A rigorous protocol for evaluating the effectiveness of gloves against nanoparticles in solution

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Context

• Majority of the studies use engineering nanoparticles (ENP) in aerosol
  Graphite – 30/40 and 80 nm (Golanski et al. 2009)
  TiO$_2$ – 10 nm (Golanski et al. 2009)
  Silver – 10 to 150 nm (Park et al. 2011)

→ Few studies with ENP in solution

• Simulate the occupational use of the gloves
  Repeated mechanical deformations (Dolez et al. 2011)
  Microclimate in the glove (sweat) (Lambers et al. 2006, Vinches et al. 2016)

→ Development of a test setup

• How to measure the real quantity of ENP which passes through the gloves?
  Use the right devices (Vinches et al. submitted)
  Evaluate the losses of ENP (Vinches et al. submitted)

Summarize the different necessary steps to evaluate the effectiveness of disposable protective gloves against ENP in solution
Materials

Nitrile rubber gloves

$ t = 73.2 \pm 3.0 \ \mu\text{m} $

- **NBR-1a**
  - Batch 1 – Box a
  - February 2015

- **NBR-1b**
  - Batch 1 – Box b
  - February 2015

- **NBR-2**
  - Batch 2
  - September 2015

- **NBR-3**
  - Batch 3
  - March 2014

Commercial gold suspension

- **5 nm, PVP, 0.05 mg/mL in MilliQ water**

  - TEM diameter = $5.0 \pm 0.6 \ \text{nm}$
  - Hydrodynamic diameter (DLS) = $9.2 \pm 0.6 \ \text{nm}$
Setup to simulate the hand flexing and the microclimate into the glove (sweat)

- Probe
- Actuator
- Exposure chamber
- Sampling chamber
- Neoprene seal ring
- Butyl rubber seal ring
- Sample
- Nanoparticle suspension
- Physiological solution

30 mm-MD each 10 s during 3 hours
Methodology

Origins in the loss of nanoparticles

- **Sampling chamber** → **LOSS OF GOLD NANOPARTICLES IN THE SAMPLING CHAMBER**
- **Storage bottle** → **LOSS OF GOLD NANOPARTICLES IN THE STORAGE BOTTLE**
- **ICP-MS analysis** → **LOSS OF GOLD NANOPARTICLES DURING ICP-MS ANALYSIS**

**Evaluation of the effectiveness of gloves in **FOUR** steps**

- **1.** Selecting the storage bottles to minimize losses
- **2.** Evaluating the losses throughout the test
- **3.** Performing the mechanical deformations test
- **4.** Analysing sampling solution by ICPMS
Step 1 – Selection of compatible storage bottles

- Preparation of a gold suspension at a nominal concentration of 10 µg/L (concentration expected based on previous work) in physiological solution at pH = 6.
- Storage in bottles of six different chemical compositions.
- ICPMS analysis after 0, 24, 48 and 72 hours.

### Restitution coefficient (%)

<table>
<thead>
<tr>
<th>Material</th>
<th>After 24 hours</th>
<th>After 72 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>75</td>
<td>65</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>70</td>
<td>50</td>
</tr>
<tr>
<td>Teflon</td>
<td>65</td>
<td>50</td>
</tr>
<tr>
<td>Low Density Polyethylene</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>High Density Polyethylene</td>
<td>50</td>
<td>30</td>
</tr>
</tbody>
</table>

**Use of glass bottles as storage bottles for gold nanoparticles in solution**
Step 2 – Evaluation of the loss coefficient for the test

• Preparation of two gold suspensions at a nominal concentration of 10 µg/L and 100 µg/L in physiological solution at pH = 6
• The physiological solution replaced by the 10 or 100 µg/L gold suspensions
• No commercial nanoparticle suspension in the exposure chamber

Loss coefficient (LC) = \frac{\text{Gold concentration after the test}}{\text{Initial gold concentration}}

For low gold concentrations (10 µg/L)
LC = 51.0 ± 0.1 %

For high gold concentrations (100 µg/L)
LC = 41.0 ± 0.1 %
Step 3 – Mechanical deformation (MD) tests

30 mm-MD each 10 s during 3 hours
Step 4: Gold nanoparticle penetration: ICP-MS results

<table>
<thead>
<tr>
<th></th>
<th>M±SD (µg/L) (n=10)</th>
<th>Maximal Concentration (µg/L)</th>
<th>Minimal Concentration (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBR-1a (Feb. 2015)</td>
<td>0.446 ± 0.162</td>
<td>0.782</td>
<td>0.319</td>
</tr>
<tr>
<td>NBR-1b (Feb. 2015)</td>
<td>0.530 ± 0.524</td>
<td>1.802</td>
<td>0.172</td>
</tr>
<tr>
<td>NBR-2 (Sept. 2015)</td>
<td>1.662 ± 2.994</td>
<td>10.028</td>
<td>0.162</td>
</tr>
<tr>
<td>NBR-3 (March 2014)</td>
<td>0.273 ± 0.132</td>
<td>0.477</td>
<td>&lt; LOD</td>
</tr>
</tbody>
</table>

1. Passage of gold nanoparticles through this model of nitrile glove indicating its low effectiveness

2. A 13 fold difference in the maximum for different batches

3. !! The oldest batch of gloves offers the best protection against gold nanoparticles and the newest batch offer the worst protection !!
RIGOROUS METHODOLOGY TO EVALUATE THE EFFECTIVENESS OF PROTECTIVE DISPOSABLE GLOVES AGAINST NANOPARTICLES IN SOLUTION

IDENTIFICATION OF FOUR IMPORTANT STEPS

1- Determine the most suitable storage bottles for the sampling solution
2- Evaluate the loss coefficient of the sampling protocol
3- Perform the permeation test
4- Measure the permeation of ENPs through disposable protective gloves

Clean the different parts of the test setup to minimise contamination.

Limitation of this methodology:
The four steps must be performed for each type of nanoparticles in solution

Effectiveness results:
• Significant concentrations of gold nanoparticles observed in the sampling solution
• Depending on the batch and on the box (variability in the manufacturing process)
• Permeation of ENP due to a loss of integrity of the elastomer (MD and swelling)
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