

Real Time Detection of Sodium in Size-Segregated Marine Aerosols

Anthony J. Hynes
Rosenstiel School of Marine and Atmospheric Science
4600 Rickenbacker Cswy.
Miami, FL 33149
phone (305) 361-4173 fax (305) 361-4689 email ahynes@rsmas.miami.edu

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<http://www.rsmas.miami.edu>

Eric S. Saltzman
Department of Earth System Science
University of California at Irvine
Irvine, CA 92697
phone (949) 824-3936 fax (949) 824-3256 email esaltzma@uci.edu

Grant Number: N00014-99-1-0066:
<http://www.uci.edu>

LONG-TERM GOALS

Our long range goals for this project are to improve our understanding of: 1) the chemistry and physical properties of seasalt aerosols, 2) the relationship between seasalt aerosol properties and the turbulence that generates them, 3) the effect of seasalt aerosols on the propagation of light through the marine atmosphere, and 4) to develop improved relationships between seasalt aerosol production and remotely observable parameters.

OBJECTIVES

The objective of this project is to develop a new capability for the characterization of marine aerosols. Specifically, we propose to develop the capability to make near real-time measurements on the quantitative chemical composition of individual marine aerosol particles of known size. The scientific goal of the work is to investigate the contribution of seasalt to the submicron aerosol mode. We have developed an instrument that has demonstrated this capability for sodium and a prototype has been deployed as part of an ONR-sponsored field campaign (SEAS). The ultimate goal of the project is to develop and deploy a field-ready instrument that could carry out the proposed measurements from land based, shipboard or airborne platforms.

APPROACH

Our approach is to introduce individual aerosols into a hydrogen/air flame and to utilize either laser induced fluorescence or emission to monitor the sodium content of aerosols. We have developed an emission based sodium aerosol detector (ASD) that can quantitatively measure the sodium content of aerosols. The ASD can detect particles that contain more than 1×10^{-14} g of sodium, equivalent to a 150 nm diameter dry sodium chloride particle. Particles can be size-segregated prior to analysis using a differential mobility analyzer. Over the last contract period we focused on a recalibration of the ASD

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and workup of the SEAS data, incorporation of design improvements based on the SEAS deployment into the emission based ASD and experiments on laser induced fluorescence detection of sodium.

WORK COMPLETED

The initial field deployment of the ASD was carried out at Bellows AFB, Oahu, Hawaii as part of the ONR-sponsored Shoreline Environment Aerosol Study (SEAS). Our effort focused on assessing the field reliability and performance of the instrument and its response to ambient marine boundary layer aerosols. Issues addressed during this study included: detection limits, inlet efficiency, coupling of the ASD to particle size /counter, and in-field calibration. As part of the overall workup of the SEAS data set we performed new measurements to gain more consistency and resolve discrepancies between measured and calculated aerosol sizes. This resulted in a new calibration and the SEAS data has been reworked to reflect this. A manuscript based on our measurements and a comparison with the University of Hawaii optical particle counting (OPC) measurements has been submitted to the Journal of Atmospheric and Oceanic Technology for inclusion in a special section on the SEAS experiment. Based on our experience during the SEAS deployment we have redesigned and completely rebuilt the emission-based ASD. We have deployed the redesigned instrument in a laboratory at RSMAS with outside sampling capability. We have also continued to work on the implementation of 10 kHz, laser induced fluorescence detection of the sodium content of laboratory aerosols. We have achieved detection limits below 100 nm (equivalent diameter dry NaCl) and used LIF to sample outside aerosol particles.

RESULTS

One of the significant advantages of the ASD technique is that it is quantitative with high accuracy and precision. One test of this is our ability to generate aerosol particles containing a known mass of sodium chloride, dry the aerosol particles and then measure an aerosol particle diameter that is consistent with that mass. In our last report we showed a figure that required that we use an aerosol density of 1 to get agreement between calculated and measured diameter. We interpreted this as an inability to completely dry our aerosols and get to the dry density of sodium chloride, 2.1. Recent laboratory work has demonstrated that our size measurements were in error and with correct sizing we get excellent agreement between calculated and measured sizes, as shown in Fig 1.

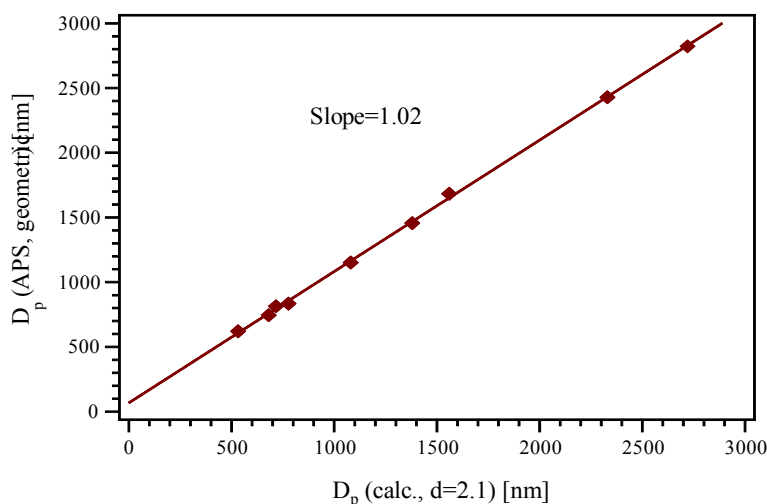


Fig. 1: Correlation between calculated dry sizes for VOAG generated aerosols and the sizes measured with the APS, assuming dry aerosols. The plot shows excellent linearity with a slope of 1.02.

Fig. 2 shows a distribution for a typical sodium mass data set from SEAS. For each time period, all sodium masses were aggregated into one data set and one size distribution generated. The error bars reflect the statistical counting error and the calibration error ($\pm 15\%$). Area and volume distributions were also calculated from the number distribution using average diameters. The observed seasalt number distributions typically peak at 500 nm. The number distributions change with time, reflecting changes in wind speed. In all four cases we measured sub-micrometer sea salt down to the instrument detection limit of 200 nm. Measurements labeled JD118.07 and JD118.3 sampled clean air before the passage of a front over the SEAS site. These ASD distributions are in good agreement with the refractory i.e. sea salt distributions obtained by the OPC. This correlation of OPC refractory particle counts, with the ASD distributions suggests that the amount of internally chemically mixed aerosols was low and that the ASD distributions shown in Fig. 2 represent particles that consist largely of seasalt. It suggests that the heated OPC measurements reliably reflected the sea salt distribution in the absence of significant concentrations of mineral dust aerosols. It further indicated that sulfate aerosol particles were the dominant constituent of the total aerosol distribution in this diameter range during clean air sampling. The distributions labeled JD119.875 and JD120.4 were obtained after the passage of the front.

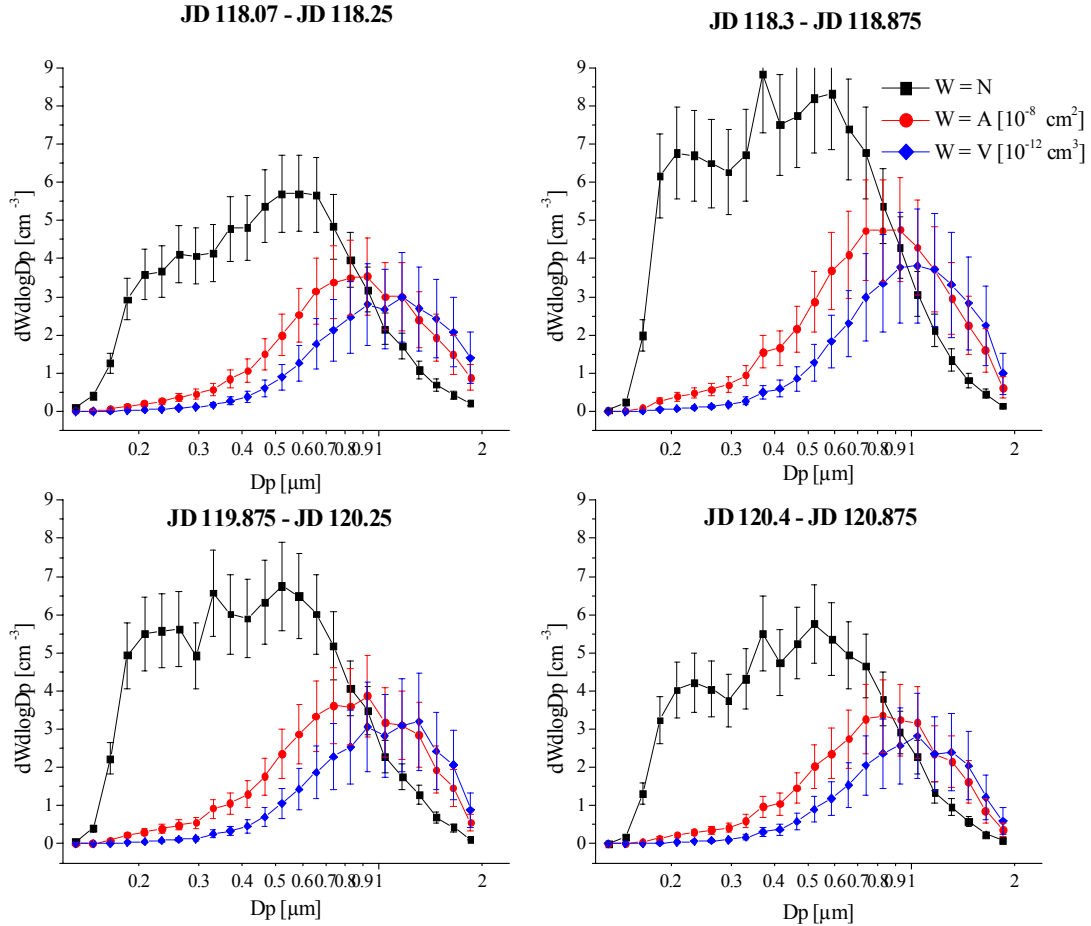


Fig. 2 Averages for $dN/d\log D_p$, $dA/d\log D_p$ and $dV/d\log D_p$ for sodium containing particles during four sampling periods during the SEAS experiment. Particle diameters are equivalent dry sodium diameters based on a density of 2.1.

Fig. 3 shows a comparison of ASD and aerosol volatility/OPC measurement after the passage of a front over the SEAS site at Bellows beach. During this period the ASD counts are lower than the refractory OPC counts. The agreement is particularly poor below 500 nm, when the OPC counted up to 5 times more aerosols at 250 nm. These differences suggest that the two instruments were measuring aerosol particles of different chemical composition. The most obvious explanation is that after the frontal passage the air mass contained a substantial fraction of refractory small particles (possibly mineral dust) that were not composed primarily of sea salt. It is suspected that this refractory material consists of organic compounds. Much of the current database on submicron seasalt has been obtained using the aerosol volatility technique. These results show that volatility is not necessarily a reliable diagnostic for seasalt under all atmospheric conditions.

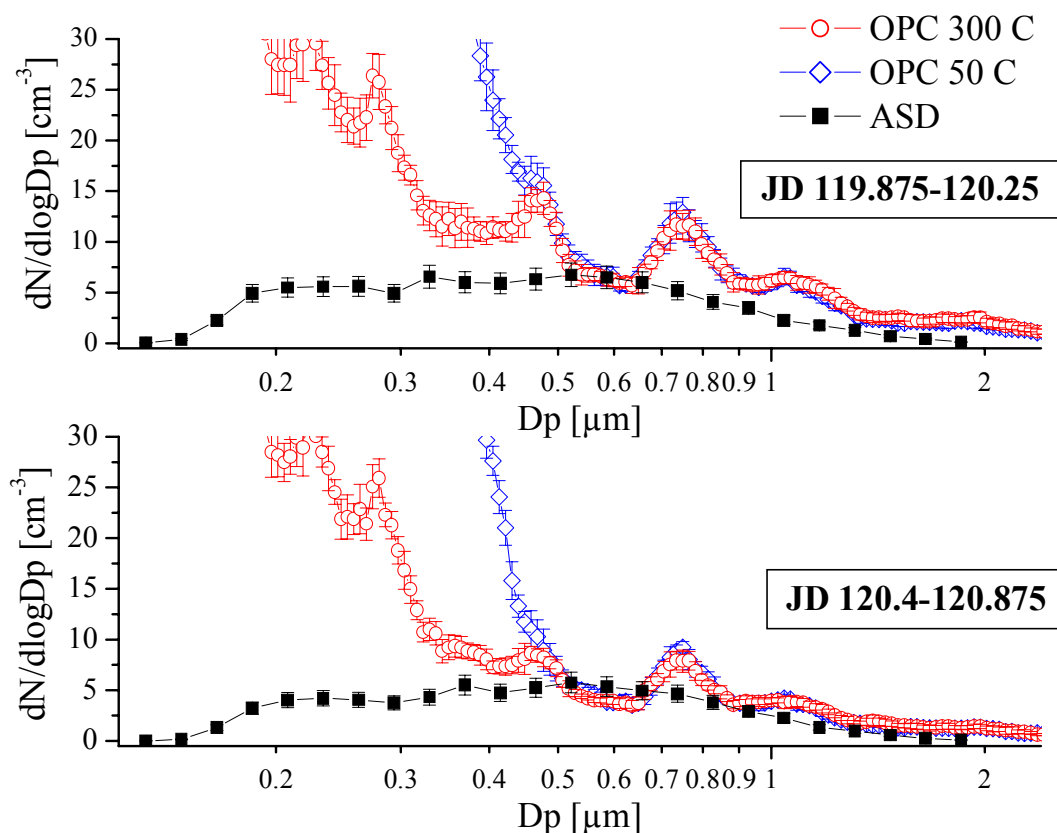


Fig. 3 Comparison of the average ASD size distributions (i.e. equivalent geometric diameter of dry sea salt) with the average of the OPC distributions after the passage of a front over the SEAS site. OPC measurements were taken 2 m below the ASD inlet, after heating the aerosols to 50 and 300 C respectively

During the past year we have reconfigured the ASD and deployed it in our rooftop laboratory at RSMAS. Modifications include increased flame shielding from ambient air, and investigating continuous (rather than triggered) data acquisition, for improved detection limits. We have used high frequency LIF for detection of outside aerosols. Our sensitivity is somewhat higher than the ASD as

currently configured (i.e. with triggered detection), with a limit of detection below 100 nm (equivalent diameter dry NaCl). Our limited set of aerosol particle measurements at RSMAS is consistent with our measurements during the SEAS campaign. We find that all our measurements with either the ASD or high frequency LIF, show the presence of a submicron sodium aerosol fraction, however this is typically a small fraction of the total aerosol number density particularly below 500 nm.

IMPACT

These results show that accurate, high precision quantitative determination of the sodium content of size resolved aerosols is possible using flame emission detection techniques. This technique can act as a benchmark for semiquantitative approaches such as laser ablation / mass spectrometry. The field measurements obtained at SEAS suggest that aerosol volatility alone is not necessarily a specific indicator of the seasalt component of the marine aerosol. The ASD instrument should be deployed under a wide range of environmental conditions to test current assumptions about the distribution of seasalt aerosols, and the interpretation of volatility measurements. These studies should be done in conjunction with qualitative techniques capable of detecting organic carbon and other aerosol components to provide insight into the nature of the refractory aerosol.

PUBLICATIONS

C. D. Clark, P. Campuzano-Jost, D. S. Covert, R. S. Richter, H. Maring, A. J. Hynes, and E. S. Saltzman, Real-Time Measurement of Sodium in Single Aerosol Particles by Flame Emission: Laboratory Characterization, *Journal of Aerosol Science*, vol. 32, 765-778, 2001

P. Campuzano-Jost, C.D. Clark, H. Maring, D. S. Covert, S. Howell, V. Kapustin, A. Clarke, E. S. Saltzman, A. J. Hynes. Near Real Time Measurement of Sea-Salt Aerosol during the SEAS Campaign: Comparison of Emission based Sodium Detection with an Aerosol Volatility Technique. Submitted to the *Journal of Atmospheric and Oceanic Technology*.