Recent Progress in Quantifying the Chemical Composition of (Biogenic) Nanoparticles Formed by Nucleation

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Outline

- Overview: What we know about the growth of biogenic nanoparticles and what we need to know
- An overview of measurements of the composition of biogenic nanoparticles
 - Indirect measurements
 - Direct offline measurements
 - Direct online measurements
- Thermal Desorption Chemical Ionization Mass
 Spectrometry
 - Urban studies
 - Recent results from Hyytiälä
- Conclusions, future needs, etc...

New particle formation by biogenic precursors

It's important to understand how particles form and grow in order to understand the impact of new particle formation on chemistry and climate.



How do nanoparticles (Dp < 50 nm) form?

- Nanoparticles form <u>in the atmosphere</u> 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**.
 - Heterogenous nucleation means the formation of liquid or solid embryos onto pre-existing particles (or ions) by condensation of vapors.

random collisions and intermolecular forces cause molecules to form and break apart

cluster grows indefinitely by condensation and coagulation until it becomes a particle



What makes nanoparticles special?

The Kelvin effect means that there are fewer compounds that can condense on nanoparticles than to larger ones. Condensation can be considered as analogous to Kohler theory for cloud droplet activation.

Saturation ratio for pure H₂O droplet



See: "Initial steps of aerosol growth," Kulmala et al., ACP, 2004

So what sorts of compounds have such a low vapor

pressure?



structures from Lim and Ziemann, ES&T, 2005

We DON'T know what compounds cause

nanoparticles to grow (sulfuric acid is not enough!)



Comparison of growth rates with values that would occur if growth were due only to H_2SO_4 condensation for data sets that include measurements of both nanoparticle growth rates and $[H_2SO_4]$.

Properties of nanoparticles that make them difficult

for study

- Difficult to size-separate: need differential mobility analyzer and aerosol charger
- Low mass:
 - difficult to collect enough on filter for lab analysis
 - Online instruments are constantly working at detection limit
- Particle diffusivity:
 - Contributes to low collection efficiency
- Low vapor pressure constituents are difficult to analyze

One approach: Indirectly measure composition using a

Tandem Differential Mobility Analyzer (TDMA)











	Volatility (~100 ℃)	Hygroscopicity
Sulfuric acid	Volatile	Very hygroscopic
Sulfates (Totally or partially neutralized by ammonia)	Non-volatile	Very hygroscopic
Organic carbons	Volatile	Not or only slightly hygroscopic

H. Sakurai, UMN

TDMA measurements of nanoparticle composition in

Atlanta, GA



• Data from Atlanta-ANARChE: 10 nm at 90% RH

Sakurai, et al., JGR, 2006

TDMA measurements of nanoparticles at a coastal site

in Ireland. • Tandem DMA data from Mace Head, Ireland

Mace Head, Ireland



Evidence of hygroscopicity of newly formed particles, made with ultrafine tandem differential mobility analyzers, show particles composed primarily of non- or weakly soluble species.

Experimental approach: Indirect measurements of

composition

- Instrument: Thermal Denuder/ Twin DMPS
 - Ambient size distribution
 - − Size distribution after exposure to 300 °C
- Data from Melpitz, Germany





Measurements show that sulfuric acid condensation explains most of the growth up to 10-20 nm, then organics play a role.

Experimental approach: Indirect measurements of

composition

- Instrument: pulse height analysis CPC
- Data from Hyytiälä

- Growth curves are synthesized from diameter spectra for each particle type.
- Observed spectrum looks more like pinic/pinonic acid than (NH₄)₂SO₄



DMA/pulse height analysis

O'Dowd et al., Nature, 2002

laboratory analysis • Data from Hyytiälä



Makela et al., Tellus B, 2001

analysis Aerodyne Aerosol Mass Spectrometer



When CH_2I_2 and O_3 were mixed and illuminated with UV radiation, rapid homogeneous nucleation was observed down to the lowest concentrations achievable in the chamber (0.015 ppb)

analysis AMS measurements at Hyytiälä during QUEST 2



Allan et al., ACP, 2006

analysis • Instrument: NanoAerosol Mass Spectrometer (NAMS)

Instrument for determining aerosol elemental composition



analysis • α -Pinene + $O_3 \rightarrow$ Secondary Organic Aerosol



Early stage of particle growth is not simply gas phase product condensation:

Pinonaldehyde:C/O = 5.0Pinic acid:C/O = 2.25Secondary ozonide:C/O = 4.0 or3.8

Fresh aerosol is highly oxygenated. Polarity likely decreases with increasing particle size.

Low C:O ratios may arise from "undetected" (by PIAMS) highly polar compounds or from co-condensation of small molecules such as H_2O .

Similar C:O ratios are observed for other monoterpene precursors.

Tolocka et al., ES&T (2006) 40, 1843-1848

Courtesy: M. Johnston

analysis • Thermal Desorption Chemical Ionization Mass Spectrometer



Recent measurements: MILAGRO

• TDCIMS measurements of 8-10 nm particles during March 21-22 2006



Recent measurements: MILAGRO

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TDCIMS measurements of NH₄+ in **20 nm** particles during 23 March



Recent measurements: MILAGRO

• TDCIMS 8 – 30 nm "mode following" experiment during 16 March 2006



ion abundance/pg

Sulfur compounds



note: 3x the scale of other plots "Organics" Nitrate (62 amu) 300 28 amu 800 ion abundance/pg 42 amu 59 amu 200 75 amu 400 100 0 0 20:00 18:00 19:00 21:00 20:00 21:00 18:00 19:00 time (UTC) time (UTC)

Early measurements: Boulder, CO

• TDCIMS measurements of sub-20 nm composition



Smith et al., AS&T, 2005

Octanoic acid sampled with TDCIMS

TDCIMS peaks for 10⁻¹⁵ g octanoic acid (144 amu), applied directly on filament



Pinic acid sampled with TDCIMS

TDCIMS mass spectrum of pinic acid, applied directly on filament



TDCIMS measurements in Hyytiälä on 1 April 2007



TDCIMS measurements show amines in 10 nm particles



TDCIMS positive ion mass spectra (low resolution) from 1 April 2007

Organic acids and other goodies in 10 nm particles at Hyytiälä



 $(H_2O)_2O_2^-$ (68, reagent ion) organic acids: formic acid (45) formic acid dimer (91), and acetic acid (59 amu).

Organics with nitrogen (78 and 92): Pyrroles, major components of humic material in forests, mildly acidic

Experimental accomplishments/needs:

- One of the most interesting unanswered questions is how nanoparticles grow.
- Past studies of the composition of particles formed by nucleation have benefited by the variety of approaches.
- Recent advances in "bridging the gap" by lowering the size range of aerosol
 instruments and raising the m/z of molecular approaches will play a crucial role in
 future research.
- Elemental composition instruments show great promise.
- We need more measurements in a greater variety of locales and longer term measurements.

TDCIMS:

• From MILAGRO ...

Ammonium and protonated amines usually dominate positive ion composition for the smallest particles.

Negative ion spectra are a rich variety of nitrate, sulfate and organic compounds. Nitrate often dominates spectra for the smallest particles (regional affect?).

• From Hyytiälä ...

Protonated amines, organic acids, and nitrogen-containing compounds usually dominate positive and negative ion spectra for the smallest particles. Suggests importance of understanding forest N cycle

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