Mass spectrometric analysis of nano particles from Diesel exhaust

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The idea:

- Particles emitted from a diesel engine at low power (≈ 20 kW) are soot particles (≈ 70 nm).
- Fuel sulfur (usually 50 ppmM) is emitted as gas-phase SO2
- At high power settings (120 km/h, 45 kW), SO2 is oxidized to SO3 at the oxidation catalyst (designed to remove NOx). SO3 is fast converted to H2SO4 which condensates on the soot particles.
- But: Ford observed a new mode (around 30 nm), the so-called "nucleation mode".

Do these particles consist of H2SO4/H2O?
Setup

- CPC
- DMA
- AMS
- DMA
- CPC
- CPC

Car exhaust pipe

Dilution device 1:100

Dilution air

Excess air

The problem:

- NI fast board output voltage \( \approx \) factor of 2.1
- Mass scale wrong
- Couldn't be corrected by AMS software
### Test Runs

<table>
<thead>
<tr>
<th>Date</th>
<th>Fuel sulfur content (ppm)</th>
<th>Power setting</th>
<th>Speed</th>
<th>Dilution</th>
<th>SMPS</th>
<th>AMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.04.02</td>
<td>1. 50</td>
<td>cold start/idle</td>
<td>-</td>
<td>1:100</td>
<td>yes</td>
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</tr>
<tr>
<td></td>
<td>2. 50</td>
<td>45 kW</td>
<td>120 km/h</td>
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<td>no</td>
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<tr>
<td></td>
<td>3. 50</td>
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<td>50 km/h</td>
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<tr>
<td></td>
<td>2. 50</td>
<td>45 kW</td>
<td>120 km/h</td>
<td>1:100</td>
<td>yes</td>
<td>yes</td>
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<tr>
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<td>3. 40</td>
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<td>120 km/h</td>
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<td>yes</td>
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<tr>
<td></td>
<td>4. 40</td>
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<td>140 km/h</td>
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<tr>
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<td>5. 40</td>
<td>45 kW</td>
<td>120 km/h</td>
<td>1:100</td>
<td>yes</td>
<td>yes</td>
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<td>1:250</td>
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<td>120 km/h</td>
<td>1:100</td>
<td>yes</td>
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<td>4. 350</td>
<td>low</td>
<td>120 km/h</td>
<td>1:100</td>
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<td>yes</td>
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<tr>
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<td>5. 350</td>
<td>low</td>
<td>140 km/h</td>
<td>1:250</td>
<td>yes</td>
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</table>
50 ppm, 120 km/h, low/high power, AMS-SMPS

350 ppb sulfur, low/high power, 03.05.2002, Mass Spectrum
350 ppm, 120 km/h, low/high power, AMS-SMPS

AMS Data:
- sulfate
- organics
SMPS Data:
- dV/dlogD

03.05.02
350 ppm
120 km/h, low power

3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
dMdlogDa (µgm$^{-3}$)

Aerodynamic Diameter (nm)

Mobility Diameter (nm)

AMS Data:
- water
- sulfate
- organics
SMPS Data:
- dV/dlogD

03.05.02
350 ppm
120 km/h, 45 kW

0.8x10$^{12}$

Aerodynamic Diameter (nm)

Mobility Diameter (nm)

350 ppm - 50 ppm

High power (45 kW)

3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
dMdlogDa (µgm$^{-3}$)

Aerodynamic Diameter (nm)

Mobility Diameter (nm)

AMS Data:
- water
- sulfate
- organics
SMPS Data:
- dV/dlogD

02.05.2002
40 ppm
120 km/h, 45 kW

1.4x10$^{12}$

Aerodynamic Diameter (nm)

Mobility Diameter (nm)

AMS Data:
- sulfate
- organics
SMPS Data:
- dV/dlogD

03.05.02
350 ppm
120 km/h, 45 kW

1.0x10$^{12}$

Aerodynamic Diameter (nm)

Mobility Diameter (nm)
"Nucleation particles" were only observed during the idle phase after a cold start.
Summary

- **High power**: lots of sulfate in the particles:
  Hot oxidation catalyst converts SO$_2$ to SO$_3$ which transforms into H$_2$SO$_4$.
  H$_2$SO$_4$/H$_2$O condensates on soot particles.
- **No nucleation** particles observed at high power load, neither with SMPS nor AMS, independent of fuel sulfur content.

**Disagreement with SMPS system of FFA**

- excellent agreement of volume/mass distribution between SMPS of MPI and AMS

- **Low power**:
  50 ppm sulfur: only organics,
  350 ppm sulfur: sulfate + organics

- **Idle after cold start**: only organic mode, similar to low power at 50 ppm

- **Where do the 350 ppb sulfur go?**