

**Analysis of the Chemical Composition of Atmospheric and Chamber  
Generated Aerosol Using Mass Spectrometry**

Thesis by  
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*To My Parents*

## Acknowledgements

I remember when I first arrived at Caltech during the visiting weekend for prospective students. I was a very unsure over which graduate school to attend and what to study, but then I met John Seinfeld and Rick Flagan. John and Rick showed me around their labs personally and instilled a great sense of excitement in me for studying aerosols, clouds, and all things atmospheric. I would never have guessed that two huge names in science would be so kind and personable. Ever since that moment, my adventure at Caltech has been an excellent one. There have certainly been high points and low points and a fair amount of stress related to field campaigns, but in the end, I could not have asked for a better experience.

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## Abstract

This thesis presents results demonstrating the use of particulate composition measurements to determine the mechanisms of aerosol formation in both chamber and field studies. Aerosol composition measurements are also used to theoretically estimate the water-uptake behavior and ability to nucleate cloud droplets of atmospheric aerosol; these estimates are compared with in-situ airborne measurements. Common to all studies presented is the use of online aerosol mass spectrometry, a technique with high time resolution and minimal artifacts.

Chemical mechanisms involved in particle formation from the photooxidation of isoprene were explored in chamber studies using both online and offline mass spectrometry. The yield of aerosol and the nature of oligomers formed was found to depend on the  $\text{NO}_x$  concentration. Peroxides were found to be important under low- $\text{NO}_x$  conditions while under high- $\text{NO}_x$  conditions the majority of the particulate mass was found to derive from reaction products of methacrolein.

Particle formation from photooxidation of aliphatic amines was shown to be a feasible route of secondary organic aerosol formation in the atmosphere. Chamber studies at low relative humidity demonstrated that particle formation is primarily the result of acid-base reactions between amines and nitric or sulfuric acid, though diverse oxidized organic compounds are also formed. Thermodynamic calculations show that certain amines can compete with ammonia to form aminium salts at atmospherically relevant concentrations. An airborne field study near a major bovine source in the San Joaquin Valley, CA, gave evidence of particulate amine formation in the atmosphere.



The composition of particulate emissions from ships was studied during a joint shipboard and airborne field project in the Eastern Pacific. Particulate emissions were found to contain significantly higher levels of organic material than accounted for in current inventories. Observed hydrophobic organic material is concentrated in smaller particles and acts to suppress hygroscopic growth and activity of ship-exhaust particles as cloud condensation nuclei.

Ongoing research involves quantifying the impact of reactions within cloud droplets on the organic composition of aerosols. A recently completed field campaign investigated the role of particle chemistry in determining if aerosols can act as ice crystal nuclei.

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