In-Situ Mass Spectrometric Analysis of Diesel Exhaust Particles

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Abstract

Size-resolved measurements of the chemical composition of the volatile and semi-volatile fraction of diesel exhaust particles were performed using the Aerosol Mass Spectrometer (AMS, developed by Aerodyne Inc.). The instrument can be operated in two modes: The bulk analysis mode which is used for total chemical composition measurement, and the time-of-flight mode, in which the size selective mass loadings of individual species can be measured (slide 3). A diesel car with a standard oxidation catalyst was used on a chassis dynamometer (slides 4 & 5). At low power settings, the mass distribution peaks at 40 nm aerodynamic diameter and the composition is dominated by organic species. At high load (45 kW), corresponding to an uphill slope of 6% at 120 km/h, the maximum of the mass distribution shifts to about 100 nm and agrees very well with the mobility diameter measured by an SMPS system simultaneously (slides 6 - 8). The composition is dominated by sulfate, which is most likely due to the conversion of SO$_2$ into SO$_3$ inside the oxidation catalyst. The SO$_3$ reacts fast to H$_2$SO$_4$ which nucleates or condenses on pre-existing particles.

Comments to the presentation

With increasing engine load at high speed, e.g. 120 km/h, a steadily rising mode of nucleation particles was observed on a chassis dynamometer (slide 7). These particles consist mainly of sulfate, which was rising from 5 µg m$^{-3}$ at 6 kW load to 160 µg m$^{-3}$ at 40 kW, whereas a simultaneously appearing organics mode was smaller and nearly constant at 10-20 µg m$^{-3}$ (slide 8). This leads to an increasing sulfate/organics ratio (slide 9).

A significant mode of 80 - 100 nm particles (mass size distribution) consisting of organics was observed during measurements in ambient air close to the German Autobahn A4 (slides
In control measurements at a rural background site these particles were not observed, the levels of sulfate, nitrate, ammonium and organics > 300 nm aerodynamic diameter were similar at the Autobahn and the background site (slide 12).

To further investigate this difference real world emissions were measured in individual car chasing experiments, where dilution of exhaust is different as compared to a chassis dynamometer (slide 13). Again nucleation particles were consisting of sulfate and were observed only when 360 ppm sulfur fuel was used and the car was driven at high speed, i.e. high engine load (slide 14). No nucleation particles appeared with low engine load, e.g. 50 km/h, or with low sulfur fuel (slides 14 & 15). Therefore, the origin of nucleation mode particles, which consist of organic material and are observed in the vicinity of busy roads such as an Autobahn is still unclear. Heavy duty diesel trucks seem to be probable emitters of organic nucleation particles.

**Conclusions and summary**

- AMS confirms chemical bulk analysis: ratio of sulfate / organics in particles increases with engine load.
- Highway experiment showed small organics mode, which is due to traffic.
- Chasing experiment with passenger diesel vehicle showed small sulfate nucleation mode in correspondence with chassis dynamometer tests.
- Oxidation catalyst leads to efficient conversion of organics and some sulfate formation.
- Difference between autobahn and chassis dynamometer / passenger car chasing: Are heavy duty diesel VOF emissions larger than passenger diesel VOF?
IN-SITU MASS SPECTROMETRIC ANALYSIS OF DIESEL EXHAUST PARTICLES

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Outline

Introduction

The Aerosol Mass Spectrometer (AMS)

Measurement Results:
  - Chassis dynamometer
  - Freeway (Autobahn)
  - Individual car chase

Discussion

Summary / Conclusions
Aerosol Mass Spectrometer (AMS)

Particle Beam Generation

Aerodynamic Focusing Lens

Ambient Pressure Sampling Orifice

Aerodynamic Sizing

Particle Beam TOF Chopper

Thermal Vaporization and Electron Impact Ionization

Particle Composition

Quadrupole Mass Spectrometer

Turbo Pump

Aerodyne Research, Inc.
Chassis Dynamometer Measurements

Chassis dynamometer at Ford Research Center Aachen (FFA):

- 48" (1.22 m) diameter role
- Max. 186 kW break power
- Max. speed 200 km h⁻¹
- Loss compensation

- Passenger diesel car (euro III), 1.8 L, 66 kW (90 hp),
- 50 ppm / 350 ppm S fuel.
- Turbo charger, direct injection, exhaust gas recirculation, oxidation catalyst.
const. speed 120 km/h:

Number distribution

Volume distribution
Size distributions at different engine loads

Vacuum aerodynamic diameter, mobility diameter (nm)

low load: more organics, aerodynamic diameter smaller than mobility diam. => density < 1.

high load: more sulfate, density ≥ 1, larger particles.
Mass ratio of sulfate to organics vs. engine load

Ford Focus
fsc: 350 ppm
speed: 120 km/h
Motorway and rural background Experiment

(A4, near Aachen, Germany)
Instrumentation of Ford Mobile Laboratory

- Soot: EC and OC
- O₃
- NOₓ / NO / NO₂
- CO
- Calibration unit
- APS
- DMA
- CPC
- PM₁₀
- Datalogger
- Zero air

Cloud Physics and Chemistry
Mass distributions

near highway

rural background site

Vacuum Aerodynamic Diameter (nm)

Sulphate
Organics
Ammonium
Nitrate
Car chasing experiment

- Diesel passenger car, same as on the dyno
- Fuel sulphur content: 30 and 360 ppm
- Speeds 50, 100, and 120 km/h
- Distance: 10 m
120 km/h with different fuel sulfur content

sulphate

organics

Nucleation mode
50 km/h with 360 ppm sulfur fuel

**sulphate**

**organics**

No nucleation mode
Summary

- AMS confirms chemical bulk analysis: ratio sulfate / organics of particles increases with engine load.
- Highway experiment showed small organics mode which is due to traffic.
- Chasing experiment with passenger diesel vehicle showed small sulfate nucleation mode.
- Oxidation catalyst leads to efficient conversion of organics and some sulfate formation.
- Difference between autobahn and chassis dyno: Heavy duty diesel VOF emissions > passenger diesel VOF?
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