Laser Vaporizer-AMS for detection of airborne metal nanoparticles

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Introduction

The possibilities with the LV-AMS is more than just detection of soot

• Nanotechnology
  – Determine the amount of impurities on produced particles
  – Determine the relative amount of constituents in alloys and oxidation degree of metaloxides.
  – Get insight of the particle shape and density without TEM analysis

• Nano safety
  – Emission measurements

Gold nanoparticle  GaAs Nanowires
Methods: Metal particle generator setup

- Generation of metal particles was performed with either a High Temperature furnace (HT) or a Spark Discharge generator (SDG)

  - Generated particles: \textbf{Au, Pd, Ag, PdAg, FeO, CuO}
Methods: Particle beam and laser alignment

- Particle beam
  - Ion extraction
    - Tungsten vaporizer
  - Laser vaporization
  - Ammonium nitrate 400 nm
  - Regal black soot (rBC) 350 nm
- Laser vaporization
- Tungsten vaporizer
- Ion extraction
- Particle beam

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Methods: Determination of relative ionization efficiencies

- \[ C_S = \frac{\sum_i I_{s,i}}{\text{RIE}_S \cdot \text{mIE}_{NO_3} \cdot Q} \] [\mu g/m^3] \quad \text{(Onasch et al. 2012)}

- \[ \text{RIE}_S = \frac{\text{mIE}_S}{\text{mIE}_{NO_3}} \]

- The mass specific ionization efficiency (mIE_s, [ions/pg]) was determined by calculating mass/particle and ions/particle.

\[
m_{tot} = N \frac{\pi}{6} \rho_{eff} d_m^3
\]

\[
\rho_{eff} = \frac{d_{va}}{d_m} \rho_0
\]

\[ I_s \quad = \text{AMS signal-strength of species S [Hz]}
\]
\[ \text{RIE}_s \quad = \text{Relative ionization efficiency of species S}
\]
\[ \text{mIE}_{NO_3} \quad = \text{Mass specific ionization efficiency of Nitrate [ions/pg]}
\]
\[ Q \quad = \text{Sampling flow} \quad [1.5 \text{ cm}^3/\text{s}]
\]
\[ N \quad = \text{Total number conc. [cm}^{-3}]\]
Results: Mass specific ionization efficiencies

30 nm ($d_m$) Au particles

- $mIE_{NO3} = 1000$ ions/PG
- $mIE_{Regal\ black} = 155$ ions/PG
- $mIE_{Au} = 18$ ions/PG

Slopes:
- $mIE_{NO3}$: $18.3$
- $mIE_{Regal\ black}$: $14.2$
- $mIE_{Au}$: $18.3$

Picogram/particle vs. ions/particle graph.
Results: Relative ionization efficiencies (RIE)

Isotopes
- Au: 197
- Pd: 102, 104, 105, 106, 108, 110
- Ag: 107, 109
- FeO: 54, 56, 57, 58 (+ 16)
- CuO: Not vaporized/detected

<table>
<thead>
<tr>
<th>Agglomerates</th>
<th>Regal black</th>
<th>Au</th>
<th>Pd</th>
<th>Ag</th>
<th>PdAg</th>
<th>Fe (FeO)</th>
<th>Cu (CuO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mRIE (ions/pg)</td>
<td>155</td>
<td>18</td>
<td>9</td>
<td>31</td>
<td>22</td>
<td>27</td>
<td>Not Vaporized</td>
</tr>
<tr>
<td>RIE (mRIE_s/mRIE_rBC)</td>
<td>1</td>
<td>0.12</td>
<td>0.06</td>
<td>0.20</td>
<td>0.14</td>
<td>0.17</td>
<td>Not Vaporized</td>
</tr>
</tbody>
</table>
Results: Laser intensity vs. signal strength

Complete vaporization!
Results: Emission measurements during maintenance of particle generator setup

A – Background
B – Cleaning HT generator
C – Cleaning SDG generator
D – Cleaning DMA
Conclusions

• The mass specific ionization efficiency for the metal particles are lower compared to soot particles
  – Alignment of laser / particle beam / ion extraction

• Promising tool to investigate important particle characteristics in nanoparticle production
  – Relative amounts in alloys
  – Amounts of impurities
  – Density/Shape of particles

• Useful technique for emission measurements
  – Free nanoparticle emissions where identified during some steps in the maintenance procedure
  – Deal with problems due to background particles
  – Can not be used on a routine basis
Extra slides
Results: Mass spectra (Au)

- All tested metal species, except CuO, were detected.

  Isotopes
  
  - Au: 197
  - Pd: 102, 104, 105, 106, 108, 110
  - Ag: 107, 109
  - FeO: 54, 56, 57, 58
  - CuO: Not vaporized/detected

30 nm ($d_m$) Au particles

\[ d_m = \text{mobility diameter} \]
Results: Mass spectra alloy (PdAg)

Isotopes
Pd: 102, 104, 105, 106, 108, 110
Ag: 107, 109
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Thank you for listening!
Results: Determination of effective density from Particle Time of Flight

Sintered HT furnace Au particles

\[ \rho_{eff} = \frac{d_{va}}{d_m} \rho_0 \]

\( d_{va} = 420 \text{ nm} \)
\( d_m = 30 \text{ nm} \)
Dens. = 14 g/cm³

Eff dens (g/cm³) vs. Mobility diameter (d_m) for Au Agglomerates

- DMA-AMS
- DMA-APM
Transit of Soot Particles Across Laser Beam

- 5-20 microsecond evaporation time
- Coatings evaporate first at relatively low temperatures (<600°C) potentially dependent upon vapor pressures
- Core evaporates last at high temperature (>1000°C) under SP2-like incandescence conditions
- Coating and core material ionized and detected with mass spectrometry

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