Challenges with the development of Standards and analytical methods for Nanotechnology

John A. Small
Surface & Microanalysis Science Division
Chemical Science & Technology lab NIST

John.small@nist.gov
Measurements/Metrology

• NIST is the U. S. National Measurement Institute (NMI)

  - MISSION: To promote U.S. innovation and industrial competitiveness by advancing measurement science, standards, and technology – in ways that enhance economic security and improve the quality of life.
Outline

Standards for nano characterization:

- Metrology/Characterization
- Materials
- Documentary

Yttria particles courtesy Nanophase Technologies Corporation. Image courtesy of John Henry Scott, NIST
Metrology / Characterization
Nano Characterization

Size Distribution:
(S)TEM, SEM, SPMs (AFM, STM), Dynamic Light Scattering, Field Flow Fractionation with Multi Angle Laser Light Scattering, Ultrafine Condensation Particle Counter (UCPC) by Pulse Height Analysis (PHA), Single Particle Mass Spectrometry, Scanning Mobility Particle Sizer, Full-Pattern Powder Analysis, Low Frequency Raman Spectroscopy, Small Angle X-ray Scattering

Agglomeration state:
Centrifugation, Analytical Ultra-Centrifugation, Zeta potential, (electric field light scattering), X-Ray Disk Centrifuge

Shape:
(S)TEM, SEM, DLS and MALLS, X-Ray Diffraction, Electron Holography, SERS, Small Angle Neutron Scattering

Crystal Structure:
X-ray Diffraction, SANS

Surface charge:
Zeta potential (DLS in an electric field), Electrophoretic mobility, Ion mobility
Nano Characterization cont.

Chemical Composition (both spatially averaged (bulk) and spatially resolved heterogeneous) Analysis:
- NMR, X-ray photoelectron spectroscopy, Auger electron spectroscopy, X-ray Fluorescence, XRD, Atomic emission spectroscopy, absorption spectroscopy, fluorescence spectroscopy, and mass spectroscopy, NSOM, SEM/EDS, (S)TEM including (SAED, CBED, EFTEM, EELS, EDS), CFM, EBSD

Surface Area:
- BET (Burnauer, Emmett and Teller) analysis

Surface Chemistry:
- SERS, X-ray photoelectron Spectroscopy, Auger electron spectroscopy, CFM

Porosity:
- BET analysis

Solubility:
- Zeta potential, Static light scattering, Phase equilibrium measurements
Measurement Problems

• What do we measure?
• What is tested in animal studies?
• What are people exposed to?
• Are they the same?
• What concentration matters?
  – Measured in what units?
    • Mass? Particle number?
      Composition? Morphology?

• WE DO NOT KNOW UNTIL WE MEASURE
  – But how many and which measurements are correct?
What do we need in a characterization tool?

- Ease of use of bulk analysis methods
- Analyses that accurately represent the whole sample (such as bulk analysis does for older technologies.)
- Spatial resolution of nanoscopic methods
- Analyzes for everything
- Speed of process control methods

THESE DESIRES (REQUIREMENTS?) CANNOT CURRENTLY BE MET
Analytical Metrology for Nano

- Size
  - indirect
  - direct
- Spatially-resolved composition
Size Indirect

Physical sizing techniques

- field flow fractionation (FFF) system
- chromatographic light scattering
- analysis of distribution (monomers vs. dimers)
- dynamic light scattering (DLS)
- size distribution, shape, surface area information

DLS measures the size of an equivalent hard sphere that diffuses with the same speed as the scattering particle.
Nanoparticle Analysis by Analytical Ultracentrifugation

• Sizing technique based on sedimentation

• Can be used for sizing particles at subnanometer and above size ranges.

• Large particles settle faster than smaller sizes

• Sedimentation rate related to particle size distribution

• Techniques yields both cumulative mass fraction as an integrated particle size distribution or particle diameter as a differential size distribution.
Size Direct (microscopy)

Scanned Probes (STM)
AFM

Detector and Feedback Electronics

Photodiode

Laser

Sample Surface

Cantilever & Tip

PZT Scanner
Electron Microscopy

SEM

TEM

John Henry Scott NIST
• Often one average “diameter” is reported for each particle
• Morphology
  – Size distribution
  – Shape
Surface "Goo"
Problems (increase inversely with particle size)

A monolayer of surface "goo"
~10% of a 10 nm particle

SRM 1963, 0.1 µm spheres
Comparison of scanning electron microscopy, dynamic light scattering and analytical ultracentrifugation for the sizing of poly(butyl cyanoacrylate) nanoparticles

Three different methods were used to determine the size and size distribution of the particle populations: scanning electron microscopy (SEM), dynamic light scattering (DLS), and analytical ultracentrifugation (ANUC). SEM on freeze-dried and Au-shadowed samples showed a relatively narrow distribution of virtually spherical particles with a mean diameter of 167 nm. DLS yielded a monomodal distribution with hydrodynamic diameters around 199 nm (in the absence of additional stabilizer) or 184 nm (in the presence of 1% poloxamer 188). The size distribution determined by ANUC using sedimentation velocity analysis was somewhat more complex, the size of the most abundant particles being around 184 nm.

Alexander Bootz a, Vitali Vogel b, Dieter Schubert b and Jörg Kreuter
European Journal of Pharmaceutics and Biopharmaceutics
Volume 57, Issue 2, March 2004, Pages 369-375
NIST future RM Au nanoparticles Sized by DLS, DMA, SANS, SAXS, AFM, SEM, and TEM.

Average size and size distribution do not agree between the different methods.

Should come as no surprise.
Spatially-resolved Characterization

NSOM

Shear-force Image
3 µm x 3 µm

Glass
775 cm\(^{-1}\)

Rhodamine -B
1350 cm\(^{-1}\)

Rhodamine -B
1650 cm\(^{-1}\)

Raman Shift (cm\(^{-1}\))

600 800 1000 1200 1400 1600 1800 2000 2200

600 700 800 900 1000

Glass 775

Rhodamine 1350

Rhodamine 1650
Electron Energy Loss Spectrometry (EELS)

High Spatial Resolution Chemical Analysis

John Henry Scott, NIST
Valence Mapping

Mn 3-window map

valence map w/ profile

25 nm

valence profile

valence map profile suggests Mn^{2+} rich surface

valence measured by EELS matches titrated value

John Henry Scott, NIST
Complex materials

Functionalized or crud

50 nm
Materials
### Current NIST Particle Size Standards: nm-µm Range

<table>
<thead>
<tr>
<th>SRM</th>
<th>Type</th>
<th>Particle Diameter, nominal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1691</td>
<td>Polystyrene (0.5 % in H₂O)</td>
<td>269 nm</td>
</tr>
<tr>
<td>1963a</td>
<td>Polystyrene (0.5 % in H₂O)</td>
<td>100 nm</td>
</tr>
<tr>
<td>1964</td>
<td>Polystyrene (0.5 % in H₂O)</td>
<td>60 nm</td>
</tr>
<tr>
<td>1659</td>
<td>Silicon Nitride</td>
<td>200 nm to 10 µm</td>
</tr>
<tr>
<td>1978</td>
<td>Zirconium Oxide</td>
<td>330 nm to 2.19 µm</td>
</tr>
<tr>
<td>1988</td>
<td>Titanium Oxide</td>
<td>100 nm to 500 nm</td>
</tr>
</tbody>
</table>

These SRMs are for evaluating or calibrating instruments used for the determination of particle size such as light scattering, electrical zone flow-through counters, optical and scanning electron microscopes, sedimentation systems.

SRM = standard reference material
NIST & Nanotechnology: Standards

On the Horizon

Article of commerce

• Proposed RM 8475 CNT: Release by FY 07. Amount of Catalyst (bulk)

John Small NIST
Ian Anderson, NIST

David Buckingham NIST

RM 8475 after purification
In final stages of Au nanoparticle RM in conjunction with NIH/NCL: 10 nm, 30 nm, and 60 nm mean particle size. (DLS, DMA, SANS, SAXS, AFM, SEM, and TEM). Limited Amount / Sample
Documentary Standards
ISO TC 229: Nanotechnologies

established 2004
Chair and Sec. with UK, 27 P members and 8 O members

Scope: Standardization in the field of nanotechnologies that includes either or both of the following:

1. Understanding and control of matter and processes at the nanoscale, typically, but not exclusively, below 100 nanometres in one or more dimensions where the onset of size-dependent phenomena usually enables novel applications,

2. Utilizing the properties of nanoscale materials that differ from the properties of individual atoms, molecules, and bulk matter, to create improved materials, devices, and systems that exploit these new properties,
WG 1: *Terminology and nomenclature (Chair Canada)*
Scope: Define and develop unambiguous and uniform terminology and nomenclature in the field of nanotechnologies to facilitate communication and to promote common understanding.

WG2: *ISO/TC 229 Working Group on Metrology and Characterization (Chair Japan)*
Scope: The development of standards for measurement, characterization and test methods for nanotechnologies, taking into consideration needs for metrology and reference materials.

WG 3: *Health, Safety and Environmental Aspects of Nanotechnologies (Chair USA)*
Scope: The development of science-based standards in the areas of health, safety, and environmental aspects of nanotechnologies.
## Work programme for ISO/TC 229

**Total number of projects in status: Critical = 0 - Warning = 0 - Deleted = 0 - Without alert = 8**

<table>
<thead>
<tr>
<th>Alert</th>
<th>Project ref.</th>
<th>Project title</th>
<th>Reg. Date [Time in months]</th>
<th>Time frame</th>
<th>Crnt stage</th>
<th>Stage date</th>
<th>Limit dates</th>
<th>VA</th>
<th>Comments</th>
</tr>
</thead>
</table>
ASTM

ASTM E56: Established 2004

Scope: 1) The development of standards and guidance for nanotechnology & nanomaterials, and 2) the coordination existing ASTM standardization related to nanotechnology needs.

Six sub-committees:

- **E56.01** Terminology & Nomenclature
- **E56.02** Characterization: Physical, Chemical, and Toxicological Properties
- **E56.03** Environment, Health, and Safety
- **E56.04** International Law & Intellectual Property
- **E56.05** Liaison & International Cooperation
- **E56.90** Executive
- **E56.91** Strategic Planning and Review
WK8985 New STANDARD GUIDE FOR HANDLING UNBOUND ENGINEERED NANOPARTICLES IN OCCUPATIONAL SETTING

Developed by Subcommittee: E56.03

Date Initiated: 08-23-2005

1. Scope

The guide will describe actions that could be taken in occupational settings to minimize human exposures to unbound, intentionally produced nanometer-scale particles, fibers and other such materials in manufacturing, processing, laboratory and other occupational settings where such materials are expected to present. It is intended to provide guidance for controlling such exposures as a precautionary measure where relevant exposure standards and/or definitive risk and exposure information do not exist...
International Electrotechnical Commission (IEC)

TC 113: Nanotechnology standardization for electrical and electronics products and systems – established 2006
- Secretariat: Germany, and Chair: US
- US TAG recently formed
- Emphasis on strong liaison with ISO TC 229

IEEE
- Standards activities under IEEE Nanotechnology Council
- Standards address materials, devices and system-level interoperability
- IEEE Nanoelectronics Standards Roadmap initiative – March 2006
- Anticipatory standards philosophy
- Standards for nanoelectronics:
  - IEEE P1650 standard test method for measurement of electrical properties of CNTs- standard approved and adopted in 2005
  - Work underway on development of standard method for characterization of CNTs used as additives in bulk materials (IEEE P1690)
Organization for Economic Co-operation and Development (OECD)

The 1st Meeting of the WPMN agreed to implement its Programme of Work 2006-2008 through six specific projects to address human health and environmental safety:

1) Development of an OECD database on EHS research
2) EHS Research strategies on Manufactured Nanomaterials
3) Safety Testing of a Representative Set of Manufactured Nanomaterials
4) Manufactured Nanomaterials and Test Guidelines
5) Co-operation on Voluntary Schemes and Regulatory Programmes
6) Co-operation on Risk Assessment and Exposure Measurement

The WPMN also decided that these projects will be managed through six steering groups comprising delegations.
TC229 Scope

Understanding and control of matter and processes at the nanoscale, typically, but not exclusively, below 100 nanometres in one or more dimensions where the onset of size-dependent phenomena usually enables novel applications.

- Currently the standards community is having trouble defining Nanoscale. The problem is the word “typically”.
- No resolution of the issue as of a few weeks ago.
- One group wants a “white-line definition 1-100 nm.
- Other group wants to soften the definition to allow for larger particles.
- If we go with a white line Definition ie 1-100 nm,
  - What do you use for size?
  - Size is highly method dependant so need a very specific std. method
  - Also size is a distribution therefore are particles 100.1 non nano??

- White-line definition does not necessarily match the actual risk. The decision is not based on actual risk.
Asbestiform

- Asbestos
  - Natural nanofibers
  - 50 years of health effect research
    - Shape, size, composition
  - Interactions with human body
  - Longevity in body
  - 20+ year latency for cancer
  - Liability is still killing companies

Nonasbestiform

Images courtesy of the Nat. Stone, Sand, & Gravel Assoc.
What We need to do

• We can produce only a limited # of standard materials. We need to have scheme to insure they are highly leveraged and matched to needs.
• Our standards cannot be only for classical calibration. Need to include other types i.e. maybe more consensus standards or materials where the homogeneity is critical.
• Need to understand size measurement at least correlation between the different methods.
• Need new faster methods for spatially-resolved chemical analysis.
• Need to make sure our documentary standards are relevant.
• Need to get a predictive system in place.

“There’s Plenty of Room at the Bottom”