

# **Real Time Detection of Sodium in Size-Segregated Marine Aerosols**

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## **LONG-TERM GOALS**

The goal of this project is to develop a new capability for the chemical characterization of marine aerosols. This involves the development of an instrument to make quantitative, near real-time sodium concentration measurements on individual size-segregated marine aerosols. The development and deployment of a single particle sodium detector would allow us to measure the size distribution of sea salt aerosols in air in a variety of sea states and to verify laboratory-derived relationships for the formation of aerosols via sea spray bubble bursting mechanisms. This information will provide a basis for relating the abundance of sea salt aerosols to remotely observable parameters reflecting the physical state of the atmosphere and surface ocean. It will also provide insight into the influence of sea salt-derived particles on the optical properties of the marine aerosol and a better understanding of how sea salt aerosols affect aerosol growth and nucleation in the marine boundary layer.

## **OBJECTIVES**

Our objective was to determine the feasibility of coupling aerosol detection and sizing instrumentation with a highly sensitive spectroscopic sodium detector utilizing laser induced fluorescence. This would allow the simultaneous quantitative determination of aerosol size and sodium content.

## **APPROACH**

For our initial feasibility study, we built a laboratory-based aerosol sodium detector (ASD). The performance characteristics of the ASD have been studied using well-characterized, synthetic aerosols to determine its sodium detection limits and response linearity.

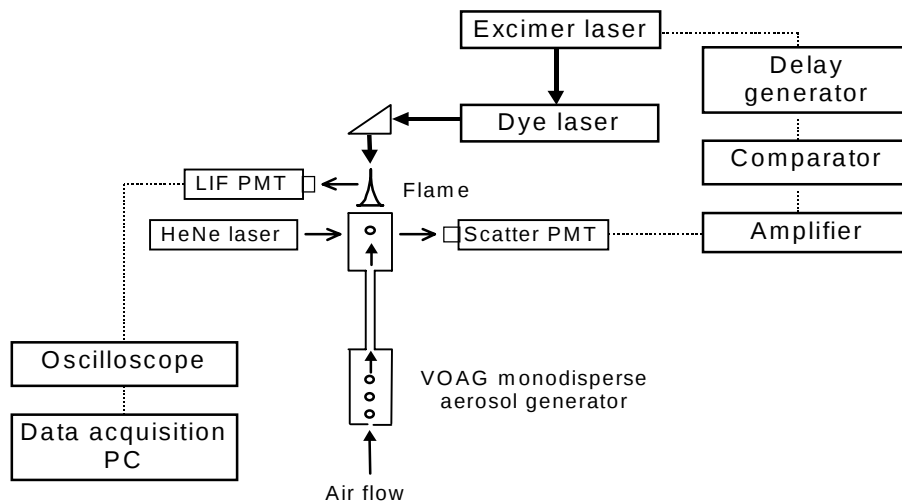
The Principle Investigator for the project is Dr. Eric Saltzman. He provides overall guidance for the project and is also responsible for the design and development of data acquisition/analysis software. Dr. Tony Hynes is co-Principle Investigator. He is primarily responsible for spectroscopy, flame chemistry, and burner design. Dr. Catherine Clark is the Post-doctoral Associate on the project. She has been involved in all phases of the project and has had the primary responsibility for construction and testing of the instrument. Drs. Dave Covert and Hal Maring are collaborators who have provided assistance on inlet design, particle sizing, and other issues involving aerosol physics.

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## WORK COMPLETED

Thus far, we have accomplished the following tasks:

1. Construction of a prototype ASD – the ASD consists of a vibrating orifice aerosol generator for calibration/testing purposes, a flame for volatilization of aerosol particles and reduction of sodium to the atomic form (Na), excimer/dye lasers and associated optics/electronics for Laser Induced Fluorescence (LIF) sodium detection. LIF detection is triggered by optical detection of a single aerosol, using a HeNe laser, and associated detection electronics. A schematic of the ASD is shown in Figure 1 (below).



**Figure 1. Schematic of the ASD**

2. Detection limit -The detection limit of the instrument was assessed using monodisperse aerosols with an aerodynamic diameter of 1  $\mu\text{m}$ . These particles were detected with a signal-to-noise ratio of approximately 1000:1 (RH=72%). Since previous near-real time field measurements of sodium in aerosols used flame emission (Vonnegut and Neubauer, 1953; Radke and Hobbs, 1969), we compared the response of LIF detection to that from thermal emission. Under the same conditions, LIF is about three orders of magnitude more sensitive than D-line emission at 589 nm.
3. Linearity - The linearity of the LIF detector was investigated using a pneumatic nebulizer to introduce large numbers of NaCl aerosols into the flame. The LIF signal levels off at very high NaCl concentrations due to self-absorption of the fluorescence (Rensberger-Weiland et al., 1993).
4. Influence of particle chemistry on LIF signal - Using the VOAG to generate monodisperse aerosols, we examined LIF as a function of aerodynamic diameter for single NaCl aerosols (0.5 - 2  $\mu\text{m}$ ) and a function of anion for different sodium salts (NaCl, Na<sub>2</sub>SO<sub>4</sub>, NaHSO<sub>4</sub>, NaNO<sub>3</sub>, 50/50 v/v mixture NaCl/NH<sub>4</sub>Cl). The measured sodium LIF signals were independent of the nature of the salt, correlating only with the amount of sodium in a single aerosol (estimated from the diameter, density and molecular weight). LIF signals increased linearly with increasing diameter up to 1.3  $\mu\text{m}$ , and

then leveled off and decreased. This behavior is characteristic of incomplete volatilization of aerosols in the flame due to low flame temperatures, short flame transit times or large aerosols (Alkemade, 1979). This was confirmed by observing scattered light from a HeNe laser directed at the aerosols above the burner, in the flame. We have now switched to a hotter H<sub>2</sub>/air flame, which avoids these problems, with complete volatilization of aerosol particles within 0.5 cm of entering the flame front. We are in the process of repeating these experiments.

5. Preparation for analysis of marine air – We are currently in the process of preparing the system for a mini-“field campaign” to be carried out using ambient marine air. This involved several modifications to the system, including construction of a low pressure flame housing and the development of a new data acquisition/processing system for continuous operation. We have also constructed a new high flow rate, aerosol inlet which is capable of delivering large particles from a roof tower into the laboratory.

## **RESULTS**

The results obtained thus far demonstrate the feasibility of using LIF for the real-time detection of sodium in marine aerosols. The detection limit obtained in laboratory experiments suggests that an LIF-based ASD would have the inherent capability of detecting particles on the order of 0.15 μm diameter. The results also suggest that the ASD should be insensitive to changes in major ion chemistry of the aerosols, and linear over a wide dynamic range. Furthermore, the experiments demonstrated that the LIF instrument can detect sodium more sensitively than one can optically detect aerosols. This suggests that the design of future instruments should incorporate high frequency “continuous” sodium detection, rather than optical triggering.

The results of our work to date have been presented at two meetings this year:

Catherine D. Clark, Tony J. Hynes and Eric S. Saltzman, Real-time Detection of Sodium in Aerosols by Laser Induced Fluorescence, American Geophysical Union Spring Meeting, Boston, MA, May 1998.  
Catherine D. Clark, Robert Richter, Hal Maring, Eric S. Saltzman, David Covert and Anthony J. Hynes, Real-time Chemical Characterization of Individual Size-Segregated Aerosols: Detection of Sodium by Laser Induced Fluorescence, American Institute of Chemical Engineers Annual Meeting, Miami Beach, FL, November 1998.

## **IMPACT/APPLICATIONS**

Our experience with this laboratory prototype instrument suggests that it would be possible to construct a rugged, field deployable ASD, and a preliminary design for such an instrument has been completed. The construction of such an instrument would provide a critical new tool for the characterization of the marine aerosol.

## **TRANSITIONS**

This project has been carried out in collaboration with Dr. Dave Covert (Univ. of Washington), who is an expert in the field deployment of aerosol physics instrumentation. As the ASD technology becomes

more fully developed and packaged as a field instrument, we envision a collaborative effort to incorporate the ASD into a wide range of field missions.

## **RELATED PROJECTS**

None.

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