Recent progress in quantifying the chemical composition of atmospheric nanoparticles

Jim Smith
Physics Dept @ Univ. Eastern Finland, Kuopio
Atmospheric Chemistry Div. @ National Center for Atmospheric Research, Boulder, CO USA

18 October 2010
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!!!

![Diagram showing the formation of a stable critical cluster and subsequent growth by condensation and coagulation.](image-url)

- Random collisions and intermolecular forces cause molecules to form and break apart.
- Cluster grows indefinitely by condensation and coagulation until it becomes a particle.
- A stable "critical cluster" forms after a certain energy threshold is reached.
- Minimum detectable diameter by particle instrumentation is ~3 nm.
Atmospheric new particle formation: The atmospheric “banana”

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?

\[ \Gamma = \frac{GR}{GR_{H_2SO_4}} \]

Stolzenburg et al., 2005; Wehner et al, 2005; unpublished, 2009
Measuring the physical and chemical properties of newly formed atmospheric nanoparticles

“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 (1839-1919)

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
Flows of clean N₂ keep ambient air away from ion source and filament.

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.
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 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 $\alpha$ particles emitted from the source, generating mostly $H_3O^+$, $O_2^-$ and $NO^-$, …

- Ionized analyte injected into a triple quadrupole mass spectrometer for analysis
July 25, 2009: Composition of 20nm particles in Atlanta

Positive ions

- 18 (ammonia-$H^+$)
- 30 (?)
- 33 (methanol-$H^+$)
- 46 (dimethylamine-$H^+$)

Negative ions

- 55 (?)
- 74 (?)
- 80 (SO$_3^-$)
- 96 (SO$_4^-$)
- 97 (HSO$_4^-$)
- 112 (SO$_5^-$)
TDCIMS observations at Hyytiälä on 9 April 2007 show aminium ions with deprotonated acids in 10nm particles

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

GF for 10nm \((\text{NH}_4)_2\text{SO}_4\)
New particle formation – a simple demonstration

\[ \text{volatile!} \quad \begin{array}{c}
\text{H}_3\text{C}-\text{NH}_2 + \text{HCl} \rightarrow \\
\text{H}_3\text{C}-\text{NH}_3^+ + \text{Cl}^- \\
\text{non-volatile!}
\end{array} \]
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.

Acknowledgements

• University of MN: **Pete McMurry**, Brent Williams, Chongai Kuang
• NCAR: **Fred Eisele**, Jun Zhao, Hans Friedli, Kelley Barsanti
• University of Helsinki: Markku Kulmala, Mikael Ehn
• University of Eastern Finland & FMI: Ari Laaksonen, Kari Lehtinen
• Funding:
  US Department of Energy
  US National Oceanic and Atmospheric Administration
  US National Science Foundation