Nanoparticles in food and non-food
Recent methods and measurements

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RIKILT and nanoparticle analysis

- Method development for the Dutch Food Authority
- Exposure to, and toxicity of nanoparticles
- Participating in EU-projects and proposals; e.g. NanoLyse
Nanoparticles in food and non-food applications

Nanomaterials for Food Applications

- Organic
  - Capsules
  - Agglomerates, polymers and emulsions
- Combined Inorganic & Organic
  - Surface modified Metals and Metalloids
  - Surface modified Clay
- Inorganic
  - Clay
  - Metals and Metalloids
Methods and measurements

- **Hydrodynamic chromatography**
  - Food, Non-food, Tox studies

- **Single particle ICPMS**
  - Food supplements, Tox studies

- **Electron microscopy**
  - Non-food, Shape, Agglomeration, Confirmation
Hydrodynamic chromatography

- Separation based on exclusion from the wall
- Larger particles elute earlier
- No chemical interaction
Hydrodynamic chromatography

- Synthetic amorphous silica (SAS, food additive E551) in powdered food products

<table>
<thead>
<tr>
<th>Product</th>
<th>Total silica content g/kg</th>
<th>Nano-silica content g/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coffee creamer</td>
<td>5.1</td>
<td>1.0</td>
</tr>
<tr>
<td>Roasted vegetable rub</td>
<td>4.9</td>
<td>0.6</td>
</tr>
<tr>
<td>Lasagna sauce</td>
<td>5.4</td>
<td>0.3</td>
</tr>
<tr>
<td>Instant soup</td>
<td>0.6</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Hydrodynamic chromatography

- **In vitro digestion:**
  Simulation of oral, stomach and intestinal digestion based on artificial human digestive juices to assess the changes and presence of digested nanoparticles.
Hydrodynamic chromatography

- Fate of nano-silica following digestion
Hydrodynamic chromatography

- Separation of organic nanoparticles
Single particle ICPMS

- Single particle ICPMS, a screening tool for metal and metaloxide nanoparticles
Single particle ICPMS

- Conventional ICPMS (right) results in a continuous signal since the metal is distributed homogeneously in the sample as ions.

- Single particle ICPMS (left) results in a discontinuous signal since the metal is distributed heterogeneously in the sample as nanoparticles.
Single particle ICPMS

- The size of the particles determines the intensity of the transient signals (peak height)
- The particle concentration determines the frequency of the transient signals (number of peaks min\(^{-1}\))
- Choosing a good dwell time is critical
Size distribution of silver nanoparticles in a suspension at 25 ng/L.

The manufacturer states a particle size of 67 ± 17 nm.
Single particle ICPMS

- Analysis of:
  - “Meso Gold”, a food supplement

- Method:
  - Dilute 500,000 times

- Result:
  - Au, 24 nm, 14 ng/L (7 ppm prior to dilution): manufacturer states ca. 30 nm, 10 ppm
Scanning electron microscopy

- TiO$_2$ particles in a facial cream
Scanning electron microscopy

- TiO$_2$ particles in a facial cream are coated with an organic silicium component, probably PDMS
Single particle ICPMS

- *In vitro* digestion model
  - Silver (Ag) nanoparticles (60 nm) in different concentrations in digestion matrix consisting of proteins, sugars and fats.
  - Samples simply diluted and directly analyzed with single particle ICPMS.
Single particle ICPMS

- *In vitro* digestion model
  - n-Ag added in concentrations of 5, 10 and 25 mg/L
  - Mass concentrations of n-Ag decreases during digestion
  - Particle size of n-Ag increases during digestion
  - Less particles following digestion
Scanning electron microscopy
Exposure study using sp-ICPMS

- Pilot study with rats to examine the potential of AgNPs to cross the intestinal wall
  - Rats orally exposed to <20 nm and 50-60 nm AgNPs for 3 days.
  - Exposure dose 500 mg/kg bw via drinking water and custard
  - Blood and liver samples analysed using sp-ICPMS to determine bioavailability of AgNPs
Exposure study using sp-ICPMS

- Results indicate presence of AgNPs in liver (ca. 2 mg/kg)
Summary

- HDC-ICPMS is a useful technique for the determination of nanoparticles in products and toxicity studies. However, it does requires sample preparation.
- Single particle ICPMS is a fast (screening) method for the determination of nanoparticles. However, it allows only single-element detection and assumptions regarding shape are made.
- Electron microscopy is very useful for confirmation and for solving questions about shape and agglomeration.
- A more generic sample preparation technique is urgently needed.
Questions ?