PHYSICAL ELECTRONICS
A DIVISION OF ULVAC-PHI

TOF-SIMS Imaging of High Mass Oligomers Localized to Marine Aerosol Particle Surfaces

Overview: Monitoring the emissions of many human activities has become a routine and important process in terms of environmental recovery and regulatory compliance. Of specific concern is the discharge of certain chemicals or metals into the local water supply or other bodies of water. Regulatory compliance is enforced by the collection and analysis of solid, liquid and gaseous effluents. In some cases the monitoring of gas phase emissions involves the collection of particulates, often on or in filters. In this Note we use the PHI *nanoTOF* to visualize low levels of processing chemicals on marine aerosol particles captured on a solid silicon substrate. A characteristic of time-of-flight secondary ion mass spectrometry (TOF-SIMS) is the ability to visualize chemical information at high spatial resolution. TOF-SIMS combines imaging with parallel detection so that the entire mass spectrum is available for chemical identification with high-mass sensitivity. The PHI *nanoTOF* is ideal for environmental chemical imaging applications due to the superior sensitivity and ultimate signal-to-background (S/B) characteristics of it's TRIFT analyzer.

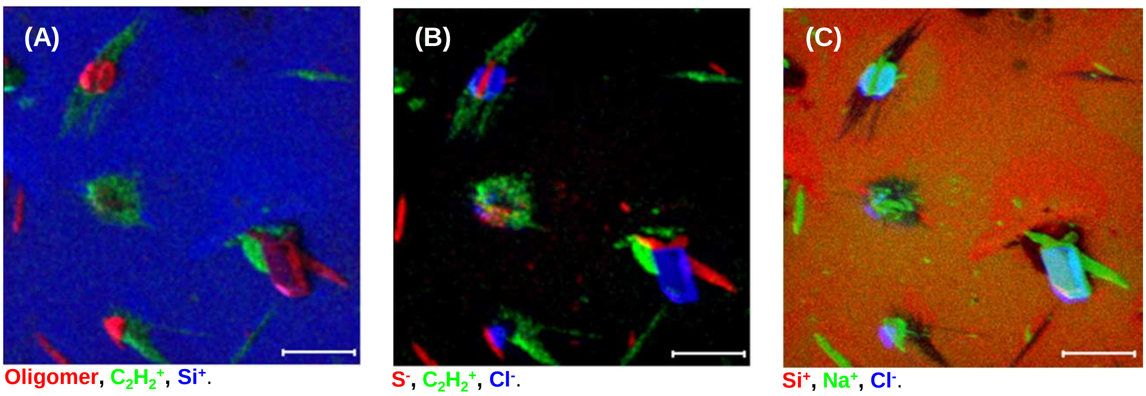

Figure 1. Chemical images of the marine aerosol particles on a silicon substrate. The field-of-view is 50 μm x 50 μm field-of-view (the marker is 10 μm). (A) False-color overlay of the oligomeric components (image sum; red), the $C_2H_2^+$ fragment (26 m/z; green), and the Si^+ substrate (28 m/z; blue). (B) False-color overlay of S^- (32 m/z; red), the $C_2H_2^+$ fragment (26 m/z; green), and Cl^- (28 m/z; blue). (C) False-color overlay of the Si^+ substrate (28 m/z; red), Na^+ (23 m/z; green), and Cl^- (28 m/z; blue). Note that the overlay images are composed of chemical images from each secondary ion polarity and are in perfect registry.

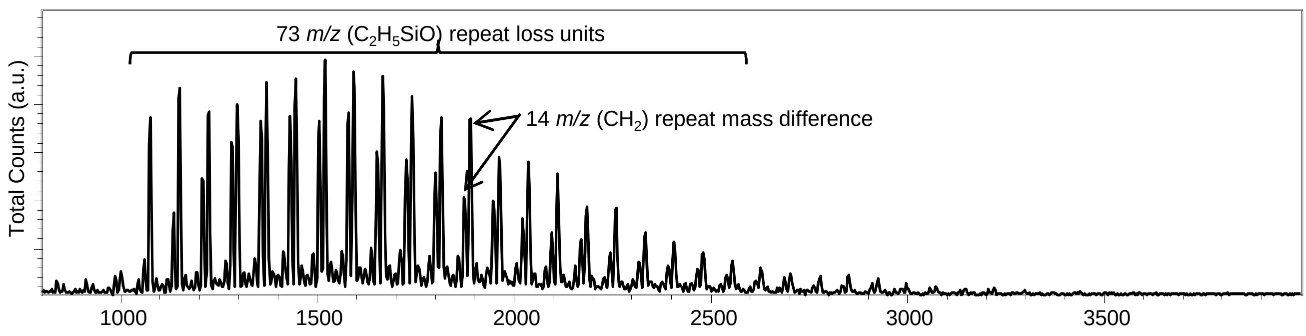

Figure 2. Positive ion polarity mass spectrum of the 800 – 4,000 m/z range. The spectrum reveals an oligomeric distribution that is indicative of a relatively low mass polymer. The 73 m/z interval indicates a repeating loss fragment of C_2H_5SiO which is consistent with a polysiloxane chemistry. A repeating methylene loss (14 m/z) is also observed.

Experimental: The aerosol particles were analyzed in the as-received state. All TOF-SIMS measurements were made on a PHI TRIFT V *nanoTOF*. A 30 keV Au^+ primary ion beam, operating at a DC current of 0.5 nA, was used to acquire chemical images of the particles in both the positive and the negative secondary ion polarities. The primary ion beam was digitally rastered at 256 pixels x 256 pixels over the 50 µm x 50 µm field-of-view, and the primary ion dose was maintained well within the static limit, i.e. < 2.6×10^{12} Au^+/cm^2, for each analysis. A raw data stream file was collected during each analysis to allow full post-acquisition evaluation (i.e. retrospective analysis) of the data.

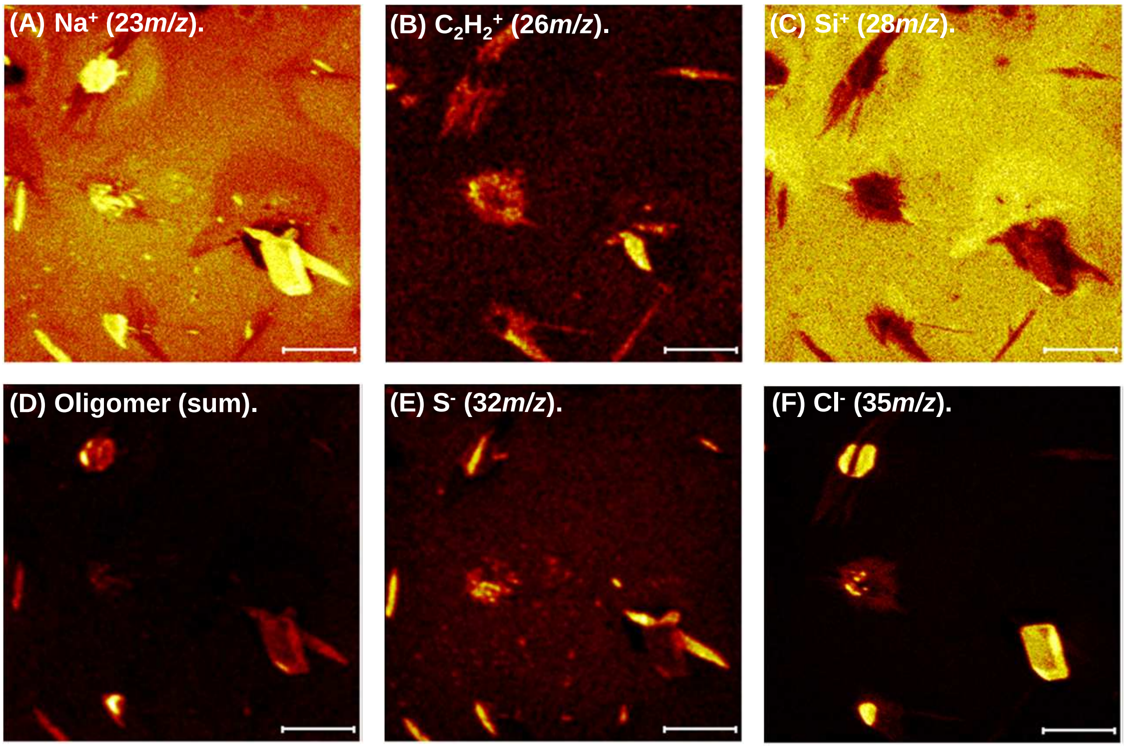

Figure 3. TOF-SIMS chemical images of the marine aerosol particles. Each image was collected, as indicated, in either the positive (+SIMS) or the negative (-SIMS) secondary ion polarity and shows specific elemental or chemical distributions across the surface of the particles observed within a 50 µm x 50 µm field-of-view (the marker is 10 µm). The oligomer image shown in panel (D) is a sum of the peaks in the mass range of approximately 1,000 – 2,500 m/z.

Results: Several elemental, organic fragment and oligomer ion images of the aerosol particles are presented in Figure 1 as false color overlay images. The oligomer, ethylene and silicon components are overlaid in panel A; the sulfur, ethylene and chlorine components are overlaid in panel B; the silicon, sodium and chlorine components are overlaid in panel C. Note that the overlay images are composed of ion images from each secondary ion polarity and are in excellent registry. The overlay images reveal the relative correlation of the organic and inorganic chemistries. The individual ion images of each component are shown in Figure 3. The NaCl crystals ostensibly arise from the marine environment. The particularly interesting features observed in these images include the sulfur-containing fibers and the oligomeric chemistry associated with both the NaCl crystals and the sulfur-containing fibers. It is interesting to note also the features containing the organic $C_2H_2^+$ fragment and that these features are independent of features containing the oligomer. It is beyond the scope of this Note to speculate on the origin of these chemical features.

A positive ion polarity (+SIMS) mass spectrum of the region containing the oligomer distribution is given in Figure 2. The oligomer distribution is centered at approximately 1,700 *m/z* which indicates a relatively low mass polymer; however, it is not known whether there is a distribution at higher mass because the data was only collected to 5,000 *m/z*. The mass spectrum reveals a repeating loss of 73 *m/z* which corresponds to a structure of $(CH_3)(CH_2)SiO$. This repeat unit is consistent with and indicative of a polysiloxane structure. There is also a repeating loss of a methylene group. This observation is also consistent with polysiloxane chemistry because the resulting siloxane ions are able to adopt a resonance-stabilized structure.

Conclusion: TOF-SIMS chemical imaging was conducted with the PHI TRIFT V *nanoTOF* to observe the chemistry of aerosol particles collected in a marine environment. The high sensitivity of the TRIFT analyzer enables the efficient detection of high mass species for chemical imaging, and the parallel detection capability of TOF-SIMS allows full molecular characterization of the matrix chemistry. The inherent qualities of the PHI *nanoTOF* and it's TRIFT analyzer provide chemical visualization without image artifacts, a specific advantage for measurements of rough surfaces and particles.

Physical Electronics USA, 18725 Lake Drive East, Chanhassen, MN 55317
Telephone: 952-828-6200, Website: www.phi.com

ULVAC-PHI, 370 Enzo, Chigasaki City, Kanagawa 253-8522, Japan
Telephone 81-467-85-4220, Website: www.ulvac-phi.co.jp