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Introduction

There is an active research program in the Union College Ion-Beam Analysis Laboratory on proton-induced X-ray emission (PIXE) analysis of atmospheric aerosols. PIXE is a powerful tool for the study of airborne pollution because it provides information on a broad range of elements simultaneously, has low detection limits, is nondestructive, does not require large samples, and the analysis can be performed in a short amount of time. However, PIXE provides only elemental information. We are investigating the use of micro-Raman spectroscopy (MRS) to complement PIXE analysis of aerosol samples by providing chemical information. In MRS, laser light is inelastically scattered from a sample and the vibrational spectrum of the scattered light is used to identify molecules and their functional groups. We are focusing on aerosol samples collected in the Adirondack Mountains that have considerable concentrations of sulfur that may contribute to acid rain [1].

Aerosol Sampling

The aerosol samples are collected using a nine stage cascade impactor that separates particles according to their size [2]. The particulate matter is impacted on thin Kapton films at each stage. The impactor and the sampling apparatus are shown in Figure 1. The pump pulls air through the impactor and the valve controls the flow rate which is monitored by the flow meter. The impactor is designed for a flow rate of 1 L/min. A microscopic image of an aerosol deposit on a Kapton impacted foil is shown in Figure 2.

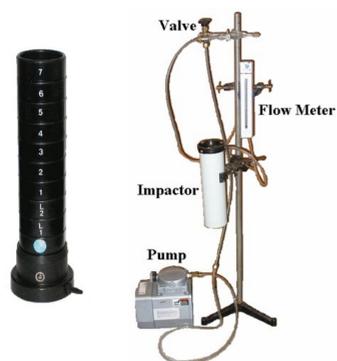


Figure 1. Nine stage impactor (left) and sampling apparatus (right).



Figure 2. A microscopic image of an aerosol deposit on one of the Kapton impactation foils.

PIXE

In PIXE, a proton knocks an inner-shell electron out of an atom and an X-ray is emitted as the vacancy is filled by an outer-shell electron. The energies of the X-rays are characteristic of the elements in the sample and the intensities of the X-ray lines can be used to calculate the concentration of the elements. This technique provides information on selected elements from Si to U with good sensitivity. Minimum detection limits for PIXE analysis of aerosol samples are typically on the order of a few ng/m³ [3].

Preliminary results of a PIXE analysis of aerosol samples collected at Piseco Lake in the Adirondacks in July 2012 are illustrated in Figures 3 and 4. Shown in Figure 3 are PIXE spectra taken on an aerosol sample (red) and a blank Kapton film (blue) with a 2.2-MeV proton beam from the Union College 1.1-MV Pelletron Accelerator. The sample is for particulate matter (PM) with an aerodynamic cutoff of 1 μm in diameter. Energy spectra were fitted with GUPIX software [4] to determine the concentrations of elements contained in the sample. Figure 4 shows the concentration measured for each element in each PM bin. These results show significant concentrations of sulfur that can be a major contributor to acid rain, a well-known problem in the Adirondacks.

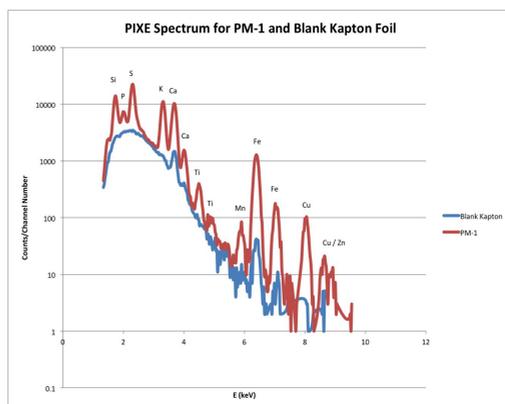


Figure 3. A comparison of PIXE spectra taken on a blank Kapton foil (blue) and a Kapton foil impacted with 0.5-1 μm diameter particles at Piseco Lake in the Adirondack Mountains of New York (red).

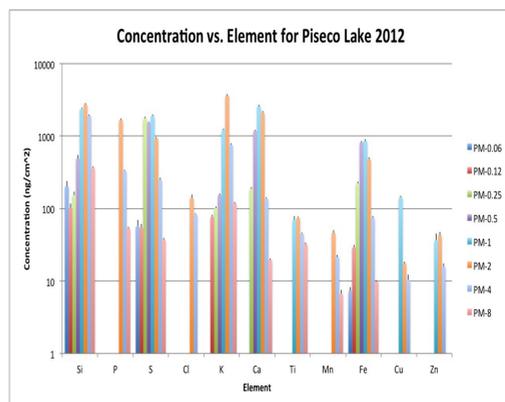


Figure 4. Concentration of elements in samples collected at Piseco Lake in July 2012.

Micro-Raman Spectroscopy

Micro-Raman Spectroscopy (MRS) uses inelastic scattering of photons to obtain information about molecular bonding in a sample. The basic principles of MRS are illustrated in Figure 5. Incident laser light excites vibrational states of molecules in a sample. The elastically scattered light is filtered while the inelastically scattered light is dispersed onto a detector to generate a spectrum. The spectrum provides information about the molecules and functional groups present in the sample.

A photograph of the Senterra MRS system at Union College is shown in Figure 6. It includes an optical microscope for viewing and aligning the sample, a monochromator to filter and disperse the scattered light, and a charge-coupled device (CCD) to detect the light. Three lasers—a He-Ne at 633 nm, a diode-pumped YAG at 532 nm, and a diode laser at 780nm—are used as photon sources.

A Micro-Raman analysis is being performed on the aerosol samples to try to understand the molecular structure in which the sulfur appears. The parameters used in the MRS analysis are as follows: the laser light frequency was set to 785nm, the co-additions were set to 10, and the objective was set to 50. Figure 7 shows the sample under the MRS microscope and a spectrum taken on one of the aerosol samples is shown in blue in Figure 9. The spectrum shows clear peaks at 1015 cm⁻¹, 1117 cm⁻¹, 1383 cm⁻¹, 1606 cm⁻¹, and 1782 cm⁻¹.

For the purpose of this study, a library of standards was created. The library included a blank Kapton foil, sulfuric acid on Kapton, nitric acid on Kapton, solid sodium sulfate on Kapton, solid sodium nitrate on Kapton, aqueous sodium sulfate on Kapton, aqueous sodium nitrate on Kapton, and distilled water on Kapton. Spectra were collected from each standard in order to identify the peaks present in the MRS spectrum from the aerosol sample.

Figure 8 contains Raman spectra of solid sodium sulfate (blue), 0.05M sodium sulfate (black), and blank Kapton (green). K.H. Fung *et al* [5] shows in their data a strong peak at 980 cm⁻¹ that corresponds to the sulfate ion (SO₄²⁻). In Figure 8, both the solid sodium sulfate and aqueous sodium sulfate spectra show a strong peak at 980 cm⁻¹. We believe this corresponds to the sulfate ion reported in the literature.

Figure 9 shows Raman spectra of a Piseco Lake sample (blue), 0.05M sodium sulfate (black), and Kapton (green). The Piseco Lake sample Raman spectra shows a peak at 1015 cm⁻¹, which may correspond to the 0.05M sodium sulfate peak at 980 cm⁻¹.

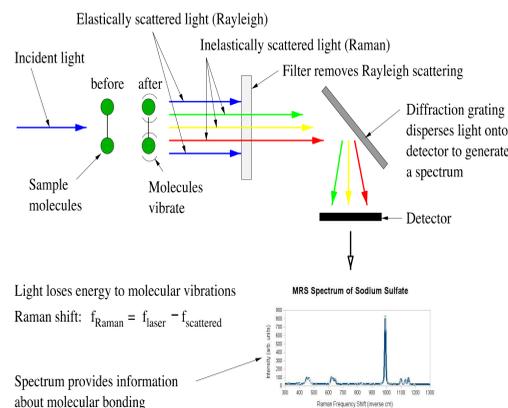


Figure 5. An illustration of the basic concept of MRS.



Figure 6. A photograph of the MRS at Union College.

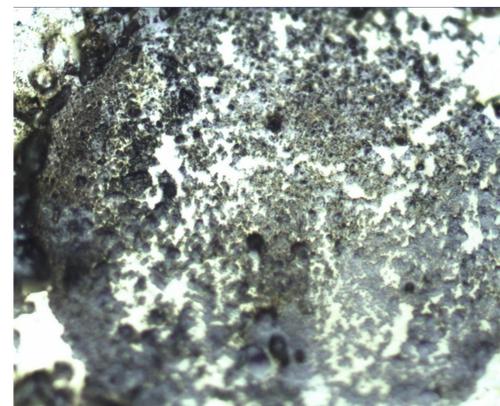


Figure 7. A photograph of an impacted foil from Piseco Lake under the MRS microscope.

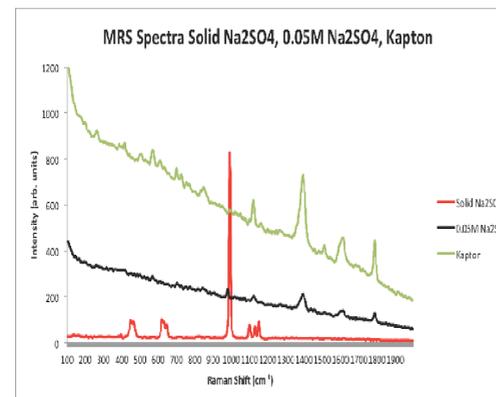


Figure 8. Raman spectra of a solid sodium sulfate standard (blue), a 0.05M sodium sulfate standard (black), and a blank Kapton foil (green).

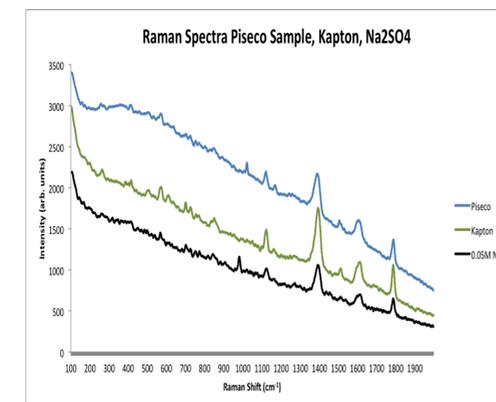


Figure 9. Raman spectra of a Piseco Lake sample (blue), a blank Kapton foil (green), and a 0.05M sodium sulfate standard (black).

Discussion

After acquiring the spectra from the Piseco Lake sample, several standards were created to generate spectra that might be able to yield insight into the molecular composition of the Piseco Lake sample. A spectrum for blank Kapton was generated. The peaks associated with the Kapton are 1117 cm⁻¹, 1383 cm⁻¹, 1606 cm⁻¹, and 1782 cm⁻¹ as seen in Figures 8 and 9. A spectrum for solid sodium sulfate was also generated as seen in Figure 8. The peaks associated with solid sodium sulfate occur most notably at 989 cm⁻¹, 1093 cm⁻¹, 1127 cm⁻¹, and 1153 cm⁻¹. Finally, a spectrum for 0.05M sodium sulfate was produced, which is shown in both Figure 8 and Figure 9.

Figure 8 clearly illustrates a peak at 980 cm⁻¹ that correlates to the sulfate (SO₄²⁻) ion. Figure 9 plots the same 0.05M sodium sulfate spectrum as seen in Figure 8 in addition to the MRS spectrum of the Piseco Lake sample and the blank Kapton. Noticeably, a peak occurs at 1015 cm⁻¹ in the Piseco Lake sample spectrum that does not occur in the Kapton spectrum. Although the peak appears to be shifted to slightly higher wave number, the peak at 1015 cm⁻¹ may be due to the presence of a sulfur oxide.

The formation of acid rain occurs in several chemical steps in the atmosphere. For example:



It is possible that the impacted particle contained a sulfur oxide ion that was not sulfate (SO₄²⁻), but rather an intermediate species of sulfur oxide like sulfur trioxide (SO₃²⁻).

Future Work

We plan to coat the impacted foil from Piseco Lake with a conductive material so that our lab may conduct SEM/EDX analysis on the sample to locate specific impacted particles that contain high concentrations of sulfur. Once those particles have been identified, they will be the main focus of future MRS work. Also, additional library research and MRS work will be conducted on sulfur oxides (SO_x).

References

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Acknowledgements

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