SEM-EDX Analysis of Atmospheric Aerosols

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Introduction

One of the important environmental issues in upstate New York is the acid rain problem in the Adirondack Mountains, which is associated with atmospheric aerosols. As a part of a systematic study to understand the transport, transformation, and effects of airborne pollutants in the Adirondack Mountains, we are performing an analysis of atmospheric aerosols collected at Piseco Lake. In previous work, we used proton induced X-ray emission (PIXE) spectrometry to measure the concentrations of elements in the aerosol samples as a function of the size of the particulate matter. The results of the PIXE analysis indicate significant concentrations of sulfur in small particles that can travel great distances and may contribute to acid rain.[1] Here we report on the investigation of the small-particle aerosol samples using scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX) to obtain elemental information on individual particles.

SEM-EDX

A scanning electron microscope (SEM) is an instrument that produces a largely magnified image of a sample by scanning it with a focused beam of electrons. In SEM, an electron gun fitted with a tungsten filament cathode and placed at the top the microscope thermionically emits a beam of electrons. The emitted electrons are focused along a vertical path down toward the sample. Shown in Figure 1 is a schematic diagram of the scanning electron microscope. When the electrons strike the sample, they interact with atoms in the sample Secondary electrons are ejected from the K-shell of the atoms in samples by inelastic scattering. These electrons have relatively low energy (< 50 eV) and are emitted within a few nanometers from the sample surface, so they are best for imaging outer surfaces of samples and are usually collected by an Everhart-Thorley detector.

Energy dispersive spectroscopy is a non-destructive method of examining samples for their elemental makeup, using X-ray spectra emitted by bombarding a solid sample with a focused beam of electrons. This process involves an electron interaction with an atom causing the inner shell electron from the atom to be ejected. Then a vacancy is created and will be filled by an electron from a higher electron orbit. To fill this vacancy, the electron with higher order needs to de-excite. During this process, an X-ray will be emitted to conserve energy. Shown in Figure 2 and 3 are schematic diagrams of this process. The energy of this X-ray generated from each element is unique, so we can determine what element the X-ray is emitted from.

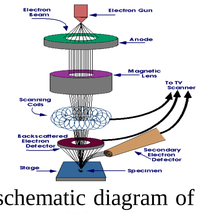

Figure 1: A schematic diagram of the scanning electron microscope.[2]

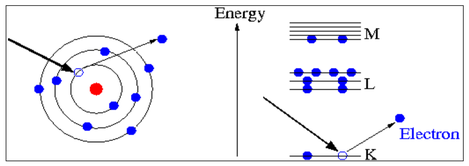

Figure 2: The ejection of an inner shell electron by a electron.

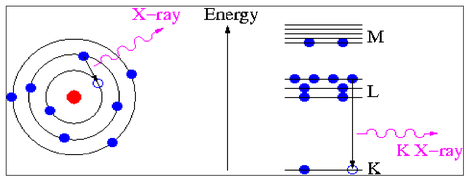

Figure 3: An X-ray is emitted when the void is filled by an outer shell electron.

Sample Collection

A nine-stage cascade impactor was used to collect the aerosols and separate them based on their particle size [2]. Shown in Figure 4 is a schematic and photograph of the impactor. The impactor was attached to a vacuum pump which drew air through the impactor at a rate of 1 L/min for approximately 48 hours. This corresponds to a total of approximately 2.7 m^3 of air that flowed through the impactor. Particles of different aerodynamic diameter ranges were impacted on Kapton foils in each stage. The thin Kapton foils, shown in Figure 5, were removed and used as targets in the PIXE experiments and the SEM-EDX experiements.

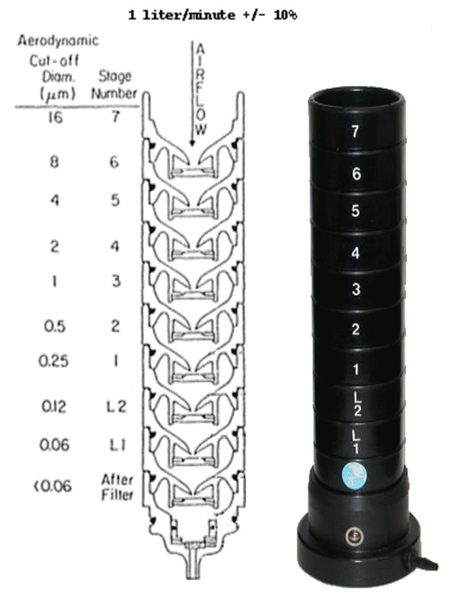

Figure 4: A schematic and photograph of the nine stage cascade impactor [1].

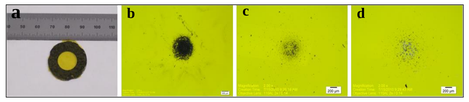

Figure 5: A photograph of an impaction foil (a) and several microscopic images of aerosol deposits (b-d).

Experiment

For this experiment, we used a scanning electron microscope (SEM), shown in Figure 6, to produce images of the sample by scanning it with a focused beam of electrons. The SEM has a Bruker Quantax 200 EDX system with a Peltier-cooled XFlash silicon drift detector for X-rays. The detector has an active area of 10 mm*mm. It has an energy resolution of better than 125 eV at count rates up to 60,000 cps. A photograph of the inside structure of the SEM is shown in Figure 7. As shown in Figure 7, the secondary-electron (SE) detector is located behind and to the left of the electron lens pole piece. Secondary electrons have relatively low energy and are emitted from the upper several nanometers of the material under the electron beam, so the wire cage around the end of the detector is usually set to a positive "bias voltage" of hundreds of volts to collect the secondary electrons even if they exit the sample traveling away from the detector. This also makes the SE detector able to produce images at very low probe currents which has a positive effect on the resolution.

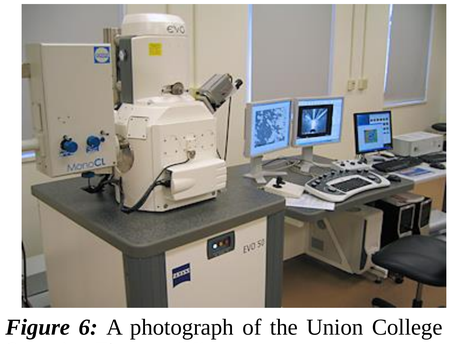

Figure 6: A photograph of the Union College Scanning Electron Microscope.

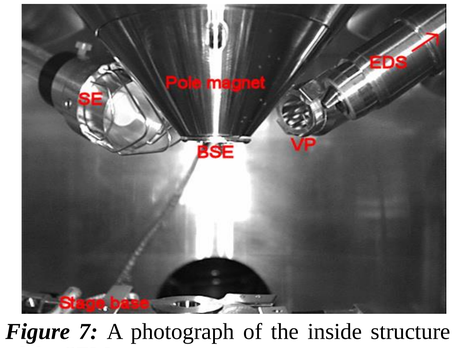

Figure 7: A photograph of the inside structure of the SEM.

Preliminary Results

Shown in Figure 8 is a graph of the measured concentrations in mass per unit area for each element and particle size determined from the PIXE analysis for the samples collected in July of 2012.[1] In the graph, we can see that the sulfur concentration peaks at aerodynamic cutoff diameter between ¼ and 2 μm. To see the morphology of these aerosol particles, we picked six particles each on stage 2 and stage 3 which are particles of PM ½ to 2 and PM 1 to 2 respectively and used SEM-EDX to analyze these particles. Due to the fact that the samples are thin films which can be penetrated easily by high current, we chose to do SEM-EDX imaging with low current. Thus, the heavy elements with high atomic numbers greater than Ca might not be shown in EDX spectrum. Shown in Figure 9-14 are some results from SEM-EDX.

The results from SEM-EDX are consistent with the previous results from PIXE in the general overall element concentrations in the sample. The results from the SEM-EDX analysis suggest that the sources are some combination of industry and airborne soil. The results also support the conclusion from the PIXE analysis that there are large concentrations of S in small particles that can be suspended in the air for long periods of time and travel great distances. However, the observed ratios of S to O are not consistent for different particles, suggesting that the S is not bound in one particular oxide.

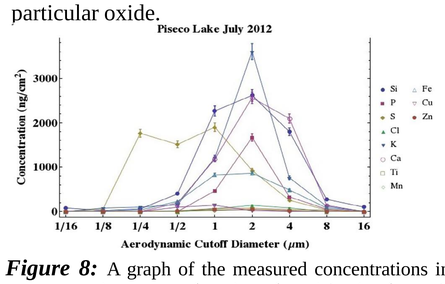

Figure 8: A graph of the measured concentrations in mass per unit area as a function of particle size for each element in the samples collected in July of 2012.[1].

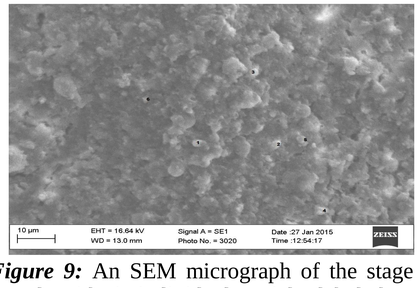

Figure 9: An SEM micrograph of the stage 2 sample with six individual particles labeled.

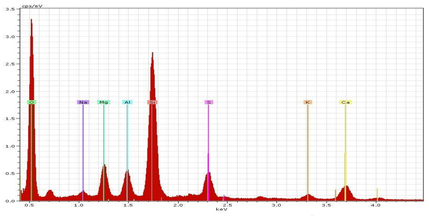

Figure 10: An EDX-spectrum taken on particle 1 in the SEM image shown in Figure 9.

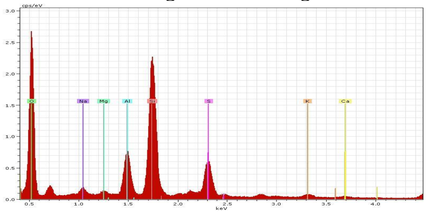

Figure 11: An EDX-spectrum taken on particle 4 in the SEM image shown in Figure 9.

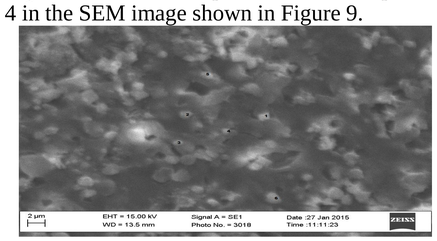

Figure 12: An SEM micrograph of the stage 2 sample with six individual particles labeled.

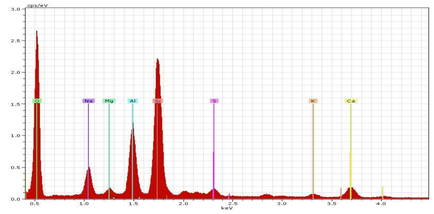

Figure 13: An EDX-spectrum taken on particle 2 in the SEM image shown in Figure 12.

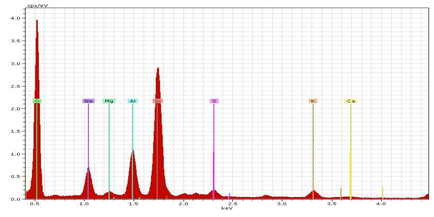

Figure 14: An EDX-spectrum taken on particle 5 in the SEM image shown in Figure 12.

References

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