Evaporation of Volatile Aerosols

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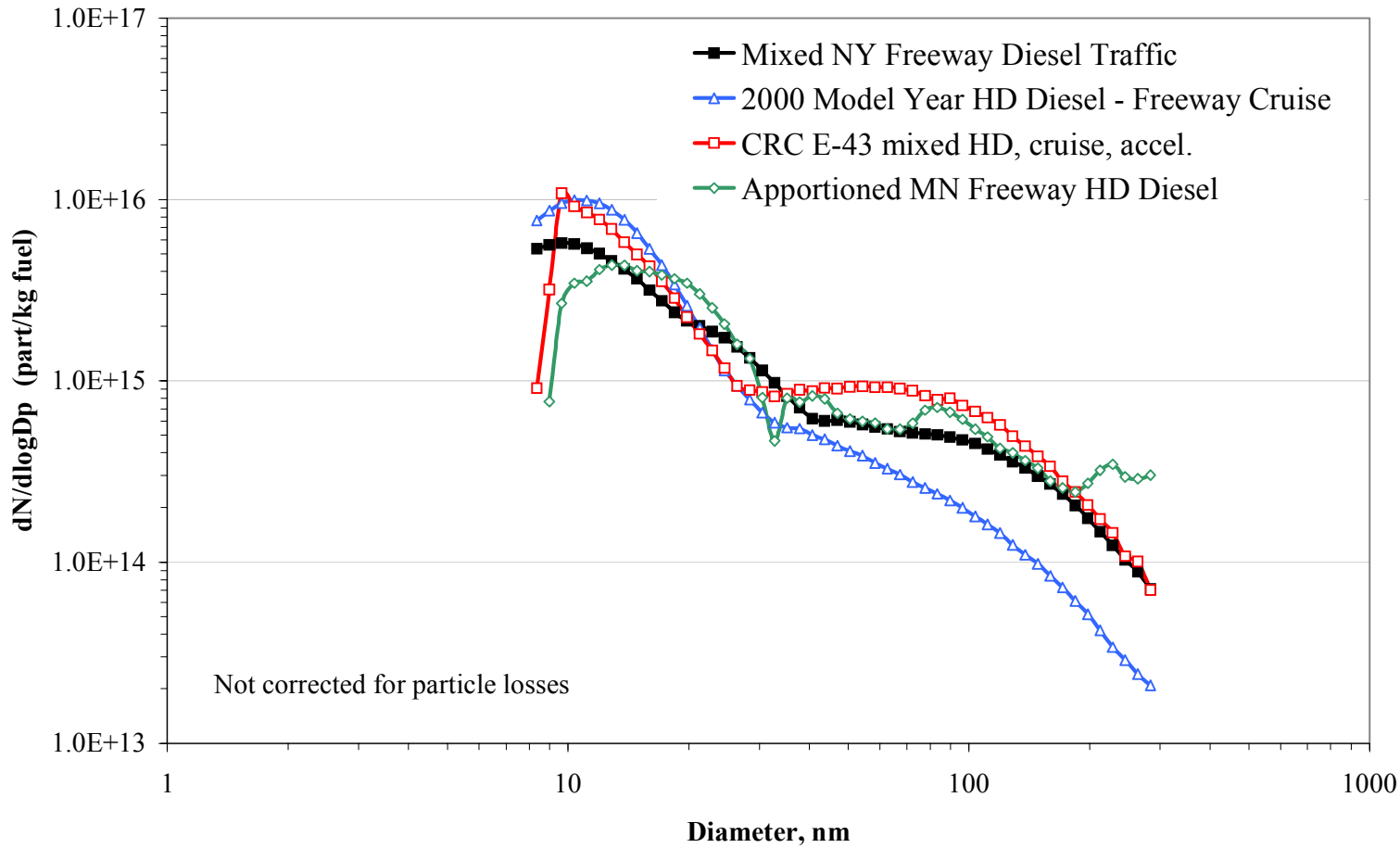
Outline

- Nature of nuclei mode
  - Engines without aftertreatment
    - » Lab measurements
    - » On-road measurements
  - Engines with aftertreament
    - » Lab measurements
    - » On-road measurements
- Aerosol evaporation
  - Typical lab setup
  - Theory
  - Experimental

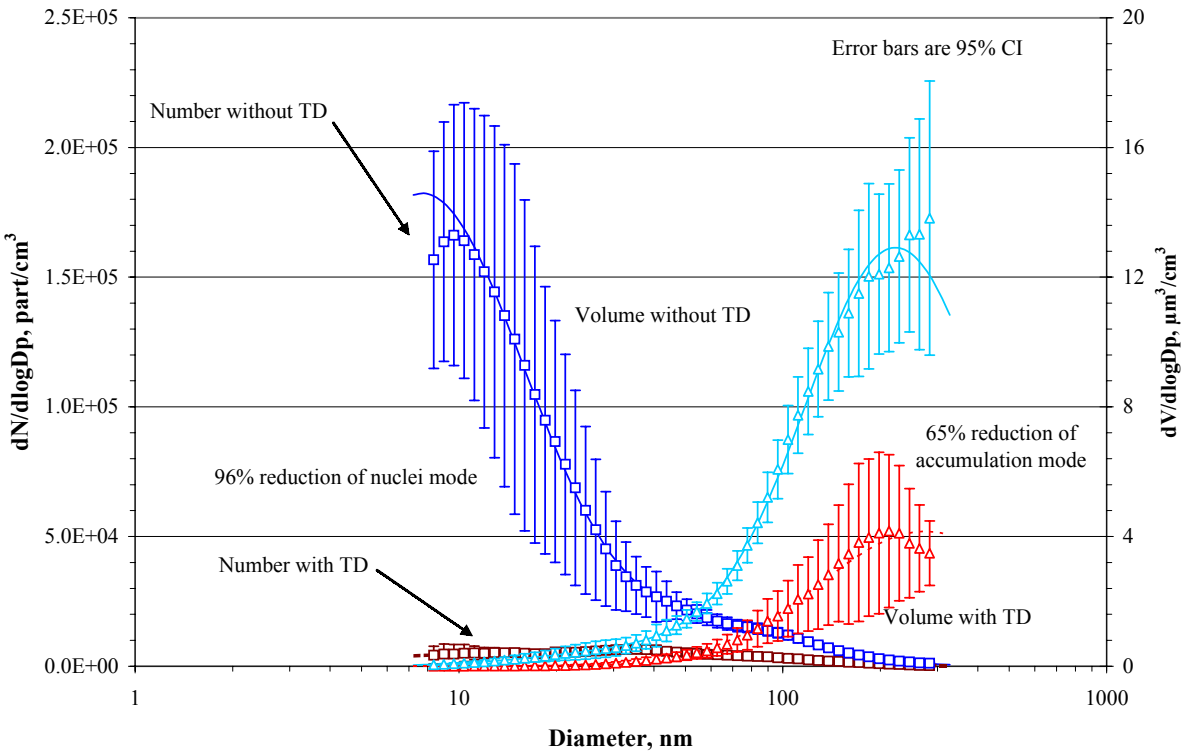
Objective

- Diesel exhaust aerosols, especially in the nuclei mode diameter range are mainly volatile, particularly for low carbon emitters like
  - Modern heavy-duty engines
  - Engines equipped with highly efficient particle filters
- A number of modern particle measurement instruments operate at reduced pressure
  - Particle mass spectrometers
  - Cambustion DMS500
  - Dekati ELPI
- Do nuclei mode particles evaporate during sampling and measurement?

On-road tests with modern heavy duty engines show a large nucleation mode

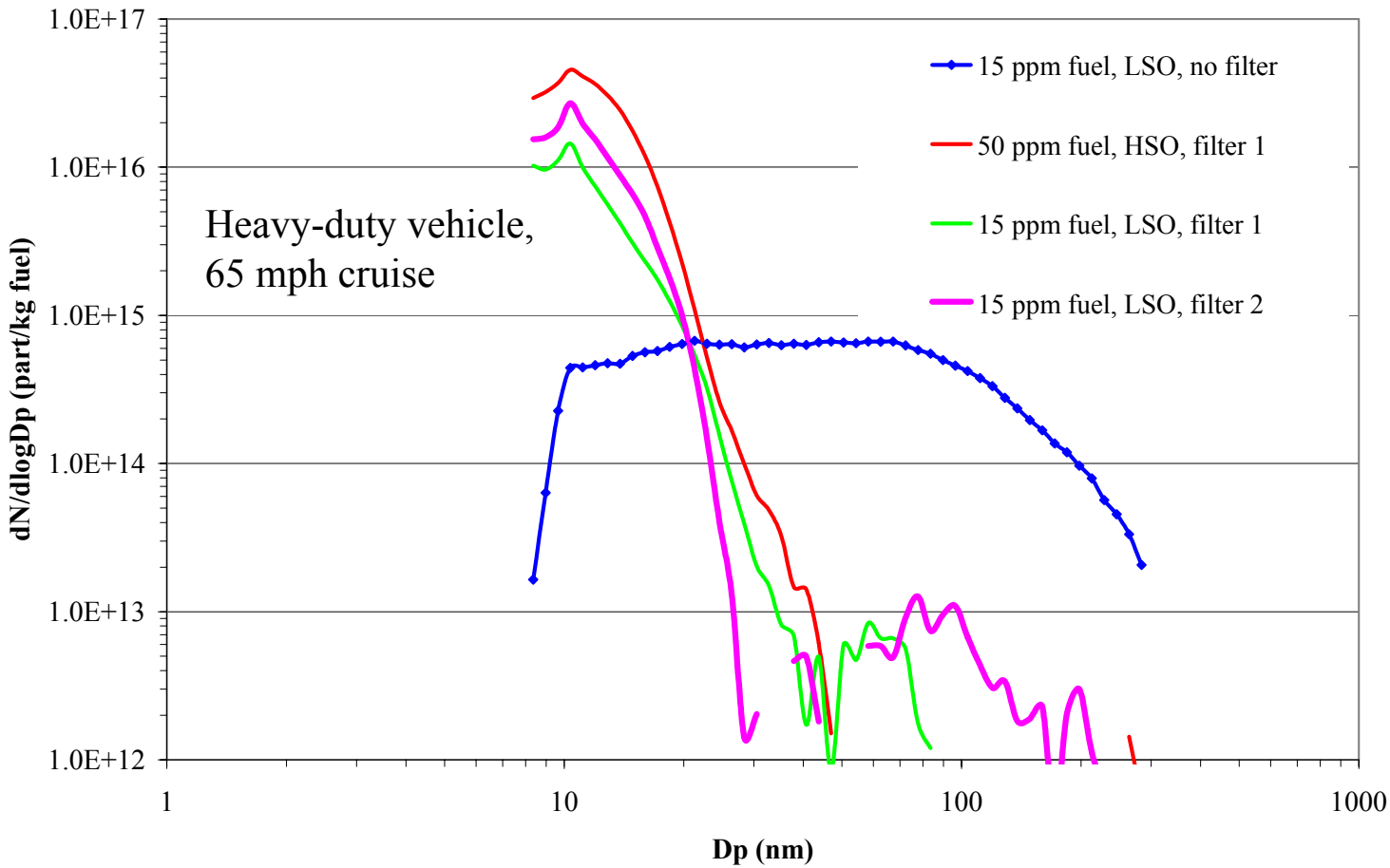


Much of the on-road aerosol is volatile, especially in the nuclei mode region

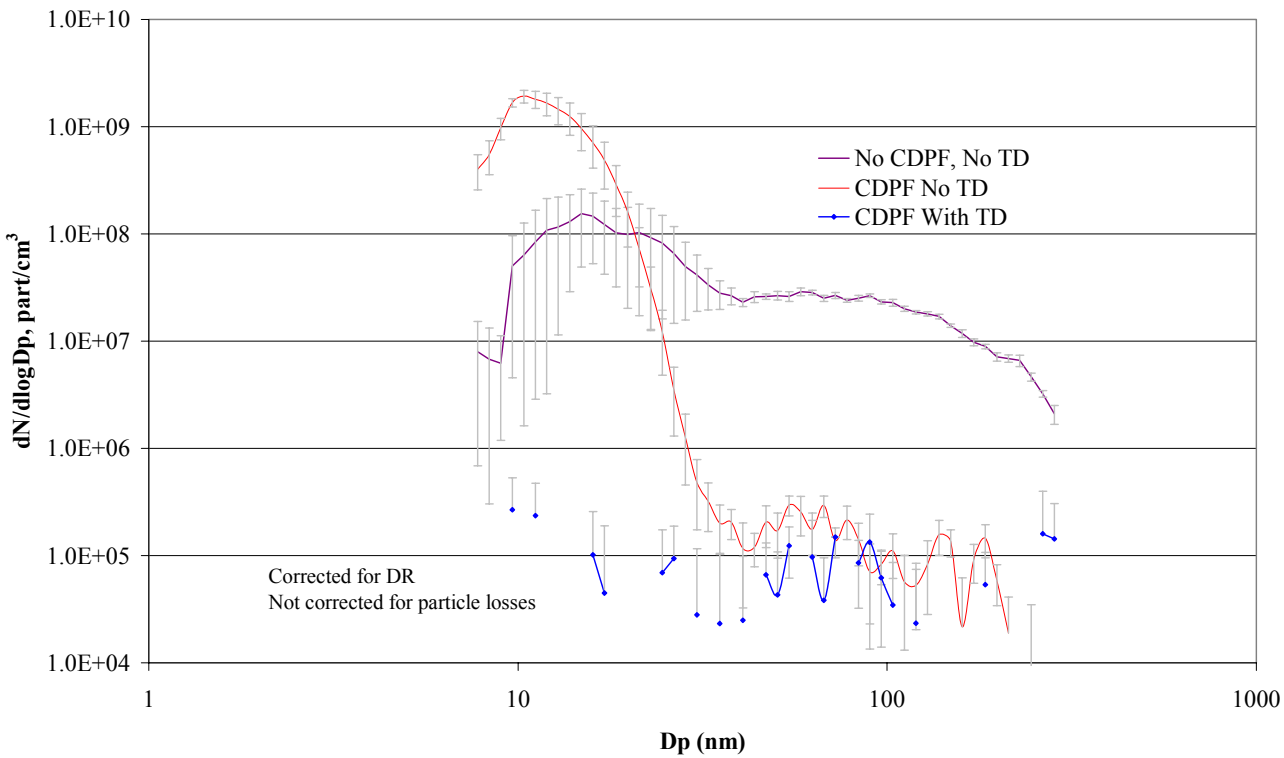


- Overall average fall 2002 on-road data
- Thermal denuder (TD) used to remove volatile particles
- 96% reduction in nuclei mode region
- 65% reduction in accumulation mode region
- Nuclei mode or nanoparticles are nearly all volatile – as expected from laboratory tests

On-road testing with efficient DPFs show nothing but a large nucleation mode



Laboratory tests shows that the nucleation mode downstream of DPFs is nearly entirely volatile



- The results shown are for a catalyzed DPF on a modern Cummins engine, 26 ppm S fuel
- DPF very efficient for solid particles
- May form a very large nuclei mode downstream of DPF at high load conditions
- Nuclei mode is essentially 100% volatile
- Sulfuric acid likely major component

Nuclei mode composition – *heavy-duty engines*

- A volatile nuclei mode is often present, with or without aftertreatment
- For engines without aftertreatment the nuclei mode consists mainly of heavy hydrocarbons
- For engines with aftertreatment the nuclei mode consists mainly of sulphates

Evaporation Theory

The rate of diameter change due to evaporation in the free molecular regime, $d_p < \lambda$, is independent of total pressure and given by:

$$\frac{d\left(d_p\right)}{dt} = \frac{2M\alpha_c\left(p - p_\infty\right)}{\rho_p N_a \sqrt{2\pi mkT}}$$

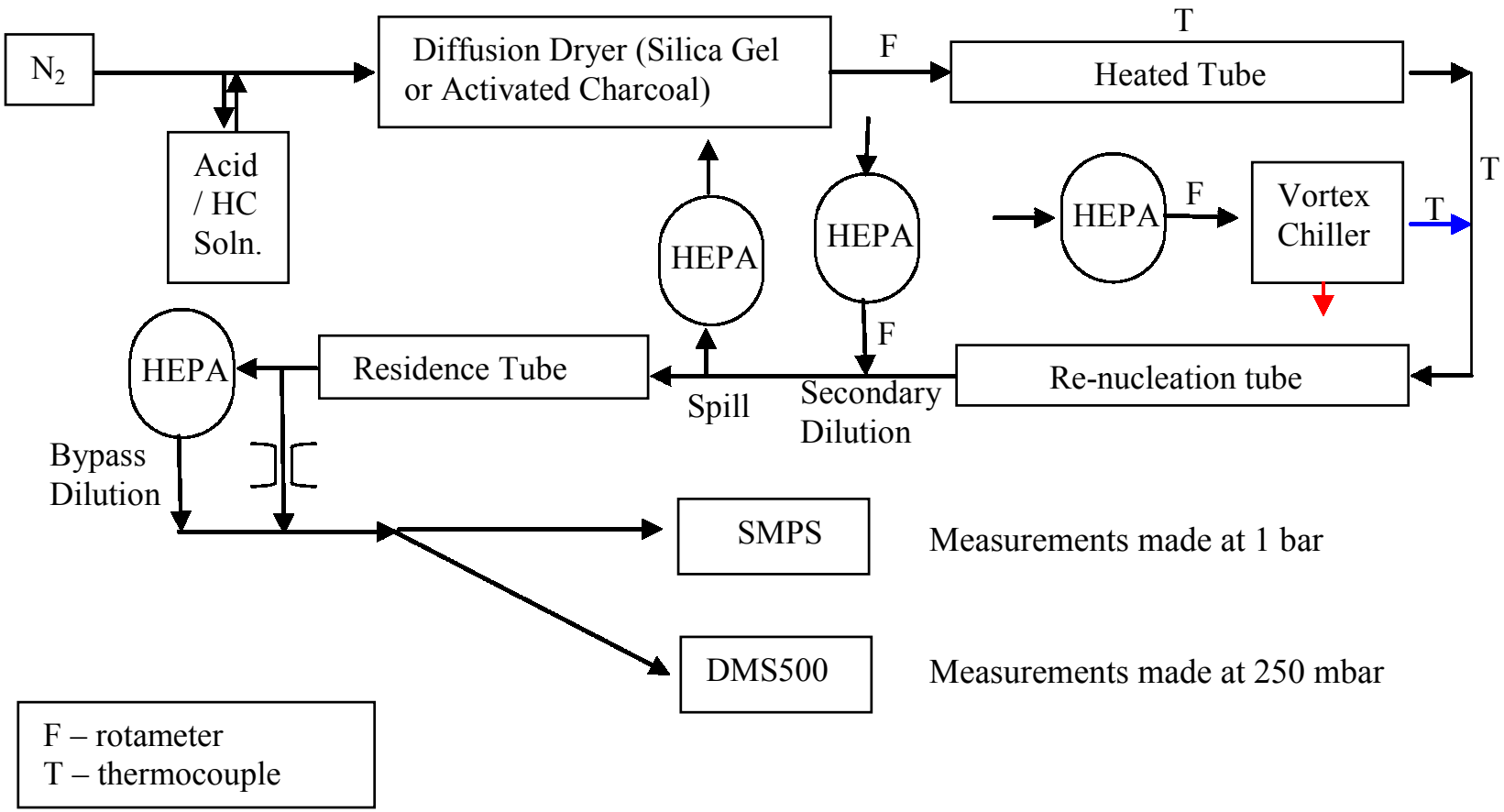
In the continuum regime, $d_p > \lambda$, it increases with decreasing pressure through the dependence of D and ϕ on pressure and is given by:

$$\frac{d\left(d_p\right)}{dt} = \frac{4DM\left(\frac{p_d}{T_d} - \frac{p_\infty}{T_\infty}\right)}{R\rho_p d_p}\phi$$

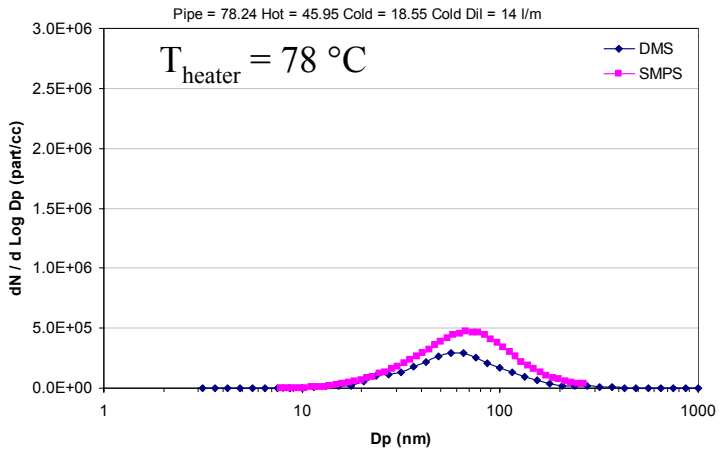
Approach

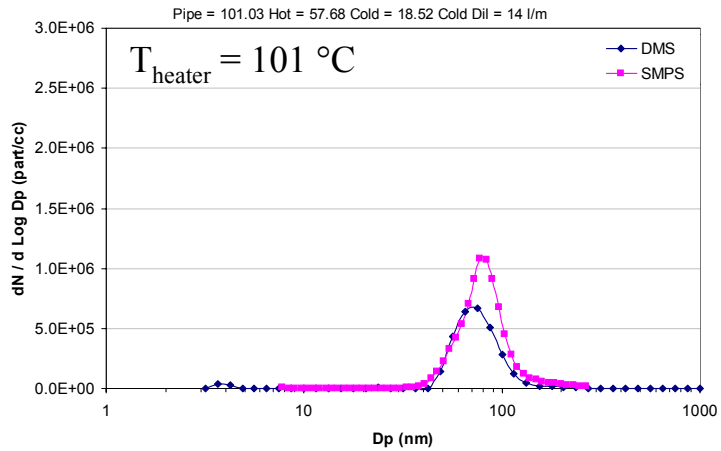
- Two types of volatile aerosols were studied
  - Eicontane a C20 normal alkane – this is a much more volatile hydrocarbon than found in the nuclei mode of typical heavy-duty engines which evaporate like C24 to C32 normal alkanes
  - Sulfuric acid / water particles which are as or more volatile than the sulfuric acid or ammonium sulfate particles than constitute much of the nucleation mode in trap equipped engines
- Two types of experiments were done to access the tendency to evaporate
  - Comparisons of simultaneous size distribution measurements made with a DMS500 operating at 250 mbar and an SMPS operating at 1 bar
  - Comparisons of nano SMPS size distributions measured with an SMPS for aerosols aged for 2 s at 250 mbar and 1 bar

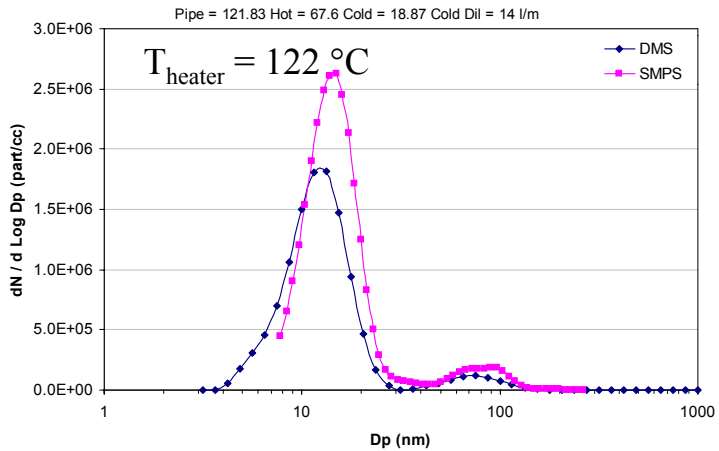
Experimental Setup – Simultaneous DMS, SMPS measurements

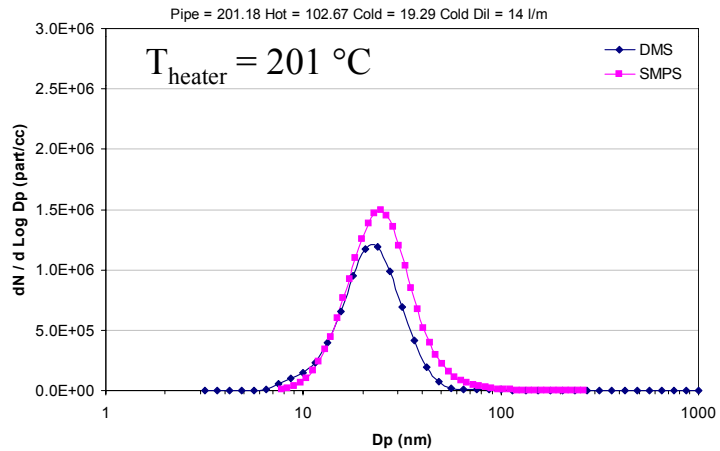


Sulfuric acid / water aerosols – comparisons of DMS and SMPS measurements

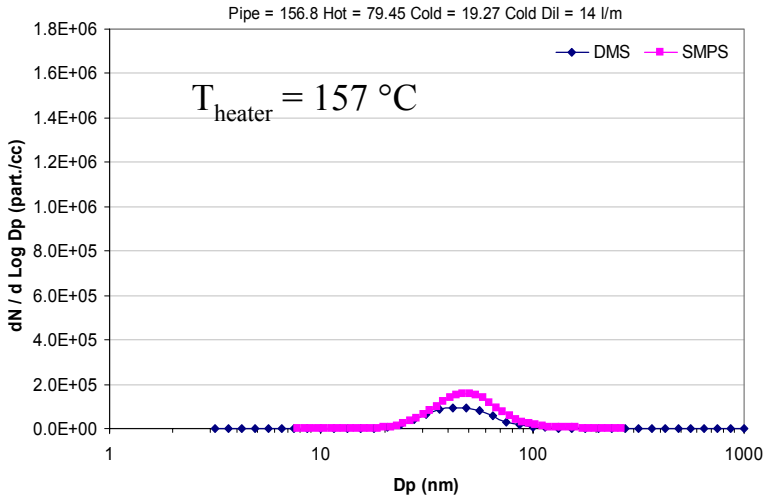


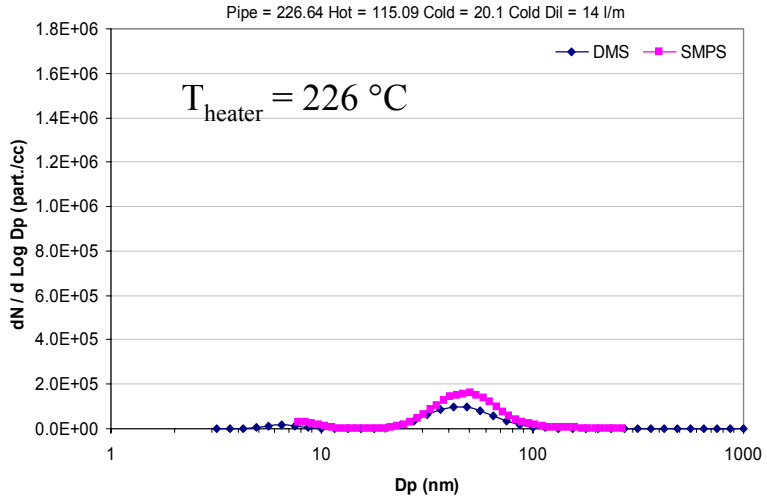


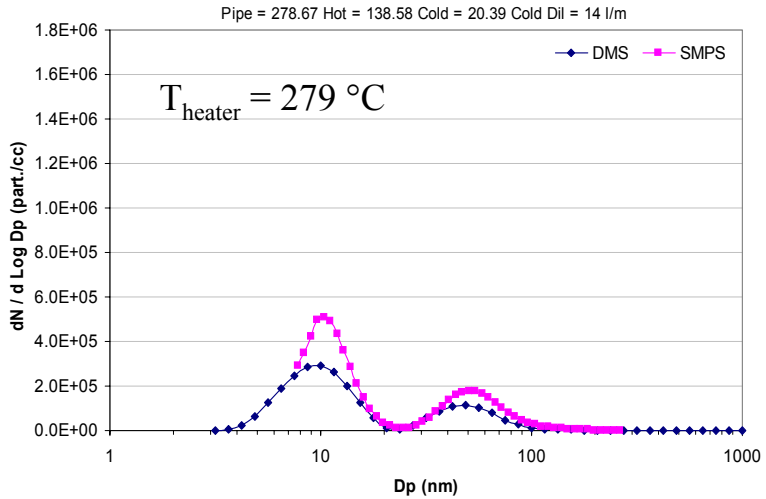


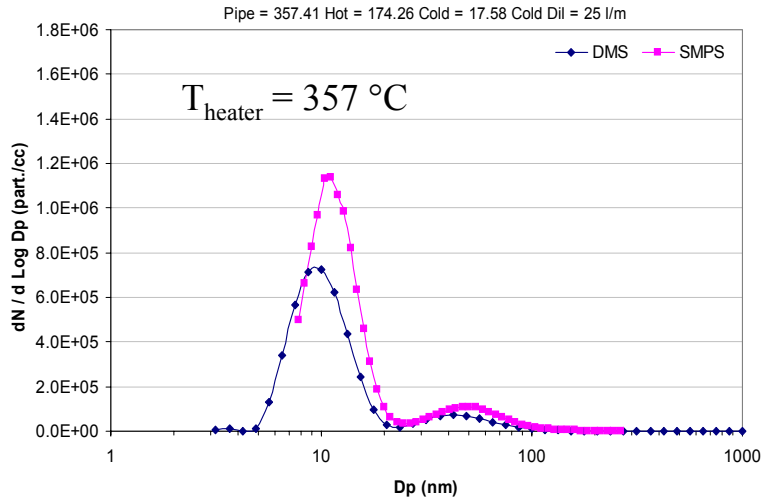


Eicosane (C20) aerosols – comparisons of DMS and SMPS measurements

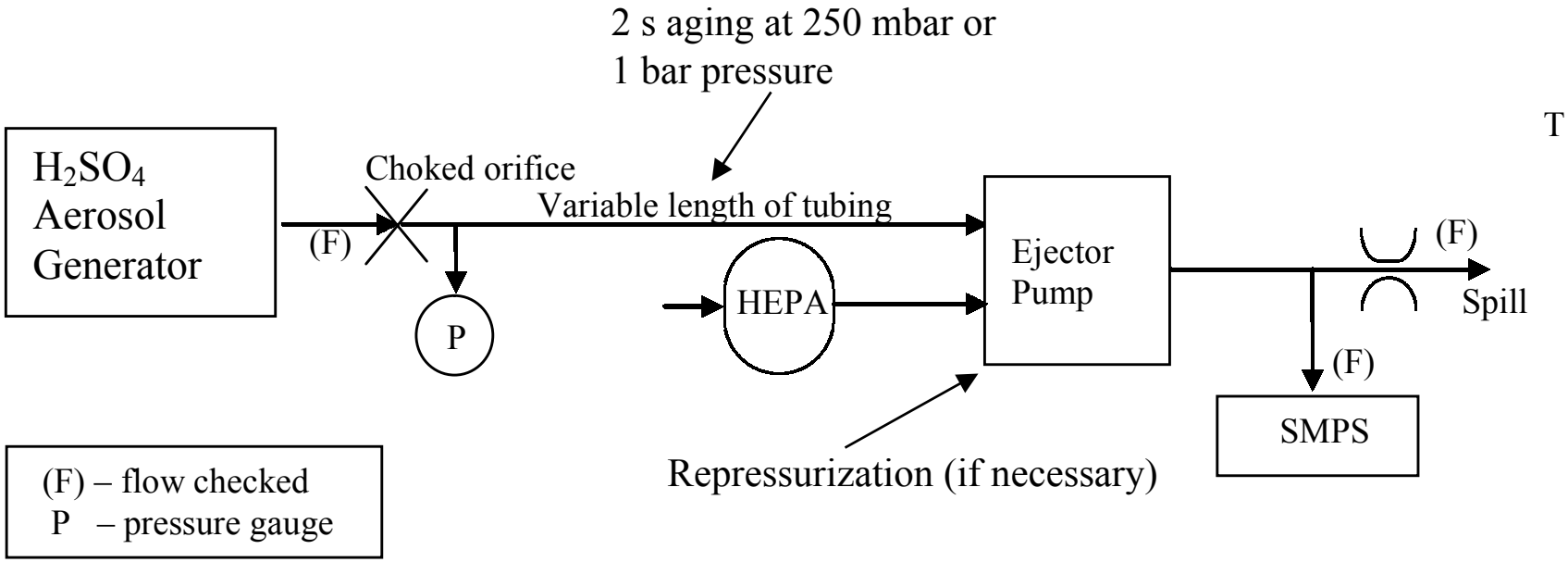




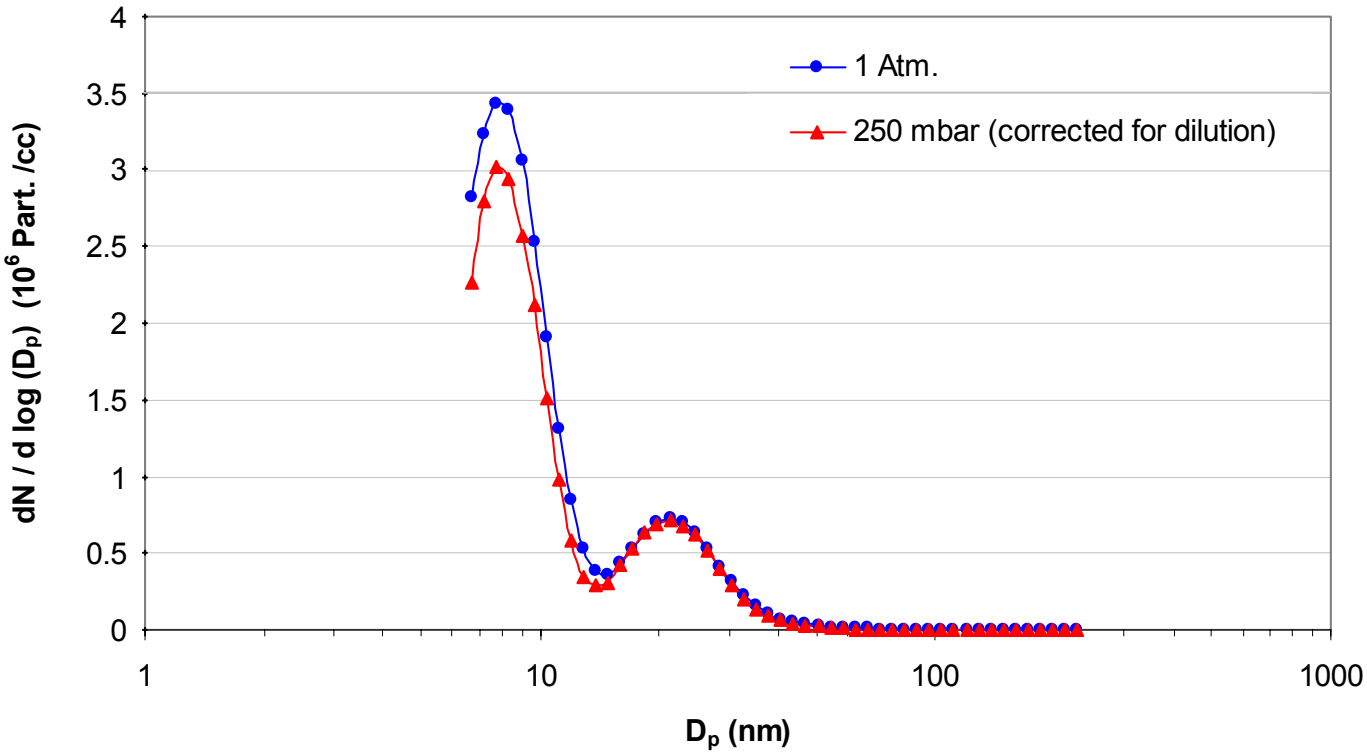




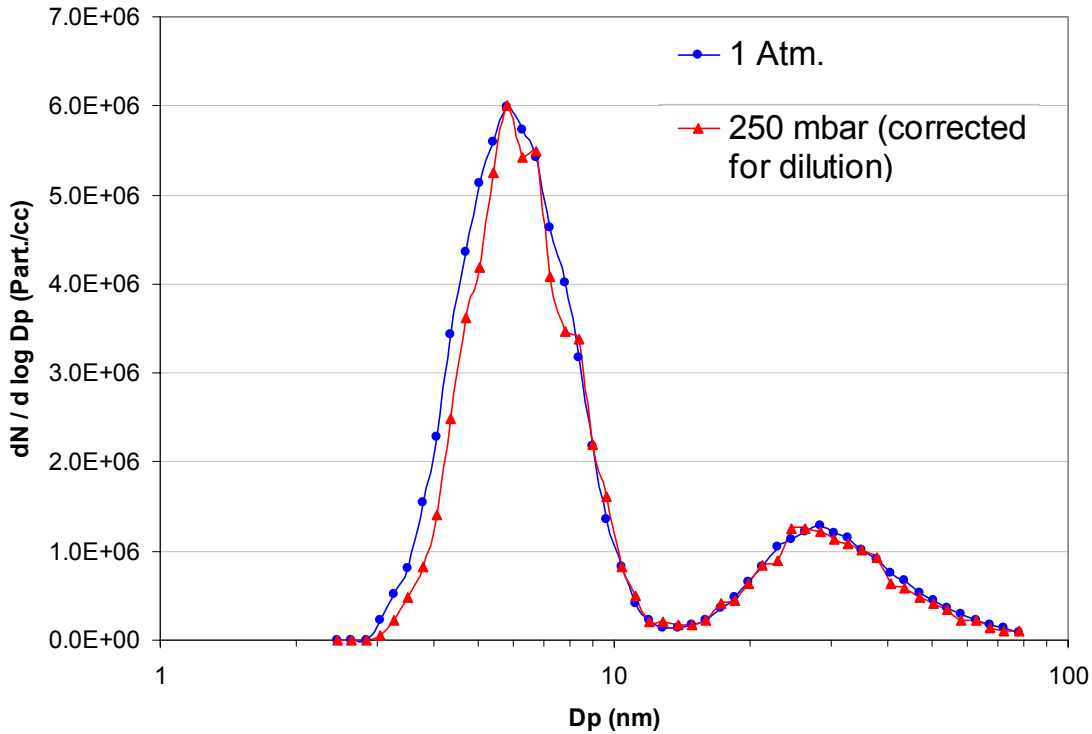
Experimental setup – SMPS measurements after aging at 250 mbar or 1 bar



Low pressure treatment of sulphuric acid / water 2 s at low p with no significant change in size



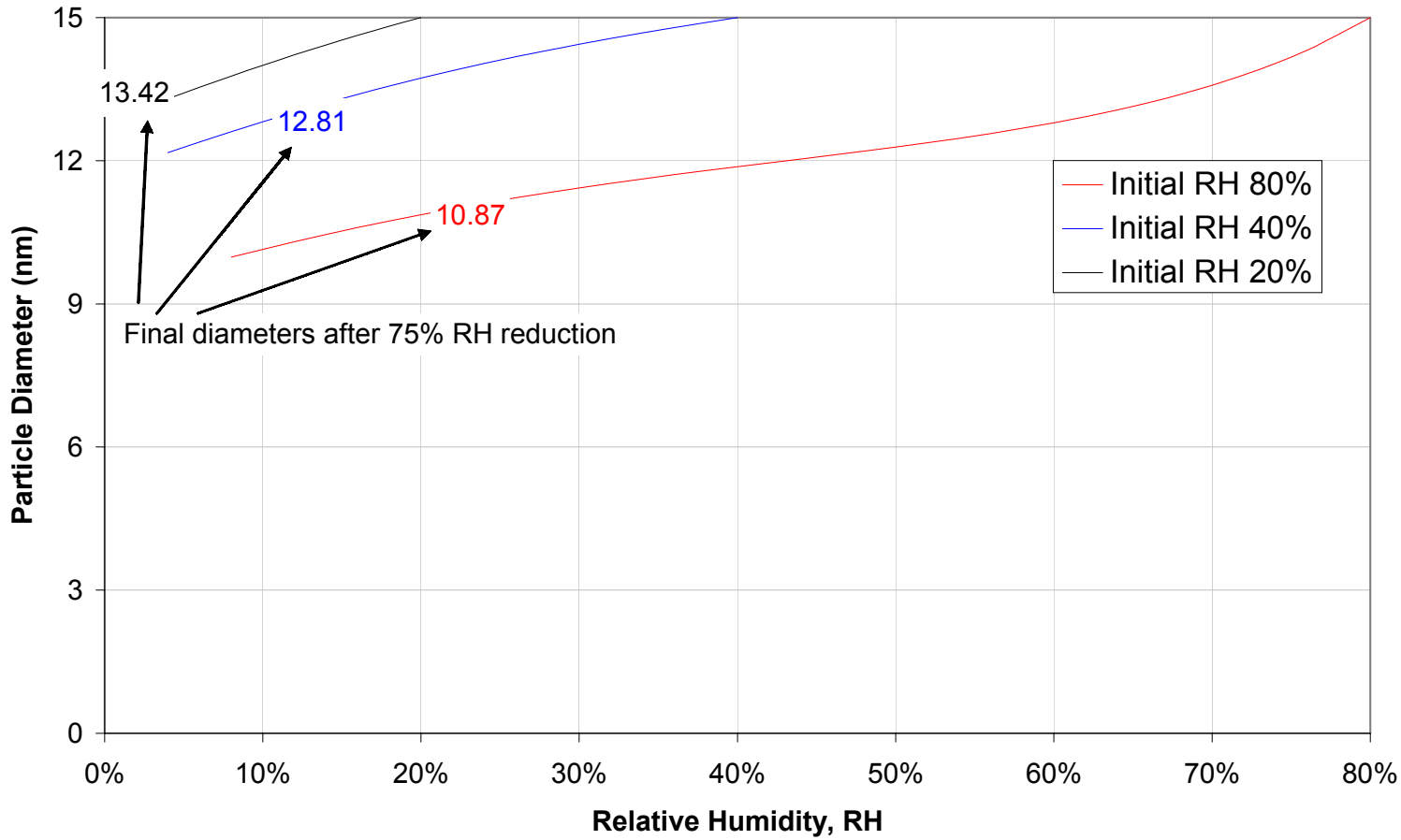
Low pressure treatment of Eicosane (C20) – 2 s at low p with no significant change



Other issues

- The only aerosol component likely to have a significant partial pressure in a diluted sample stream is water
- Thus sulfuric acid / water aerosols should change size if relative humidity changes do to
  - Heating or cooling
  - Dilution
  - Pressure changes
- However the process is reversible so that we don't see it in our reduced pressure experiments

Water uptake and loss from sulphuric acid is very fast
Final diameters of 15 nm droplets after RH reduction



Conclusions

- For particles in the free molecular regime ($d_p < \lambda \sim 65$ nm) theory predicts and experiments show that evaporation of volatile particles in diluted exhaust aerosols is not influenced by pressure (constant T)
- This does not mean that very volatile aerosols do not evaporate – just that pressure does not influence the process
- In our experience with engine aerosols most of the very volatile materials have evaporated before measurement – in the atmosphere and in the laboratory
- However hygroscopic aerosols will lose of gain water when relative humidity is changed by dilution or pressure change – the resulting diameter change is small at low relative humidity