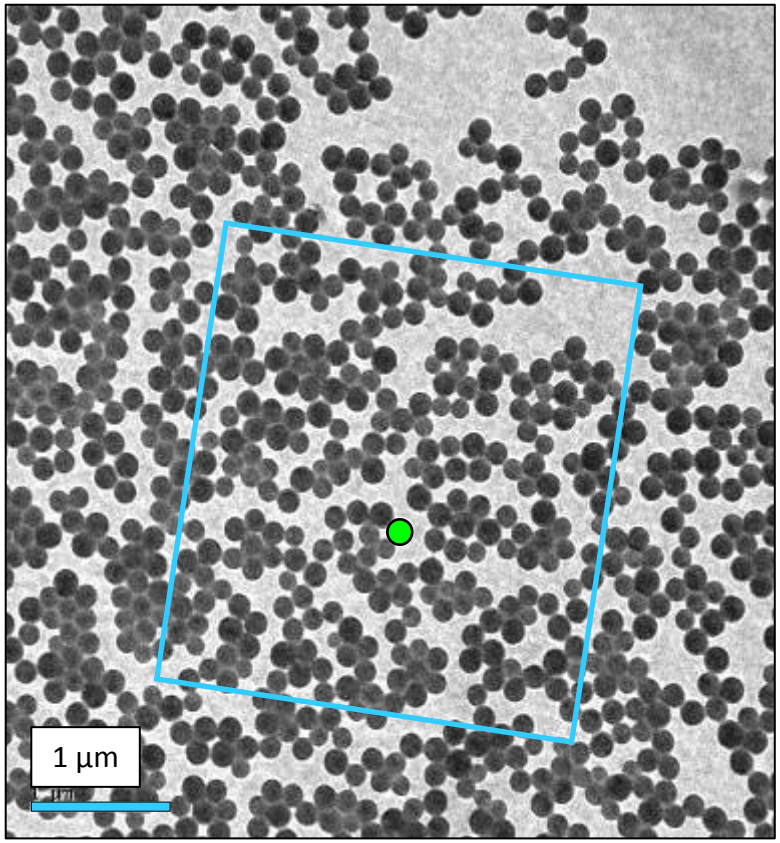
Australian Government
National Measurement Institute

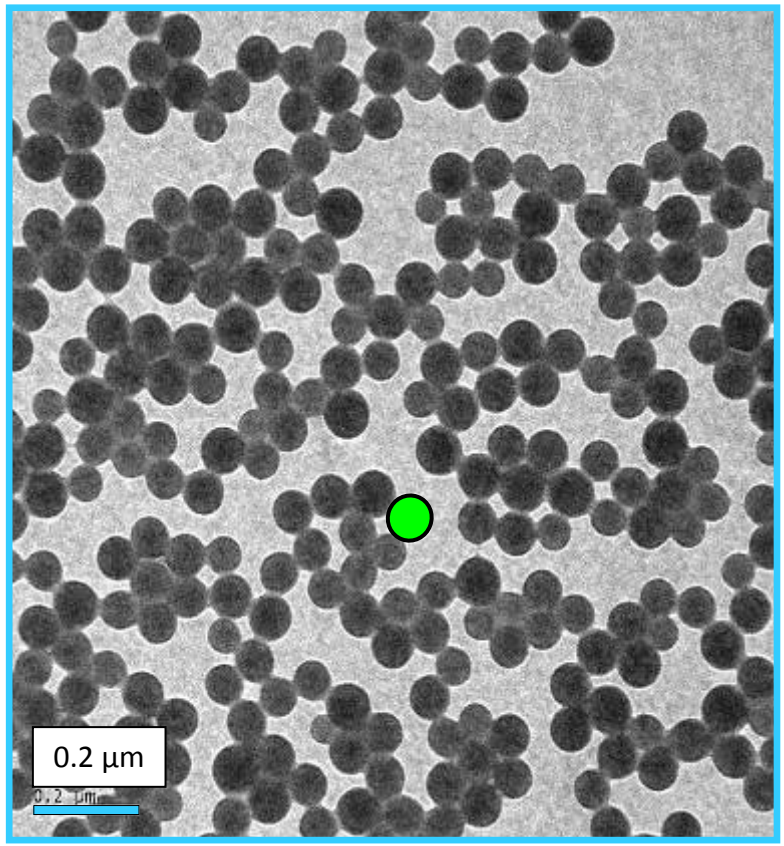
Nanometrology and Documentary Standards for Nanotechnology

Dr. John Miles
Nanometrology Section, Physical Metrology Branch
National Measurement Institute Australia

Nanotechnology Work Health and Safety Symposium
9 – 10 September 2010 Canberra

Australian Government
National Measurement Institute





● *d* = 170 nm

● *d* = 80 nm

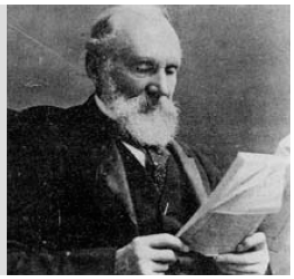
CRM polystyrene latex CRM (Duke Scientific); certified mean diameter *d*=(81.0±2.7) nm
Å Jämting (NMI), B Bojarski (CSIRO)

Australian Government
National Measurement Institute

Measurement is fundamental.

When you can measure what you are speaking about, you know something about it. But when you cannot measure it, your knowledge is of a meagre and unsatisfactory kind. It may be the beginning of knowledge, but you have scarcely advanced to the stage of science.

William Thomson, Lord Kelvin 1883

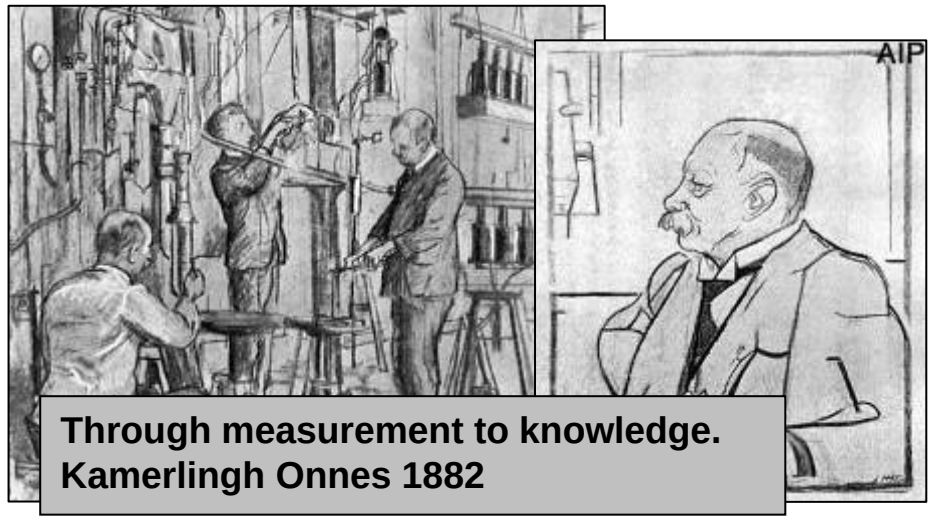


There are two possible outcomes: if the result confirms the hypothesis, then you've made a measurement. If the result is contrary to the hypothesis, then you've made a discovery.

Enrico Fermi

On careful examination the physicist finds that in the sense in which he uses language no meaning at all can be attached to a physical concept which cannot ultimately be described in terms of some sort of measurement.

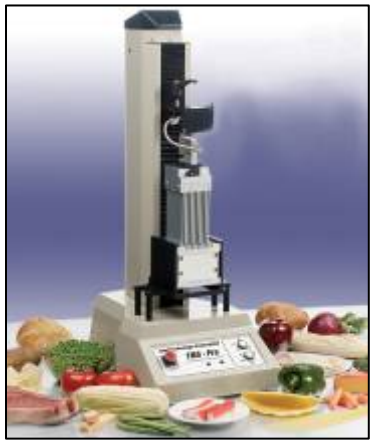
Percy Bridgman

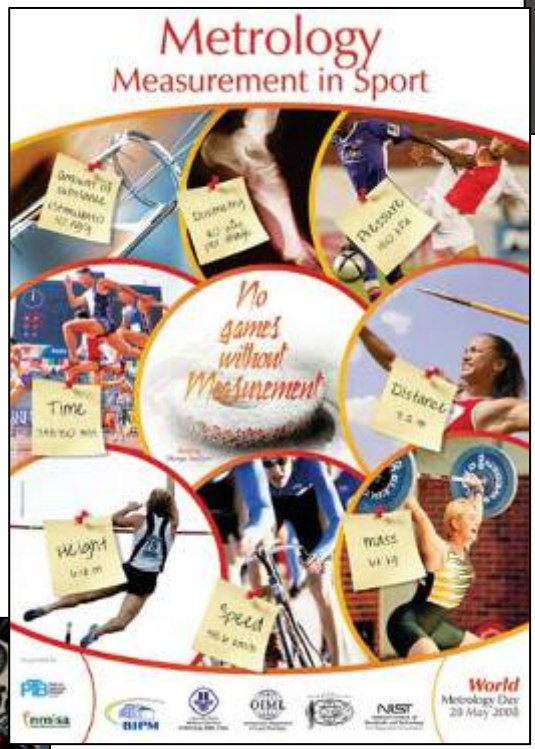


Through measurement to knowledge.
Kamerlingh Onnes 1882

Australian Government
National Measurement Institute

Measurement: The central nerve of modern society

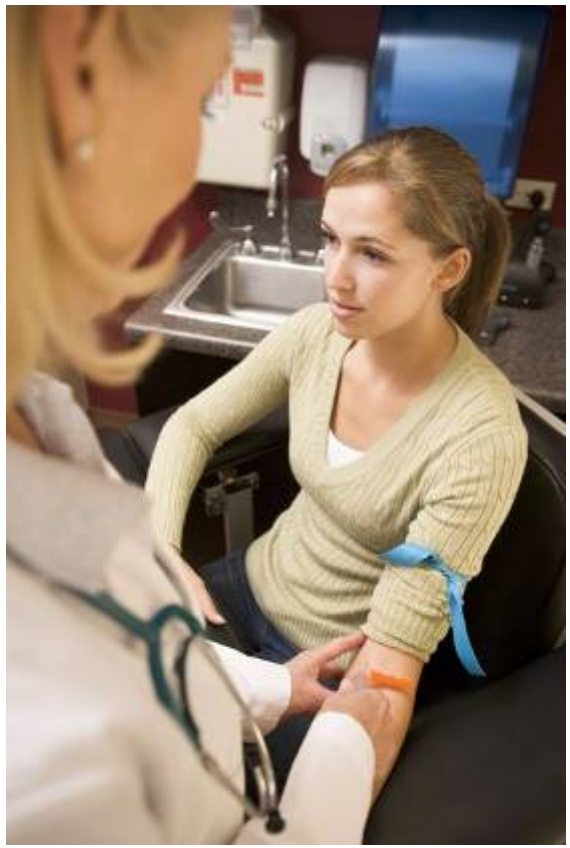




- Getting measurements right is critical in today's society


LICE

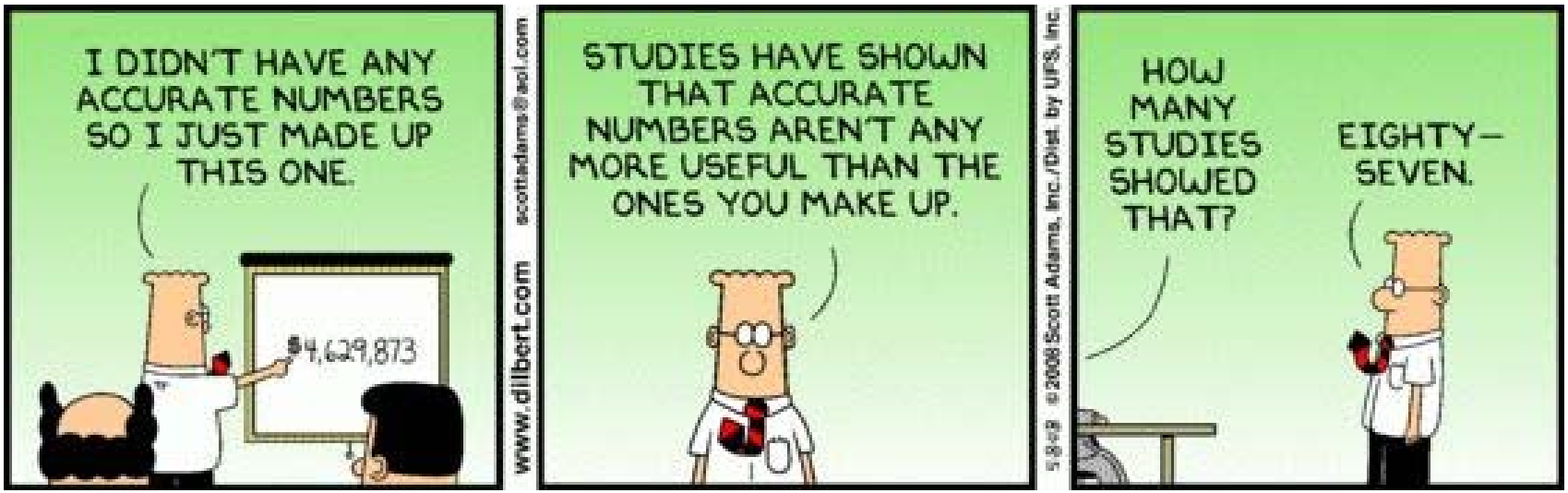

9
8
7
6
5



The quality of measurements

- Workplace health and safety regulations demand high-quality measurements in the workplace

The quality of a measurement is given by its uncertainty.



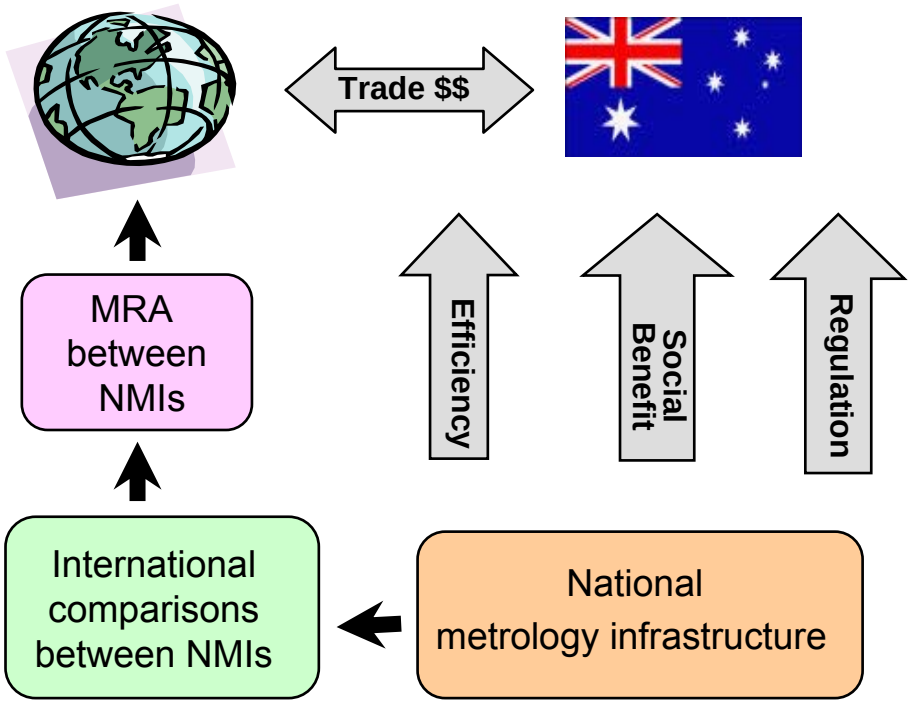
What are the requirements for high quality, low uncertainty measurements?

- International and national measurement systems;
- Measurement standards and/or reference materials;
- Validated test methods;
- Repeatable and reliable instruments with known influence parameters;
- Trained operators;
- Stable environment
- …

Australian Government
National Measurement Institute

The International Measurement System

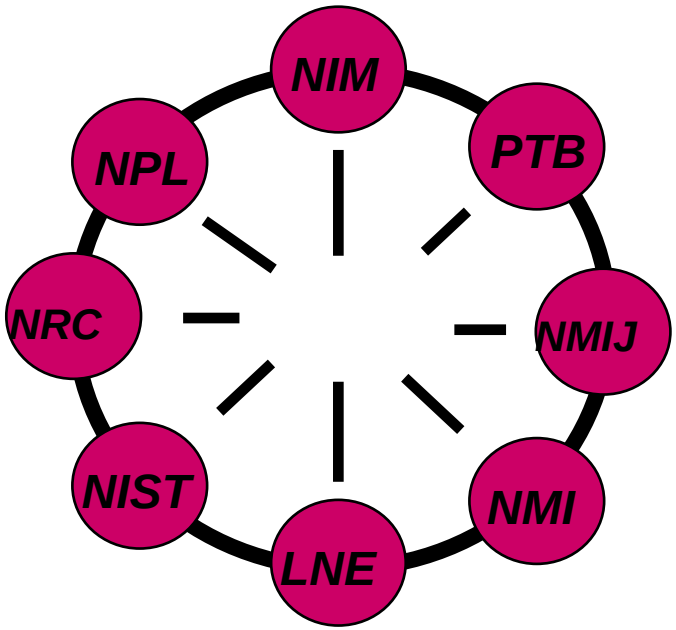
The task of the BIPM is to ensure world-wide uniformity of measurements and their traceability to the International System of Units (SI).



BIPM

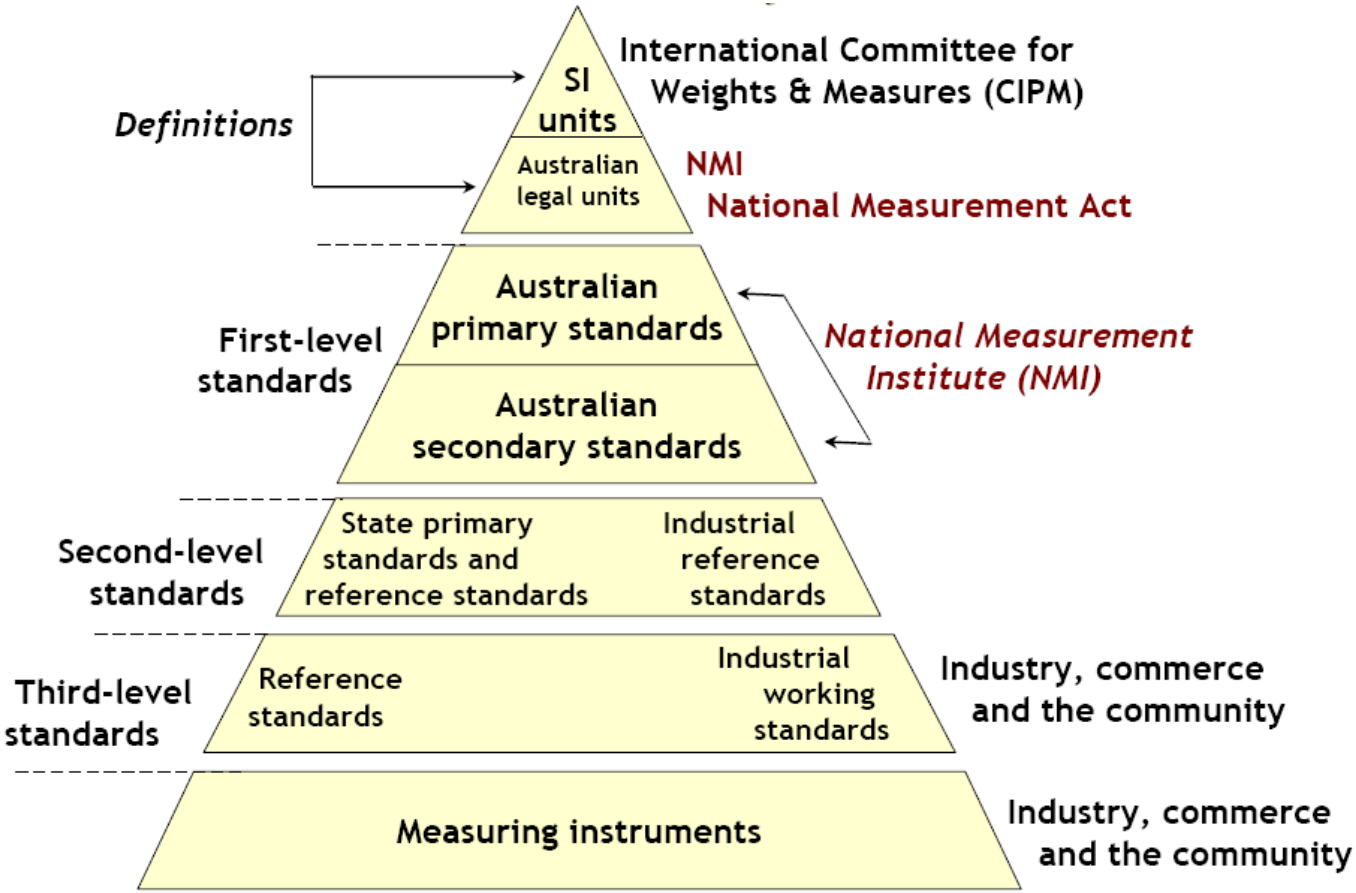
National Measurement Institutes

- Each developed country has a National Measurement Institute;
- A critical role of an NMI is to establish, maintain and disseminate the national standards of measurement, providing traceability to the SI system;



Headquarters of Australia's NMI in Sydney

Australia's Measurement System



Australian Government
National Measurement Institute

National Measurement Institute Australia

Australia's peak measurement organisation

Establishes, maintains and realises Australia’s units and standards of measurement

~500 staff

>20 sites across Australia

Australian Government
National Measurement Institute

NMIA: Functions

Responsible for Australia's national infrastructure
in physical, chemical, biological and legal metrology
and in national trade measurements

Coordinates Australia's national measurement system
(NMI, NATA, SA, JAS-ANZ)

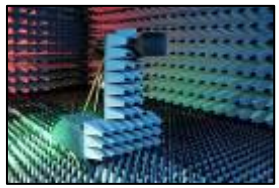
Establishes, maintains and realises
Australia's units and standards of measurement

Represents Australia under international measurement treaties
$\Rightarrow$ mutual recognition, intercomparisons










Australian Government
National Measurement Institute

Government support for nanometrology

National Enabling Technologies Strategy
(07/2009–06/2013)

NETS "…provides funding for new and enhanced biotechnology and nanotechnology measurement laboratories and research so that measurement standards can be established for regulators and industry."

"Australian researchers, industry, workers and the community will benefit from the establishment of the best possible standards and regulation based on research."

Australian Government
Department of Innovation
Industry, Science and Research

BUDGET
2009-10

INNOVATION

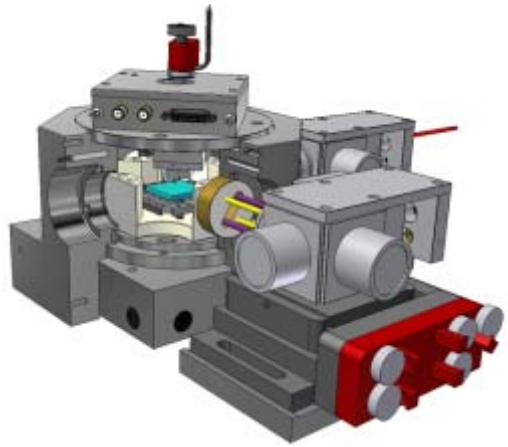
Powering Ideas
An Innovation Agenda
for the 21st Century

Australian Government
National Measurement Institute

NMIA nanometrology: Key areas

Linking the nanometre to the metre:

Provide traceability for nanoscale dimensional measurements using a Metrological Scanning Probe Microscope (mSPM)



C Freund

Metrology of nanomaterials:

Nanoparticle characterisation laboratory
Evaluation of instrumentation
Instrument and method development
Reference materials

Dissemination through:

publications, calibration services, consultancy, workshops, research collaborations

NMIA nanoparticle laboratory
Sep-2009

Australian Government
National Measurement Institute

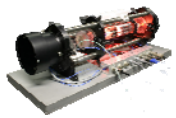
Traceable dimensional nano measurements

SI definition of the metre

The metre is the length of the path travelled by light in vacuum during a time interval of 1/299 792 458 of a second.

Realisation of the metre

Iodine-stabilised laser



Frequency comb

Calibration of the laser wavelength

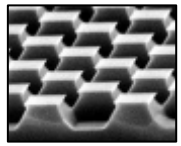
Laser used in interferometry measurements is calibrated using iodine-stabilised laser or frequency comb.

Metrological SPM

Position read-out using laser interferometry

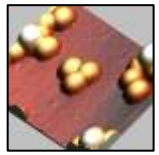
Calibration of standards for microscopy

Step height, flatness, 1D and 2D pitch length



Calibration of standards for dimensional particle characterisation

Particle size and shape



Calibration of 'secondary' NMI or client instruments

SPM, SEM, TEM, DLS, FFF, ...

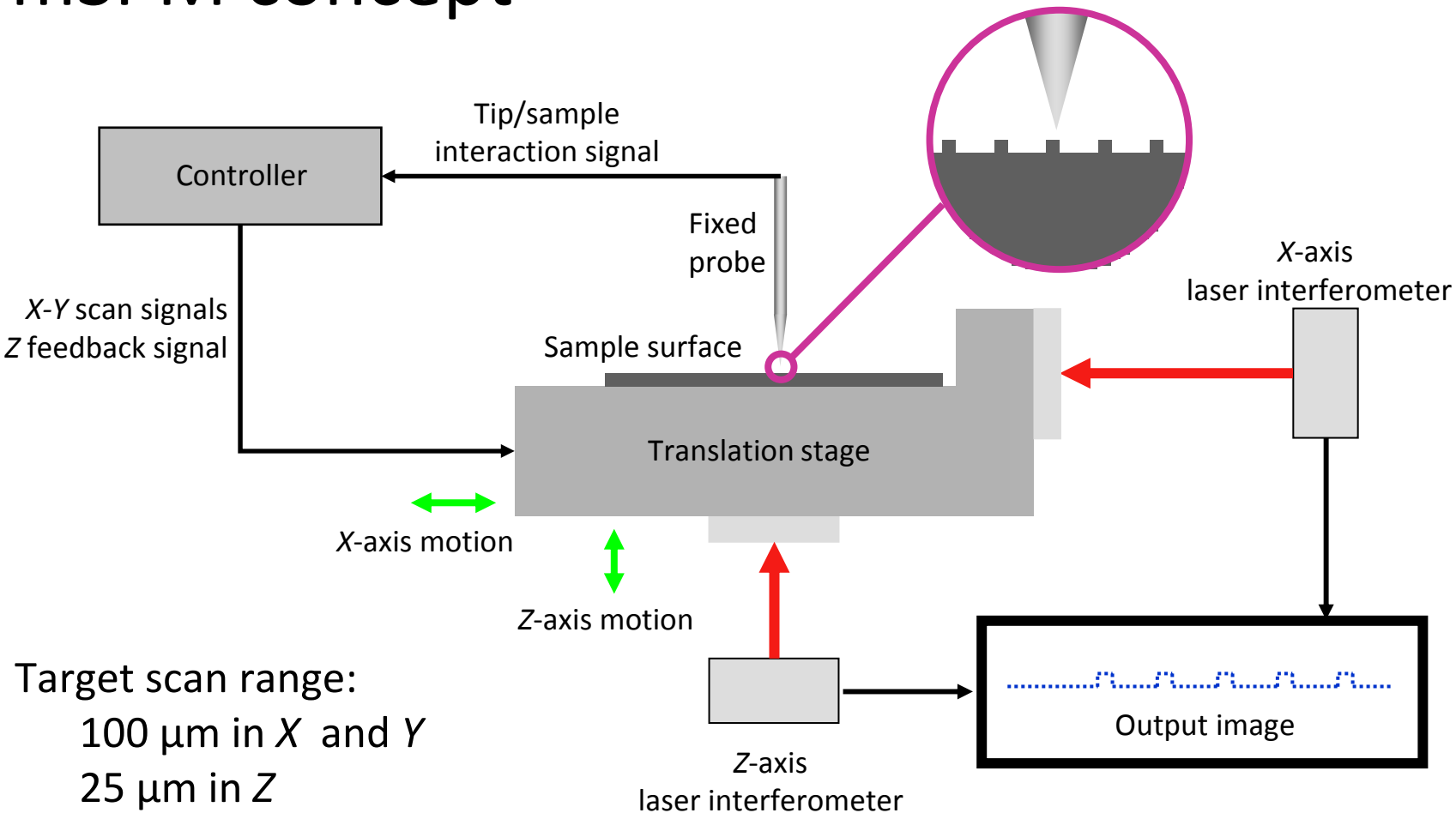
Transfer Standards

Calibration of user instruments

SPM, SEM, TEM, DLS, FFF, ...

Traceable dimensional measurements of nanomaterials and nanostructures

mSPM concept



Target scan range:

100 µm in *X* and *Y*

25 µm in *Z*

Target uncertainty:

≤1 nm.

M Lawn

mSPM: Probe

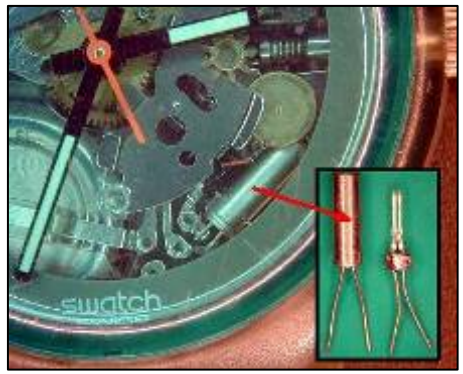
Atomic Force Microscopy (AFM)
- non-contact mode

Quartz tuning fork cantilever
- piezoelectric actuation/detection

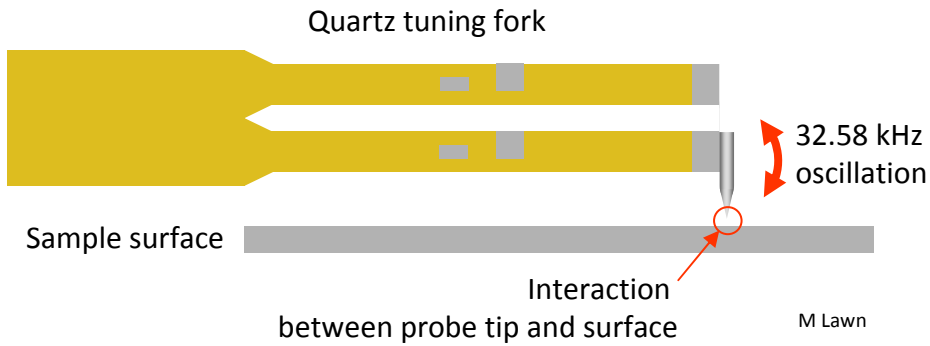
Tip-sample interaction detunes
- free air mechanical oscillation

Feedback loop maintains
- frequency/amplitude/phase

Advantages:
- reduced tip and sample wear
- simple actuation and readout
- low power dissipation



Swatch Group



mSPM: Design principles

Short measurement loop

High symmetry

Kinematic mounting

Materials selection
- low thermal expansion
- high thermal conductivity
- high stiffness of metrological fram

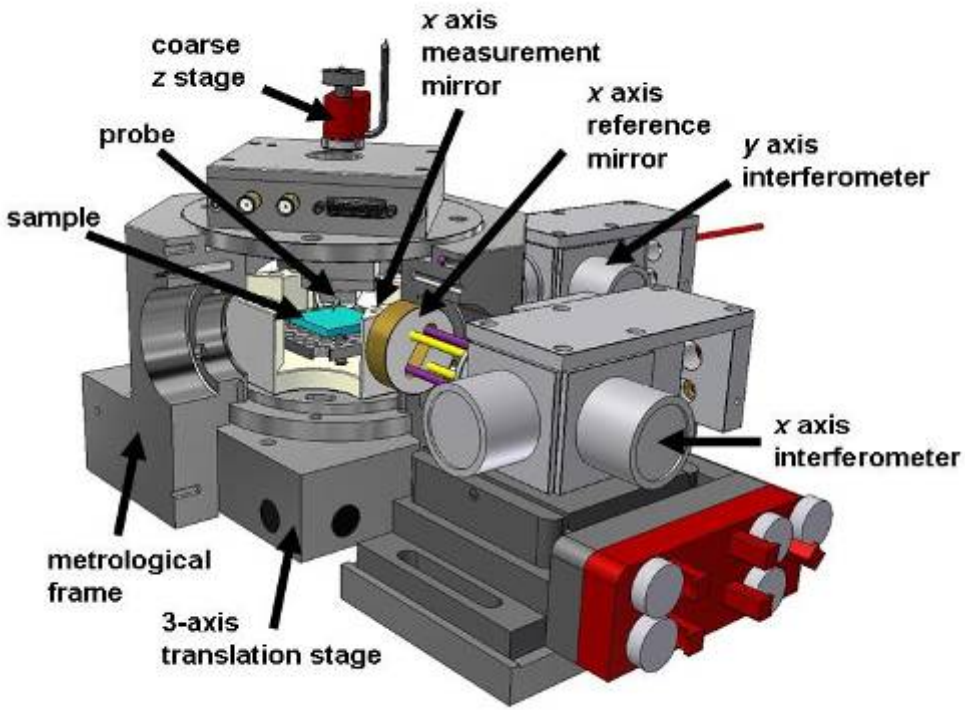
Interferometry – minimise dead path

Alignment – minimise Abbé offsets

Temperature management

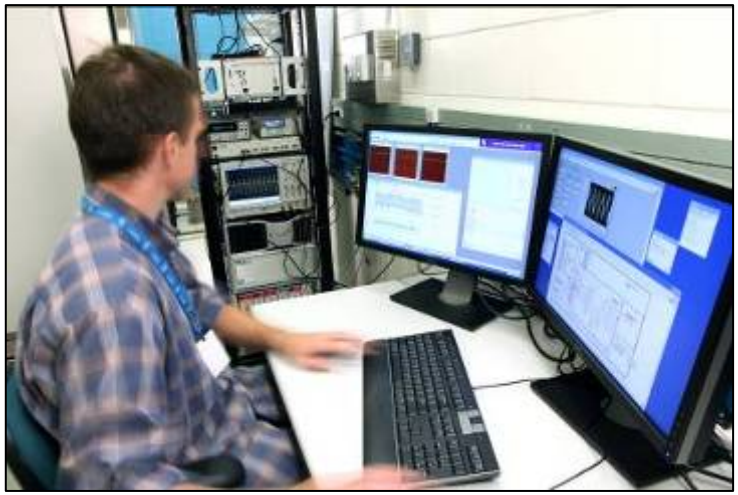
Vibration isolation

…



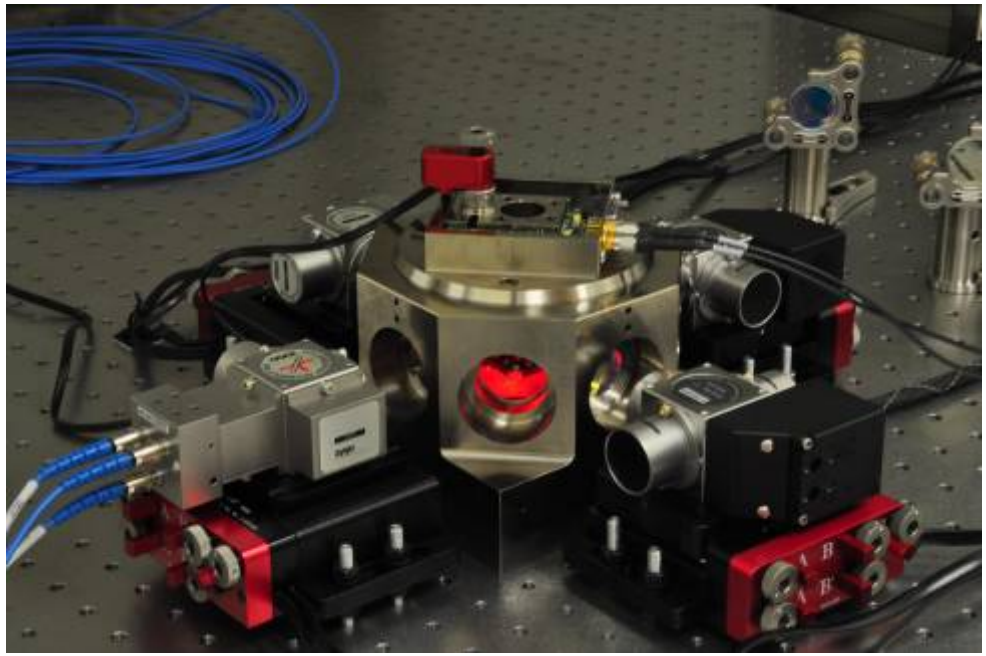
Australian Government
National Measurement Institute

NMI mSPM development



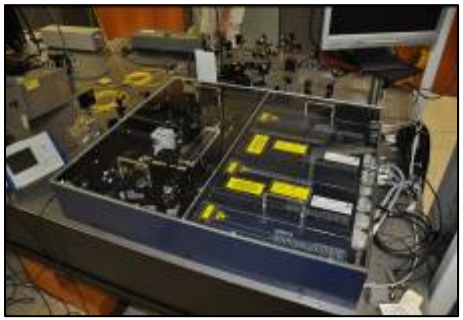
Developing the control systems

Beginning the assembly

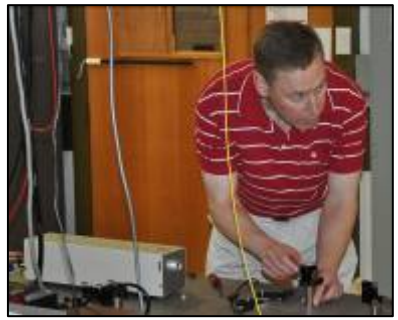


Australian Government
National Measurement Institute

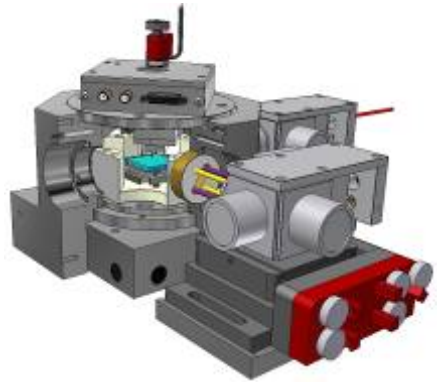
Practical traceable length nanometrology



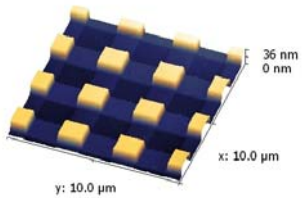
SI metre



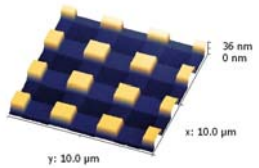
Calibration of mSPM
Interferometry Laser



"*Type A*" mSPM



Traceable calibration artefact



Transfer
standard

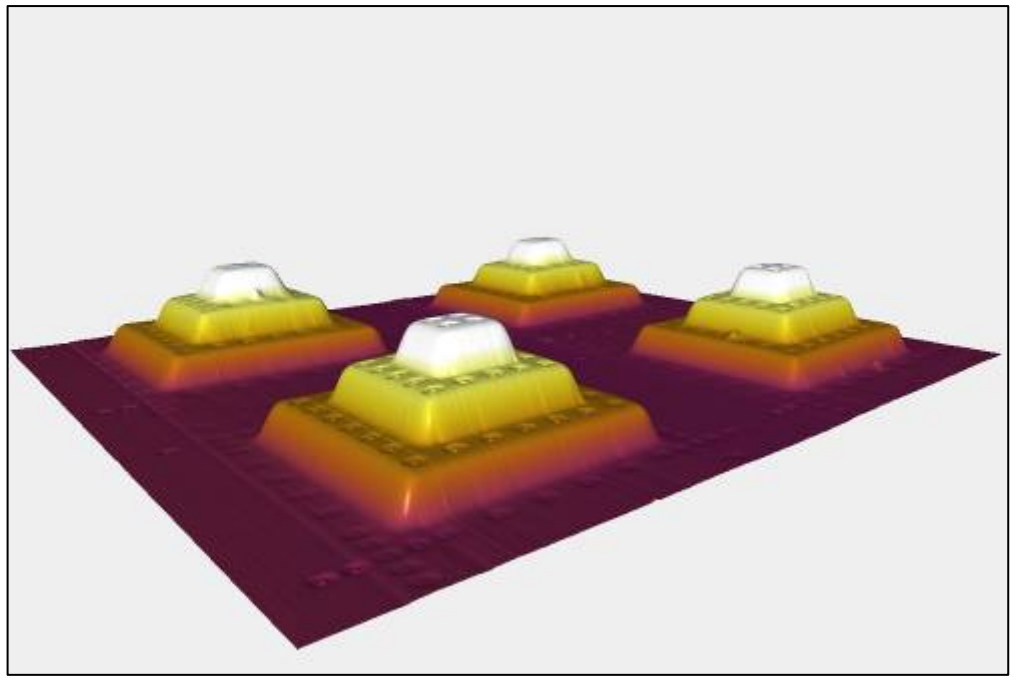
Traceable measurements
of nanoparticles

"*Type B*" SPM

Australian Government
National Measurement Institute

Images taken with NMI Type B AFM

100nm diameter Polystyrene Latex particles deposited on a silicon substrate.



Three dimensional calibration structure ion beam fabricated in silicon

The metrology of nanomaterials

ISSUES

Properties cannot be extrapolated from the macro scale.

Enormous variety of nanomaterials and characterisation techniques.

Physico-chemical metrology is still in its infancy.

No consensus about which properties are the crucial ones for both beneficial and detrimental effects.

The interaction of nanomaterials with the environment (e.g., in tissue or food) is crucial but poorly understood.

No routine methods are available for analysing nanomaterials in matrices (e.g., in tissue, soil, food).

CSIRO

Evident Technologies

What is the ‘right’ particle diameter?

Different techniques measure different things.

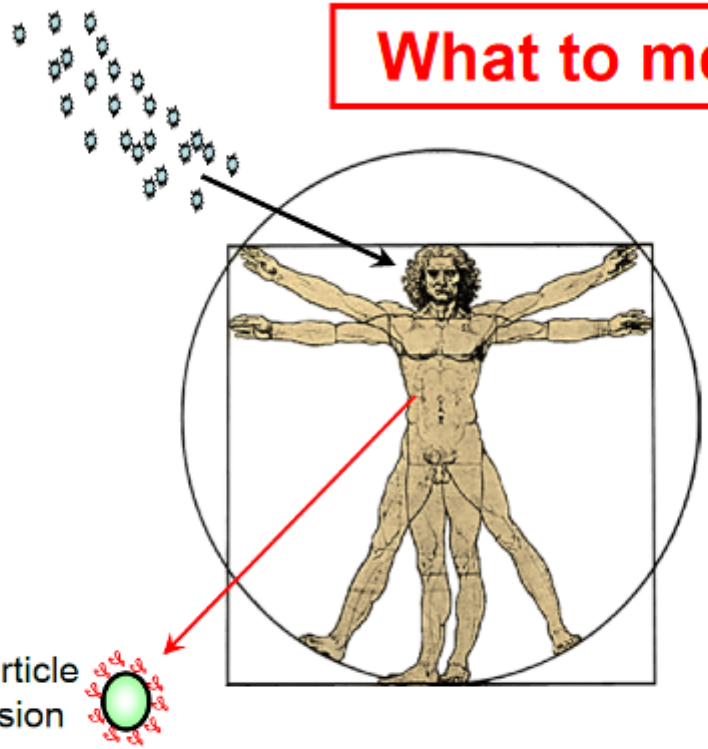
Table 1. Reference Value Mean Size and Expanded Uncertainty [a]
Average Particle Size (Diameter), in nm

Technique	Analyte Form	Particle Size (nm)
Atomic Force Microscopy	dry, deposited on substrate	24.9 ± 1.1
Scanning Electron Microscopy	dry, deposited on substrate	26.9 ± 0.1
Transmission Electron Microscopy	dry, deposited on substrate	27.6 ± 2.1
Differential Mobility Analysis	dry, aerosol	28.4 ± 1.1
Dynamic Light Scattering	liquid suspension	
173° scattering angle (backscatter)		28.6 ± 0.9
90° scattering angle		26.5 ± 3.6
Small-Angle X-ray Scattering	liquid suspension	24.9 ± 1.2

[a] The expanded uncertainties, U, are calculated as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the combined standard uncertainty calculated according to the ISO and NIST Guides [2]. The coverage factor, k, for 95 % expanded uncertainty intervals is based on a t multiplier with the appropriate associated degrees of freedom.

NIST Report of Investigation, RM 8012, Dec-2007.

Issues with nanoparticle measurements



What to measure? Which unit?

- identifying & counting particles in air [😐😊😊]

⇨ identifying & counting their 'metabolites' in biological matrices [☹😐☹]

⇨ measuring their functional properties [☹☹😐]

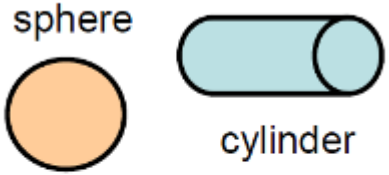
but: particles unstable & reactive ↷ various transformations

⇨ measure also dynamics

Issues with nanoparticle measurements

symmetric objects

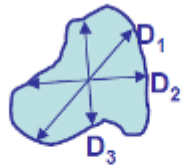
sphere



cylinder

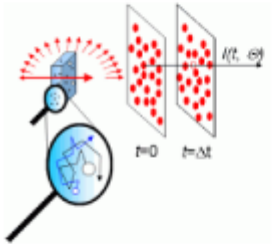
Morphology parameter(s)

but



etc.

Dynamic Light Scattering



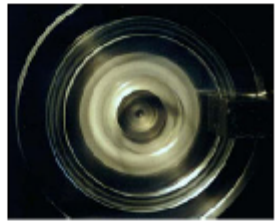
46 ± 2 nm

Hydrodynamic diameter

Nanoparticle size in suspension

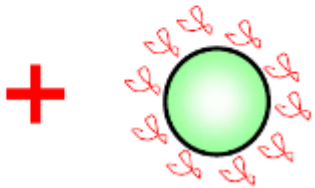
Disc sedimentation

35 ± 1 nm



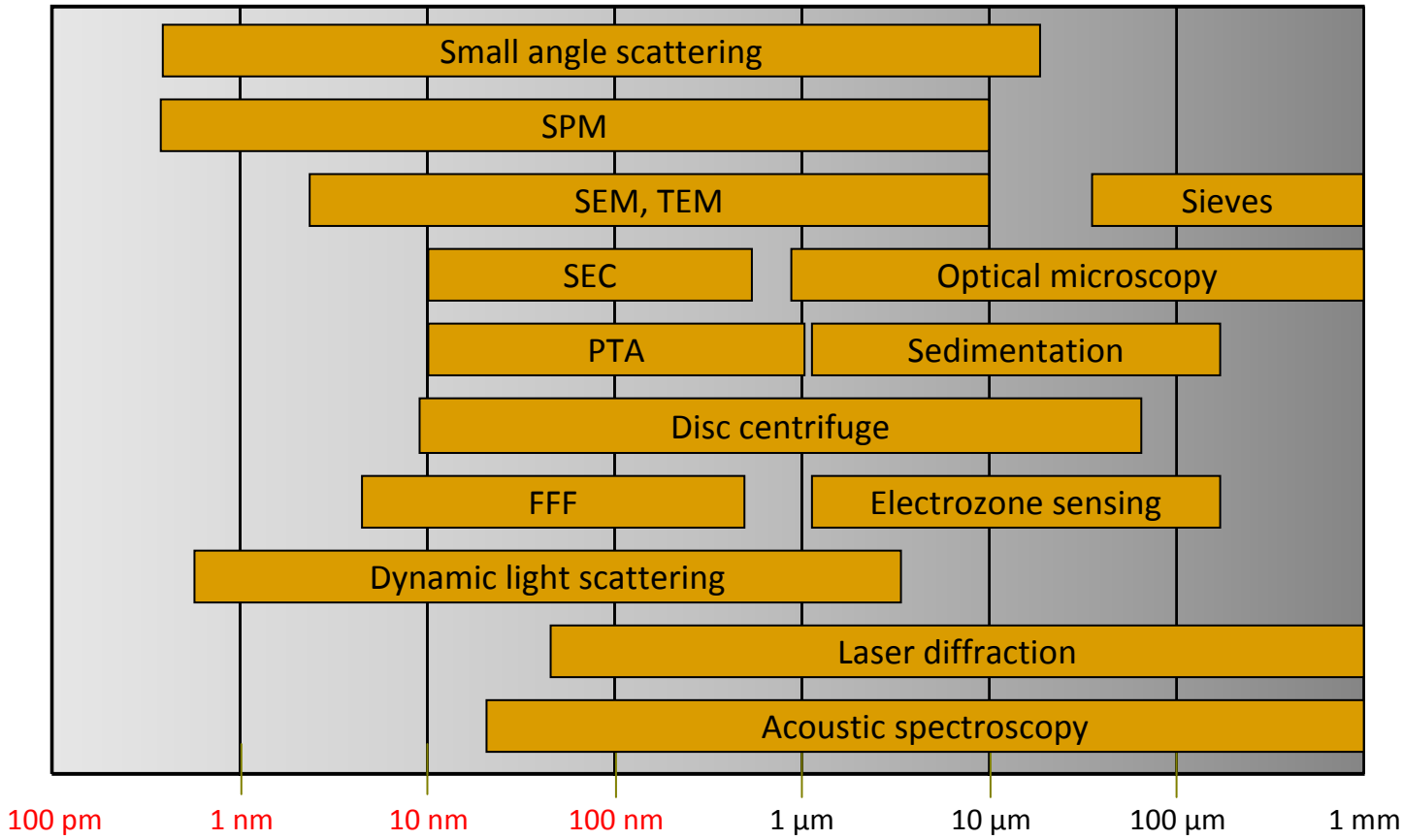
Stokes diameter

EHS-(decision) relevant parameter?



Molecular interfacial structures & properties

Particle sizing techniques



Australian Government
National Measurement Institute

Nanoparticle measurement laboratory at NMI

Laser diffraction

Micro channel resonance

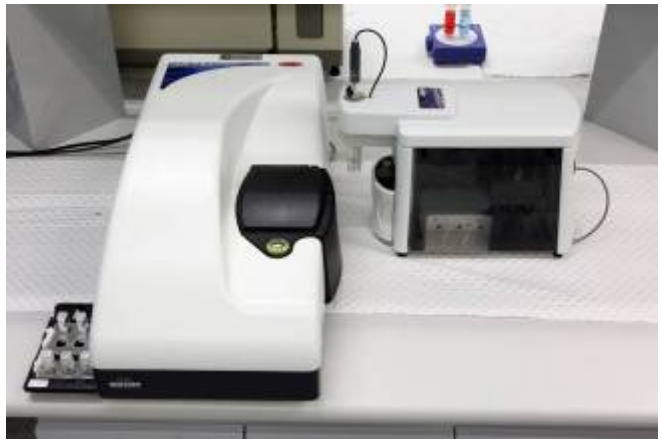
Disc centrifuge

Australian Government
National Measurement Institute

Particle measurement techniques at NMI

Particle tracking analysis system

Dynamic light scattering



BET surface area

Nuclear magnetic resonance

Australian Government
National Measurement Institute

Particle measurement techniques at NMI

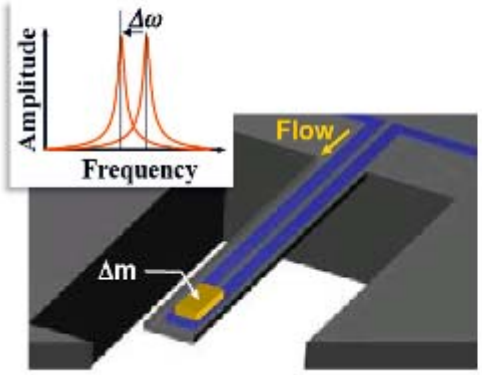
Zeta potential

Microscopy

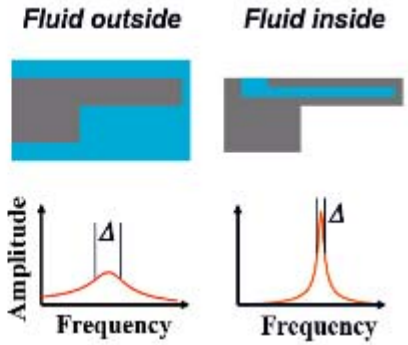
Processing equipment

The Micro Channel Resonator

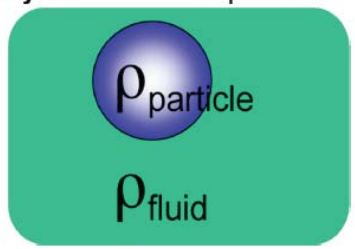
- New instrument developed in collaboration with researchers at MIT
- Principle of detection based on Archimedes principle
- Uses a micro resonator (the probe) with a microfluidic channel etched through the centre.
    - A change in the mass of the resonator (i.e. when a particle flows through) causes a change in resonant frequency.
    - This allows us to measure buoyant mass
    - From buoyant mass we can calculate a dry mass (if we know the density of the particles and the fluid)
    - From dry mass, particle diameter can be determined (assuming particle shape is known).



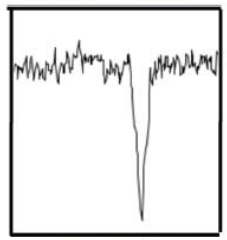
Fluid flows through hollow resonator.



$$M_{Buoyant} = Vol * (\rho_{particle} - \rho_{fluid})$$

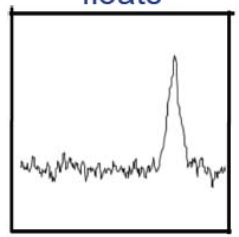


Particle in light fluid "sinks"



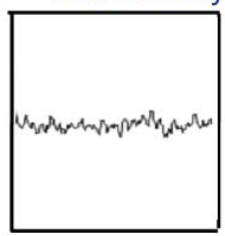
= negative frequency shift

Particle in dense fluid "floats"



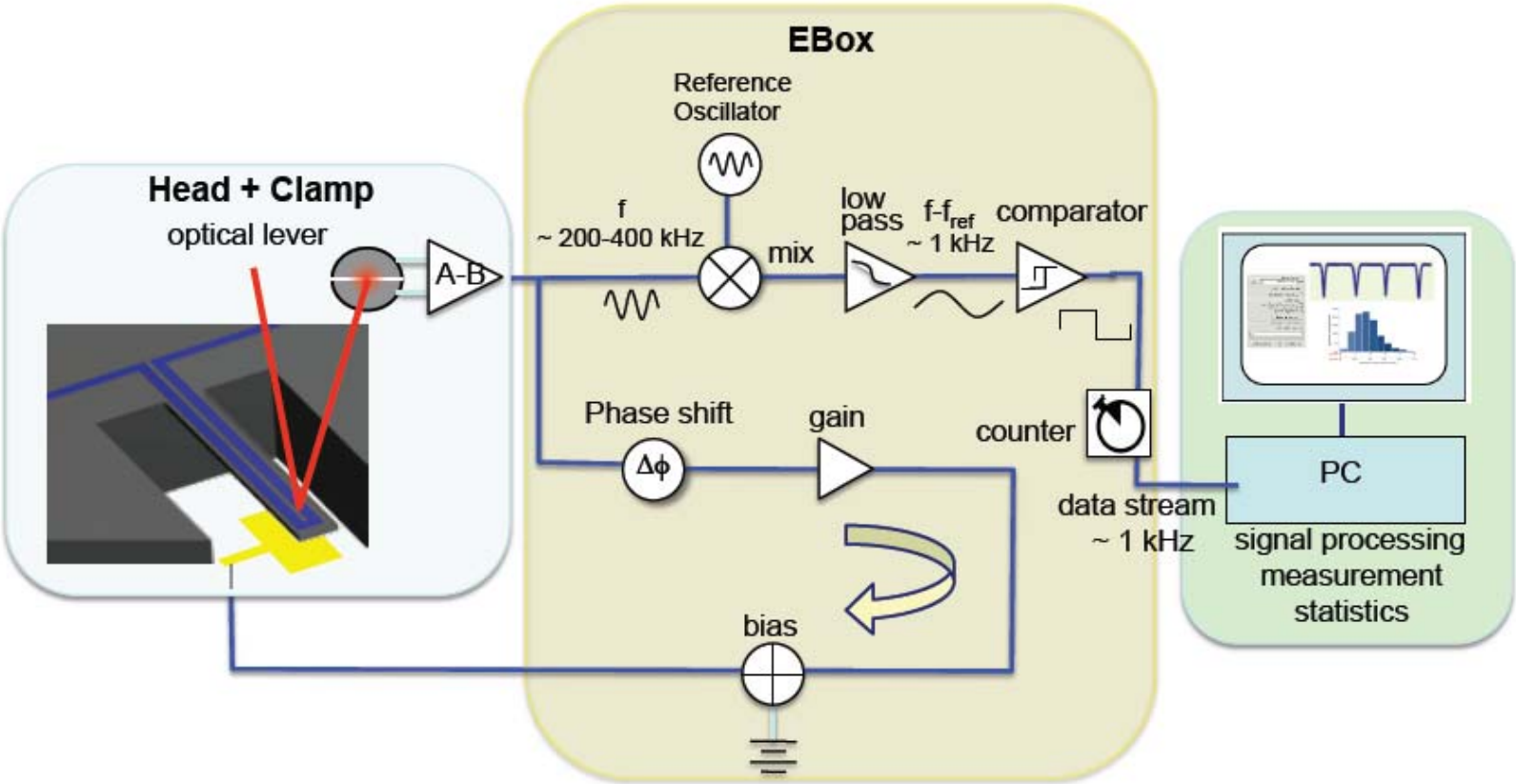
= positive frequency shift

Particle density = fluid density



= **zero** frequency shift

Frequency Measurement



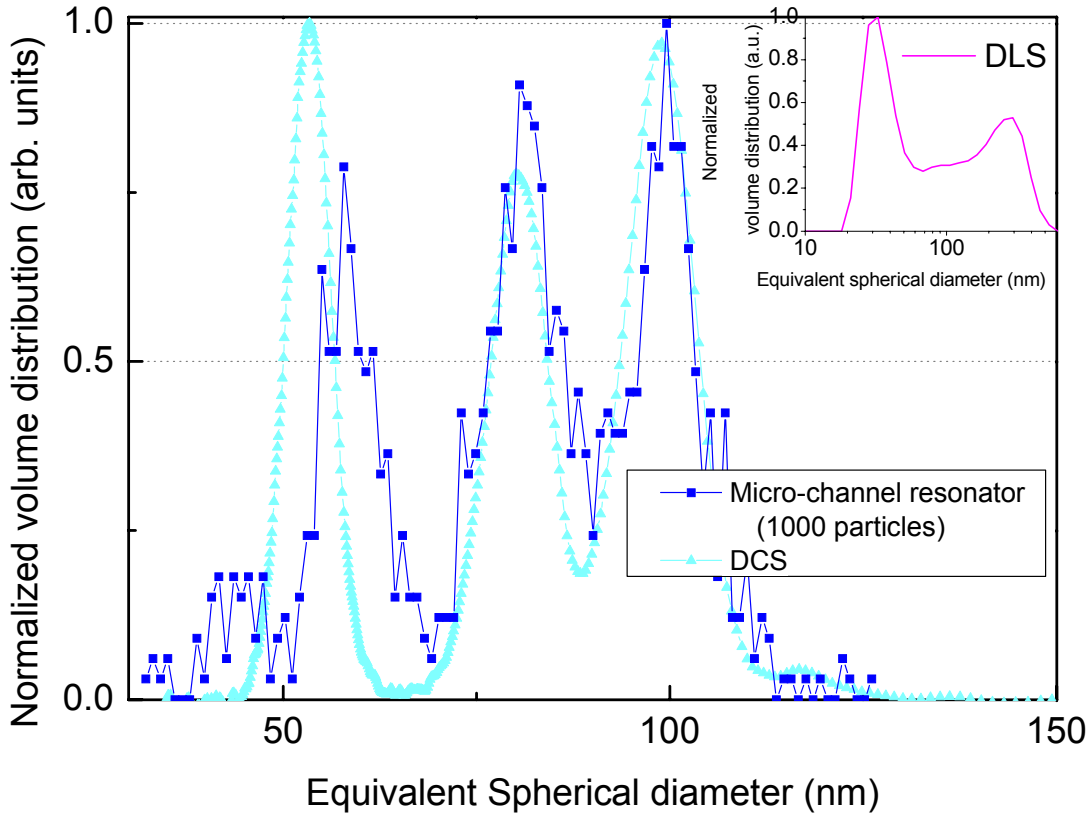
Self resonant circuit using gain control oscillator – allows for very quick response to changes in resonant frequency

Probe frequency is 'mixed down' with reference oscillator to produce signal at ~1kHz.

Frequency resolution 40 ppb @ 1kHz.

Resultant mass resolution ~ 1 Femto (10^{-15} g) g!!!

Comparing micro channel resonator, disc centrifuge and dynamic light scattering



Australian Government
National Measurement Institute

NMIA Nanometrology team:
Bakir Babic; Heather Catchpoole; Victoria Coleman; Chris Freund; Jan Herrmann; Åsa Jämting; Malcolm Lawn; John Miles.

John Miles

Nanometrology

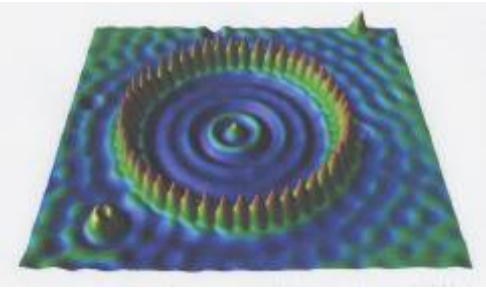
National Measurement Institute

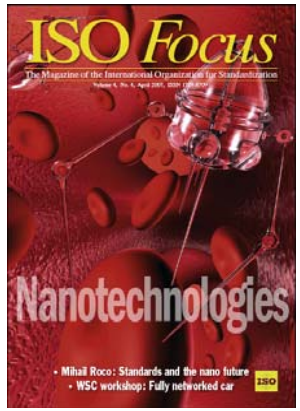
Bradfield Road, West Lindfield NSW 2070, Australia

Email: john.miles@measurement.gov.au

measurement.gov.au

Australian Government
National Measurement Institute





Documentary Standards for Nanotechnologies

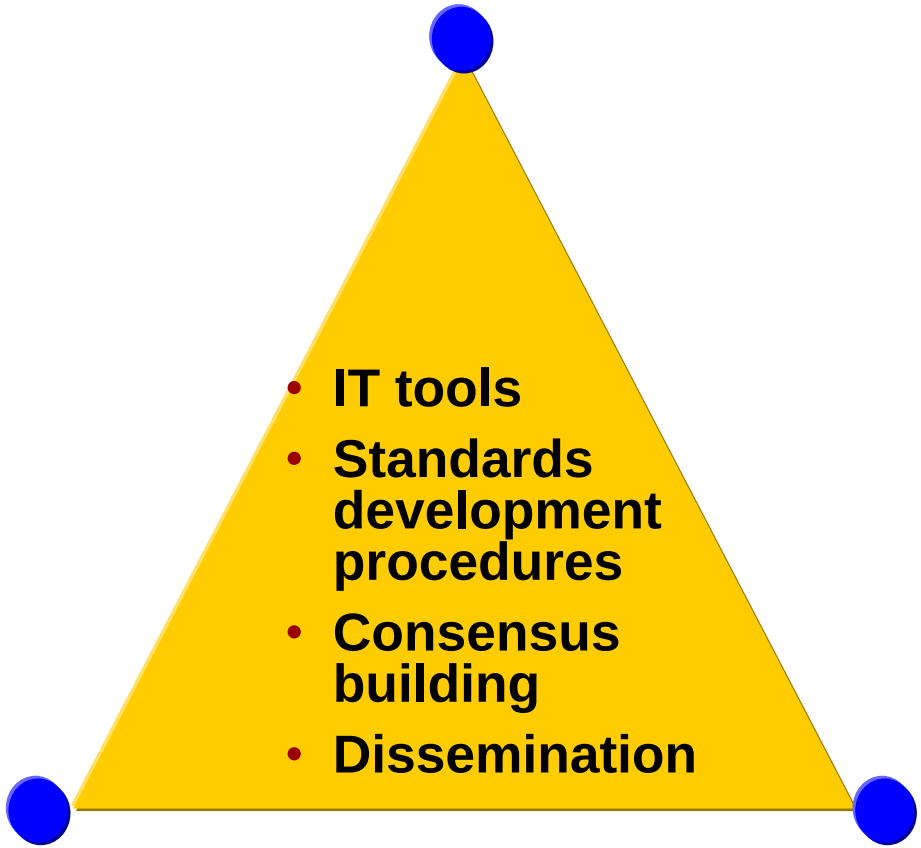
International Organization for Standardization

www.iso.org

Australian Government
National Measurement Institute

The 3 pillars of the ISO system

156 national members



190 TCs

3 000 technical bodies

50 000 experts

Central Secretariat in Geneva

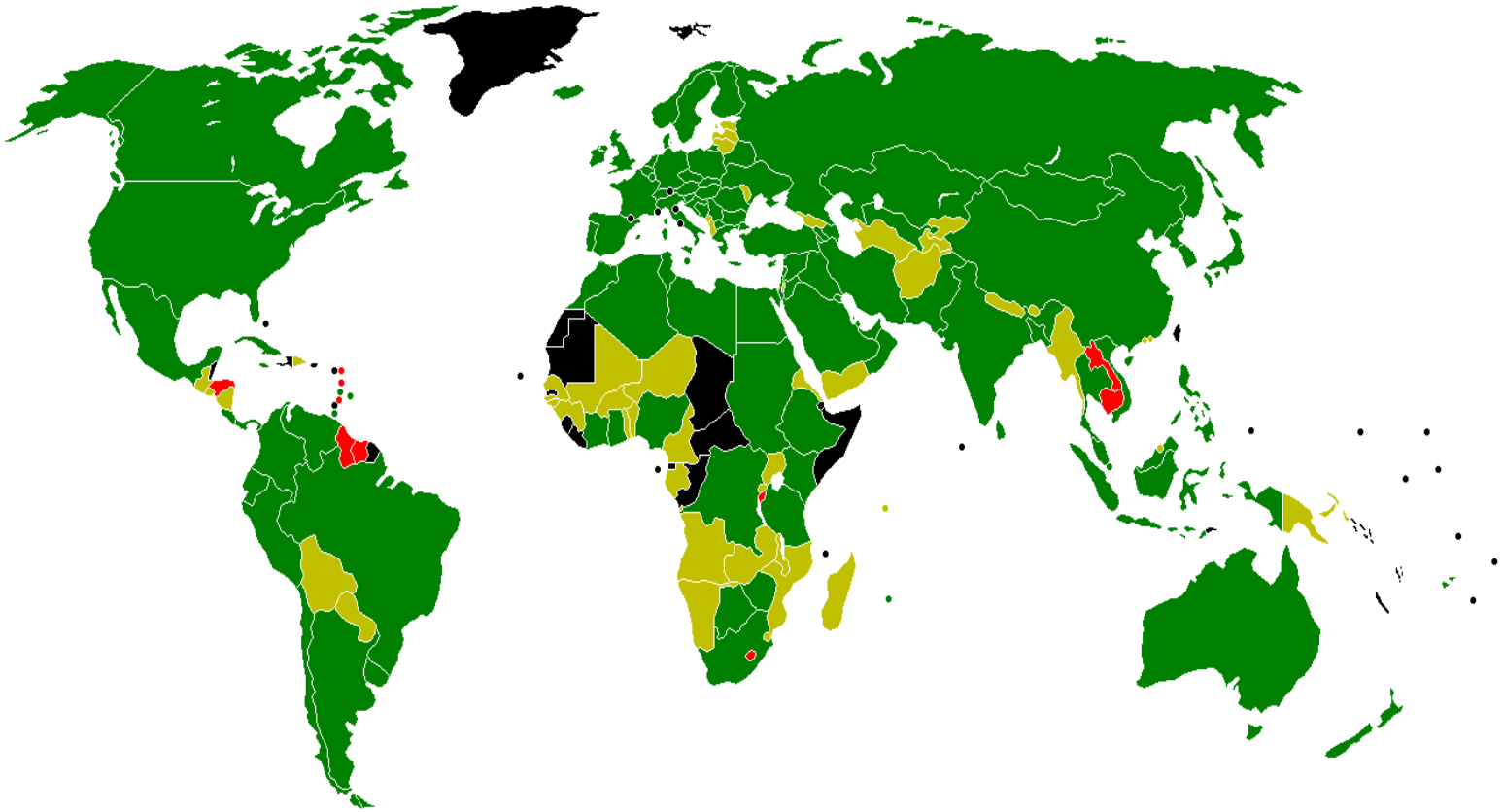
150 staff

Members - general

- ISO is made up of its 156 members
  - one member per country
  - ISO member = ISO entrance door in the country
  - three categories of members
    - member body (full member) (101)
    - correspondent member (45)
    - subscriber member (10)

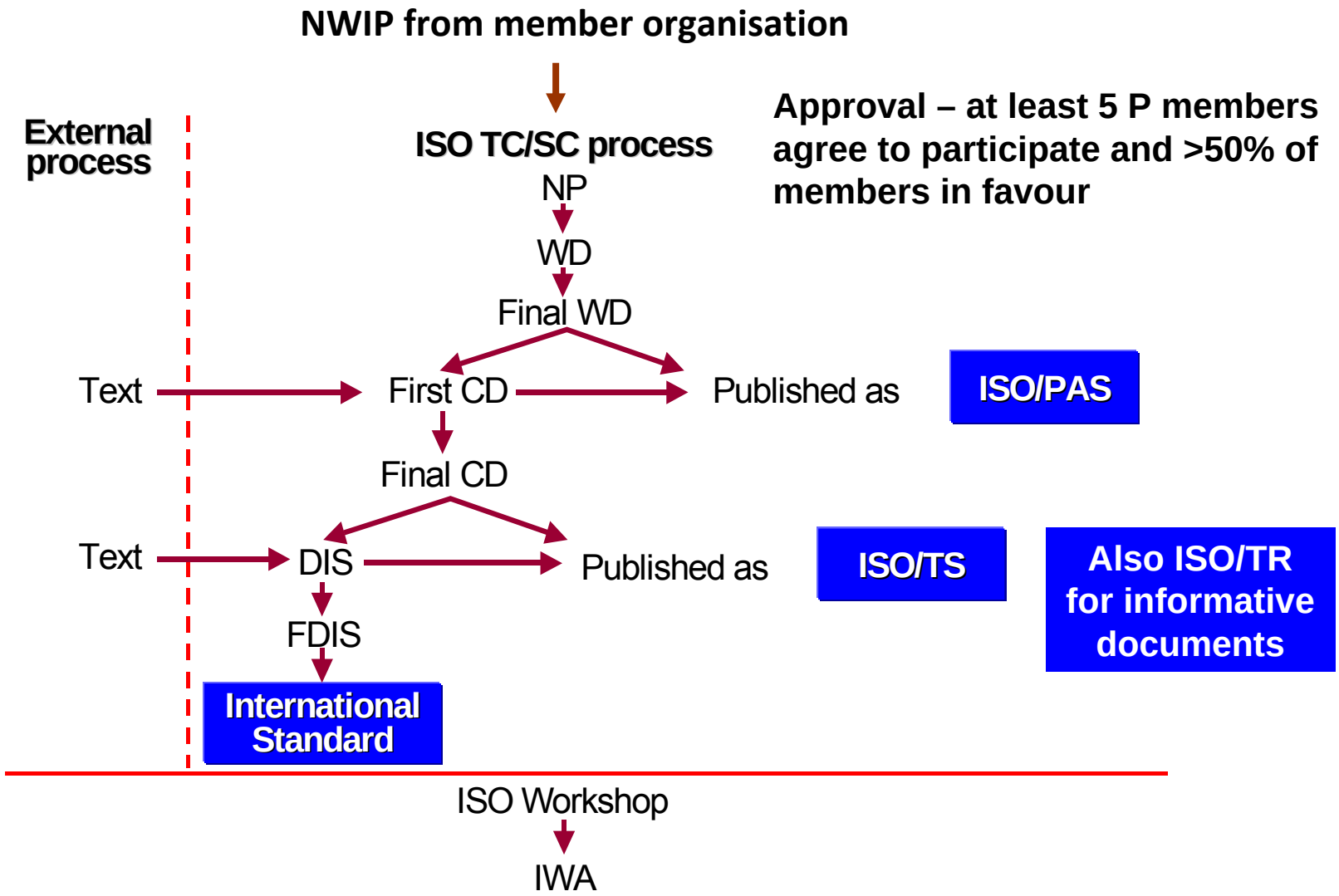
Australian Government
National Measurement Institute

ISO members



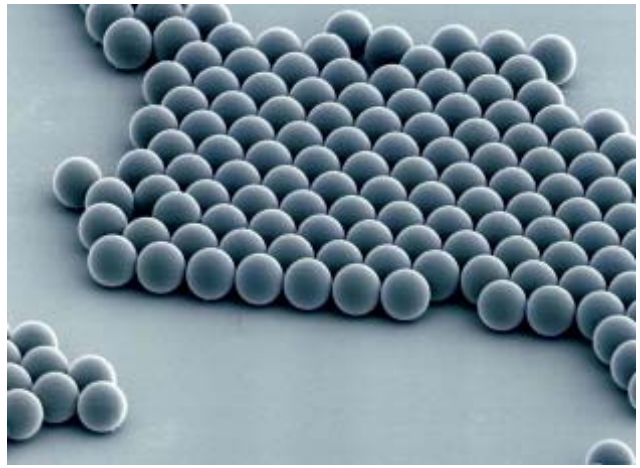
Members **Corresponding members** Subscriber members Non members

Development of International Standards
Process accommodates special needs



ISO TC 229 - nanotechnologies

- Established June 2005 – UK Secretariat and Chair (Peter Hatto)
- Currently 43 members – 32 “P” and 11 “O”
- First plenary 9 – 11 November 2005 in London
- Standards Australia attended London meeting as a “P” member



ISO TC 229 - nanotechnologies

- SCOPE:
  - "Standardization in the field of nanotechnologies that includes either or both of the following:
    - » 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,
    - » 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

ISO TC 229 - nanotechnologies

» Specific tasks include developing standards for: terminology and nomenclature; metrology and instrumentation, including specifications for reference materials; test methodologies; modelling and simulation; and science-based health, safety, and environmental practices.

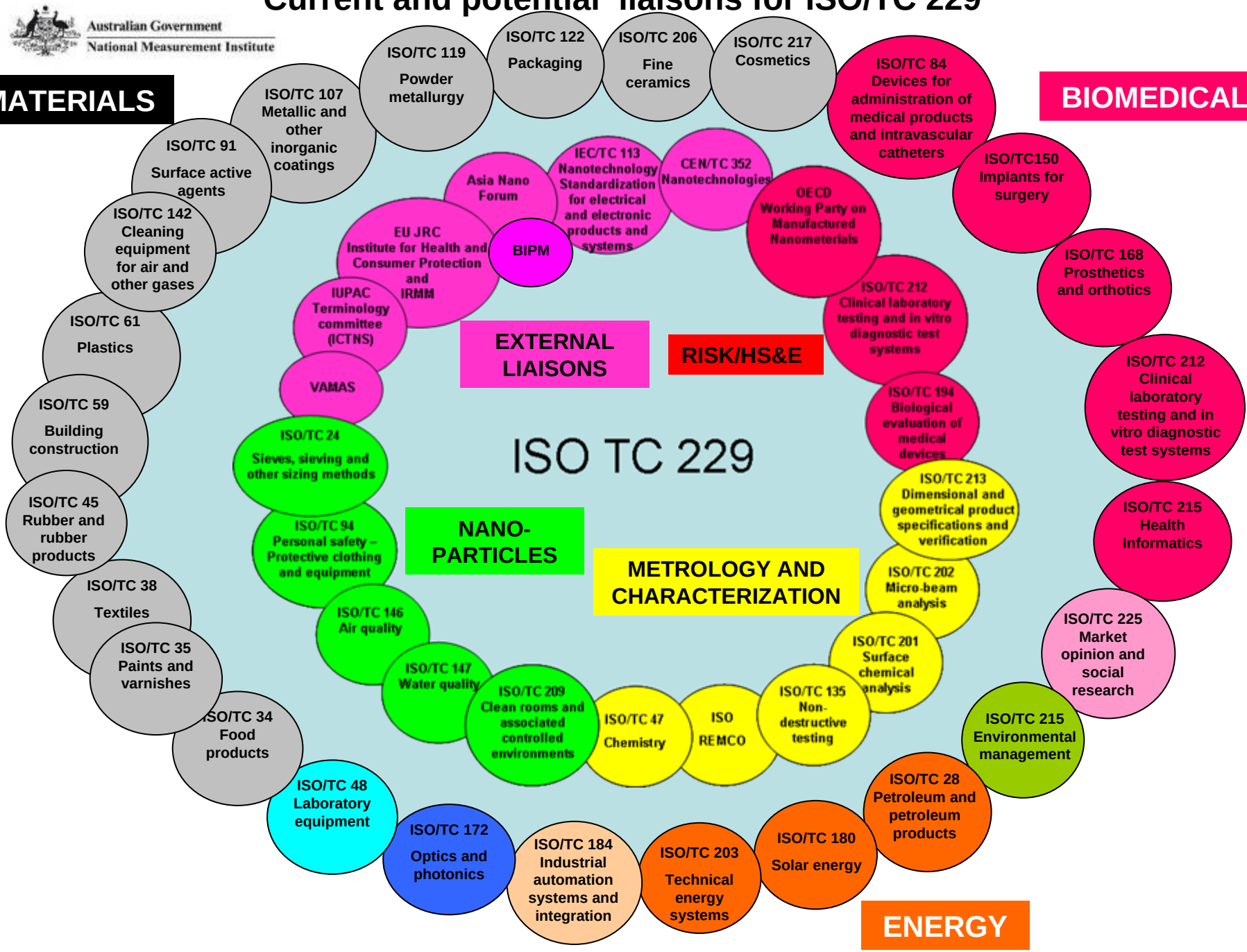
Australian Government
National Measurement Institute

ISO/TC 229 - Nanotechnologies

- ***43 members – 32 "P" and 11 "O"***
- ***Liaisons with around 25 other ISO/IEC/CEN TCs and SCs and 8 external bodies – Asia Nano Forum, BIPM, ECOS, EC JRC, IRMM, IUPAC, OECD and VAMAS***
- ***Exploring additional external liaisons with other groups, e.g. International Alliance for NanoEHS Harmonization, NanoAf-Net, other emerging economies.***
- ***Established in June 2005***

TC229 meeting in Maastricht in May 2010

Current and potential liaisons for ISO/TC 229

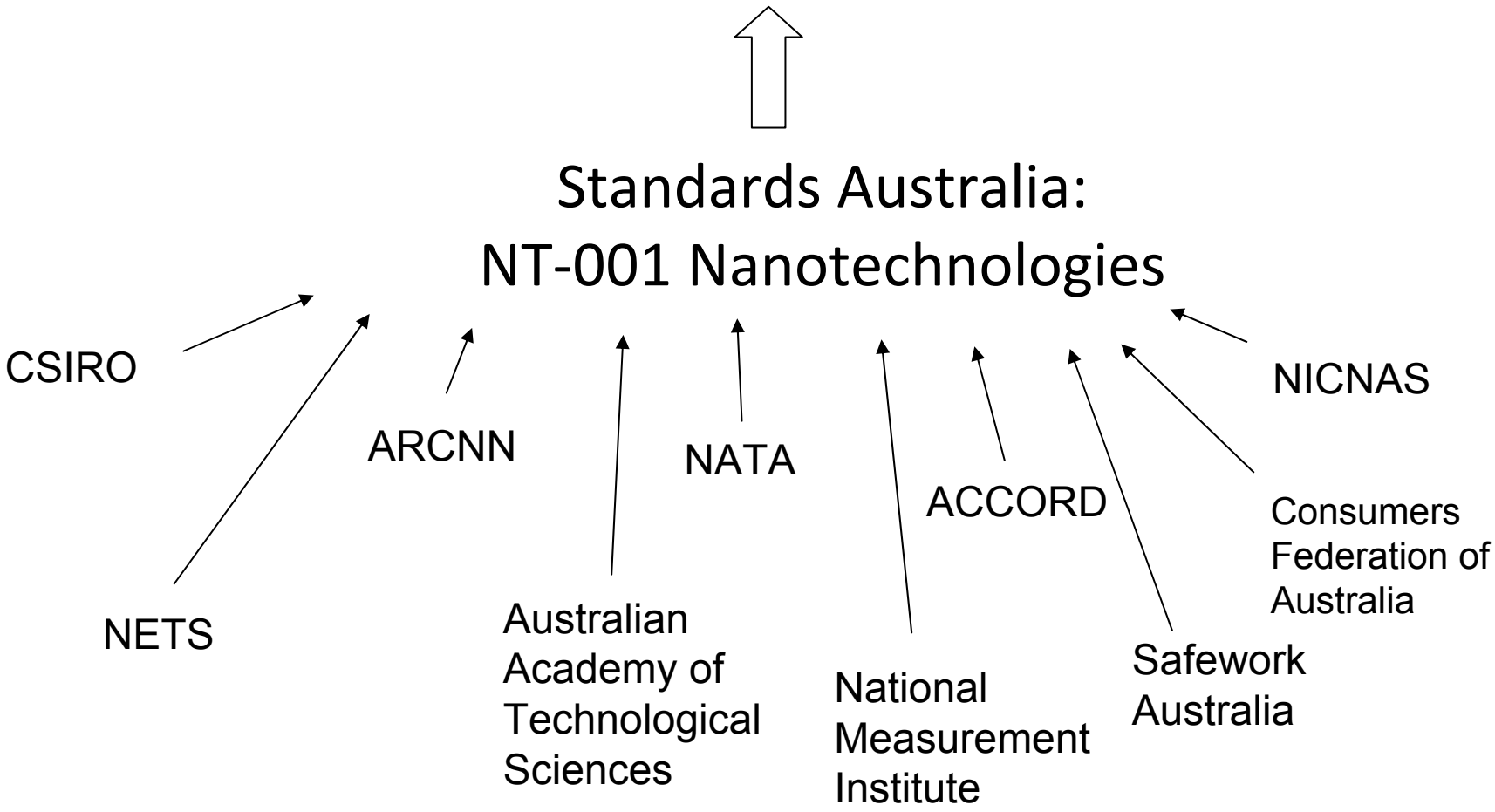


Standards Australia NT-001

- NT-001 established in March 2006
- Mirror committee to TC229
- Has representation from a wide range of Australian nanotechnology

Australian Government
National Measurement Institute

TC229 Nanotechnologies

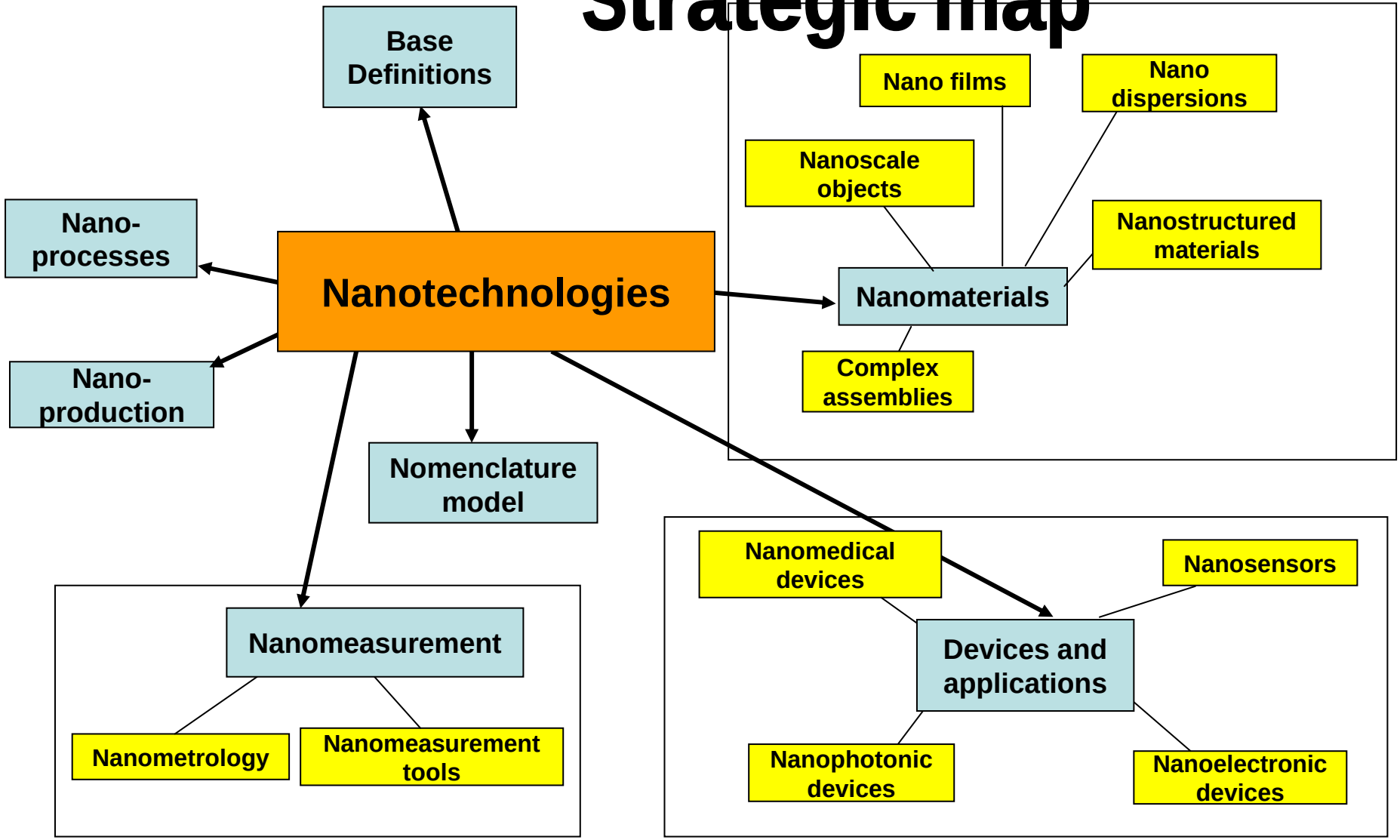


TC 229 – Structure/working areas

Terminology and Nomenclature (JWG 1)
"what you call it" - Convened by Canada

Australian Government
National Measurement Institute

ISO/TC 229 JWG1: Strategic map



Recent important ISO definitions

Nanoscale

The size range from approximately 1 nm to 100 nm

- *NOTE 1 Properties that are not extrapolations from a larger size will typically, but not exclusively, be exhibited in this size range. For such properties the size limits are considered approximate.*

- *NOTE 2 The lower limit in this definition (approximately 1 nm) is introduced to avoid single and small groups of atoms from being designated as nano-objects or elements of nanostructures, which might be implied by the absence of a lower limit.*

Recent important ISO definitions

Nanoparticle

A nano-object with all three external dimensions at the nanoscale

Note: If the lengths of the longest and the shortest axes of the nano-object differ significantly, the terms nanorod or nanoplate should be considered. "Significantly" is considered to mean more than three.

Recent important ISO definitions

Nanotechnology

The application of scientific knowledge to manipulate and control matter in the nanoscale to make use of size- and structure-dependent properties and phenomena distinct from those associated with individual atoms or molecules or with bulk materials.

- *NOTE: manipulate and control includes material synthesis*

Recent important ISO definitions

Nanomaterial

Material with any external dimension in the nanoscale or having internal structure or surface structure in the nanoscale

NOTE: This generic term is inclusive of nano-object and nanostructured material

Engineered Nanomaterial

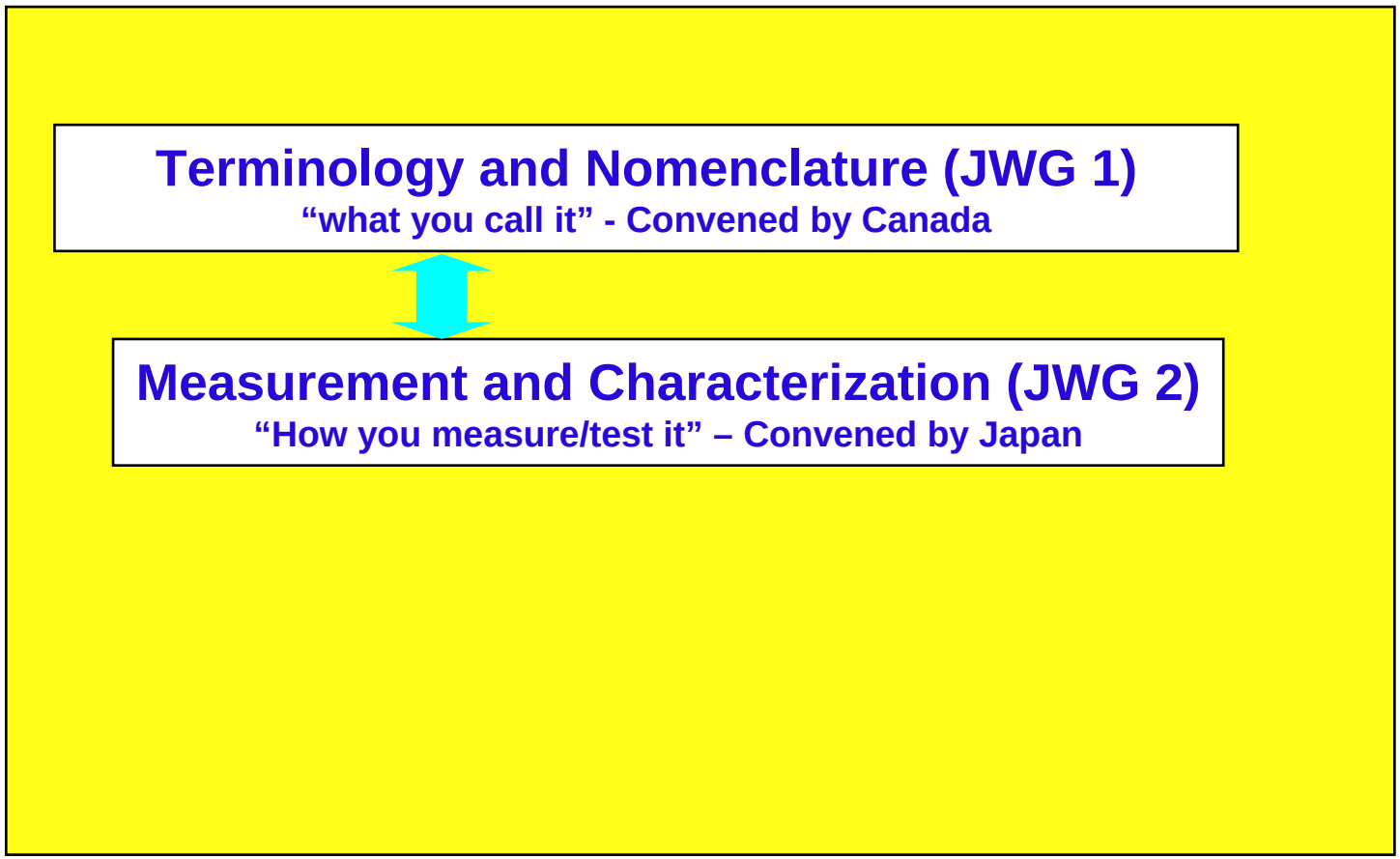
Nanomaterial designed for specific purpose or function

Manufactured Nanomaterial

Nanomaterial intentionally produced for commercial purpose to have specific properties or specific composition

Australian Government
National Measurement Institute

TC 229 – Structure/working areas



Australian Government
National Measurement Institute

ISO/TC 229 JWG2: Outline Roadmap

2005 2010 2015

Carbon Nano-Materials

Basic Character set
Purity Geometrical property
Morphology Dispersability Tube type

Advanced Character set
Electrical, Magnetic, Mechanical , Optical properties

Manufactured nanoparticles

Basic Character set
Purity Composition, Geometrical property, Sampling method.

Advanced Character set
Elemental structure, Chemical functionality,
Electrical, Magnetic, Mechanical , Optical properties

Coatings/ Nanostructured materials

Basic Character set
Geometrical property, Composition, Density

Advanced Character set
Electrical, Magnetic, Mechanical , Optical properties

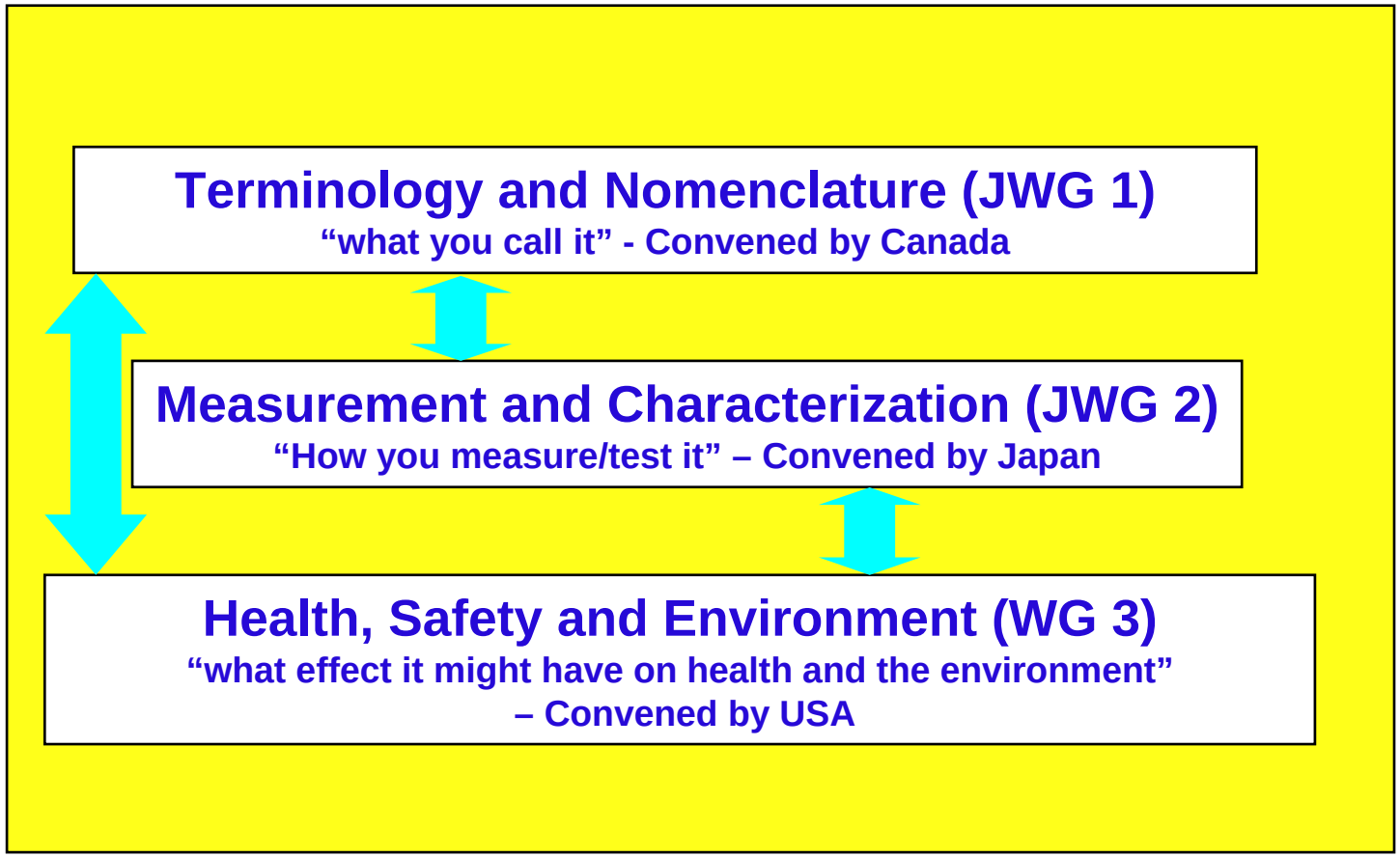
Basic Metrology

Length, Depth, Force, Traceability, Definition of Measurand, Uncertainty

Interoperability

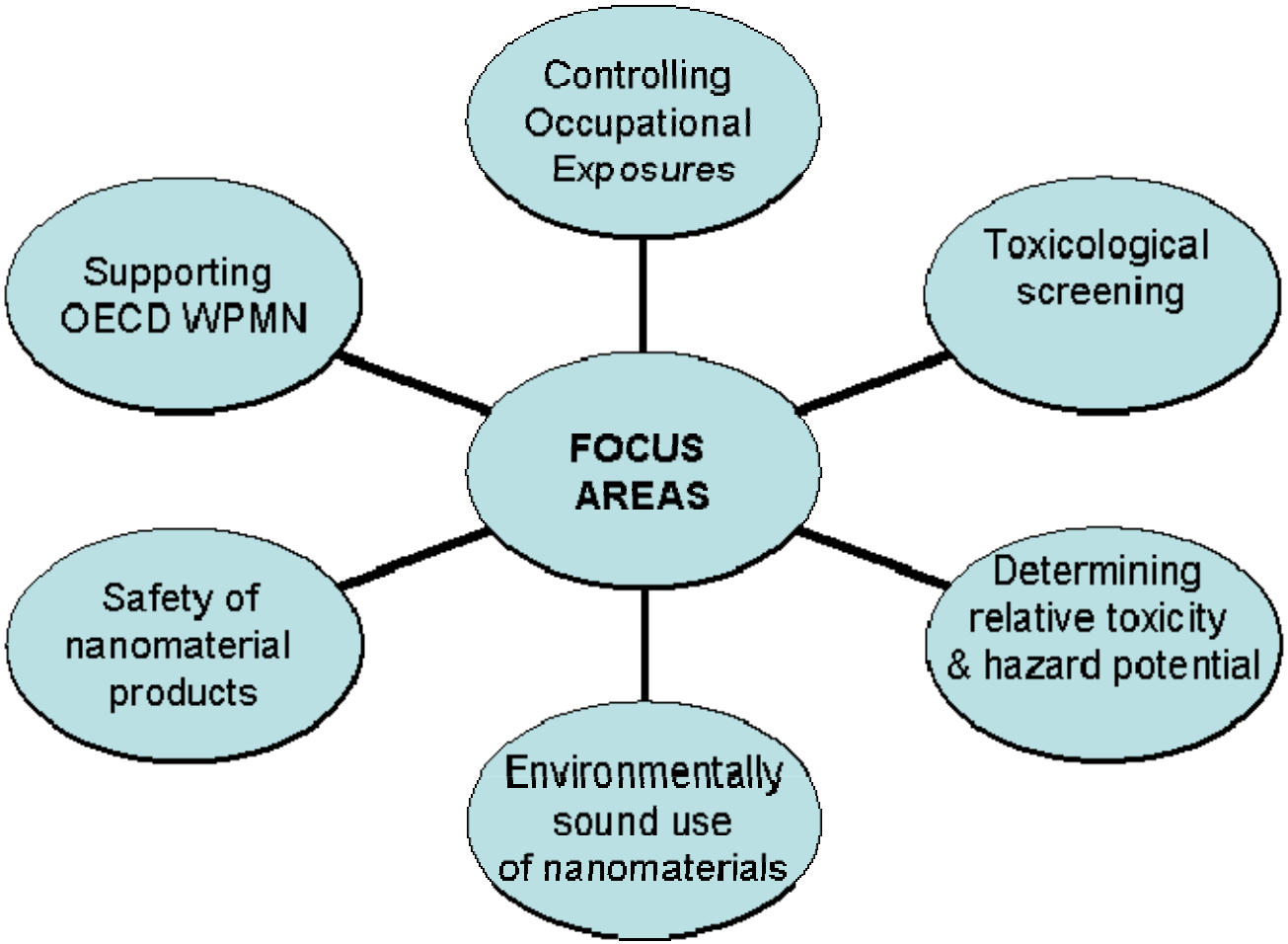
Support for WG3 activities

TC 229 – Structure/working areas



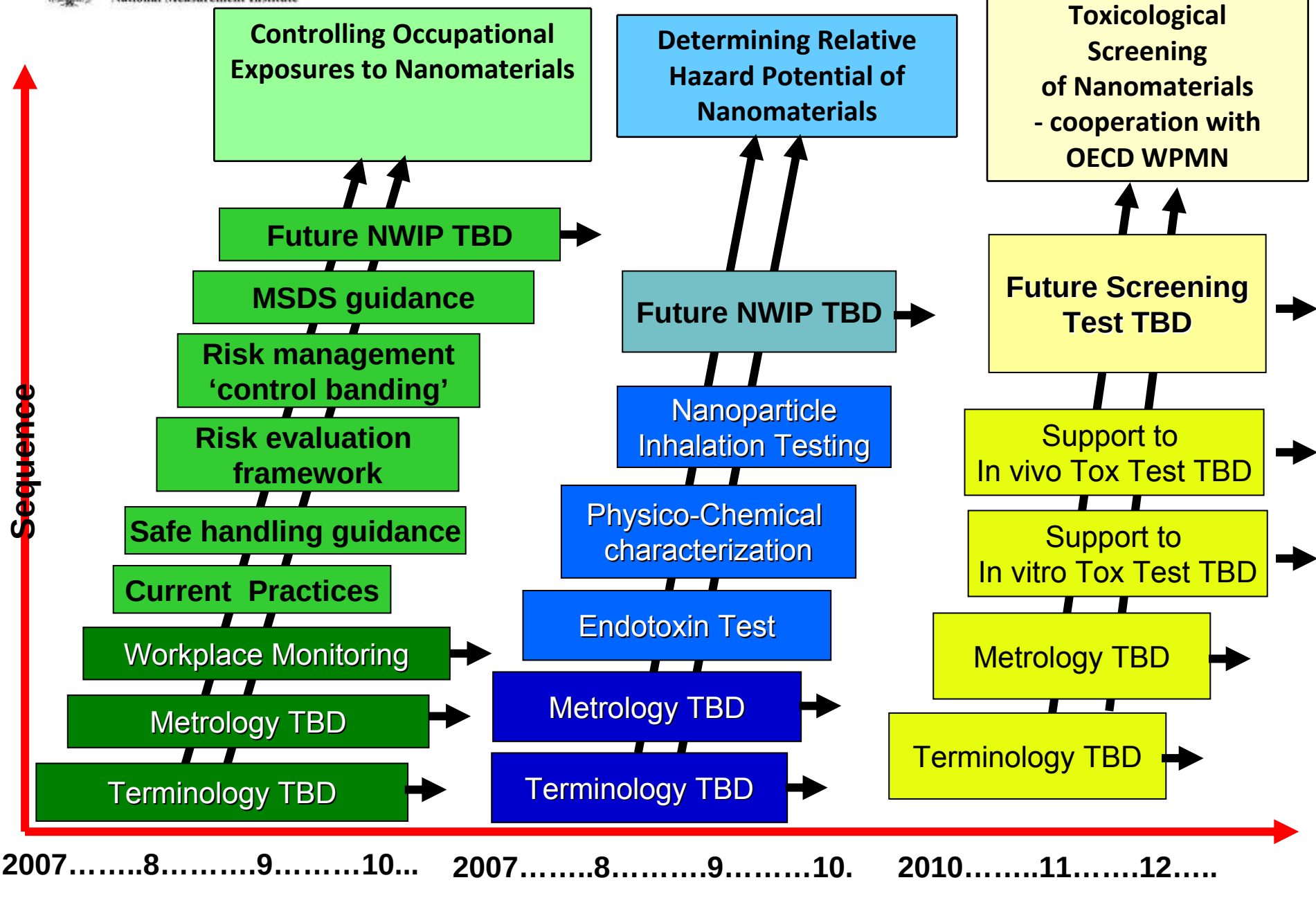
Australian Government
National Measurement Institute

WG3 Focus Areas



ISO/TC 229 WG3 : Strategic Roadmap

Australian Government
National Measurement Institute



Australian Government
National Measurement Institute

TC 229 Work programme – WG3

Controlling Occupational Exposures to Nanomaterials

- *ISO/TR 12885 - Safe Practices in Occupational Settings Relevant to Nanotechnologies (Published)*
- *TR Nanomaterial risk evaluation framework*
- *TS Guidance on safe handling and disposal of manufactured nanomaterials*
- *TS Guidelines for occupational risk management of nanomaterials based on "control banding“*
- *TR Preparation of Material Safety Data Sheet (MSDS) for nanomaterials*

Australian Government
National Measurement Institute

WG3

Determining Relative Hazard Potential of Nanomaterials

- *TR: Guidance on physico-chemical characterization of nanomaterials for toxicology testing.*
- *IS: Endotoxin test on nanomaterial samples for in vitro systems*
- *IS: Generation of Metal Nanoparticles for inhalation toxicity testing*
- *IS: Characterization of nanoparticles for inhalation toxicity testing*

Australian Government
National Measurement Institute

WG3

Toxicological Screening of Nanomaterials
- cooperation with OECD WPMN

- *TS Surface characterization of gold nanoparticles for nanomaterial specific toxicity screening - FT-IR method*

New Work Item Proposals:

- *TR Guidance on toxicological screening methods for manufactured nanomaterials*
- *TR Guidance on sample preparation methods and dosimetry considerations for manufactured nanomaterials (for toxicology screening)*

Other projects under development

- ***Joint developments with CEN (CEN lead):***
  - *Guidance on labelling of manufactured nano-objects and products containing manufactured nano-objects*

Published ISO Standards

- **ISO/TR 11360:2010**
  Nanotechnologies -- Methodology for the classification and categorization of nanomaterials
- **ISO/TR 12885:2008**
  Nanotechnologies -- Health and safety practices in occupational settings relevant to nanotechnologies
- **ISO/TS 27687:2008**
  Nanotechnologies -- Terminology and definitions for nano-objects -- Nanoparticle, nanofibre and nanoplate
- **ISO 29701:2010**
  Nanotechnologies -- Endotoxin test on nanomaterial samples for in vitro systems -- Limulus amebocyte lysate (LAL) test
- **ISO/TS 80004-3:2010**
  Nanotechnologies -- Vocabulary -- Part 3: Carbon nano-objects

Australian Government
National Measurement Institute

Thank you for your attention

John Miles
Nanometrology
National Measurement Institute
Bradfield Road, West Lindfield NSW 2070, Australia

Email: john.miles@measurement.gov.au

measurement.gov.au