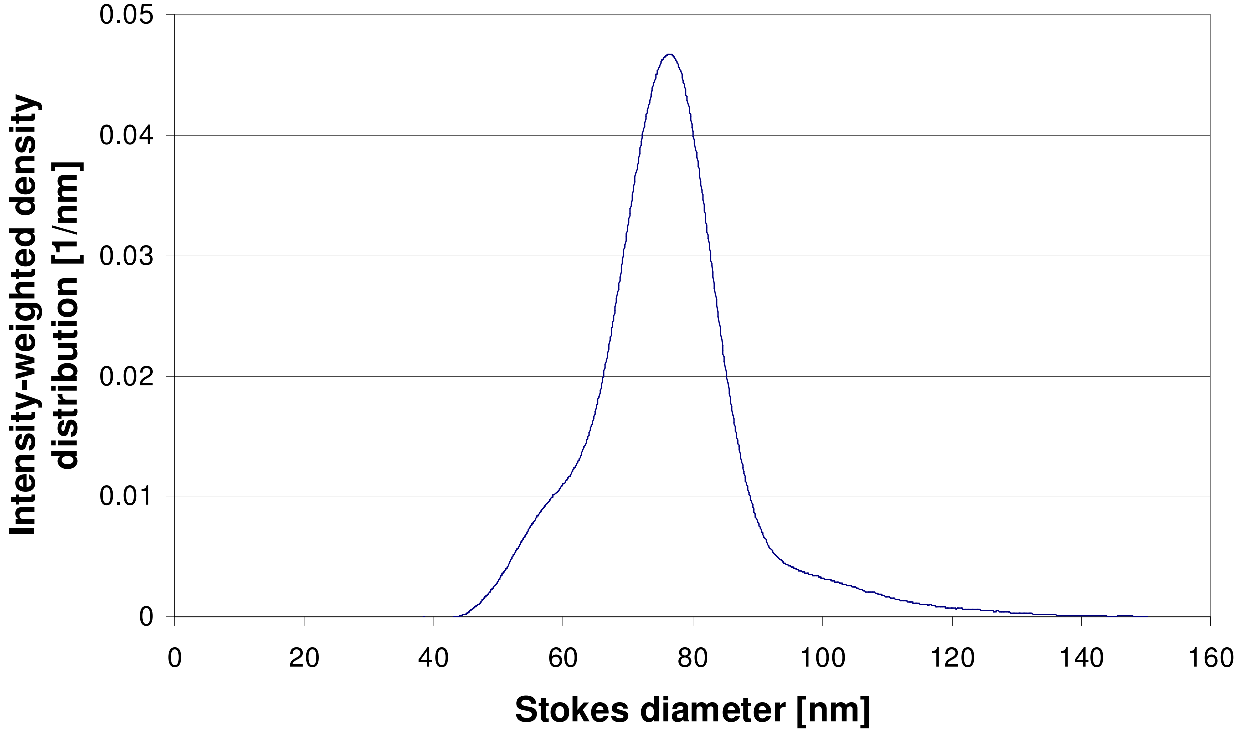
not "trivial" for:
nano-structured materials



enzyme

Nanoparticle-specific characterisation issues: examples

– What is the measured property?
  - Sedimentation test on colloidal silica A: modal Stokes diameter = 75 nm



Courtesy A. Braun, V. Kestens (JRC-IRMM)

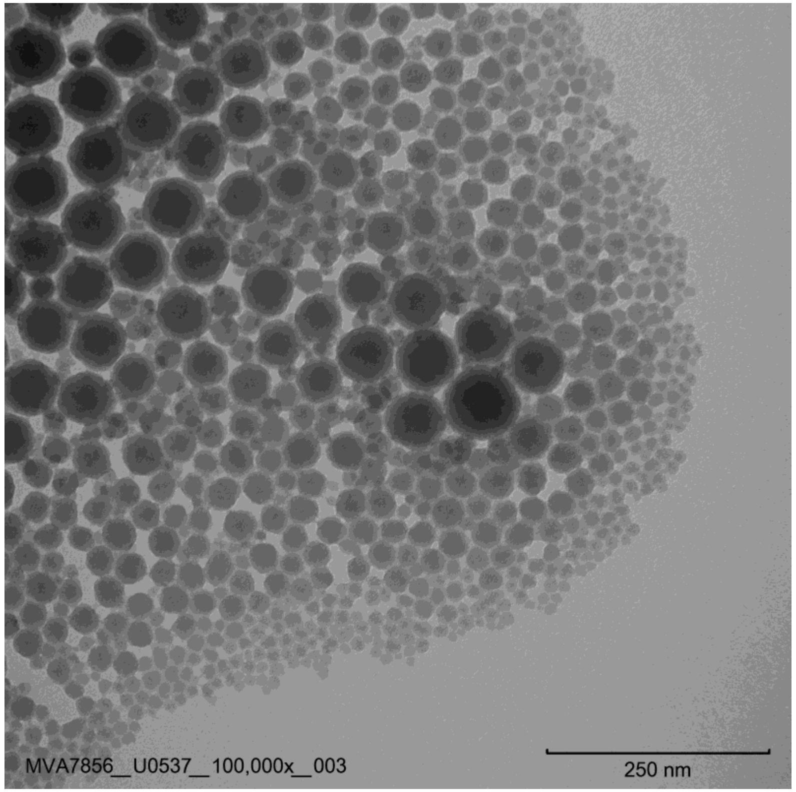
Nanoparticle-specific characterisation issues: examples

– What is the measured property?
  - TEM image analysis on the same colloidal silica A

Observations:

1) aspect ratio = 1.14

2) Many particles < 75 nm



TEM images and analysis by MVA Consultants

Nanoparticle-specific characterisation issues: examples

- How are the results presented?
  - non-linear weighting of the particle population
    - Finsy et al., Part. Part. Syst. Charact., 8 (1991) 187-193

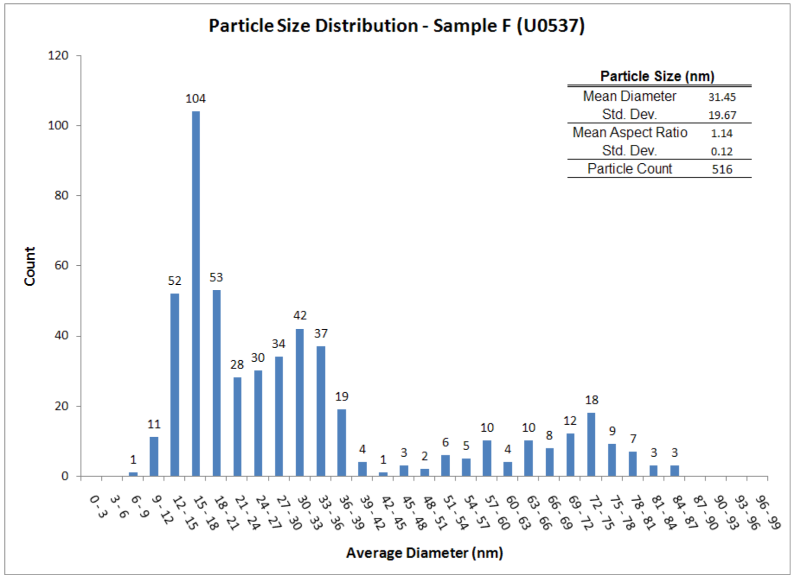


Image analyis: ‘1 particle = 1 vote’, mean value = 31 nm

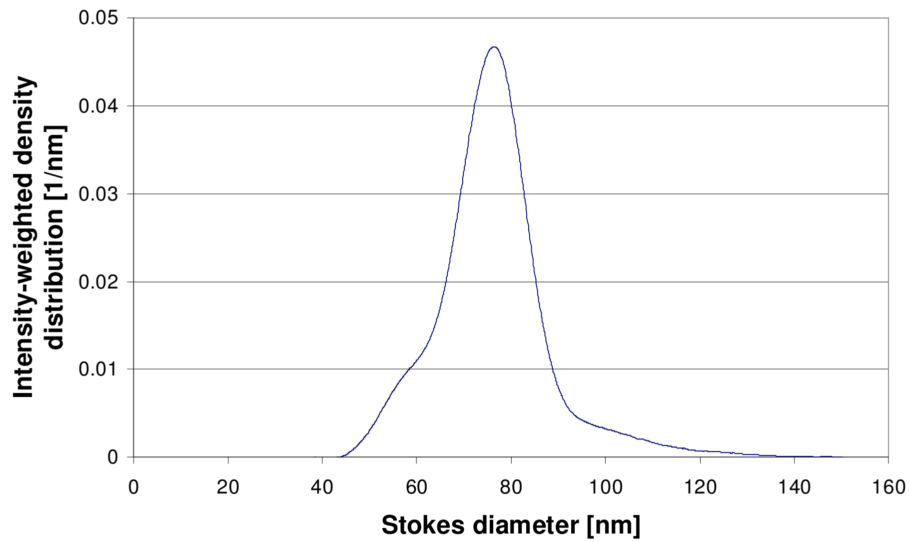


Photo-detection sedimentation: ‘bigger particles get more votes’, mean value = 75 nm

Where to find nano-relevant measurement standards?

ISO/TC 24/SC 4 Particle Characterisation

- Particle size distribution in aerosols, in suspension or on substrate/in solids
  - Available standards: see www.iso.org
  - Many are applicable to nanoparticles.
- Recent nanoparticle-relevant developments:
  - ISO 15900:2009 Determination of particle size distribution -- Differential electrical mobility analysis for aerosol particles
  - ISO/PWI 27891 Validation and calibration of aerosol particle number counters
  - ISO 22412:2008 Particle size analysis -- Dynamic light scattering (DLS)
- New working groups:
  - Working Group 16 “Characterisation of particle dispersion in liquids”
    - new work item “Guide for the characterization of dispersion stability”.
  - Working Group 17 “Methods for zeta potential determination”

Where to find nano-relevant measurement standards?

ISO/TC 229 Nanotechnologies

- WG 2: Measurement and characterisation:
  - ISO/CD 12025: General Framework for Determining Nanoparticle Content in Nanomaterials by Generation of Aerosols
- WG 3: EHS issues:
  - ISO/CD 10801 Nanotechnologies – Generation of nanoparticles for inhalation toxicity testing
  - ISO/CD 10808 Nanotechnologies - Monitoring nanoparticles in inhalation exposure chambers for inhalation toxicity testing
- Joint Task Group WG 2/WG 3
  - Guidance on Measurement and Characterization for EHS issues relevant to nanomaterials

Where to find nano-relevant measurement standards?

ISO/TC 201, ISO/TC 202, …

– See lectures by W. Unger (BAM, DE) and T. Dziomba (PTB, DE)

How to use a measurement standard?

Choice of appropriate standard via a clear definition of the intended use

- What will the measurement results be used for?
  - On-line analysis? (repeatable and quick)
  - Mechanistic modeling? (accuracy)
  - …

Perform laboratory quality control checks

- Validation (in-house)
  - Repeatability – intermediate precision: to establish whether operator training was successful, to assess infrastructure/instrumentation, ...
- Proficiency (round-robin)
  - To establish relative performance with respect to other laboratories using the same method.

How does Co-Nanomet intend to contribute?

- **Co-Nanomet Workshop: "European Nanometrology"**
  - September 8-9, 2009, Berlin
- **Co-Nanomet Workshop "Instruments, standard methods and reference materials for traceable nanoparticle characterisation"**
  - May 3-4, 2010, Nuernberg (after Partec and ISO/TC 24/SC4 meeting)
  - List existing measurement methods, their limits and assumptions
  - Standardisation: status, application of current standards, future requirements
  - Operational practices and use of equipment: links to best practices
  - Metrological traceability to improve inter-laboratory and inter-method equivalence
  - Reference materials as tools for metrological traceability and quality assurance

Conclusions

- Standardisation of measurement methods is a requirement to achieve comparability of results in the complex field of nanoparticles characterisation.
- Key documentary standards for nanoparticle characterisation have become available mainly through the work of ISO/TC 24/SC 4.
- Guidance (documents, workshops) for measurements on nanoparticle populations is being developed in Co-Nanomet, and in ISO/TC 229 and CEN/TC 352 (the ‘Nanotechnologies’ TCs).
- To improve existing standards and make them applicable in the nano-range, the nanoparticle-community will have to invest in :
  - Method validation
  - Laboratory qualification via proficiency testing and accreditation
  - Development of certified reference materials

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- **Thank you for your attention.**