Size-Resolved Element Characterization of Aerosol Particles Emitted from Thermal Wood Treatment

20th ETH Conference on Combustion Generated Nanoparticles :: June 13-16, 2016
Motivation: Characterization of aerosol particles

- Process gases
- ENP release (production and application)
- Nanomaterial and waste treatment
- Emission control (engines, turbines, incinerators)
- Human exposure
- Environmental aerosol studies

Traditionally no size-resolved online element characterization available

<table>
<thead>
<tr>
<th>Year</th>
<th>Specific applications</th>
<th>Couplings</th>
<th>Specific applications</th>
<th>Couplings</th>
</tr>
</thead>
<tbody>
<tr>
<td>2002-2013</td>
<td>Hess et al. Empa and PSI</td>
<td>RDD-SMPS-ICPMS</td>
<td>Idea: Versatile real aerosol instrument</td>
<td>Empa and PSI</td>
</tr>
<tr>
<td>2015-2016</td>
<td>Hess et al. Paul Scherrer Institut</td>
<td>Biomass emissions</td>
<td>Time / size resolved element analysis</td>
<td>Paul Scherrer Institut</td>
</tr>
</tbody>
</table>
Instrumental Arrangement
Typ. 30 ppm Cu in waste wood
→ no Cu signal

**Impregnation:**
100 times more:
→ 0.3 % Cu

**2 g impregnated sawdust batches**
- KCl
- CuSO₄
- CuCl₂
- CuSO₄·KCl

**200 mg into die**
F = 60 kN
t = 1 min

**Impregnated sawdust pellets**
φ = 10 mm
d ≈ 2.5 mm
m ≈ 200 mg
Measuring Results

Non-treated sawdust

Volume weighted PSD (SMPS)

<table>
<thead>
<tr>
<th>Mobility diameter (nm)</th>
<th>TGA temperature / °C</th>
<th>Experiment run time / min</th>
<th>Vol. conc. dV/dlog dP / nm³ cm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>105</td>
<td>0</td>
<td>10⁸</td>
</tr>
<tr>
<td>10</td>
<td>130</td>
<td>15</td>
<td>10¹⁰</td>
</tr>
<tr>
<td>20</td>
<td>200</td>
<td>30</td>
<td>10¹¹</td>
</tr>
<tr>
<td>50</td>
<td>300</td>
<td>45</td>
<td>10¹²</td>
</tr>
<tr>
<td>100</td>
<td>400</td>
<td>60</td>
<td>10¹³</td>
</tr>
<tr>
<td>200</td>
<td>500</td>
<td>75</td>
<td>10¹⁴</td>
</tr>
</tbody>
</table>

280 °C highest particle conc.

Cu and K no enhanced signal

Gaseous C no particle diameters emphasized

$^{13}$C mass intensity (ICPMS)

<table>
<thead>
<tr>
<th>Mobility diameter (nm)</th>
<th>TGA temperature / °C</th>
<th>Experiment run time / min</th>
<th>$^{13}$C mass intensity / cps</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>105</td>
<td>0</td>
<td>10⁶</td>
</tr>
<tr>
<td>10</td>
<td>130</td>
<td>15</td>
<td>10⁸</td>
</tr>
<tr>
<td>20</td>
<td>200</td>
<td>30</td>
<td>10¹⁰</td>
</tr>
<tr>
<td>50</td>
<td>300</td>
<td>45</td>
<td>10¹⁰</td>
</tr>
<tr>
<td>100</td>
<td>400</td>
<td>60</td>
<td>10¹¹</td>
</tr>
<tr>
<td>200</td>
<td>500</td>
<td>75</td>
<td>10¹¹</td>
</tr>
</tbody>
</table>

$^{63}$Cu mass intensity (ICPMS)

<table>
<thead>
<tr>
<th>Mobility diameter (nm)</th>
<th>TGA temperature / °C</th>
<th>Experiment run time / min</th>
<th>$^{63}$Cu mass intensity / cps</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>105</td>
<td>0</td>
<td>10³</td>
</tr>
<tr>
<td>10</td>
<td>130</td>
<td>15</td>
<td>10⁴</td>
</tr>
<tr>
<td>20</td>
<td>200</td>
<td>30</td>
<td>10⁵</td>
</tr>
<tr>
<td>50</td>
<td>300</td>
<td>45</td>
<td>10⁵</td>
</tr>
<tr>
<td>100</td>
<td>400</td>
<td>60</td>
<td>10⁶</td>
</tr>
<tr>
<td>200</td>
<td>500</td>
<td>75</td>
<td>10⁶</td>
</tr>
</tbody>
</table>

$^{39}$K mass intensity (ICPMS)

<table>
<thead>
<tr>
<th>Mobility diameter (nm)</th>
<th>TGA temperature / °C</th>
<th>Experiment run time / min</th>
<th>$^{39}$K mass intensity / cps</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>105</td>
<td>0</td>
<td>10⁴</td>
</tr>
<tr>
<td>10</td>
<td>130</td>
<td>15</td>
<td>10⁶</td>
</tr>
<tr>
<td>20</td>
<td>200</td>
<td>30</td>
<td>10⁷</td>
</tr>
<tr>
<td>50</td>
<td>300</td>
<td>45</td>
<td>10⁸</td>
</tr>
<tr>
<td>100</td>
<td>400</td>
<td>60</td>
<td>10⁸</td>
</tr>
<tr>
<td>200</td>
<td>500</td>
<td>75</td>
<td>10⁹</td>
</tr>
</tbody>
</table>

Measuring Results

Non-treated sawdust

KCl impregnated sawdust

Measuring Results

**KCl impregnated sawdust**

**Potassium**

- A clear coincidence with SMPS signal

**Sodium**

- Mobilized by Cl⁻ ions from KCl

---

# Measuring Results

## KCl impregnated sawdust

### Chlorine
Gaseous (HCl) and particulate (salts) Cl

### Copper
Mobilized by KCl impregnation

---

Measuring Results

Copper impregnations

KCl impregnated sawdust

Conclusion

Application
- RDD allows SMPS-ICPMS application for biomass combustion aerosol
- Detected elements: Alkali metals, Cu, Cl (also other isotopes and S)
- TGA: Reproducible experiment conditions (O₂ content, furnace temperature, gas flows)

Experiment results
- Cu release dominated by KCl and not CuSO₄ or CuCl₂ impregnation
- Cl⁻ ions added to the fuel provoke the release of alkali and heavy metals

Element map diagrams
- Time-resolved size and element analysis of gas-borne nanoparticles
- Gaseous and particulate matter visually distinguished
Data processing
- Implement correction for multiple particle charges
- Establish calibration for detected elements → quantitative measurements i.e. mass concentration instead of intensity

Technical adaptations
- Mobile installation in container → leave the lab
- Other instrument configurations e.g. sheath gas recirculation e.g. air operated DMA and gas exchange device

Applications
- Engines on test bench (diesel and aircraft engines)
- Behavior of particles in waste incineration
Acknowledgements

Assistance and discussions:
Mohamed Tarik, Debora Foppiano, Chrigu Ludwig, Martin Gysel

Financial support:
- Competence Center for Materials Science and Technology CCMX
- Swiss National Science Foundation SNF
- Swiss Nanoscience Institute (NanoArgovia)
- Swiss Competence Center for Energy Research – Biomass for Swiss Energy Future SCCER BIOSWEET