Consumer exposure to silver (nanoparticles) in consumer products

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The “blue man”

Paul Karason after 15 years of oral intake of colloidal silver
(source: www.telegraph.co.uk)
Silver in consumer products

The Nanotechproject: 313 products (24% of the inventory) use silver nanoparticles

- Medication: alternative medicine → “Blue man”, sporadic
- Medication (treatment of burns): since 50 years, routine treatment
- Textiles: since 10 years, especially functional textiles
- Biocidal sprays for indoor use
- Toothpaste (US, Poland), toothbrush
- Facial cream (e.g. CH)
- Tupperware (US, Korea)
- Toys (US)

www.nanotechproject.org

Silver in consumer products
Inhalation: EU consumer sprays

Household Sprays

Biocides: NanoSys

Personal Care Products

Antiperspirant: Nivea Silver Protect

NanoSpray I: ETH and EMPA, 2008-2010

Foot Spray: e.g. Hansaplast Silver Active Fußspray

NanoSpray II: Sabrina Losert, Andrea Ulrich, EMPA, Start 2011

Shoe sprays
Analysis of spray dispersion

TEM

ICP-MS [ppm]

propellant gas spray

pump spray

<table>
<thead>
<tr>
<th>Component</th>
<th>Ia</th>
<th>IIa</th>
<th>IIIa</th>
<th>IVa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al, C, Cl, Mg, O, Si</td>
<td>C, Cl, F, O, Zn</td>
<td>C, Cl, F, O</td>
<td>Ag, C, O, Si</td>
<td></td>
</tr>
<tr>
<td>6.8±0.7 silver</td>
<td>470±10 zinc</td>
<td>no metals</td>
<td>9.1±0.1 silver</td>
<td></td>
</tr>
</tbody>
</table>

Lorenz et al, 2011, J Nanoparticle Research, 13, 3377-3391
Hagendorfer et al, 2010, J Nanoparticle Research, 12, 2481-2494

Analysis of aerosol

- **Particle shape/size/elemental analysis:**
  
  Transmission electron microscopy (TEM) with EDX

- **Particle size distribution** 10-100 nm (No. of particles per cm$^3$ air):
  
  Scanning mobility particle sizer (SMPS)

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**Diagram:**

- Size distribution
- SMPS
- Electrostatic sampler
- Air-in
- Vent, Vacuum
- HEPA Filter
- Thermo-desorber
- Spraying: 0.2-3.5 g

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Exposure to nanoparticles in sprays

BUT: no silver confirmed in aerosol!!

Deposition of nanoparticles in different regions:
- Nasal region
- Tracheobronchial region
- Alveolar region

ICRP model

BUT: NP/ND if sprayed with propellant gas

## Nanoparticles in US consumer sprays

<table>
<thead>
<tr>
<th>Publication</th>
<th>Quadros &amp; Marr, 2011</th>
<th>Nazarenko et al, 2011</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>design comparable to Hagendorfer et al, 2010</td>
<td>focus on nanoparticles in general, not silver</td>
</tr>
<tr>
<td>Sprays</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Antiodor spray</td>
<td></td>
<td>1. Disinfectant personal care silver spray</td>
</tr>
<tr>
<td>2. Surface disinfectant</td>
<td></td>
<td>2. Nasal spray (water based)</td>
</tr>
<tr>
<td>3. Throat spray</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spray dispersion</td>
<td>1-100nm (size specific conc)</td>
<td>1. 3-65 nm particles</td>
</tr>
<tr>
<td>1. 1.7 ppm</td>
<td>2. 1.8 ppm (mainly Ag+)</td>
<td>2. &lt;3-435 nm particles</td>
</tr>
<tr>
<td>3. 16.5 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag in aerosol</td>
<td>0.24-56 ng silver per spray action</td>
<td>no quantification, only size distribution</td>
</tr>
<tr>
<td>Size of aerosols</td>
<td>1-2.5 µm</td>
<td>particles 13nm - 20µm</td>
</tr>
<tr>
<td>general</td>
<td></td>
<td>nanoparticles also from non-ENP containing products</td>
</tr>
</tbody>
</table>
Ingestion from food contact materials

Target: Commercial tupperware and PE-bags claiming “Nano silver inside”

- Product Analysis with scanning ICP-MS and TEM
- Release experiments with food simulants, analysis with ICP-MS and TEM

<table>
<thead>
<tr>
<th>Tradename</th>
<th>Producer</th>
<th>Bulk Material/Description</th>
<th>Origin</th>
<th>Silver content in µg/g plastic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic Go Green Nano Silver Basic</td>
<td>Kinetic, Pathway Davenport, US</td>
<td>Polypropylene</td>
<td>US</td>
<td>18.7</td>
</tr>
<tr>
<td>Kinetic Go Green Nano Silver Premium</td>
<td>Kinetic, Pathway Davenport, US</td>
<td>Polypropylene</td>
<td>US</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Nanosilber-Frischhaltedosen, Everin®</td>
<td>Newlife Co., Korea</td>
<td>Rubber sealing</td>
<td>Germany</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>FresherLonger™</td>
<td>Sharper Image Corporation, US</td>
<td>Polyethylene</td>
<td>US</td>
<td>37.1</td>
</tr>
</tbody>
</table>
Release from food boxes

Multiple use, after 10 d

MD-ICP-MS: 10-20% Ag as particles

N von Goetz, L Fabricius et al., 2012, submitted
Exposure to Ag from food boxes

Worst case assessment:

30 ng/cm² (worst case new box, acetic acid)

100 ml food in tupperware will cover 140 cm² (1x10x10)

→ worst-case acute exposure to 4.2 µg silver

Comparison to natural sources:
- Ag concentrations in drinking water in the US: 0.1 to 9 µg/L (1969)
- also food contains trace amounts of silver

→ exposure to Ag from these food boxes very low, but might consist of nanoparticles
→ product claim is questionable (under threshold of bactericidal activity)
Dermal exposure from PCP&C

Remederm repair cream: 0.1% Ag

silver lotion

silver antiperspirant

\[ E = w_{\text{Prod}} \cdot a_{\text{Ret}} \cdot f_{\text{Event}} \cdot \frac{q_{\text{Prod}}}{m_{\text{bw}}} \]
Aggregate dermal exposure

Lorenz et al., 2011, “Potential exposure of German consumers to engineered nanoparticles in C&PCP”, Nanotoxicology, 5 (1), 12-29

→ Personal hygiene (medium case)  
  0.5 * 60 kg = 30 µg/day
→ Cremes: e.g with 0.1% Ag in Remederm Repair  
  hand cream + face cream, 3 times a day, both 0.8 g  
  4500 µg/day
Uptake of silver nanoparticles

- **Inhalation:** no data for silver; gold: **1.5% for 40 nm**
  (Sadauskas et al, 2009 Chemistry Central Journal (3) 16)
- **Oral:** not more than **1% (largest for 30 nm)**
  (Bouwmeester et al, 2011 ACSNano (5) 5)
- **Dermal:** less than **0.01%**
  (Larese et al, 2009 Toxicology (255))

**BUT:** potentially size, surface (coating), shape dependent

Project: Gerald Bachler “The total exposure to silver”
Conclusions

- Spray: mind the generation of secondary nanoparticles
- Oral: current use in food contact material not alarming
- Dermal: external exposure comparatively large → uptake crucial

Silver in consumer products further means

- depletion of resources
- destruction of a potent antibiotic (resistance building)
Acknowledgement

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