Nanotechnology – A Primer for Health and Safety Specialists

Troy Winters
Senior Health & Safety Officer
Canadian Union of Public Employees
Vice Chair, CSA Technical Committee OHS - Nanotechnology

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What is Nanotechnology?

• Nanoscience and nanotechnology are the study and application of extremely small things.
• Application of nanotechnology involve the ability to see and to control individual atoms and molecules.
• Nanomaterials are being used across all the other science fields, such as chemistry, biology, physics, materials science, and engineering.
Emerging Technologies...

- Agriculture Biomedical
- Displays
- Electronics
- Energy
- Manufacturing
- IT & Communications
- Material Science
- Military
- Neuroscience
- Robotics
- Transportation
- Others...

Brief History...

1936 - Invention of the field emission microscope
The field emission microscope is a type of electron microscope that can achieve magnification up to x1,000,000.

1951 - Invention of the field ion microscope
The field ion microscope is a development of the field emission microscope enabling magnification up to approximately x10,000,000, representing resolution on an atomic scale.
Brief History...

1959 - “There’s Plenty of Room at the Bottom”, Richard Feynman
Feynman’s lecture at CalTech is the first to mention of some of the distinguishing concepts in nanotechnology (but predates the use of that term). He described a process by which the ability to manipulate individual atoms and molecules might be developed.

1974 Term nanotechnology is coined
Professor Norio Taniguchi coined the term “nano-technology” as “the processing of, separation, consolidation, and deformation of materials by one atom or by one molecule”.

Brief History...

1981 - Scanning Tunneling Microscope (STM) invented
An STM is a microscope that uses a tiny stylus to “feel” the surface of objects too small to be viewed by conventional microscopes or even powerful electron microscopes

1985- Discovery of buckminsterfullerene – “buckyballs”
Discovery of new forms of the element carbon - called fullerenes - in which the atoms are arranged in closed shells.
Brief History...

1986 - The Atomic Force Microscope (AFM) Invented
The AFM not only images the surface in atomic resolution but also measures infinitesimal forces at nano-newton scale.

1988 - Nanoscale materials in personal care products (Australia)
First use of microfine titanium dioxide in a cosmetically acceptable sunscreen.

1991 - Carbon nanotube discovered

2002 - National Institute of Nanotechnology founded
NINT on the University of Alberta campus - a partnership between the National Research Council, the University and the Governments of Canada and Alberta.

2007 - Environment Canada and Health Canada jointly issue a “Proposed Regulatory Framework for Nanomaterials under the Canadian Environmental Protection Act, 1999”
This proposed framework seeks to address nanomaterials in a manner which ensures the responsible introduction of nanomaterials to the Canadian market through a program which scientifically assesses and appropriately manages any potential risks.

In this document, Health Canada states its working definition of nanomaterials and lays out a strategy for coordinating its own internal efforts to collect and aggregate information on regulated nanomaterials.
How Small is Small?

The Nanoscale...

<table>
<thead>
<tr>
<th>Unit</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metre (m)</td>
<td>1 m</td>
</tr>
<tr>
<td>Centimetre (cm)</td>
<td>0.01 m</td>
</tr>
<tr>
<td>Millimetre (mm)</td>
<td>0.001 m</td>
</tr>
<tr>
<td>Micrometre (µm)</td>
<td>0.000001 m</td>
</tr>
<tr>
<td>Nanometre (nm)</td>
<td>0.000000001 m</td>
</tr>
</tbody>
</table>
That’s pretty small...

- Carbon nanotube next to a human hair is about the equivalent as putting a human hair next to a 4-lane highway.

50,000 x

Comparing other ‘small’ things

<table>
<thead>
<tr>
<th>Electron Microscope</th>
<th>Optical Microscope</th>
<th>Dotted Eye</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>Glucose</td>
<td>Antibody</td>
</tr>
<tr>
<td>Antibody</td>
<td>Virus</td>
<td>Bacteria</td>
</tr>
<tr>
<td>Virus</td>
<td>Cancer cell</td>
<td>A period</td>
</tr>
<tr>
<td>Bacteria</td>
<td>Baseball</td>
<td></td>
</tr>
</tbody>
</table>

Size (nm)
Definitions

- **Nanotechnology** – the science, engineering, and technology conducted at the nanoscale, which is about 1 to 100 nanometers.
- **Nanoscale** - size range from approximately 1 nm to 100 nm
- **Nanostructured material** - material having internal nanostructure or surface nanostructure
- **Nanomaterial** - material with any external dimension in the nanoscale or having internal structure or surface structure in the nanoscale

Definitions

- **Nano-object** - material with one, two or three external dimensions in the nanoscale
  - **Nanoparticles** - nano-object with all three external dimensions in the nanoscale
  - **Nanofibre** - nano-object with two similar external dimensions in the nanoscale and the third dimension significantly larger
  - **Nanoplate** - nano-object with one external dimension in the nanoscale and the two other external dimensions significantly larger
Definitions

• **Nanofibres** are further divided into:
  – **nanotubes** (hollow nanofibre)
  – **nanorods** (solid nanofibre)
  – **nanowire** (electrically conducting or semiconducting nanofibre)

• **Nanoproduct** – a product that contains or has been enhanced by the application of nanomaterials

Health Canada's Working Definition of Nanomaterial

• Health Canada considers any manufactured substance or product and any component material, ingredient, device, or structure to be nanomaterial if:
  – It is at or within the nanoscale in at least one external dimension, or has internal or surface structure at the nanoscale, or;
  – It is smaller or larger than the nanoscale in all dimensions and exhibits one or more nanoscale properties/phenomena.

Health Canada's Working Definition of Nanomaterial

For the purposes of this definition:
• The term "nanoscale" means 1 to 100 nanometres, inclusive;
• The term "nanoscale properties/phenomena" means properties which are attributable to size and their effects; these properties are distinguishable from the chemical or physical properties of individual atoms, individual molecules and bulk material; and,
• The term "manufactured" includes engineering processes and the control of matter.


Nano vs Macro

Macro or ‘Bulk’  Nano
Natural Nanomaterials

- Carbon Black and smoke
- Volcanic ash
- Sea spray

Man Made Nanomaterials

Incident versus Engineered
The good the bad, the ugly...

Nanotechnology in Today’s World

• The next industrial revolution is already here...
• By the end of 2011 the total government funding for nanotechnology research worldwide will be $65 billion, rising to $100 billion by 2014. (2011 estimate, Cientifica)*
• All told, nanotechnologies are estimated to have impacted $251 billion across the global economy in 2009. This is estimated to grow to $2.4 trillion by 2015 (Lux Research, 2010)
Nanomanufacturing

- Top-down fabrication reduces large pieces of materials all the way down to the nanoscale
  - Example – the Creation of Silicon based technology

- The bottom-up approach to nanomanufacturing creates products by building them up from atomic- and molecular-scale components
  - Example – condensation of a nanomaterial to create a nano-thin film

Where do we find nanomaterials

- General Products
  - Eddie Bauer - is currently using embedded nanoparticles to create stain-repellent khakis
  - Intel Processor and Memory
  - Lubricants (motor oil)
  - Wetsuits (silicon coating)
  - Cleaners
    - Concrete Cleaner & Degreaser
    - Mold & Mildew Stain Remover
    - Siding & All Purpose Cleaner
    - Anti-Fog application on glass
In the absence of mandatory product labeling, it is difficult to estimate the number of cosmetics, sunscreens and personal care products containing nanoparticles that are now commercially available.

But...

Personal Use Products

- Deodorant
- Soap
- Toothpaste
- Shampoo
- Hair conditioner
- Sunscreen
- Anti-wrinkle cream
- Moisturizer
- Foundation
- Face powder
- Lipstick
- Blush
- Eye shadow
- Nail polish
- Perfume
- After-shave lotion
Food and Water

- More efficient food production, seed treatment
- More hygienic food processing (surface treatments)
- Preservation of food (packaging)
- Smart Labels
- Water treatment improvements
- Pesticides, soil treatment etc.

DuPont Hybrid Membrane Technology

Air filtration
- air/oil coalescing
- HVAC pleatable
- dust and product collection

Liquid filtration
- Microfiltration

Energy storage
- EDLC/battery separator
Carbon Nanotubes

- Tennis and badminton racquets
- Car bodies
- Silicon coated carbon nanotubes in anodes for batteries
- Antibody-carrying nanotube for cancer treatment
- Pores in membranes to run reverse osmosis desalination plants
- Integrated circuits built with nanotube transistors.
- Nanotubes used to direct electrons to illuminate pixels, resulting in a lightweight, millimeter thick display panel.
- Transparent, flexible electronic devices using arrays of nanotubes

Nanogold

- First used in stain glass hundreds of years ago.
- Photodynamic Therapy
- Health Diagnostics
- Sensory probes
- Drug delivery in biological and medical applications
- Electronics
- Catalysis
Nanosilver

**Very potent antimicrobial**

- NanoSilver Anti-odor Healthy Socks and other sports wear
- Nanocide™ Antimicrobial gel
- Sprays, Soaps, Wipes
- Toothpastes
- Baby bibs and Blankets
- Silver Nano Health System™ – a series of products including washing machines, refrigerators, air conditioners, air purifiers and vacuum cleaners introduced by Samsung in 2003 that have ionic silver nanoparticles coating

Benny the Bear Plush Toy

- From the manufacture:

  “With the additive of Silver Nanoparticles, our product has been clinically proven to fight against harmful bacteria, molds and mites.”
Full Inventory

Consumer Products Inventory

“While not comprehensive, this inventory gives the public the best available look at the 1,600+ manufacturer-identified nanotechnology-based consumer products introduced to the market.”

http://www.nanotechproject.org/cpi/

The Bad...

• Nanotechnology has the promise of a new era, but there are health concerns for workers and consumers.

• Are they all bad?

• Of course not, but we must be careful...
Nanotubes

- Asbestos was a consumer product that is now a scourge on workers across the country.
- Nothing like that would happen again... right?
- Research shows that agglomerates of Carbon Nanotubes resemble asbestos fibres both for their appearance and their toxicity (IRSST, 2010).

Nanosilver

- Exposure to soluble silver compounds may induce toxic effects, including liver and kidney damage, irritation of the eyes, skin, respiratory, and intestinal tract, and changes in hematological parameters (Drake and Hazelwood, 2005).
- Both in vitro and in vivo studies have demonstrated toxic effects of NanoSilver (Foldbjerg et al., 2011, 2009; Kawata et al., 2010)
- Studies have reported that Nanosilver is genotoxic to plant cells (Patlolla, 2012)
- Considerable amounts of silver could enter sewage plants and seriously trouble the biological purification process of waste water, and negatively impact the greater ecosystem.
General Ugliness... Determine the Risks

- So what are the other concerns for nanotechnology, specifically in the workplace.
- First and most important?
- **Do we even know it is there??**

Health Risks of Nanomaterials

To quantifying the human health risks, we need to answers many questions, including:
- How can the material enter the body?
- Where does it go and how does it change once it gets there?
- What aspects of the material end up causing harm?
- How much material is needed for serious harm to occur?
- How should the toxicity of the material be assessed?
- How will people end up being exposed to the material?
- How should exposure be measured? and
- Can exposures be adequately controlled?
How can the material enter the body?

• There are three main routes by which workers can be exposed to nanomaterials:
  – inhalation;
  – ingestion;
  – skin contact

How can the material enter the body?

**Ingestion**

• In the workplace, nanomaterials in particulate form could be ingested by
  – swallowing the mucous that traps and clears particles deposited in the airways
  – ingestion of contaminated food or water;
  – oral contact with contaminated surfaces or hands.
How can the material enter the body?

**Skin contact**
- Skin might be exposed to nanomaterials during their manufacture or use or by contact with contaminated surfaces. It is still not fully known to what extent nanoparticles in general are able to penetrate the intact skin and cause adverse effects.
- Exposure through the parenteral route can occur in the workplace primarily due to accidents such as needle-stick injuries. Workers who could be at risk from needle-stick injuries will mostly include, but are not limited to, those in workplaces in the health care sector.
- Once the worker’s skin is broken, punctured, or scratched nanomaterials can enter the bloodstream and hence can translocate throughout the body.

**Inhalation probably most common...**

**Inhalation and Deposition**

**Diffusion**
- The smaller the particle size, the more vigorous the movement is.
- Diffusion is the most important mechanism for deposition in the small airways and alveoli (as opposed to Interception, Impaction, Sedimentation).
- Very fine particles 1nm or smaller are also trapped in the upper airway.
Where does it go and how does it change once it gets there?

• Once in the blood stream, nanomaterials can be transported around the body and are taken up by organs and tissues including the brain, heart, liver, kidneys, spleen, bone marrow and nervous system (Oberdörster, 2005).

• Several studies showed that inhaled insoluble or low solubility nanoparticles can translocated to mammel (monkey and mice) brain by the olfactory nerve. (De Lorenzo 1970, Oberdorster et al. 2004, and Wang et al. 2005)

Where does it go and how does it change once it gets there?

• Nanoparticles may be transported through membranes to within cells and be taken up by cell mitochondria and the cell nucleus. This can cause major structural damage to mitochondria, cause DNA mutation and even result in cell death (Li 2003, Savic 2003, Geiser 2005).

• One study showed the possibility that gold particles injected into gestating female rates are transferred to the fetus (Wootliff, 2004).
What aspects of the material end up causing harm?

Novel Properties at the Nanoscale

- When the particle size is decreased to the nanoscale range, fundamental physical and chemical properties of a substance can change, often resulting in completely new and different than before physical/chemical properties.
- For example
  - Bulk silver does not react much, but nanosilver becomes a potent antimicrobial
  - $\text{TO}_2$ particles lose their white colour and become colourless at decreasing size ranges below 50 nm.

What aspects of the material end up causing harm?

- **Surface- area** presented to target organ (dose)
- When compared to the same mass of material in bulk form, nanoscale materials have a relatively larger surface area
What aspects of the material end up causing harm?

Surface-area
- American Silver Eagle coin. This silver dollar contains 31 grams of coin silver and has a total surface area of approximately 3000 square millimeters.
- If the same amount of coin silver were divided into tiny particles – say 10 nanometer in diameter – the total surface area of those particles would be 7000 square meters (which is equal to the size of a soccer field)
- That’s 2.3 million times more surface area

Quantum Effects
- The so-called *quantum size effect* describes the physics of electron properties in solids with great reductions in particle size.
- Quantum effects can begin to dominate the behavior of matter at the nanoscale - particularly at the lower end (single digit and low tens of nanometers) - affecting the optical, electrical and magnetic behavior of materials.
What aspects of the material end up causing harm?

**Coatings**

- Often nanoparticle surfaces are intentionally modified with coatings or functionalized in order to prevent agglomeration of particles and to achieve desired properties (i.e. pharmacological activity).
- Such modifications, as well as the contamination of particle surfaces with impurities, can lead to changes in biological responses.

http://www.cdc.gov/niosh/topics/nanotech/

What aspects of the material end up causing harm?

- Studies have indicated that low solubility nanoparticles are more toxic than larger particles on a mass for mass basis.
How toxicity of the material can be assessed?

**Main Parameters for Proper Characterization of Nanoparticles for Toxicological Studies**

Parameters
- Mass, concentration
- Solubility
- Specific surface
- Number of particles
- Hydrophilicity/hydrophobicity
- Shape, porosity
- Biopersistence
- Crystalline structure
- Lung deposition site
- Age of the particles

How toxicity of the material can be assessed?

- Surface properties (charge, reactivity, chemical composition, functional groups, potential to generate free radicals, presence of metals, surface covering, etc.)
- Chemical composition (purities and impurities)
- Degree of agglomeration/aggregation
- Size and grain-size distribution
- Producer, process and source of material used
How will people end up being exposed?

Common Occupational Nanomaterials

- **Construction** – in products improving wear-resistance, rigidity, but also used in pigments; windows, more efficient insulation materials, cutting tools that don’t get dull as easy

- **Health care** – in new drugs and active agents, drug-delivery systems, oral vaccines, tissue engineering and production of biocompatible materials

How will people end up being exposed?

- **Energy conversion and use** – increasing efficiency of energy conversion and low-wastage storage of energy, including new generation photovoltaic cells, more economical lighting, and compact combustion cells

- **Automobile (and aerospace) industry** – reinforced and stronger materials, sensors optimising engine use, fuel additives, scratch-resistant and dirt-repellent coatings
How will people end up being exposed?

- **Chemical industry** – catalysts, adhesiveless bonding techniques, multi-functional and more efficient ceramics, products used for surface functionalisation and finishing, such as pigments, corrosion-inhibitors, self-cleaning and anti-static surfaces.

- **Electronics and communication** – optical/optoelectronic components including lasers, high-density memories, pocket electronic libraries, ultra fast compact computers

How should exposure be measured

- Very technical.
- See related ISO standards
Can exposures be adequately controlled?

• Absolutely!

• Risk assessment is an essential preliminary step to determine what control level must be implemented

• However, in the absence of adequate knowledge of the toxicity and behaviour of airborne nanoparticles, and the absence of specific standards or regulations, strict control measures should be put in place to minimize, as much as possible, the risk to workers of pulmonary and cutaneous absorption.

Control

• Elimination
• Substitution
• Engineering techniques
• Administrative means
• Personal protective means
Controls – not really that exotic...

• While the means of control are relatively well known for ultrafine particles such as welding fumes, control of NP exposure faces a special challenge, namely that the clientele targeted by this control is not necessarily familiar with UFP control technologies.
• Control Banding – will talk about shortly

So what does the law say??
Regulations

- Regulation – a document specifying mandatory rules created by an authority through the powers established under legislation
- Government/jurisdiction imposed requirement, which specifies product, process or service characteristics with which compliance is mandatory in an applicable jurisdiction
- Nothing specific on nanomaterials in OHS Laws

Regulatory Framework in Canada

- Canadian Environmental Protection Act (CEPA, 1999) – New Substances Notification Regulations
- Canada Consumer Product Safety Act (CCPSA) formerly Hazardous Products Act (HPA) – June 20, 2011
  - Controlled Products Regulations
  - Ingredients Disclosure List
  - Consumer Chemicals and Containers Regulations
Regulatory Framework in Canada

- Food & Drugs Act (F&DA)
  - Food & Drugs Regulations
  - Medical Devices Regulations
  - Cosmetics Regulations
  - Natural Health Products Regulations
  - Safety of Human Cells, Tissues and Organs for Transplantation Regulations
- Pest Control Products Act
  - Pest Control Products Regulations

Regulatory Framework in Canada

- *New Substances Notification Regulations (NSNR) of CEPA 1999*
- Jointly administered by Environment Canada and Health Canada
- Conducts pre-market human health and environmental risk assessments of chemicals and polymers imported to or manufactured in Canada
- Uses traditional risk assessment methodology
  - Examines potential exposure and hazards to humans and the environment to determine potential risk
- Can enact measures to obtain more information or limit use of substances.
New Substances Program

- The nanoscale form of a substance on the DSL is considered a "new substance" if it has unique structures or molecular arrangements.
- In addition, nanomaterials which are intended to be manufactured in or imported into Canada that are not listed on the DSL are also considered "new."
- As all new substances, new nanomaterials are subject to notification under the New Substances Notification Regulations (NSNR) (Chemicals and Polymers).

Regulations in Canada – more information

- Refer to Canada’s Nano Portal at: http://nanoportal.gc.ca for more information
- Canada and the U.S. have recently finalized a Work Plan for Nanotechnology under the Canada-United States Regulatory Cooperation Council (RCC)
- Canada’s government participates in OECD’s Working Party for Nanotechnology (WPN) and Working Party for Manufactured Nanomaterials (WPMN), to promote international co-operation with other nations on the human health and environmental safety of manufactured nanomaterials
Standards

A standard, defined as:

**standard** – a document, established by consensus and approved by a recognized body that provides for common and repeated use, rules, guidelines or characteristics for activities or their results, aimed at achievement of the optimum degree of order in a given context

- Standards should be based on the consolidated results of science, technology and experience, aimed at the promotion of optimum community benefits
ISO/TC229, Standards for Nanotechnologies

• Standards development in nanotechnologies is active concurrently with worldwide research and commercialization, for economic and social benefits through technical innovation

• Standards help business reduce barriers to trade and assist to ensure safety in materials, components, products and systems
Standards for Nanotechnologies

- ISO and IEC, the two major, globally-relevant standards development organizations that have been developing standards for safe and responsible use of nanotechnologies since 2005.
- The Technical Committees (TCs) are ISO/TC229 and IEC/TC113 with 47 member countries, including Canada.

Standards for Nanotechnologies

- ISO/TC229 has the following objectives:
  - Support the sustainable and responsible development of nanotechnologies
  - Facilitate global trade in nanotechnology-enabled products and systems
  - Improve quality, safety, security, consumer and environmental protection, together with the rational use of natural resources
  - Promote good practice in production, use & disposal of nanomaterials / nano-enabled products.
Standards for Nanotechnologies

- At the TC level, activities are subdivided into working groups with a country designated to convene each WG’s activities.
- End deliverables include technical reports, technical specifications, and international standards.
(Joint) Working Groups

ISO/TC229, Nanotechnologies, and IEC/TC113, Nanotechnology standardization for electrical and electronic products and systems, the working groups are:

- JWG1: Terminology and Nomenclature - ISO/IEC (19)
- JWG2: Measurement and Characterization - ISO/IEC (5)
- WG3: Health, Safety and Environment – ISO (19)
- WG3 of IEC/TC113: Performance Assessment – IEC
- WG7 of IEC/TC113: Reliability – IEC

Canada

- Canada, as a member ISO/IEC country, participates through a mirror committee of volunteers (referred to as the Nano SMC) which is a SCC Mirror Committee (SMC) for both ISO/TC229 and IEC/TC113.
- The committee is facilitated by Standards Council of Canada (SCC) and CSA Group (CSA).
- International standards in various forms are developed with input from volunteer Canada experts.
Canada

- When published these international consensus documents may be nationally-reviewed and adopted as National Standards of Canada.
- They may be applied in Canada for voluntary use or for reference in regulations following a SCC-accredited process facilitated by CSA Group.
- It includes Public Review open to comments from any source, with review and ballot by a national Technical Committee with interest area balance.

Canadian Standards

- **CSA Z12885-12** Nanotechnologies - Health and safety practices in occupational settings relevant to nanotechnologies
- **CAN/CSA-ISO/TR 13121:13** Nanotechnologies - Nanomaterial risk evaluation
Canadian Standards

- ISO/TR 13329:2012 Nanotechnologies – Safety Data Sheet (SDS) preparation for manufactured nanomaterials (edited)

CSA Z12885-12

- CSA Z12885-12 is based on ISO/TR 12885:2008 – the first WG3 OHS standard from ISO/TC229
- Significantly different with CAN/CSA Z1000, Occupational Health and Safety (OHS) Management framework
- Added Canada-generated content, related to OHS nano-research in Canada
- CSA Technical Committee has balanced membership from government, industry, labour, and users in Canada
CAN/CSA-ISO/TR 13121:13

The contents include:
- Nanomaterials' properties, hazards and exposure
- Evaluating and managing risks
- Deciding, acting, reviewing and adapting
- Informative annexes including:
  - Physical and chemical properties
  - Tiered testing approach
  - Health and environmental hazard data
  - Output worksheet and other reference material

CSA Z13329-15 (SDS)

- Provides guidance on the development of safety data sheets (SDSs) for manufactured nanomaterials (and materials or products that contain manufactured nanomaterials), and provides additional information on safety issues associated with manufactured nanomaterials.
CSA Z12901-15 Control banding

- The concept of control banding or performance-based occupational exposure limits (Figure 5) was developed in the late 1980s by occupational health experts in the pharmaceutical industry.
- This industry uses large numbers of new chemical compounds with few toxicity data.
- The experts reasoned that such compounds could be classified based on their potential toxicity (e.g., structural relationship to chemicals with known toxicity) and by their need for restriction of exposure.

- As the principle of control banding was applied to dangerous chemicals, chemical mixtures, and fumes
- The premise of CB is that the greater the potential for harm, the greater the degree of control needed to manage the situation and make the risk “acceptable.”
CSA Z12901-15 Control banding

• Although there are various approaches, four main control bands have been described for exposure to chemicals by inhalation:
  – Band 1: Use good industrial hygiene practice and general ventilation.
  – Band 2: Use engineering control, typically local exhaust ventilation.
  – Band 3: Enclose the process.
  – Band 4: Seek expert advice.

CSA Z12901-15 Control banding

• As the risk from new nanomaterials is sometimes unknown, the standard, unlike many other models recommends the highest control for unknown chemicals.
Other References

Other References

- Engineered Nanoparticles Current Knowledge about OHS Risks and Prevention Measures, IRSST, 2010