Diesel exhaust nanoparticle volatility studies by a new thermodenuder with low solid nanoparticle losses

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Diesel exhaust undergoes rapid cooling dilution process when the exhaust is released into the atmosphere. During this process, gas-to-particle processes like nucleation and condensation can take place, modifying the size distribution and physical and chemical characteristics of the exhaust particles.

Particle volatility studies are a practical way to study the gas-to-particle processes of diesel exhaust. In addition to the emission characterizations, volatility studies can produce information about the particle formation processes and about the technical factors affecting them (e.g. exhaust after-treatment, fuel quality). For example, the changes of fuel and lubricant oil sulfur content affect mostly to the emissions of totally volatile nucleation mode particles (Kittelson et al 2008, Karjalainen et al. 2011). On the other hand, in several studies the diesel exhaust nucleation mode is found to include a non-volatile fraction (core particle mode) (Rönkkö et al. 2007). The initial formation of nonvolatile nucleation mode particles have been shown to take place at high temperature conditions before the exhaust entered into the atmosphere and the formation is affected e.g. by fuel injection pressure and exhaust after-treatment (e.g. Heikkilä et al. 2009, Lähde et al. 2011).

In the studies above, the particle volatility has been studied using a thermodenuder (TD) where the semi-volatile particle compounds are first evaporated in the heating part and, after that, collected onto the surface of active charcoal in denuder part. The diesel exhaust nucleation mode studies require that, in addition to the effective evaporation of volatile components, the penetration of small non-volatile particles is high enough. Therefore, we built a TD based on the following designing criteria:

1) TD is able to evaporate all semi-volatile species of diesel exhaust particles
2) Evaporated vapors are efficiently collected into the activated charcoal
3) Flow range of TD is 0-10 slpm and the inlet temperature is 300 K or higher.
4) Aerosol cools in the denuder part nearly to the inlet temperature of 300 K.
5) TD provides a high penetration for non-volatile particles larger than 3 nm.

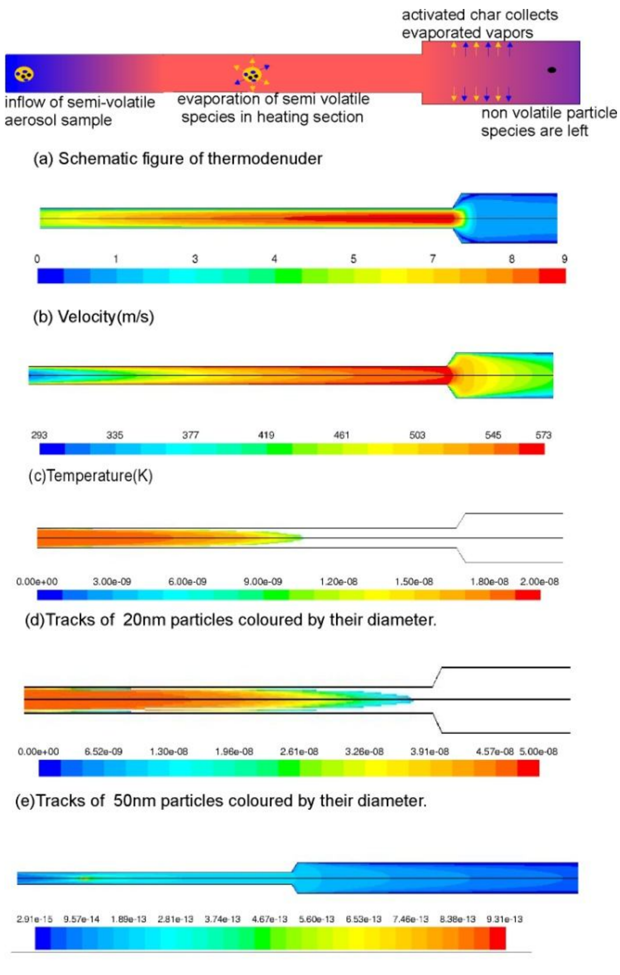

Figure 1. Schematic figure of the thermodenuder (a) and flow field inside the TD ((b)-(f)).

Designing of the TD was based on simulations by Ansys Fluent and Comsol Multiphysics CFD packages. Losses of non-volatile particles were simulated as a function of particle size by solving the transport equation for different particle sizes in combination with the flow field and heat transfer equations. Diffusion and thermoforesion where the simulated deposition mechanisms of aerosol particles and vapors. Evaporation rates of 10–100 nanometer sulfuric acid – water particles with concentration of 10^8 particles/cm^3 were simulated. Flow rate was 10slpm and heater temperature was 300^{o}C. Results of the simulations and schematic of the thermodenuder is presented in figure 1. It can be seen that the particles evaporate in the heating part. Particles smaller than 100nm evaporated completely in the heating section. In addition, simulations showed that the concentration of the initial and evaporated sulfuric acid was reduced by a factor of approximately 10 in the denuder part. Sulfuric acid vapor concentration is 100 times less than saturation vapor pressure of it at the end of the denuder part. This should effectively prevent possible re-nucleation and the condensation of vapors onto solid particles.

A laboratory measurement of the TD operating with sulfuric acid-water particles is presented in figure 2. The TD operating at 265 °C was able to remove all the particles when the nucleation mode mean diameter was around 25 nm. This is in agreement with the results of the simulations. The non-volatile particle losses were tested by generated solid particles.

In addition to the simulations and laboratory tests, the TD has been used in the diesel exhaust particle studies in engine and vehicle laboratories and on-road. These field measurements showed that the TD is able to remove the volatile nucleation mode particles and condensates from the soot and core mode particles (Rönkkö et al. 2011, Karjalainen et al. 2011). In addition, the size distribution measurements of the non-volatile core mode particles agreed well with the results obtained by using a hot dilution setup. Also the studies related to nucleation mode particle charge supports the results (e.g Lähde et al. 2011).

In summary, simulations, laboratory tests and real engine exhaust measurements shows that the TD performs well. However, the use of the TD has to be limited to the conditions where the sample flow is near 10 slpm or lower, the aerosol sample reaches the planned temperature and the concentration and size of the studied particles is below the certain case-specific values. Thus, especially in diesel particle studies, the use of the TD can require e.g. additional sample dilution before the TD treatment.

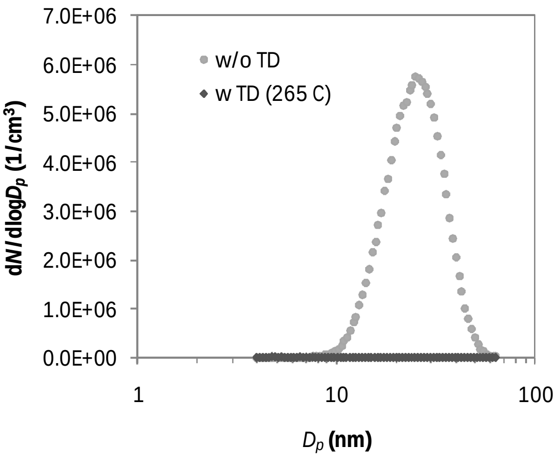

Figure 2. Effect of the new thermodenuder on the sulfur driven nucleation mode.

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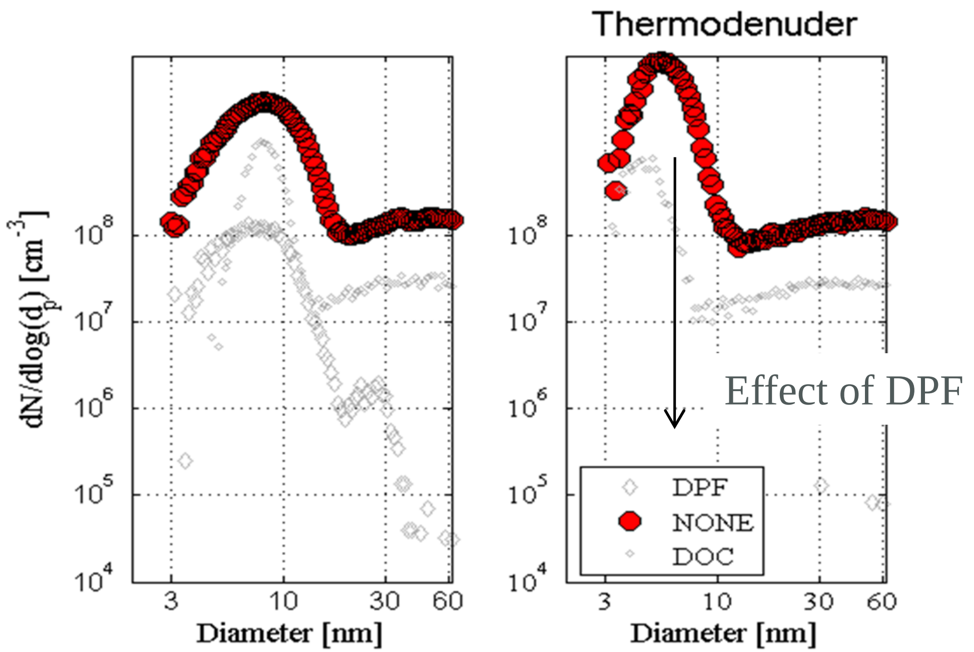
Contents

1. Background
2. Designing criteria and simulations for a new thermodenuder
3. Laboratory tests
    - Solid nanoparticles
    - Volatile nanoparticles
4. Engine exhaust measurements
    - Volatile nucleation mode particles
    - Nonvolatile nucleation mode particles
    - Externally mixed volatile and nonvolatile nucleation mode particles
5. Summary

Background



Lähde et al. 2009

- **Diesel exhaust nucleation mode particles may have non-volatile core (GMD < 10 nm)** **E.g. Rönkkö et al. 2007, Lähde et al. 2009**
- **Vehicle and engine technologies affect nucleation mode**
  - **Nonvolatile core**
  - **Formation of volatile particles in cooling dilution**
  - **Compounds condensed on core particles surfaces**

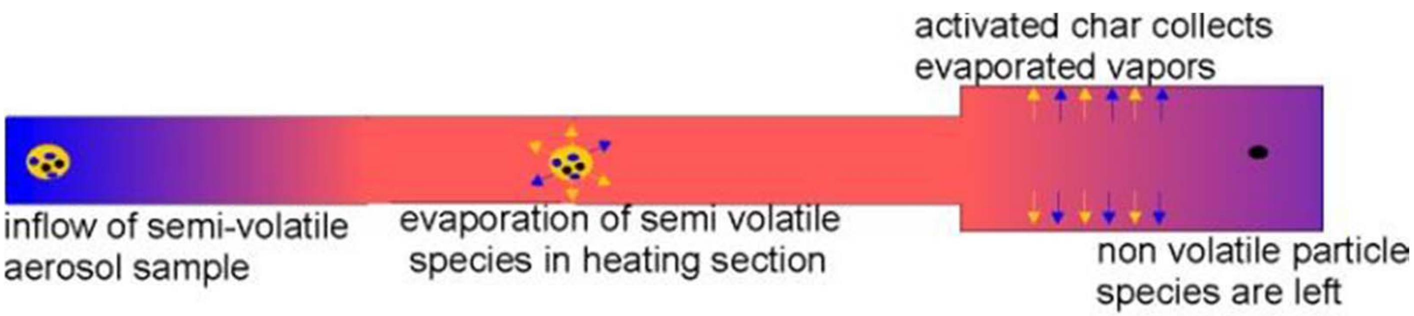
Criteria

1. Evaporation of semi-volatile species
2. Efficient collection of evaporated vapours
3. Flow range 0-10 slpm
4. Cooling of the aerosol in the denuder part (-> ~300 K).
5. High penetration for nonvolatile particles larger than 3 nm.

Simulations

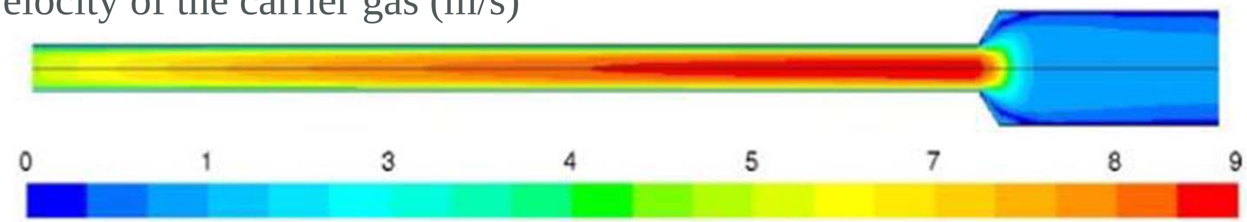
Simulated case
- •Flow rate 10slpm
- •Heater wall temperature 600K
- •Denuder part wall temperature 300 K
- •Collection mechanisms diffusion + thermophoresis

Simulation tools
- ANSYS Fluent
- turbulence model: realizable k-ε
- enhanced wall treatment of Fluent

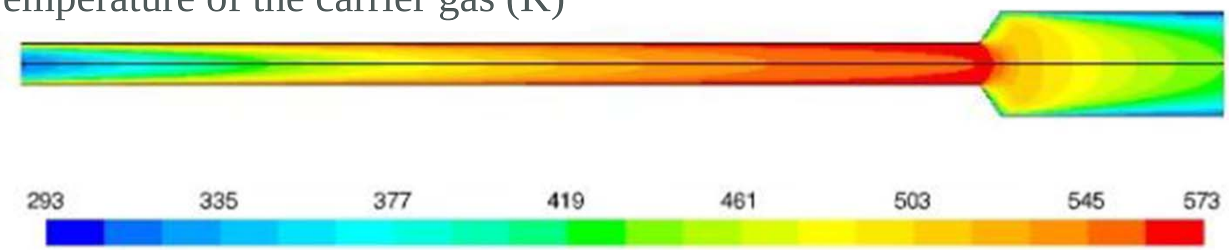


Simulations

Velocity of the carrier gas (m/s)

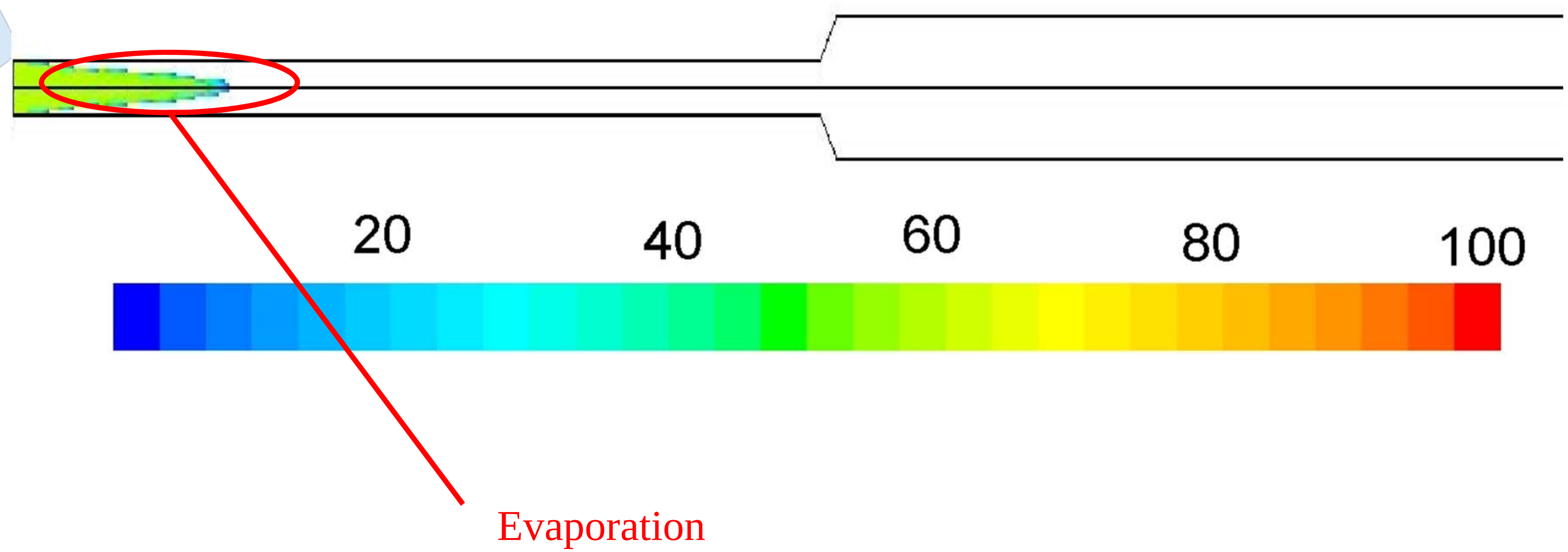


Temperature of the carrier gas (K)



Simulations

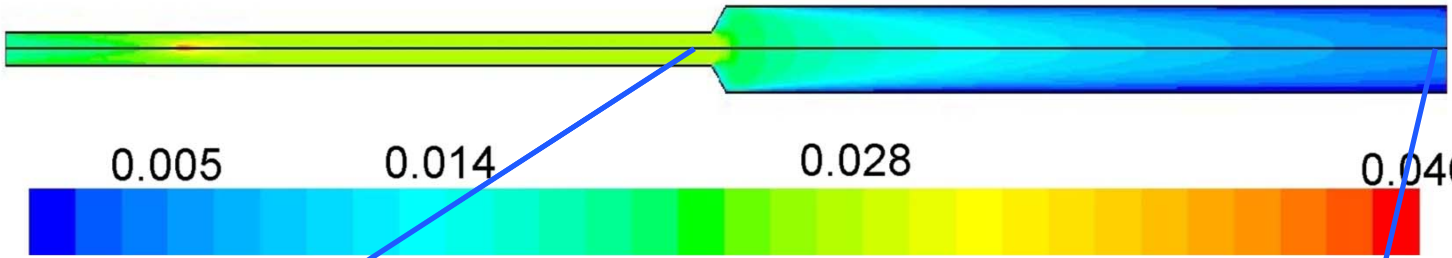
Evaporation of 100 nm sulphuric acid – water particles (scale nm)



Simulations

sulfuric acid feed:
- background concentration 0.02ppm
- particles 4.8ng/s

Sulphuric acid concentration (mole fraction)

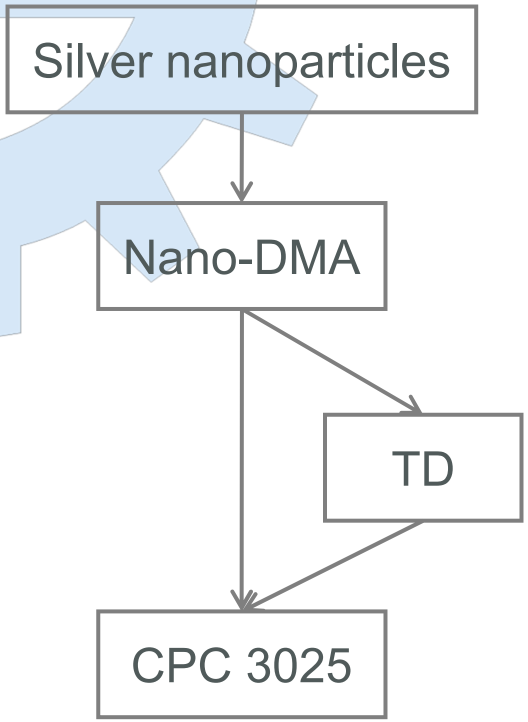


sulf. acid average mole fraction before denuder appr. 0.03ppm

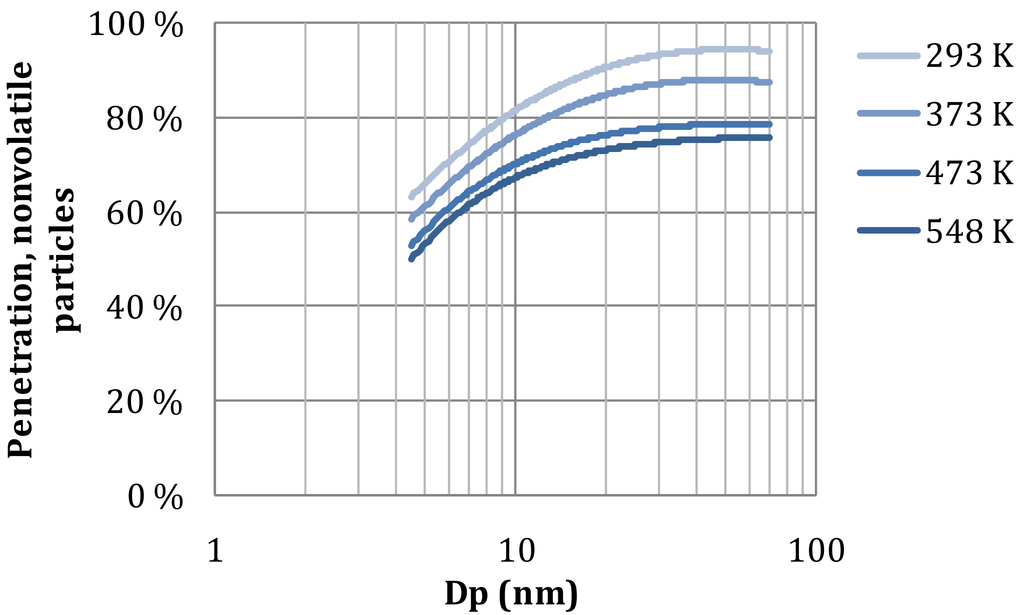
sulf. acid mole fraction at the outlet 0.003ppm

reduction of sulfuric acid by 90%

Laboratory tests: nonvolatile particles



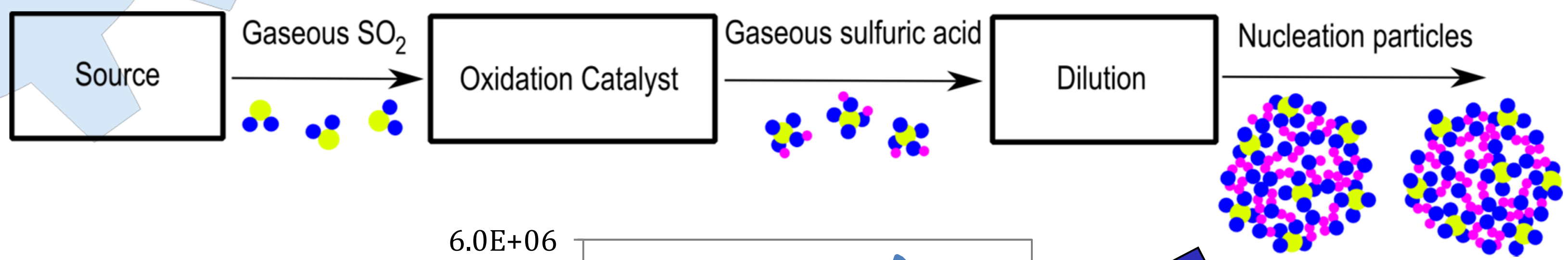
TD temperature



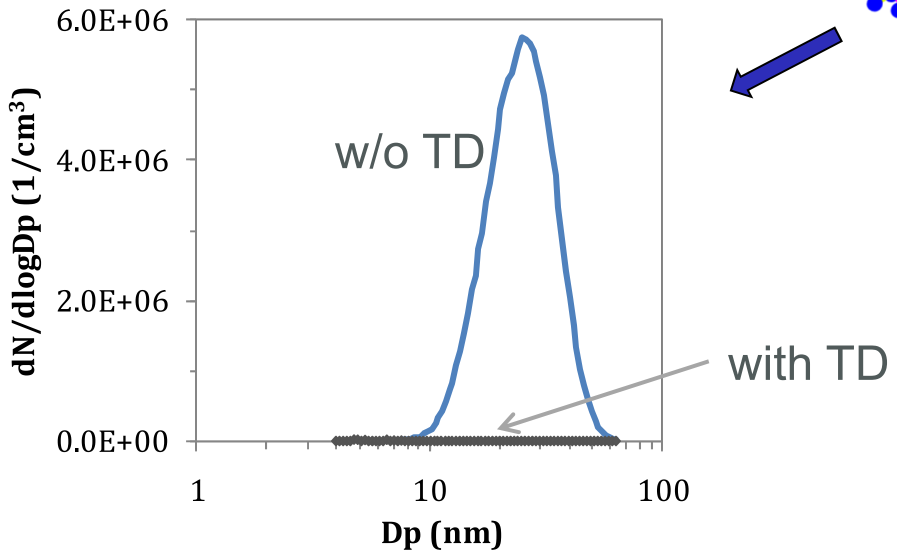
Laboratory tests: volatile particles

Mimicking the volatile particle formation in diesel exhaust (Karjalainen et al. 2011)

- SO_2 – air mixture, small scale "exhaust after-treatment"
- Cooling dilution (like in real-world) (Keskinen and Rönkkö, 2010)



Nano-SMPS:



Engine exhaust: volatile mode

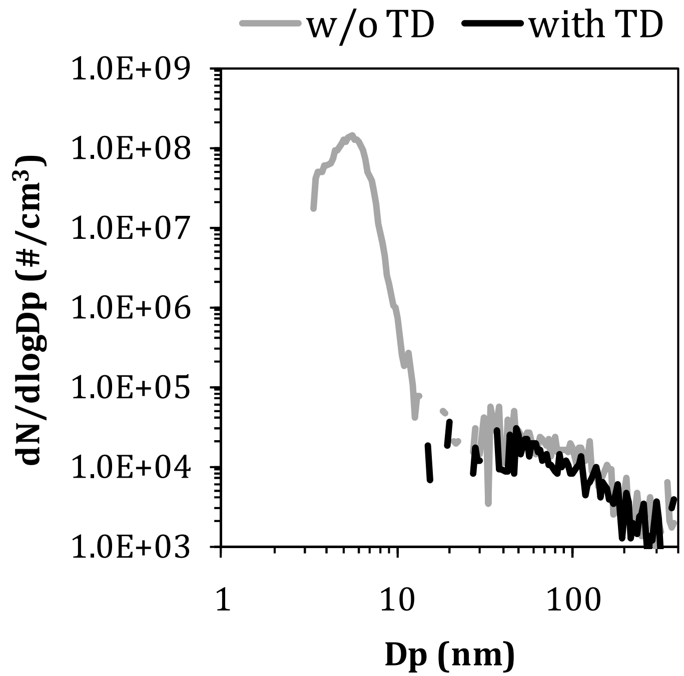
Heavy duty diesel engine with DOC+DPF

High load

Cooling dilution

Sulphur driven nucleation mode

Particles evaporated in TD

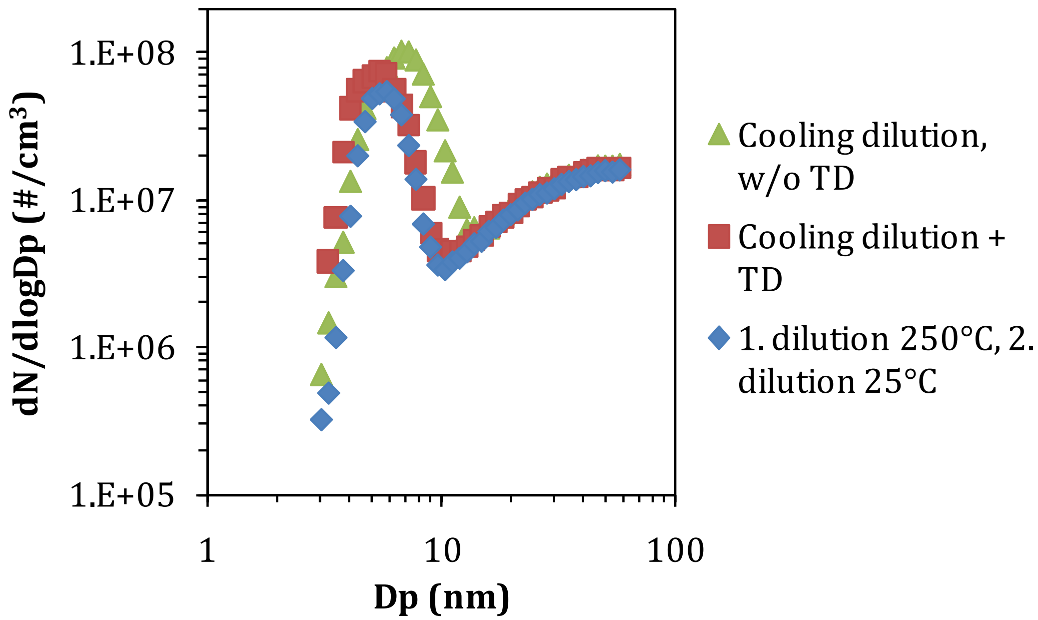


Engine exhaust: nonvolatile mode

Similar results using

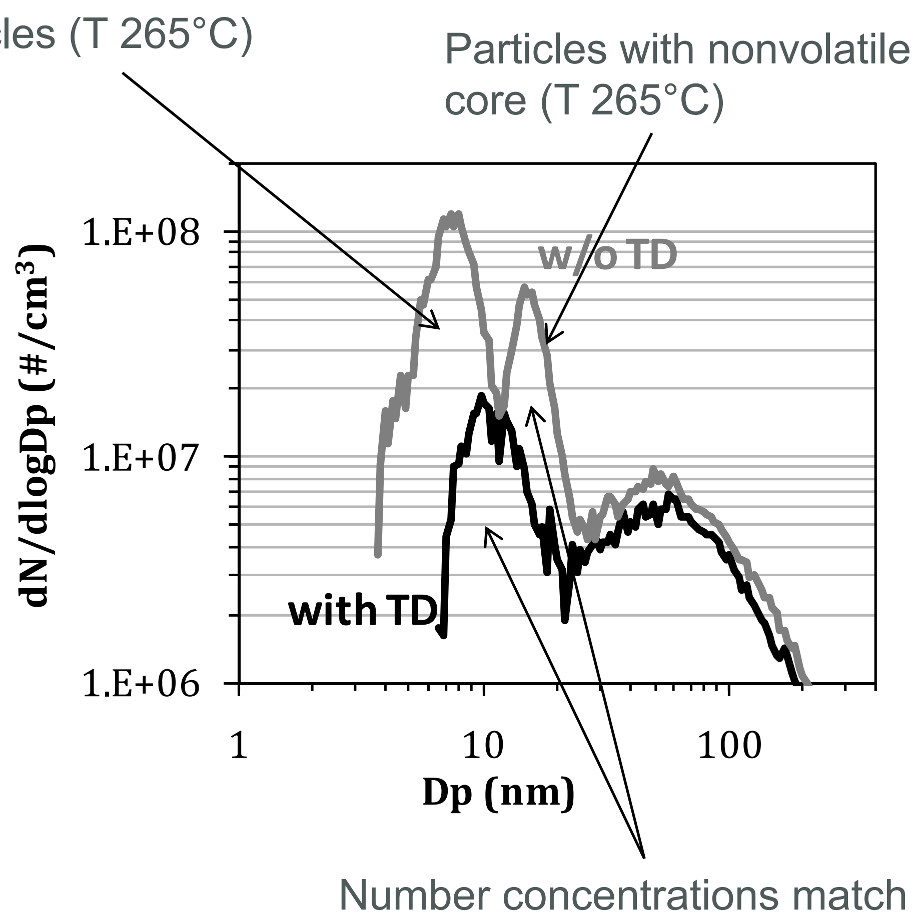
-Cooling dilution + TD

-Heated dilution air in primary diluter (250°C, Dr 8), 25°C air in secondary diluter



Measurements with heavy duty diesel engine, see Lähde et al. 2011.

Engine exhaust: both modes



Externally mixed nucleation mode particles:
Particles can be separated based on volatility in the new TD

Measurement:
Heavy duty diesel engine
Cooling dilution
Rönkkö et al. 2011

Summary

- Simulations, laboratory tests and engine exhaust studies:
  - The new thermodenuder is a practical and well-defined tool for diesel exhaust nanoparticle studies
- Limitations / requirements:
  - Maximum sample flow ~12lpm
  - Gas temperature after heater must be checked to be high enough
  - Sufficient exhaust dilution needed before thermodenuder
    - Typically DR ~100
    - Additional dilution may be needed upstream the TD if high FSC or high THC

- Focus of our particle volatility studies
  - Nucleation mode formation mechanisms
  - Effect of technologies

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