

# **Report for 2002VT6B: Substrate- and size-dependent measurement of particle-phase mercury in the atmosphere by aerosol mass spectrometry**

- Other Publications:

- Holmes, B. and G.A. Petrucci, 2002. Measurement of atmospheric particle-phase mercury by laser aerosol mass spectrometry. Federation of Analytical Chemistry and Spectroscopy Societies, FACSS, Providence, RI, USA, October 13-17.

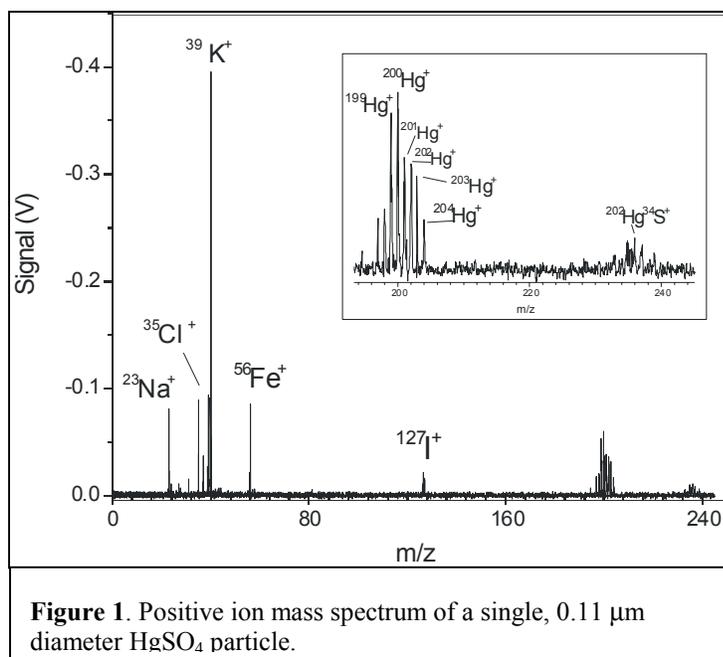
**Report Follows:**

Substrate- and Size-dependent Measurement of Particle-phase Mercury in the Atmosphere by  
Aerosol Mass Spectrometry

Annual Progress Report for the Period March, 2002 – February, 2003

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**Project Overview:** The primary objective of this work is to optimize an aerosol mass spectrometer (AMS) to sample, size and analyze single mercury particles. Targeted photoionization of Hg in single particles was proposed to improve ionization efficiencies, thereby decreasing minimum detectable limits. To date, we have been able to measure Hg from single particles of  $\text{HgSO}_4$  or  $\text{Hg}_2\text{Cl}_2$  from particles as small as  $0.11 \mu\text{m}$ . A typical mass spectrum (positive ion only) obtained from such a test particle generated in our laboratory is shown in Figure 1. From the Hg signal-to-noise shown, we estimate a limit of detection of  $\sim 10^{-16}$  g of Hg. Our estimated detection limit corresponds to 1 ppm Hg in a 10 mm particle or 100 ppm in a 1



$\mu\text{m}$  particle. On average, the atmospheric particulate Hg burden is estimated to be 10 pg per 10  $\mu\text{g}$  of atmospheric particulate, or 1 ppm in single particles (assuming a homogeneous distribution of Hg in all particles). Therefore, our present capabilities fall short of the needed sensitivity to measure Hg in single atmospheric particles at normal ambient levels. Having developed a better understanding of the laser-particle interaction and possible ionization dynamics, we now wish to pursue several different avenues to improve the sensitivity of the method. We wish to be clear, however, that we cannot guarantee that we will be able

to achieve the necessary detection capabilities to measure atmospherically relevant levels of particle phase mercury.

Progress to date:

Results from this project were recently presented at the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS) conference in Providence, RI, in mid-October 2002. (A copy of the presentation is available upon request.) FACSS is considered the premier international conference for analytical chemistry and applied and fundamental spectroscopy.

We have adapted our aerosol mass spectrometer to Hg analysis. In accordance with risk management, we've set-up a system to safely handle ultrafine mercury aerosols in our

laboratory. We've also developed the expertise needed to generate ultrafine mercury particles with different chemical compositions and oxidation states of mercury.

The proposed plan involved using a tunable laser to vaporize and photoionize Hg particles. However, energy densities available with our tunable laser and optical system were not sufficient to overcome the lattice energies of the study particles. A modification has been made to the optical setup to increase the energy density in the relevant (laser) wavelength range by about a factor of 50, which should be sufficient for particle vaporization. In anticipation of this modification, the AMS was evaluated for Hg particle analysis with a laser operating at a fixed wavelength of 266 nm. Note that this wavelength is not sufficient to ionize neutral Hg by the simultaneous absorption of only two photons. Therefore, ionization efficiencies were expected to be low at this fixed wavelength, with a correspondingly poor sensitivity.

Both Hg(I) and Hg(II) salt aerosols were generated to test the capabilities of the AMS. We wanted to test whether the oxidation state of the Hg in the particle could be maintained during the vaporization process (thereby permitting some degree of speciation). Much to our disappointment, however, we saw no evidence of Hg(II) in our particle mass spectra when analyzing ultrafine HgSO<sub>4</sub> particles. We believe that upon particle vaporization and ionization, the large local electron density results in a high degree of electron attachment to the Hg ions, resulting directly in the measured Hg(I) ions. Another possibility is full reduction of the Hg(II) to the neutral atom that is then photoionized by multiphoton absorption from the laser. If the latter is prevalent, then we can anticipate a significant increase in photoionization efficiency, and hence sensitivity, by tuning the laser to about 237.5 nm. At this wavelength, photoionization to Hg(I) can occur by absorption of only two photons. As stated above, we have the new optical setup in place that will allow us to use the tunable laser to determine the extent of electron attachment and evaluate the possibility of improving the sensitivity of the aerosol mass spectrometer to Hg.

*Dissemination of information and educational objectives* – Due to equipment problems and the complexity of the filtration setup to meet risk management guidelines, our first results were obtained late in 2002. This being the case, we have not yet deemed it appropriate to conduct the planned formal meetings with our colleagues at the Vermont Agency of Natural Resources of the School of Natural Resources at the University of Vermont. A half-day workshop is now being planned for either mid-December (immediately after Final Exams) or in the beginning of the new year (2003) before the beginning of the spring semester. Finally, we also feel it important to note that the development of the AMS for mercury analysis has been an important learning tool for the graduate students in the group as well as one undergraduate student, who has been working in the group since the beginning of the Fall 2002 semester.