Chemical Imaging Analysis of Environmental Particles

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Purpose

- Fundamental understanding of particle chemistry pertinent to atmospheric and occupational environments
- Develop novel analytical platforms for comprehensive analysis of gas-particle reacting systems

Key Successes

Scientific accomplishments

- Probing internal chemical heterogeneity of mixed organic/inorganic particles during atmospheric hydration-dehydration cycles
- Chemical imaging analysis of soot particles by multi-dimensional characterization
- Study of morphological distribution, 3D structures, and evolution of PAHs in atmospheric secondary organic aerosol (SOA) particles
- Chemical imaging analysis of cross-sectioned fly ash particles to explore internal heterogeneity

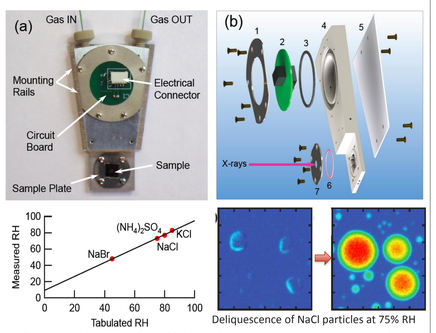
New capabilities

- Micro-reactor for scanning transmission X-ray microscopy/near edge X-ray absorption fine structure spectroscopy (STXM/NEXAFS) beamline at ALS
- New vacuum UV (VUV) ionization module for single-particle mass spectrometer – SPLAT II

Research Accomplishments

I. Electron Microscopy and Soft X-Ray Spectro-Microscopy of Immobilized Particles

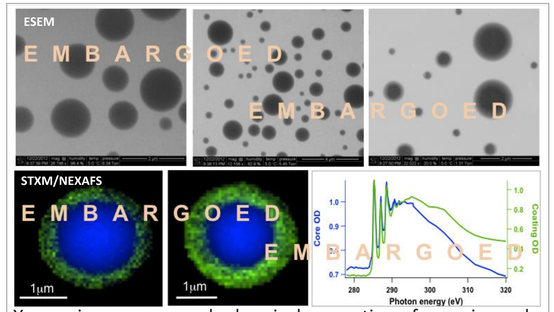
Micro-reactor for chemical imaging of particles at environmental relative humidity (0-95%)



- Compatible with STXM instruments worldwide
- Ongoing efforts to modify the existing reactor for particle-liquid studies

Kelly S et al. 2013. *Rev. Sci. Instr.*, In press.

First detection of concentration gradients within individual liquid particles



X-ray microscopy reveals chemical separation of organics and sulfate inside liquid particles undetected by conventional microscopy

These observations challenge current assumption of homogeneous mixing of water-soluble components in atmospheric particles

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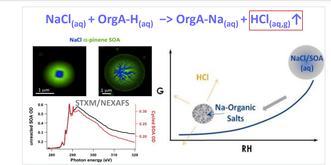
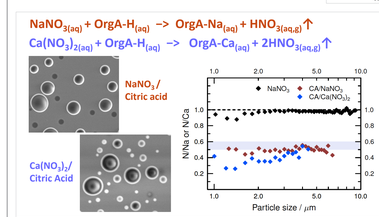
Irreversible changes in chemical composition of atmospheric particles after hydration-dehydration cycles

Hydration/dehydration of mixed sea salt/organic acid particles results in irreversible chemical composition and physicochemical properties changes





Hydration/dehydration of nitrate and carbonate particles mixed with organic acids results in similar chemical composition and properties changes

These observations challenge current assumption of reversible transformations of particle composition during hydration/dehydration cycles

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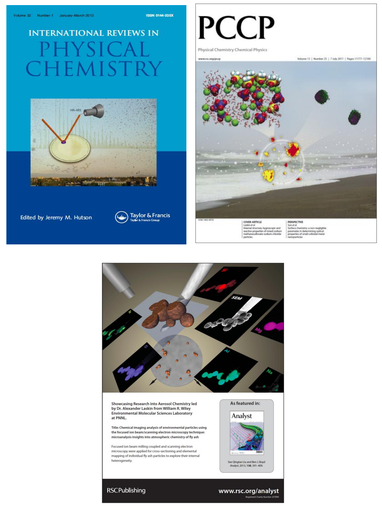
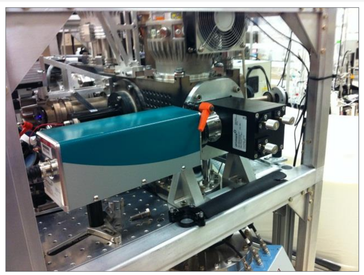


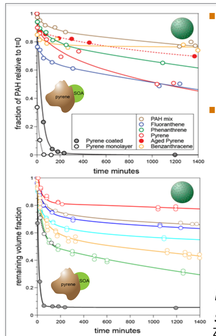
II. Mass Spectrometry of Individual Airborne Particles

Individual particle morphology using IR/VUV depth-profiling approach

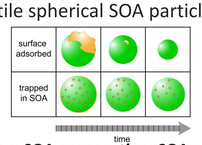


- Brilliant, pulsed VUV module designed, constructed, and incorporated into SPLAT II
- IR laser layer-by-layer evaporation followed by soft VUV ionization yields particle morphology
- IR/VUV mode improves multidimensional characterization of individual particles (composition, size, mass, density, shape, phase, and morphology)

Synergy between SOA and PAHs explains long-range transport (LRT) of toxins



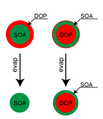
- Characterized the morphology of SOA particles formed in presence of PAHs and PAH-coated after formation
- PAHs acquired during SOA formation are trapped inside viscous, non-volatile spherical SOA particles



PAHs slow SOA evaporation; SOA particles serve as vessels for PAH LRT

Zelenyuk A et al. 2012. *Environmental Science & Technology* 46(22):12459-12466.

- Studied evaporation of dispersed oil particle- (DOP) coated SOA particles and SOA-coated DOP particles
- SOA coating prevents DOP evaporation



Results explain long lifetimes of atmospheric organic compounds such as oleic acid

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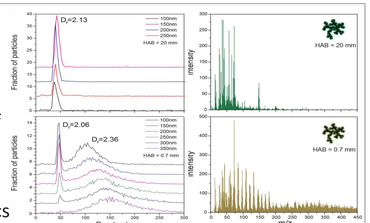
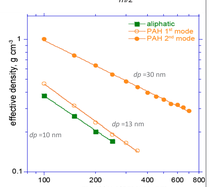
Single-particle analysis of soot

- Detailed characterization of properties of soot particles generated under different combustion regimes
- High T soot: agglomerates of 10-nm primary spherules with 2.13 fractal dimension, made of elemental carbon, coated with aliphatic organics
- Low T produces 2 soot particle types coated with PAHs: comprised of primary spherules 13- and 30-nm diameter and fractal dimensions of 2.08 and 2.36
- Relative fractions of 2 types are size-dependent





Particles generated at different combustion regimes have different composition and morphologies

Rich regions produce smaller primary spherules, lean regions generate fractal agglomerates with larger primary spherules

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Next Steps

- Proposals to DOE-BER, NASA, and NOAA
- Proposal "Combined Laboratory and Field Characterization of Nitrogen-Containing Light-Absorbing Organic Compounds" submitted to NOAA (decision pending)
- Application of developed techniques in engineered nano-particles, toxicology (LDRD opportunities)

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