Applications of Complementary Analytical Techniques to Study Chemical Composition and Properties of Atmospheric Particles

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Aerosol – a mixture of liquid or solid particles suspended in a gas.
Motivation for Aerosol Research:

• Climate Change and Environmental Effects: Aerosol-Cloud interactions, Air Pollution, Haze and Visibility Issues

• Human Health Effects, Industrial and Occupational Hygiene, Impact on Earth’s Ecosystem.

• Scientific Input and Feedback to Environmental Regulations

Fundamental Aerosol Measurements:

• Particle Concentration, Size, Shape, Morphology, Chemical Composition

• Differentiation of Internally vs. Externally Mixed Aerosols

• Physical and Chemical Properties of Aerosols: Optical Properties, Atmospheric Lifetimes and Fate, Phase Transitions, Chemical Reactivity …
Aerosol Research at EMSL

Development and Field Deployment of in-situ aerosol instruments
“Bringing Lab to Field”

Analyses of field collected aerosol samples
“Bringing Field to Lab”
Off-line Analysis of Particles Collected on Substrates in Laboratory and Field Projects

- Field sampling devices

- Laboratory Analysis (EMSL)
  - CCSEM/EDX, ESEM
  - TOF-SIMS

- Laboratory Analysis (ASL)
  - TEM/EDX, EELS, SAED
  - STXM/NEXASF
  - FTIR/Raman Microscopy
  - TOF-SIMS

- EMSL
- Berkeley Lab
Particle Sampling Devices for Field and Laboratory Studies

- Applications of different analysis techniques require different sampling approaches
- An array of sampling devices is used.

MOUDI  DRUM  PILS  TRAC  SAM  TAQ
EMSL Instruments for Characterizing “Microscopic Details” of Aerosol Particles

**Scanning Electron Microscope (SEM)**

- Standard, environmental and computer controlled modes of operation
- Microscopy and EDX analysis of particle elemental composition; studies of particle hygroscopicity; automated analysis of statistically relevant number of individual particles in samples

**Time-of-Flight Secondary Ion Mass Spectrometry (SIMS)**

- Analysis of particle surface composition
- Depth profiling of particle internal structure
  - Mapping of particles and surfaces

**Additional Techniques:** high-resolution TEM, AFM, FIB, … allow additional focused studies
Synchrotron (ALS) based X-ray Microscope

Scanning X-ray Transmission Microscope (STXM)

Absorbance (OD) = \ln \left( \frac{I_0}{I} \right) \approx \mu(E) \cdot \rho \cdot d

Beer’s law
~35 nm spatial resolution

- Micro-Spectroscopy of particle composition; analysis of particle internal molecular and chemical bonding information.
Chemical Analysis of Particle Samples

**Molecular Characterization**

- Molecular-level Understanding of Chemical Changes in Particle Composition
- Reaction Mechanism

**Microscopic Details**

- Detection of Changes in Morphology and Elemental Composition of Individual Particles
- Reaction Kinetics

**Techniques**

- HR-MS with soft, atm. pressure ionization methods
- Micro-FTIR
- TOF-SIMS
- STXM-NEXAFS (ALS/LBNL, MK Gilles et al)
- SEM-EDX
- TEM-EDX/EELS
- DESI/DART HR-MS analysis
- HR-MS with soft, atm. pressure ionization methods
- Ionization methods

**Imaging**

- CCSEM/EDX
- HR TEM
- TOF-SIMS
- STXM/NEXAFS at LBNL (Mary Gilles)
- TEM
- TEM
Chemical Analysis of Particle Samples

- Comprehensive Analysis Using Complementary Analytical Techniques is Needed!

- Systematic Approach from “General” to “In-depth” Analysis to Optimize Collaborative Research Efforts and Cost!
Partitioning of Methanesulfonate and nss-Sulfate in individual Sea Salt particles


Pt. Reyes Field Study (July 2005)

Biogenic DMS $\Rightarrow$ $\text{H}_2\text{SO}_4$, $\text{CH}_3\text{SO}_3\text{H}$ + SeaSalt $\Rightarrow$ Na*$_2$SO$_4$/CH$_3$SO$_3$Na*

Partitioning of CH$_3$SO$_3^-$ and nss-SO$_4^{2-}$ in individual Sea Salt particles is indicative of Sulfur oxidation mechanism in MBL. Data for model validation.
Partitioning of Methanesulfonate and nss-Sulfate in individual Sea Salt particles

Collected samples reveal external mixture of pure Sulfate and mixed SeaSalt/CH$_3$SO$_3^-$/$\text{SO}_4^{2-}$-particles

Single particle characterization qualitatively confirms expected particle composition!
Partitioning of Methanesulfonate and nss-Sulfate in individual Sea Salt particles

**CCSEM/EDX analysis:**

\[
\frac{[S]_{\text{total}}}{[\text{Na}]} = \frac{[\text{ss-SO}_4^{2-}]}{[\text{Na}]} + \frac{[\text{nss-SO}_4^{2-}]}{[\text{Na}]} + \frac{[\text{CH}_3\text{SO}_3^-]}{[\text{Na}]} = 0.06 + \frac{[\text{nss-SO}_4^{2-}]}{[\text{Na}]} + \frac{[\text{CH}_3\text{SO}_3^-]}{[\text{Na}]} \]

**STXM/NEXAFS analysis:**

\[
\frac{[\text{CH}_3\text{SO}_3^-]}{[\text{total-SO}_4^{2-}]} = \frac{[\text{CH}_3\text{SO}_3^-]/[\text{Na}]}{[\text{ss-SO}_4^{2-}]/[\text{Na}]+[\text{nss-SO}_4^{2-}]/[\text{Na}]} = \frac{[\text{CH}_3\text{SO}_3^-]}{[\text{Na}]} \frac{0.06 + \frac{[\text{nss-SO}_4^{2-}]}{[\text{Na}]}}{[\text{Na}]} \]
Partitioning of Methanesulfonate and nss-Sulfate in individual Sea Salt particles

$\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-}$ ratios in sea salt particles plotted for different size bins:
(combined CCSEM/EDX and STXM/NEXAFS data)

- The Results Utilize Combined Data from Three Complementary Techniques!
Particles Containing Zn, Pb, and Cl from an Industrial Region of Mexico City


Particles Containing Zn, Pb, and Cl from an Industrial Region of Mexico City

Source – Night-Time Industrial Activity:

• Concentrations were high over Midnight – 10 am
• Concentrations were low on the holiday and weekends
Particles Containing Zn, Pb, and Cl from an Industrial Region of Mexico City

SEM images of particle morphologies (night time particles)
Particles Containing Zn, Pb, and Cl from an Industrial Region of Mexico City

Particle-Type Classification

Metal Containing Particles Are Most Abundant!
Particles Containing Zn, Pb, and Cl from an Industrial Region of Mexico City

Particle Morphology (SEM - imaging)

A - Zn containing crystal attached to soot

B - Needle-like Zn containing particles

C - Spherical Fe>Zn>Mn containing particle

D - Needle-like particles containing Pb, Zn and Cl

E - Tetrahedral Zn containing particles

F - Spherical Pb rich particles.
Particles Containing Zn, Pb, and Cl from an Industrial Region of Mexico City

- Particles were apportioned to waste incineration

STXM images:

Particle type A - Zn crystals internally mixed with elemental carbon

Particle type B - Needle-like Zn particles.

Corresponding Zn L-edge NEXAFS spectra with standards

Particle type A and Zn(NO₃)₂•6H₂O standard

Particle type B and ZnO standard.
Transformation of Carbonaceous Aerosol in the Outflow from Mexico City


Work in Progress...

MILAGRO 2006, March 22 – a Day of T0→T1→T2 Transport
PIXE analysis

- Particle samples collected by DRUM impactor in 3 stages
  - 6-hour data averages

Teflon substrates

Chemical composition of non-volatile PM$_{2.5}$

Stage C
(0.07 – 0.34 μm)

Stage B
(0.34 – 1.15 μm)

Stage A
(1.15 – 2.5 μm)

PIXE/PESA/STIM analysis done at EMSL, Pacific Northwest National Laboratory (PNNL)
Transformation of Carbonaceous Aerosol in the Outflow from Mexico City

PIXE Data Confirms the Transport Event

DRUM - PIXE Sulfur Mass Concentrations

Sulfur Mass Concentration (µg/m³)

Day of Year

PIXE Data Confirms the Transport Event
Evolution of Particle-type Composition During the Transport Event
(CCSEM/EDX data)

Increase of carbonaceous content
Transformation of Carbonaceous Aerosol in the Outflow from Mexico City

Particle Morphology at T0

SEM/EDX line scan analysis of individual particles

Particles are Coated by Organic Material
Transformation of Carbonaceous Aerosol in the Outflow from Mexico City

Organic Coating is evident for particle samples collected at all three sites!
Transformation of Carbonaceous Aerosol in the Outflow from Mexico City

Molecular Structure of Particles
(Mapping Using Carbon K-edge STXM/NEXAFS Spectral Image)

- optically thick inorganic phase (In)
- Organic/secondary (OC)
- High sp², usually from elemental carbon (EC)
Transformation of Carbonaceous Aerosol in the Outflow from Mexico City

Evolution of Particle Composition (STXM/NEXAFS data)

- Organic/secondary (OC)
- Inorganic coated with OC (InOC)
- Elemental carbon coated with OC (ECOC)
- Mixed EC/In coated with OC (InECOC)
Transformation of Carbonaceous Aerosol in the Outflow from Mexico City

Evolution of Particle Composition
(STXM/NEXAFS data)

T0 → T1 → T2

- Organic/secondary (OC)
- Inorganic coated with OC (InOC)
- Elemental carbon coated with OC (ECOC)
- Mixed EC/In coated with OC (InECOC)
Transformation of Carbonaceous Aerosol in the Outflow from Mexico City

SUMMARY OF FINDINGS:

- Rapid coating of particles with organic material
- Remarkably more organics in T1 and T2 samples
- The fraction of sp² carbon decreases in aged particles – Growth of organic coating
- Consistent with reported increase in specific absorption of ES in aerosol advected T0→T1→T2

(Doran et al, ACP, 8, 1377, 2008)
SUMMARY:

- Complementary Microanalysis Techniques offer a reach set of qualitative and quantitative data on the Chemistry of Atmospheric Particles

- Application of different analysis methods is interdependent: information from one method guides and triggers further measurements