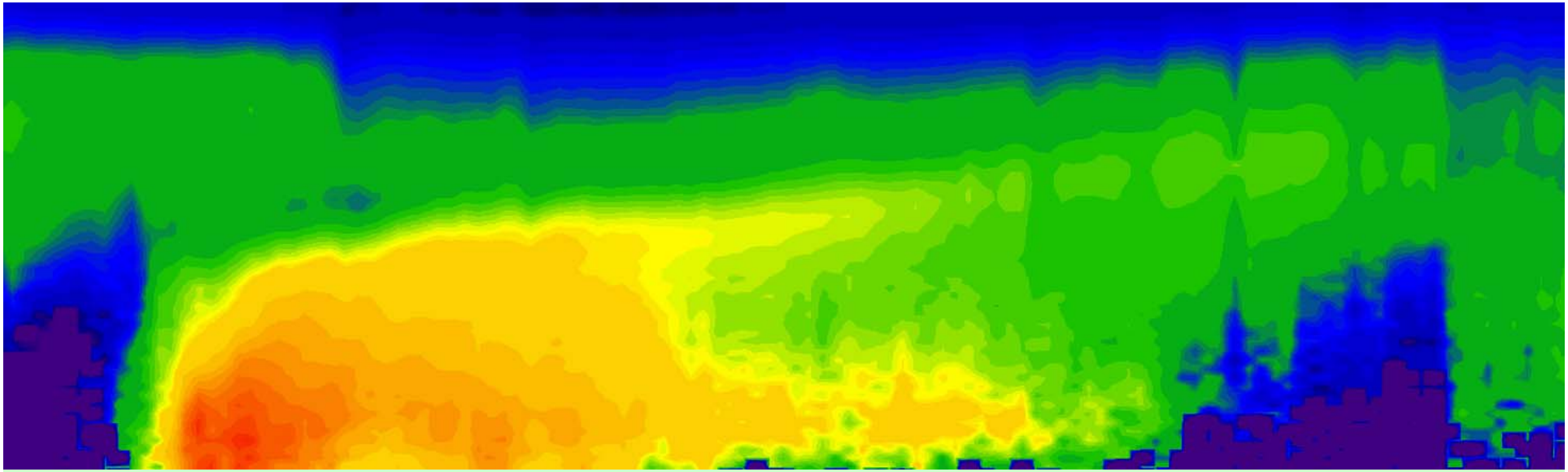

Recent progress in quantifying the chemical composition of atmospheric nanoparticles

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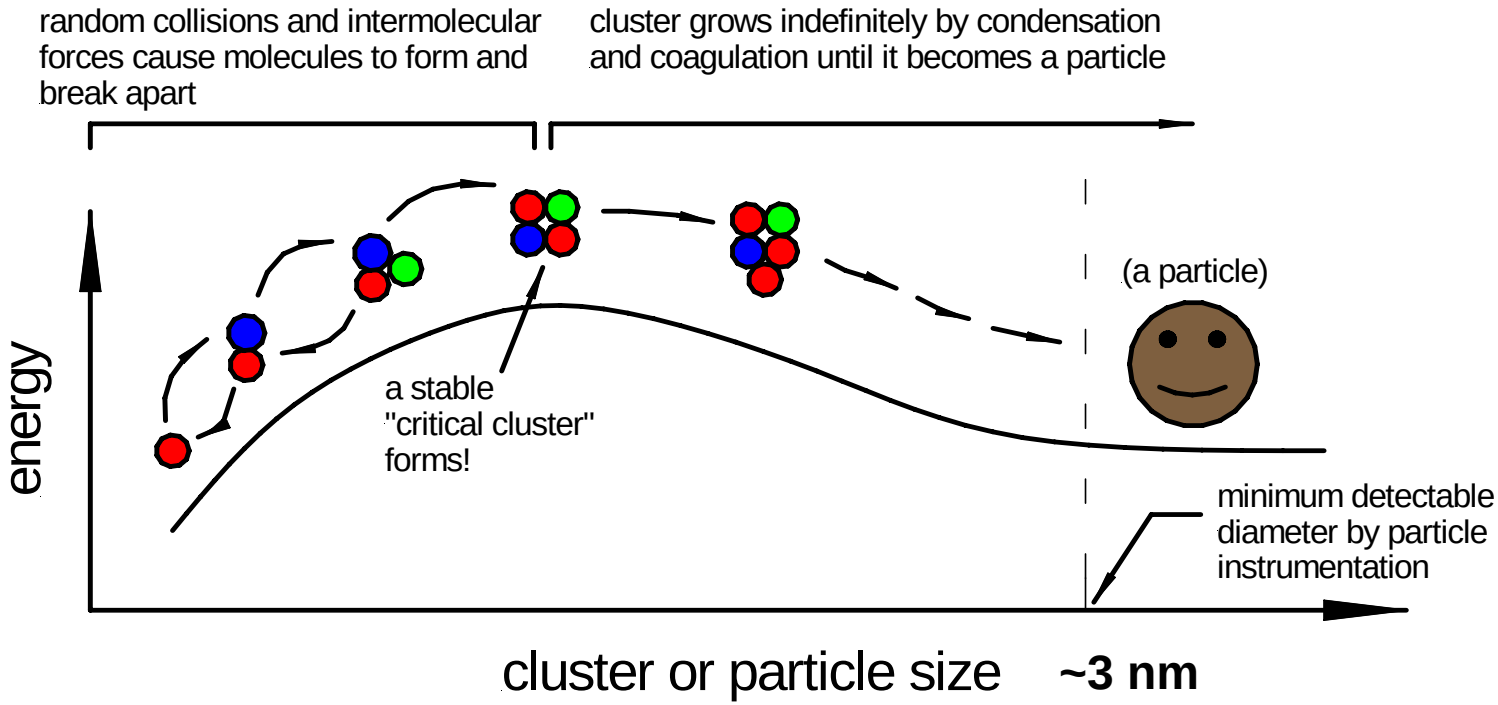
National Science Foundation

NCAR

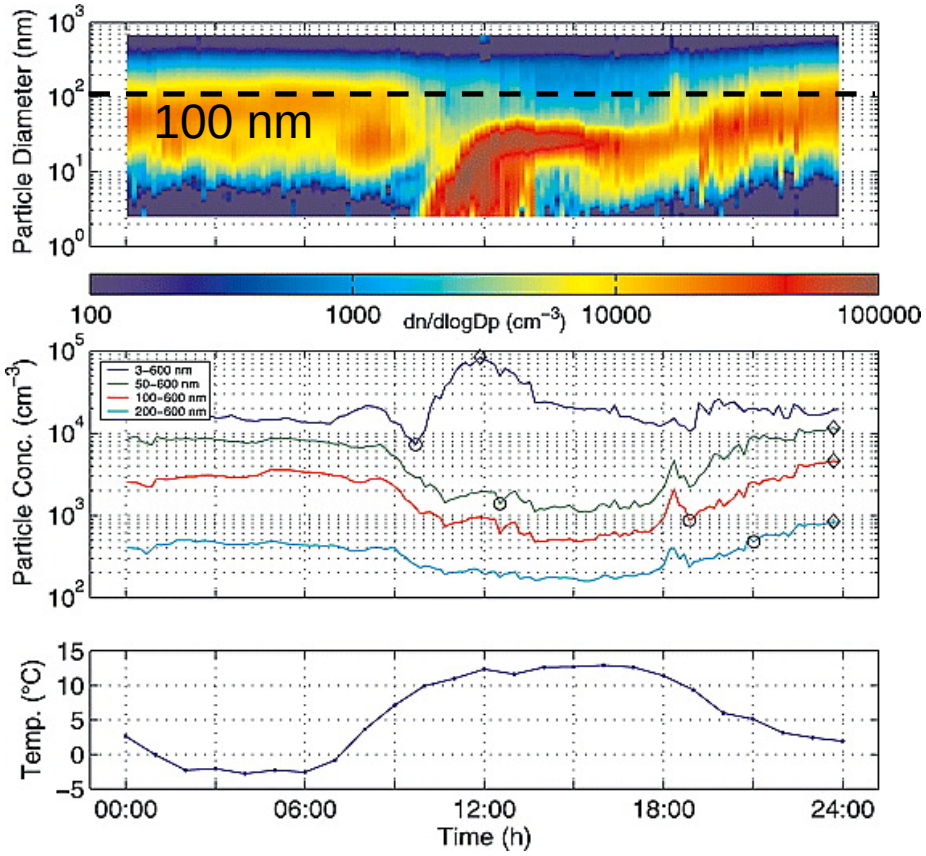
How do nanoparticles form and grow in the atmosphere?

- Nanoparticles form in the atmosphere by condensation to stable clusters formed by nucleation. They can also be emitted directly, e.g., by diesel engines.
- So how are stable clusters formed in the atmosphere?
  - The formation of stable clusters from low vapor pressure atmospheric species is known as **homogeneous nucleation**.
  - **See Jun Zhao's poster this evening to see direct measurements of neutral atmospheric stable clusters!!!**



Atmospheric new particle formation: The atmospheric “banana”

Po Valley in Italy



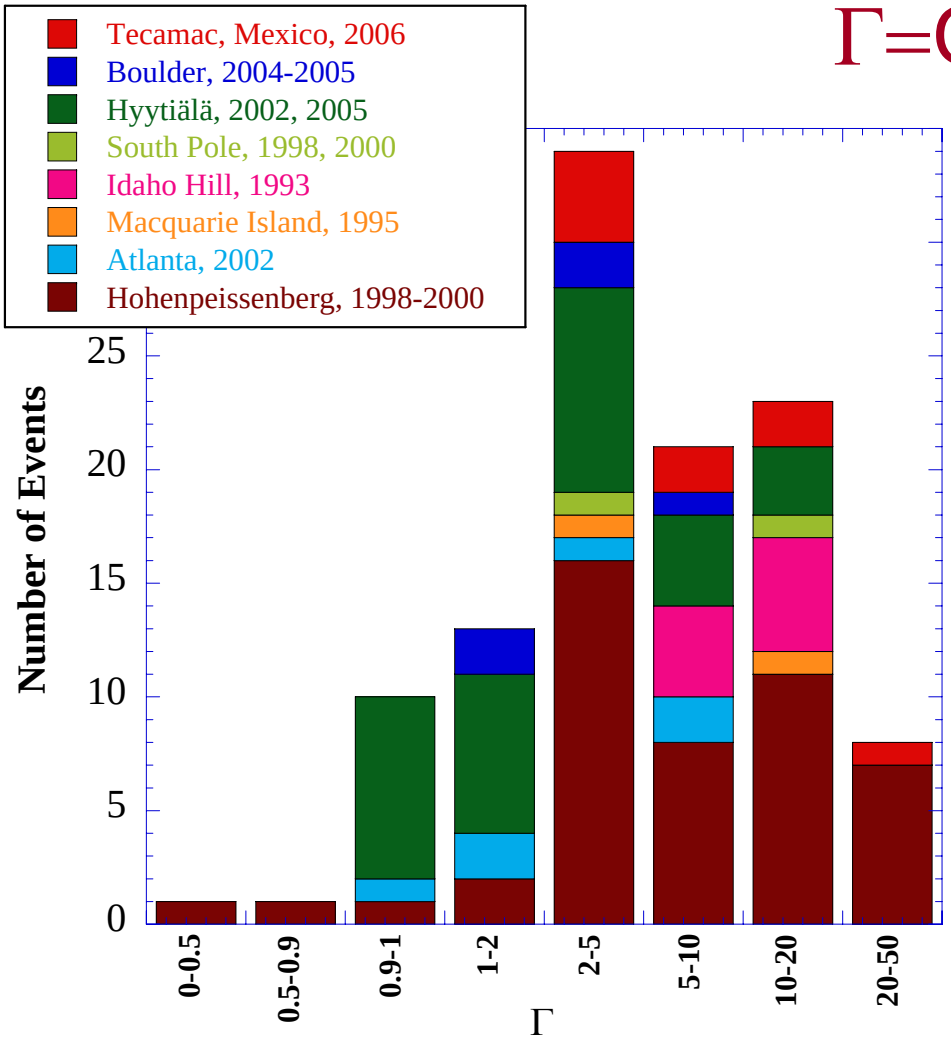
Laaksonen et al., GRL, 2005

Why should we care about new particle formation?

- There are huge uncertainties in predictions of the role of aerosols in climate, especially as related to cloud formation and precipitation.
- Model estimates suggest that new particle formation can contribute up to 40% of the CCN at the boundary layer, and 90% in the remote troposphere (Pierce and Adams, ACP, 2007).
- New particle formation is estimated to add as much as a 8 times more particles to the remote southern ocean atmosphere than anthropogenic primary particles (Spracklen et al., ACP, 2006).

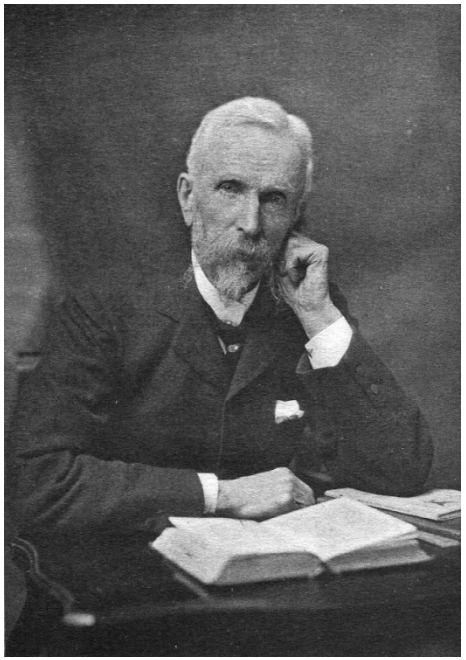
We still don't understand why nanoparticle growth rates are so high … what species, other than sulfuric acid, contribute to this?

$\Gamma = GR/GR_{H2SO4}$



Stolzenburg et al., 2005; Wehner et al, 2005; unpublished, 2009

Measuring the physical and chemical properties of newly formed atmospheric nanoparticles



John Aitken (1839-1919)

"The great difficulty in investigations of this kind is the extremely minute quantities of matter which produce surprising results and make the work full of pitfalls for the hasty."

John Aitken, Proc. R.S.E., 1923

A few words on sample size and sensitivity when analyzing atmospheric nanoparticles

If we sample 10^4 cm^{-3} particles at 10 slpm for 10 min we will collect (ideally):

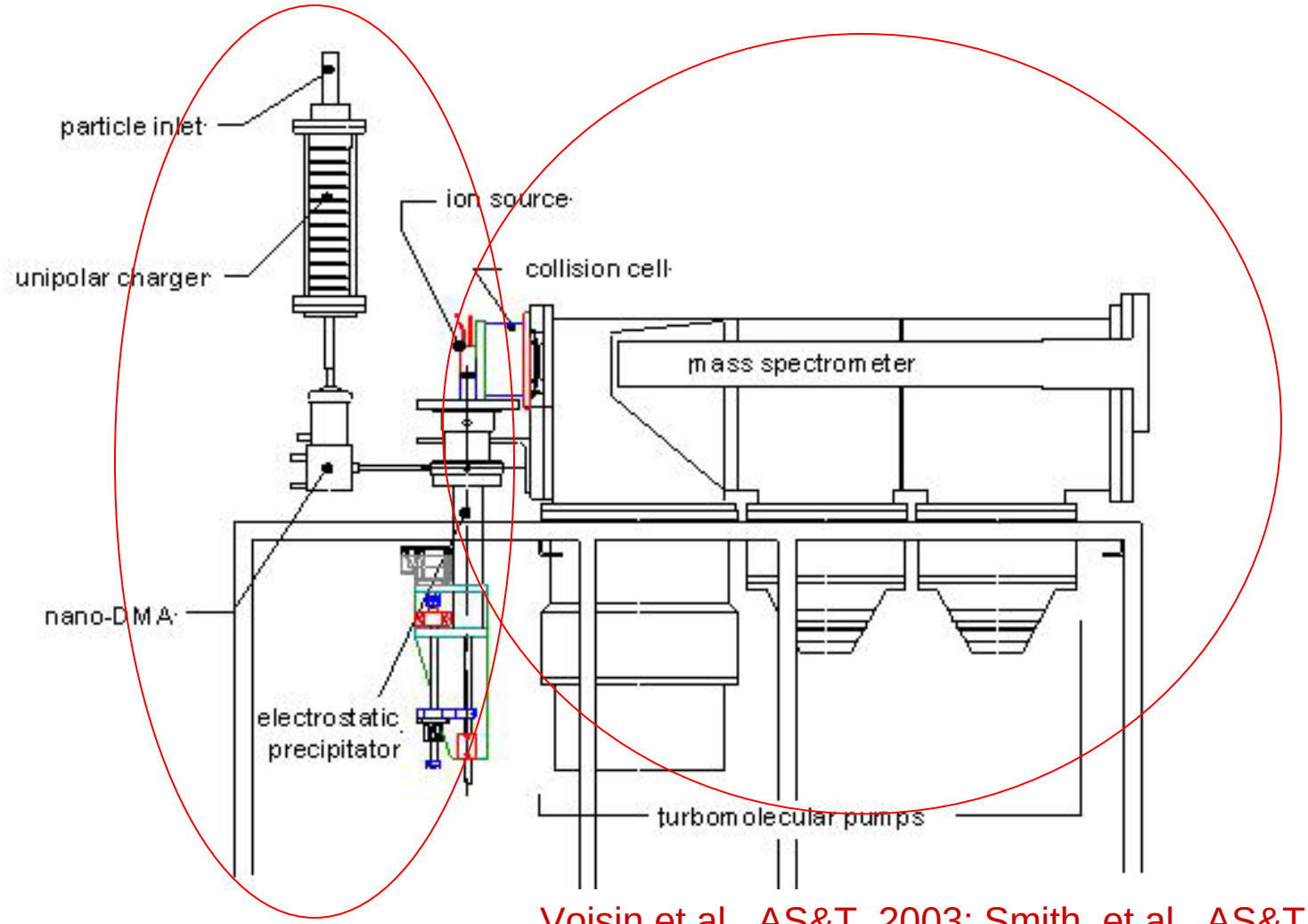
- 13 pg of 5 nm particles
- 100 pg of 10 nm particles
- 800 pg of 20 nm particles

Thus we must be sensitive to ~1 pg of sample

Typical aerosol chemical analysis techniques that are suitable for nanoparticles require about a million times more sample!

Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS)

an instrument for characterizing the chemical composition of ambient particles from **8 to 50 nm** in diameter

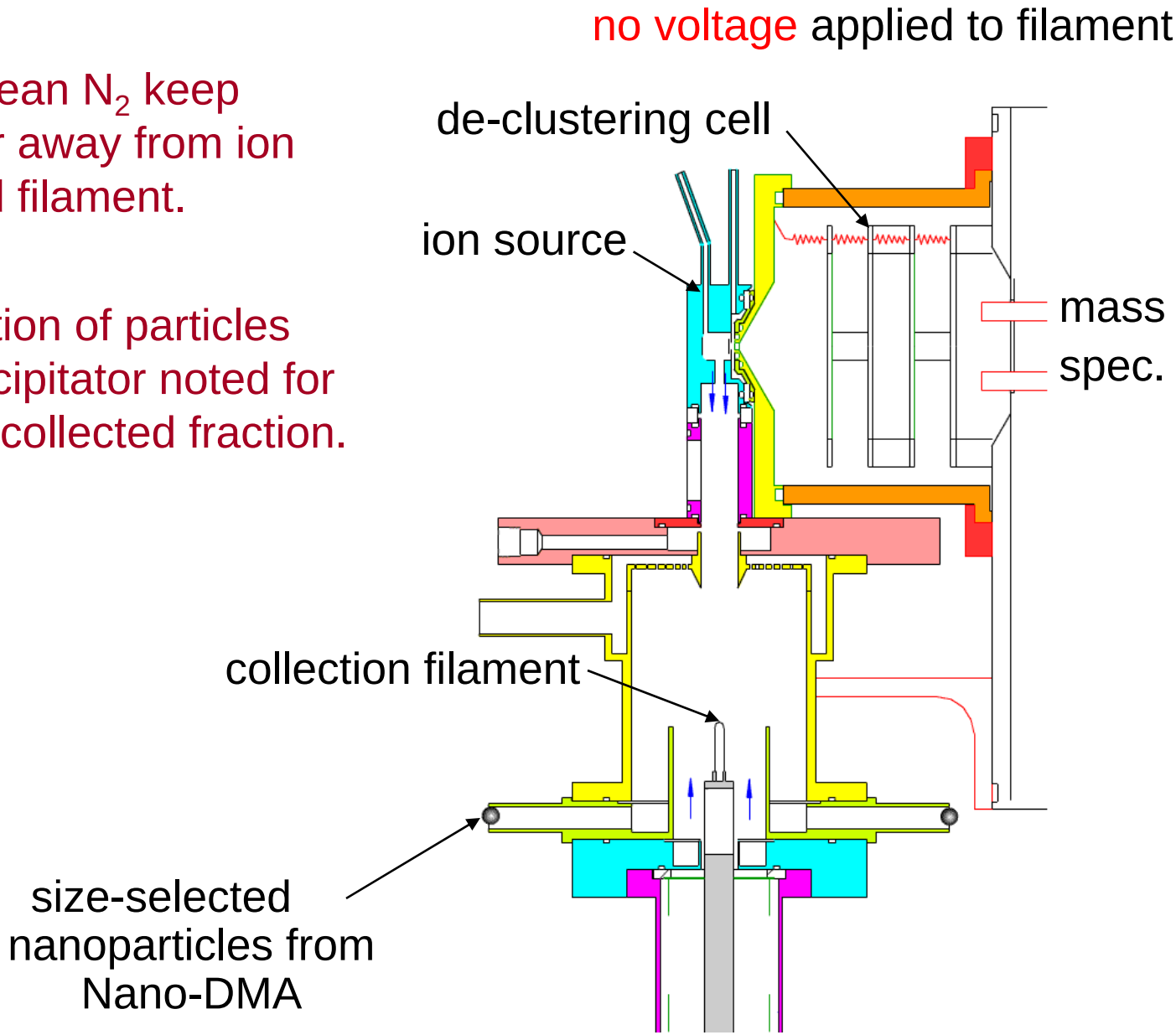


Voisin et al., AS&T, 2003; Smith, et al., AS&T, 2004

TDCIMS electrostatic precipitator

Flows of clean N_2 keep ambient air away from ion source and filament.

Concentration of particles exiting precipitator noted for estimating collected fraction.



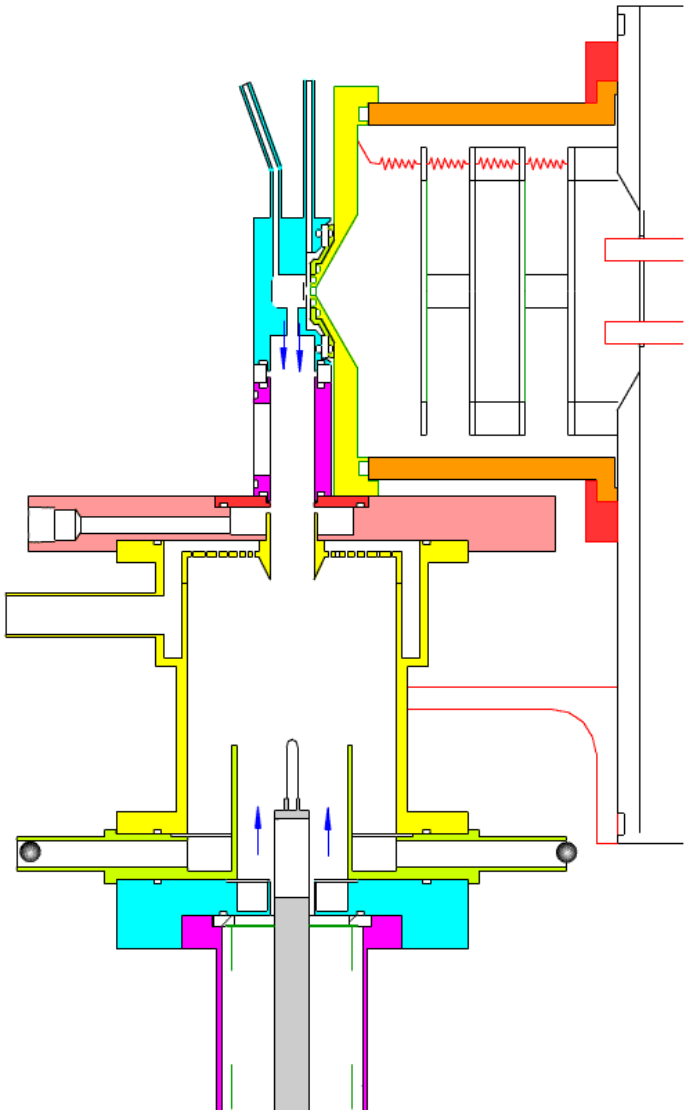
TDCIMS electrostatic precipitator

4000 V applied to filament

Charged particles are attracted to the filament by the electric field.

Collection is done at RT and atm, for ~5 – 15 min in order to collect ~10-100 pg sample.

Concentration of particles exiting precipitator noted for estimating collected fraction.



TDCIMS electrostatic precipitator

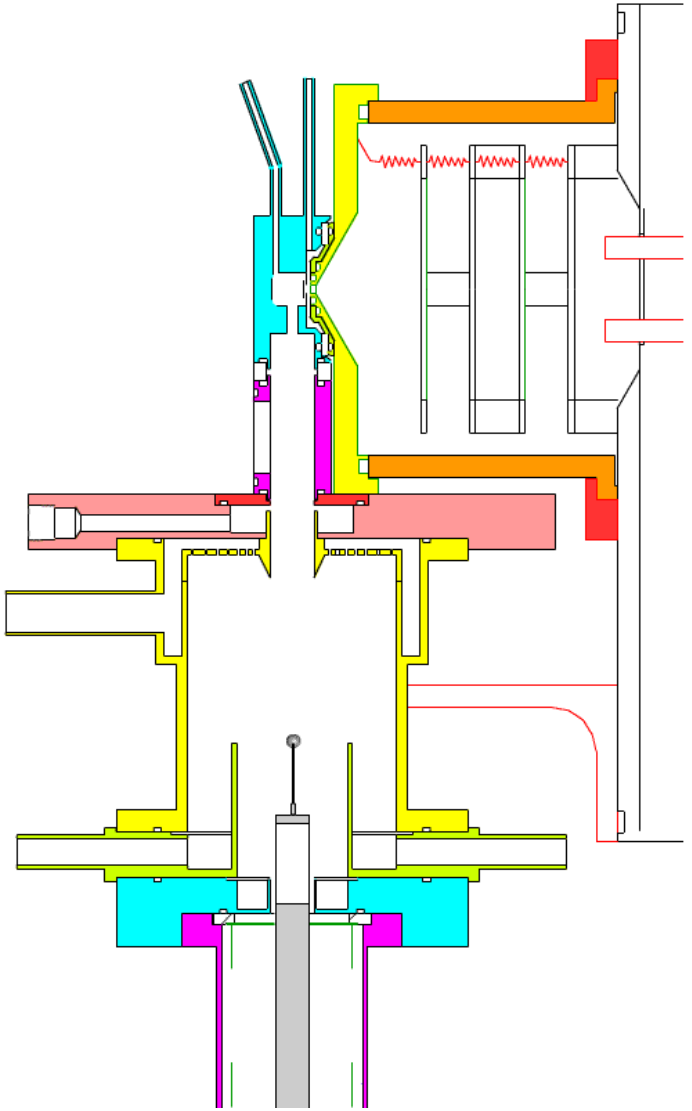
Charged particles are attracted to the filament by the electric field.

Collection is done at RT and atm, for ~5 – 15 min in order to collect ~10-100 pg sample.

Concentration of particles exiting precipitator noted for estimating collected fraction.

collection complete

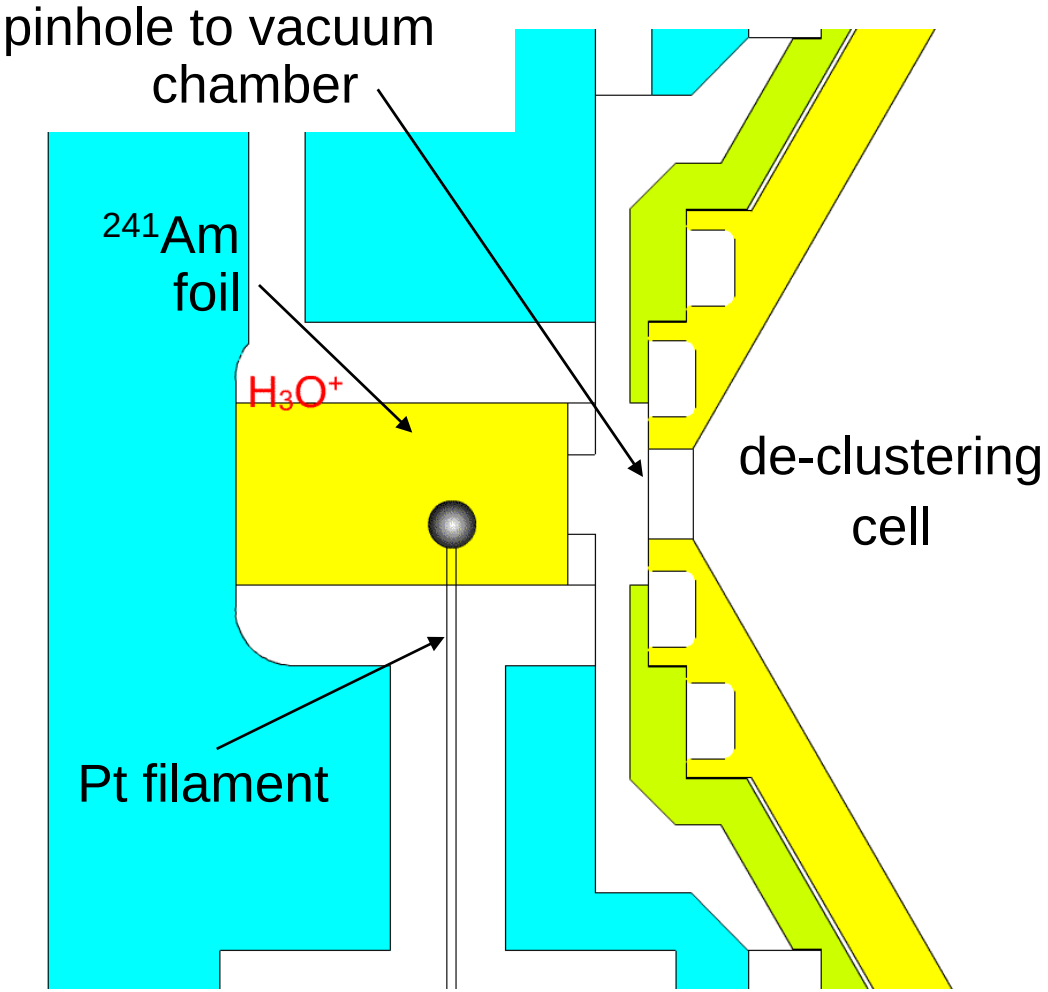
filament moved into ion source



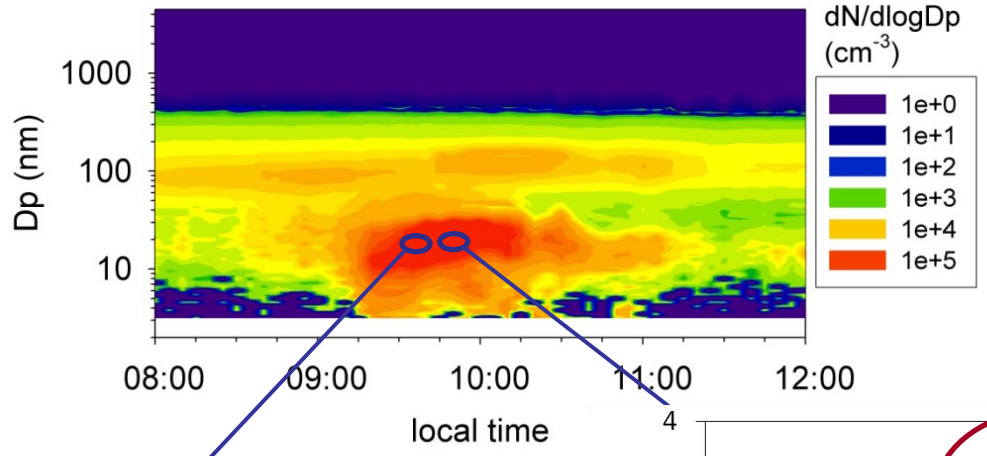
TDCIMS ion source

- Pt wire ramped from room temperature to ~550 °C to desorb sample
- Neutral compounds are ionized using chemical ionization,
  e.g.: $(H_2O)_nH_3O^+ + NH_3 \rightarrow (H_2O)_mNH_4^+ + (H_2O)_{n-m}$
- Reagent ions are created by α particles emitted from the source, generating mostly H_3O^+, O_2^- and NO^-, …
- Ionized analyte injected into a triple quadrupole mass spectrometer for analysis

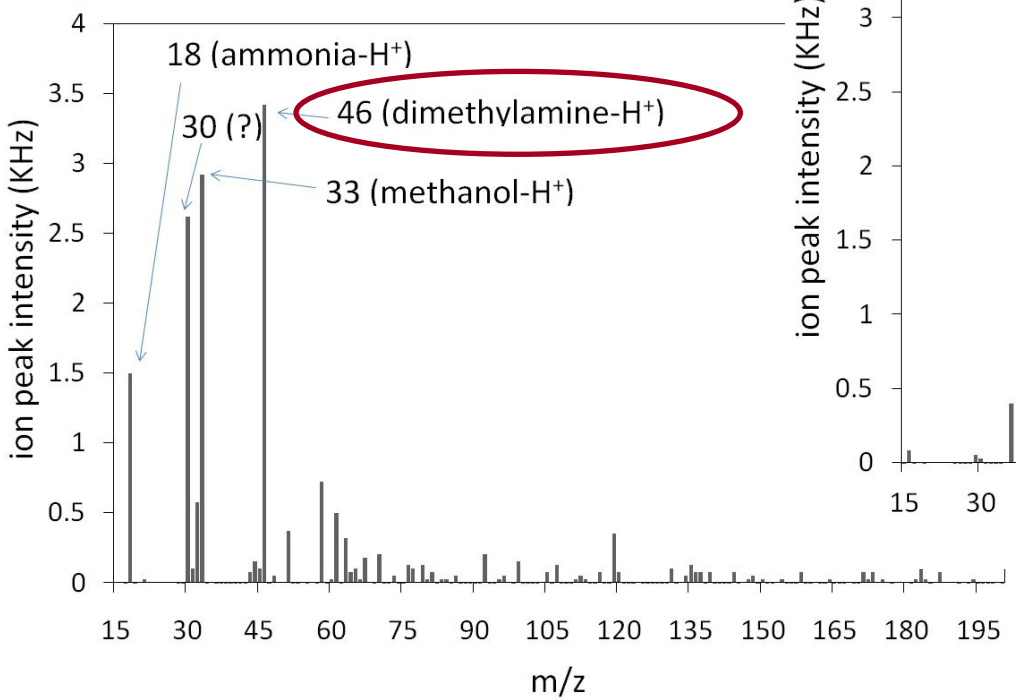
Close-up of ion source during sample desorption



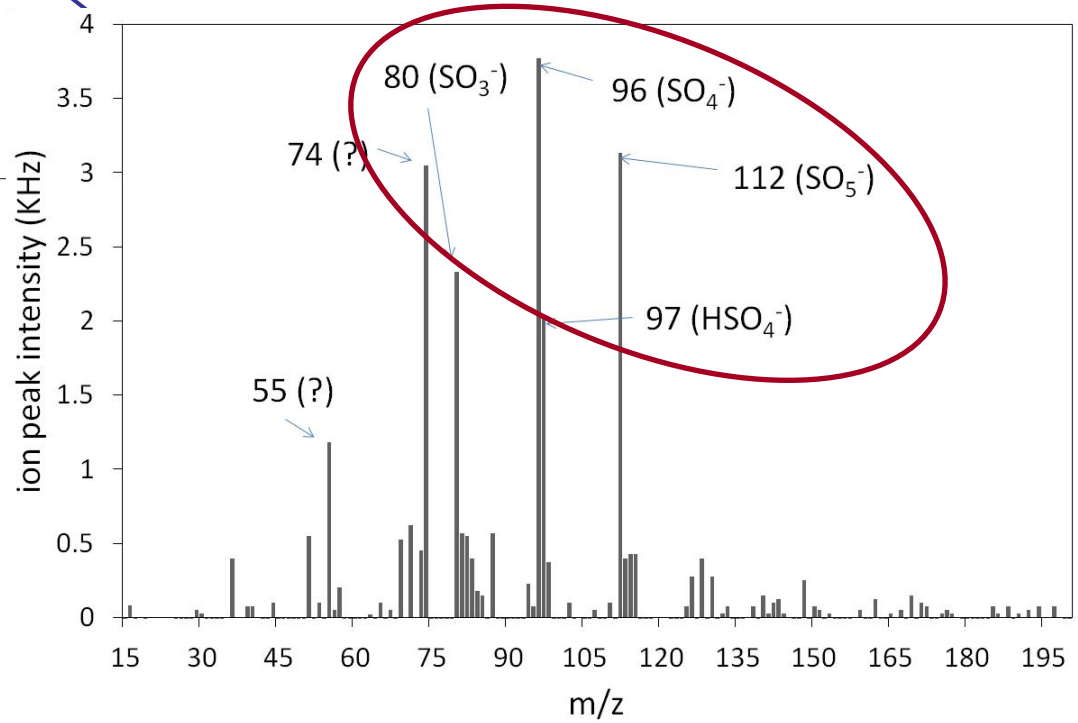
July 25, 2009: Composition of 20nm particles in Atlanta



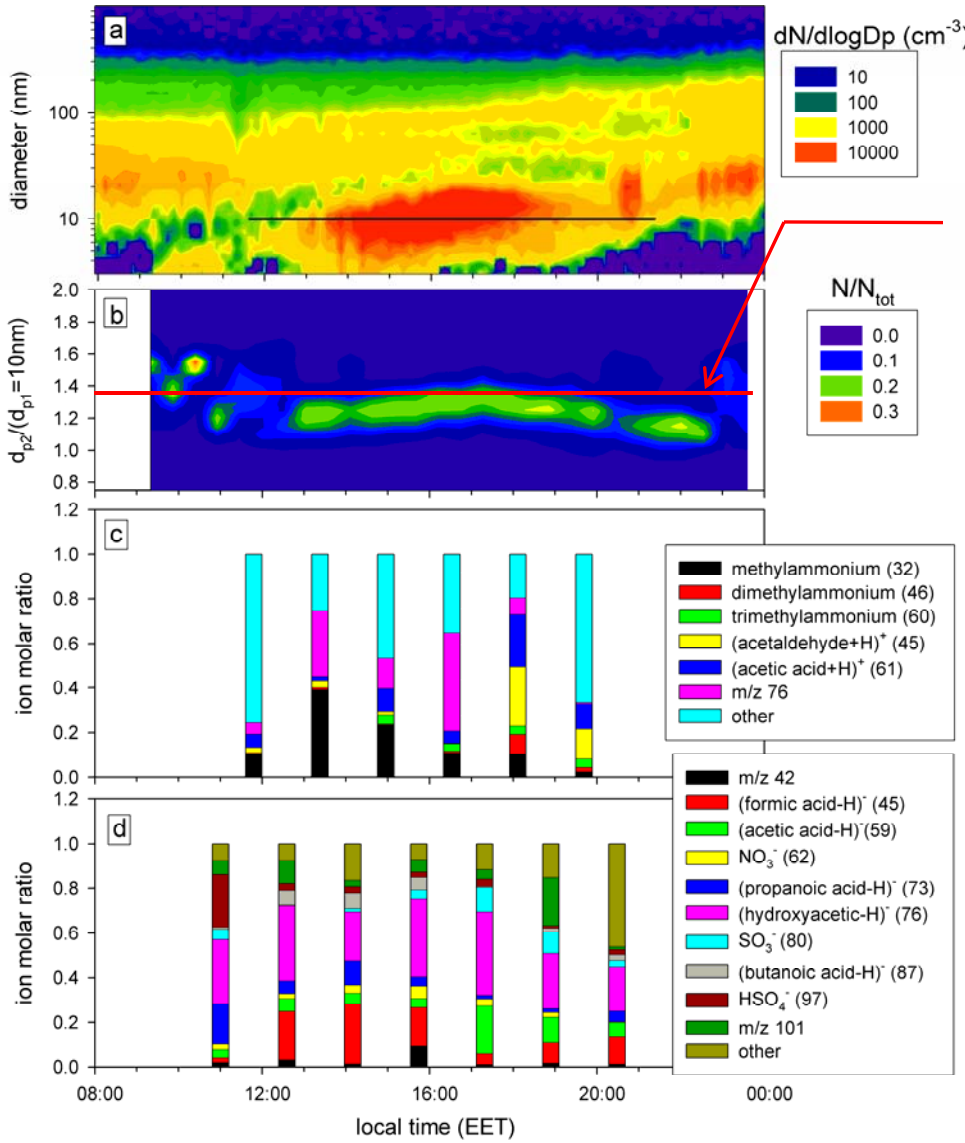
Positive ions



Negative ions



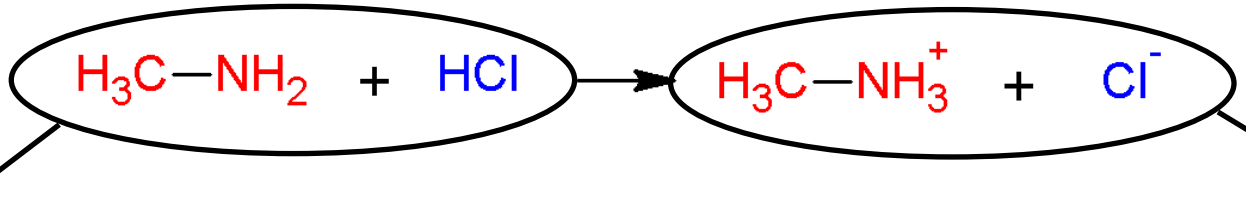
TDCIMS observations at Hyytiälä on 9 April 2007 show aminium ions with deprotonated acids in 10nm particles



GF for 10nm $(NH_4)_2SO_4$

- On average, aminium ions comprise about 23% of positive ion spectrum
- 10 nm particles had an average 90%RH growth factor of 1.27

New particle formation – a simple demonstration



volatile!

non-volatile!

a base (CH_3NH_2)

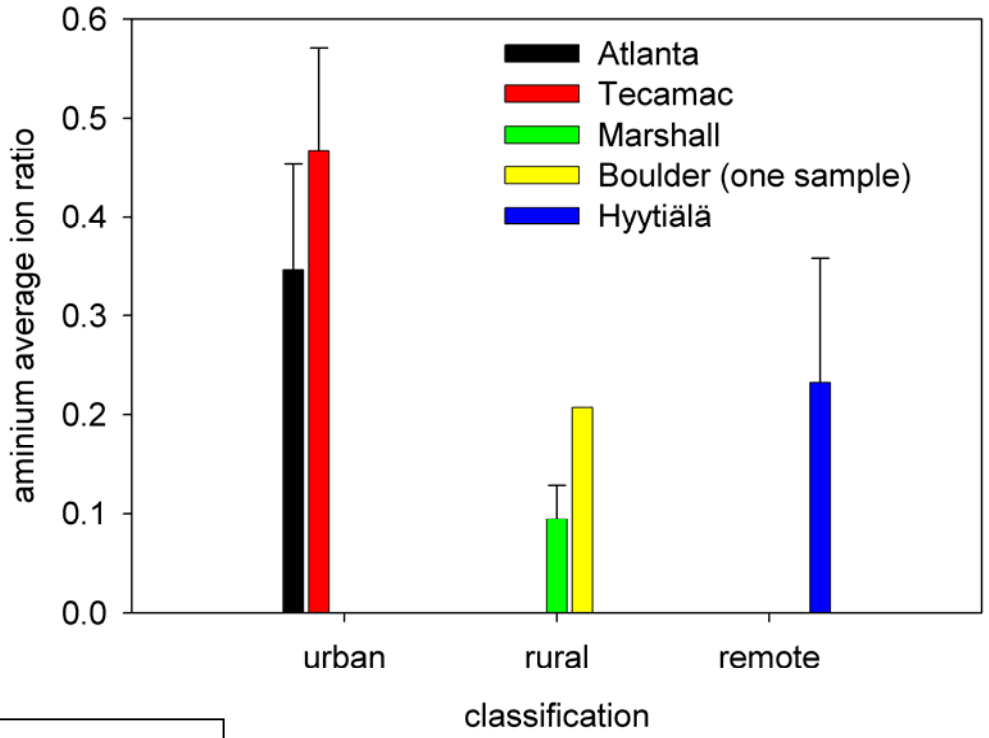
an acid (HCl)

Experiment performed by H. Friedli

Aminium ion ratios suggest that organic and inorganic salt formation may be a universal, and important, growth process

To equate aminium ion ratios from mass spectra to those in particles

- Nanoparticles formed from nucleation are composed of non-refractory oxidized species (thus are quantified by TDCIMS).
- Normalize ratio by non-acid ion peaks in positive ion spectrum.
- TDCIMS has equal sensitivity towards bases, acids, and other oxidized organics.



Aminium salt formation is an important mechanism for nanoparticle growth

Conclusions

- Acid-base chemistry plays an important role in the formation and growth of new particles.
- Amines appear as important compounds in many measurements of newly formed particles.
- The lack of information on atmospheric concentrations and sources of amines limits our ability to predict their impact in new particle formation and growth.

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