REACTIONS OF BROMIDE IONS WITH
ATMOSPHERIC TRACE GASES AND AEROSOLS

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ATMOSPHERIC TRACE GASES AND AEROSOLS

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LIST OF SYMBOLS AND ABBREVIATIONS

ACIMS…………………………..................active chemical ionization mass spectrometry

CDC…………………………………………………..collision dissociation chamber

CIMS………………………………………………...chemical ionization mass spectrometry

GC/ECD…………………………………………gas chromatography/electron capture detector

ISCAT…………………..Investigation of Sulfur Chemistry in the Antarctic Troposphere

MPAN……………………………..peroxymethacryloyl nitrate ($CH_2C(CH_3)C(O)O_2NO_2$)

PAN……………………………………………………………..peroxy acetyl nitrate

PILS………………………………………………………...particle-into-liquid sampler

PIT-MS…………………………………………proton transfer ion trap - mass spectrometry

PPN…………………………………………peroxypropionyl nitrate ($CH_3CH_2C(O)O_2NO_2$)

PTR-MS………………………………………..proton transfer reaction - mass spectrometry

SIFDT……………………………………………………….selected ion flow drift tube

slpm…………………………………………………………...standard liters per minute

TD-CIMS…………………...thermal desorption – chemical ionization mass spectrometry

VT-SIFT…………………………………….variable temperature – selected ion flow tube

SUMMARY

The use of Br⁻ as a reagent ion for the measurement of gas-phase peroxy acetyl
nitrate (PAN), nitric acid, and particulate phase sulfate and nitrate was investigated using
chemical ionization mass spectrometry (CIMS). PAN was thermally dissociated into
peroxy acetyl radicals ($CH_3C(O)O_2$) and detected as acetate. Nitric acid was detected as
NO_3^- via a proton transfer reaction with Br⁻. Aerosols were volatized into sulfuric and
nitric acid and these products were detected in an analogous fashion with Br⁻. The rate
constant for the reaction of Br⁻ with peroxy acetyl radicals was estimated to be 3×10^{-10} (at
293 K). The typical sensitivity of the CIMS instrument to PAN was found to be ~6 Hz
pptv⁻¹, with a limit of detection of ~0.4 pptv for a 1-second integration period (defined by
a signal-to-noise ratio of 3). The effect of humidity on the detection of PAN was also
investigated, and the sensitivity of the instrument dropped by ~80% for a relative
humidity of 16%; at the maximum relative humidity achieved (83%), the PAN signal
dropped by ~93%. The typical sensitivity of the CIMS to nitric acid was ~18.8 Hz pptv⁻¹,
with a limit of detection of ~13.8 pptv for a 1-second integration period. The sensitivity
of the CIMS to the sulfate aerosol was also investigated and was found to be 7000
Hz µg⁻¹ m⁻³ for a 1-second integration period, with a limit of detection of ~3 ng m⁻³.
CIMS measurements of aerosol sulfate and nitrate were compared to those of a particle-
into-liquid sampler (PILS) instrument. An excellent correlation between the two
instruments was found for sulfate measurements (e.g. $R^2 = 0.91$ for March 25, 2005
measurement), but the correlation for nitrate measurements was poor ($R^2 = 0.36$ for
March 24, 2005 measurement), indicating a problem with the variability of the nitrate

background of the CIMS. Mass spectra were taken of ambient air in both aerosol and gas-phase detection mode. These spectra largely confirmed the selectivity of the Br⁻ detection scheme. The excellent sensitivity of the CIMS instrument to aerosol sulfate indicated that this is a promising method for time response measurements of this species. However, the water dependence on the PAN sensitivity limits the use of this technique to high altitudes (i.e. low dew points).

CHAPTER 1
INTRODUCTION

A variety of chemical ionization mass spectrometry (CIMS) techniques have been developed to detect a spectrum of atmospheric species using just a handful of reagent ions. The CIMS technique uses ion-molecule reactions to selectively ionize species of interest in the complicated matrix of ambient air. For example, CO_3^- has been traditionally used to ionize and detect HNO_3 by the following reaction.

$$CO_3^- + HNO_3 \rightarrow NO_3^-(HCO_3) \qquad\qquad (1)$$

In this example, CO_3^- is the reagent synthesized in a CIMS to selectively ionize HNO_3. At the present time the species that can be detected by CIMS are limited by the availability of viable reagent ions. The choice of the reagent ion to be used for a given detection scheme depends on the species to be measured, as well as the experimental conditions (i.e. pressure, humidity). Several CIMS techniques have used reagent ions such as SiF_5^-, SF_6^-, CO_3^- and NO_3^- hydrates, H_3O^+, CF_3O^-, and I^- to detect a variety of trace species in air (notably HNO_3, pernitric acid, SO_2, HCl, PAN, and N_2O_5).

SiF_5^- was found to be an excellent CIMS reagent ion for the selective detection of HNO_3 in the lower troposphere in a study by Huey et al. [1996a]. Neuman et al. [2000] also achieved the selective, fast-time detection of nitric acid with a CIMS on an aircraft using SiF_5^- as the reagent ion. This technique was also used by Neuman et al. [2002] during the Texas 2000 Air Quality Study to take measurements of HNO_3 in the planetary boundary layer and free troposphere. Unfortunately, SiF_5^- has proven to be a viable reagent ion only for HNO_3 measurements.

Nitric acid was also measured along with pernitric acid and sulfur dioxide during ISCAT 2000 using SF_6^- as a reagent ion [Huey, et al. 2004]. Detection limits for HNO_3 and pernitric acid of less than 5 pptv were found for 1 min integration periods. SF_6^- was used as the reagent ion in this study because it detects a broader spectrum of molecules. There is a potential for interference from the slow second-order reaction of SF_6^- with water, but the low humidity found at the South Pole negated the concern for this study. Studies of the heterogeneous chemistry of several atmospheric trace species (including HNO_3, $ClNO_3$, N_2O_5, HCl, $HOCl$, $HOBr$, $BrNO_3$, and CF_2O) using SF_6^-, I^-, and F^- as reagent ions by Hanson and Ravishankara [1991a, 1991b, 1992,1993] and Hanson [1992] were expanded upon by Huey et al. [1995], who determined the product yields and rate constants of SF_6^- and I^- with many of these same atmospheric species, as well as two others: O_3 and Cl_2O.

Mohler and Arnold [1991] measured the product ion distributions and rate coefficients of the reactions of CO_3^- and NO_3^- hydrates (as well as bare CO_3^- and NO_3^-) with gaseous HNO_3 by ACIMS (Active Chemical Ionization Mass Spectrometry). This method for detection of atmospheric HNO_3 measurements was first used by Arnold and Knop [1989]. Fehsenfeld et al. [1975] measured the rate coefficient of the reaction of bare CO_3^- with HNO_3. The reactions of CO_3^- hydrates with SO_2 were studied by Seeley et al. [1997] to try and understand atmospheric measurements, using a variable temperature-selected ion flow tube (VT-SIFT). Rate constants for the reactions of a range of CO_3^- hydration levels were determined at temperatures above 150 K (below which SO_2 condensed on the inlet). Absolute and relative uncertainty values were determined with ±25% and ±15% uncertainty, respectively. An effective rate constant

for conversion of the CO_3^- hydrates to SO_3^- was also determined with an uncertainty of ±30%.

Hansel and Wisthaler [2000] studied the reactions of H_3O^+ and $(H_2O)_2H^+$ with PAN, PPN and MPAN using a selected ion flow drift tube (SIFDT) apparatus and a proton transfer reaction mass spectrometer (PTR-MS) system along with a whole host of other compounds. They found detection limits of 70 pptv or less for all three species with S/N = 2 and a 15 s integration time. PTR-MS has also been used to measure volatile organic compounds (VOCs) without significant interference, as has Proton Transfer Ion Trap-Mass Spectrometry (PIT-MS) [deGouw, et al. 2003; Warneke, et al. 2004]. PTR-MS employs proton-transfer reactions to ionize the species of interest and mass spectrometric detection of the product ion. The PIT-MS operates similarly to the PTR-MS, but uses an ion trap mass spectrometer to detect ions instead of a quadrupole mass filter [Warneke, et al. 2004].

The reactions of CF_3O^- with $ClONO_2$, HNO_3, HCl, N_2O_5, SO_2, HI, and H_2O were studied by Huey et al. [1996b]. The rate coefficients and product yields were measured at 295 K and ~0.4 Torr using the flowing afterglow technique. It was demonstrated that CF_3O^- is a selective reagent ion for the simultaneous in situ measurement of $ClONO_2$, HNO_3, and HCl (trace species important in the heterogeneous chemistry resulting in the Antarctic polar ozone hole) in the stratosphere.

Slusher et al. [2004] developed a TD-CIMS technique for the fast-time detection of PAN, other peroxyacyl nitrates, and dinitrogen pentoxide using I^- as the reagent ion. For a 1 s integration period, detection limits of 7 pptv and 12 pptv were determined for PAN and the sum of N_2O_5 and NO_3, respectively. The technique was found to be as

sensitive and selective as the previously used GC/ECD (gas chromatography/electron capture detector) method, while greatly increasing the time resolution of the data, making it useful in measuring pollution plumes from aircraft.

As a follow-up to the I^- work, this study investigates the use of Br^- as a comparable reagent ion for gas-phase measurements of PAN and its possible use in detecting aerosol chemical composition. Because Br^- is the conjugate base of a weaker acid than I^-, it is likely to be a less reactive reagent ion and has the potential to react with a broader range of acids. Gas-phase measurements of PAN and nitric acid were conducted, as well as measurements of several aerosol components, primarily sulfate and nitrate. A major goal of this study is to obtain fast, sensitive measurements of nitrate and sulfate, which could be useful for aircraft missions, and to ascertain if gas phase PAN and HNO_3 could be measured at the same time. PAN and HNO_3 sensitivities were tested as functions of temperature and humidity. Sensitivities to sulfate and nitrate aerosols were tested as a function of temperature and were compared to PILS (particle-into-liquid sampler) measurements.

CHAPTER 2
EXPERIMENTAL

2.1 Instrumentation

The TD-CIMS instrument (Figure 1) used in this study is similar to that described

by Slusher et al. [2004] and is only briefly described here.

CIMS with Br- Reagent Ion
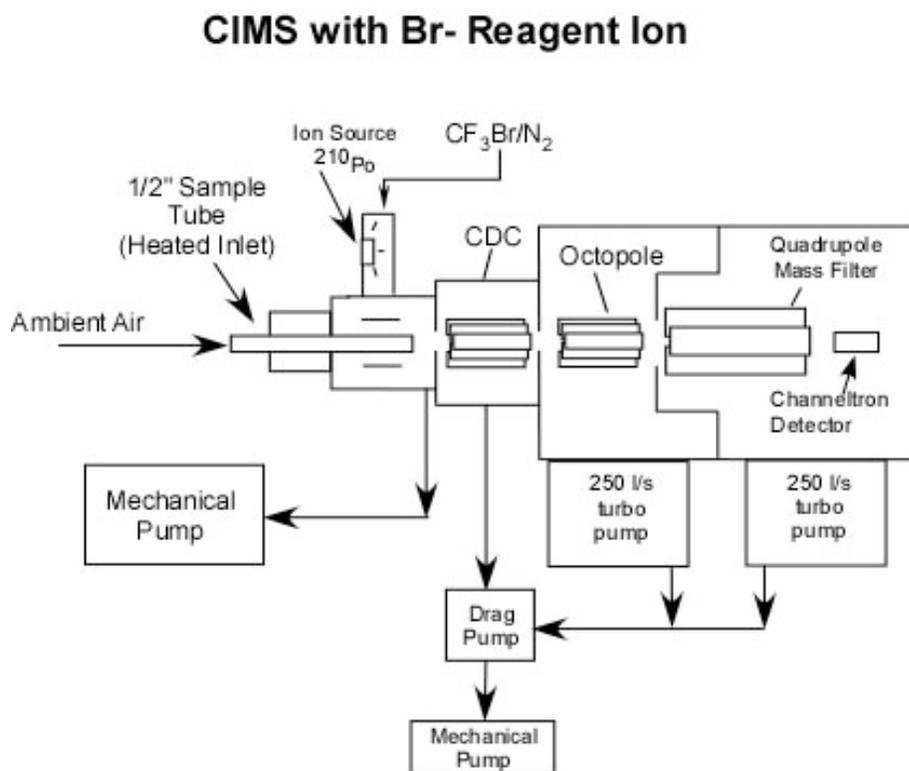
Figure 1. Instrument schematic.

A 29.2-cm long, 1.27-cm o.d. PFA Teflon tube was used for the inlet during the gas-

phase experiments. This material was found to cause the least amount of nitric acid

absorption (<5%) by Neuman et al. [1999]. The final 14.6 cms of the inlet tube were

heated by a thermostatted aluminum cylinder to 150°C. A 24.1-cm long, 1.27-cm i.d.

stainless steel tube was used for the inlet during the aerosol-phase measurements, and

was heated to 450°C with a 5-cm cube steel block containing four high-temperature

cartridge heaters (Figure 2).
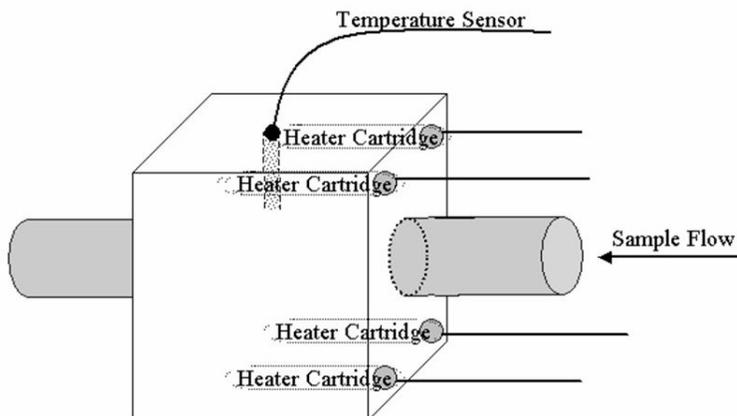
Figure 2. Heater schematic.

Zero-air and dry nitrogen, at flow rates of either 4 or 6 slpm, were both mixed with the

PAN and nitric acid calibration flows. Both indoor and outdoor ambient air was sampled

into the instrument to obtain gas and aerosol phase mass spectra. Outdoor air was

sampled through conductive carbon-filled silicon tubing (TSI Inc., Shoreview, MN). The

inlet was maintained at ambient pressure, ~740 torr (9.87×10^4 Pa). The instrument

sample flow rate was approximately 3.8 lpm, and any excess flow was vented through an

opening in the flow tube. The air was drawn into the low-pressure flow tube (~30 torr)

through a 0.025 m conical skimmer where it mixes with the Br⁻ directly introduced from

the ^{210}Po ion source. The ionized species that result from the ion-molecule reactions in

the flow tube are then drawn through a 0.0572-cm pinhole into the CDC, which operates

under parameters similar to those described by Slusher et al. [2004].

2.2 Ion Chemistry

Br$^-$ was used to detect PAN, nitric acid, and aerosol sulfate and nitrate. Similarly to the I$^-$ study by Slusher et al. [2004], Br$^-$ was synthesized by dissociative electron attachment to either CH$_3$Br (k ~6.0 x 10^{-12} cm^3 s^{-1} at 20°C) or CF$_3$Br (k ~1.2 x 10^{-8} cm^3 s^{-1} at 20°C) [Burns et al., 1996]. However, CF$_3$Br was preferred in this case because it provided a cleaner mass spectrum (a large chlorine impurity at 35 and 37 amu was observed in the mass spectrum of CH$_3$Br). A 0.19% mixture of CF$_3$Br /N$_2$ was flowed into the ion source with an additional 3 slpm of nitrogen.

PAN thermally dissociates in the inlet to form a peroxyacyl radical and NO$_2$, then the peroxyacyl radical reacts with Br$^-$ to form CH$_3$C(O)O$^-$ and BrO.

$$CH_3C(O)O_2NO_2 + M \rightarrow CH_3C(O)O_2 + NO_2 + M \qquad (2)$$

$$CH_3C(O)O_2 + Br^-(H_2O)_n \rightarrow CH_3C(O)O^-(H_2O)_n + BrO \qquad (3)$$

Because the CDC was held at low pressure with a high electric field, high-energy collisions readily dissociated water clusters (n = 0).

$$X^- \cdot H_2O + M \rightarrow X^- + H_2O \qquad (4)$$

Gas phase nitric acid is detected as NO$_3^-$, and reacts with Br$^-$ by the following reaction:

$$Br^- + HNO_3 \rightarrow HBr + NO_3^- \qquad (5)$$

The rate coefficient for this reaction was found to be approximately 7 x10^{-10} at 335 K [Davidson, et al., 1977]. This rate constant was estimated to be that for room temperature, 293 K, as the rate constant was found by Davidson, et al. to be highly insensitive to changes in temperature.

For the aerosol measurements, ammonium sulfate volatizes as it enters the heated inlet to form gas-phase sulfuric acid, which undergoes the following reaction with Br^-:

$$Br^- + H_2SO_4 \rightarrow HBr + HSO_4^- \tag{6}$$

HSO_4^- is the ion then detected by the mass spectrometer. Nitric acid contained in the nitrate aerosol undergoes a similar change from aqueous to gas form when the aerosol is heated in the inlet, and the resulting HNO_3 gas undergoes reaction (5) and is detected as NO_3^-.

2.3 Calibration

Calibrations for each of the measured species were performed by adding known amounts to the inlet. As in the investigation by Slusher et al. [2004], PAN was generated by a photolytic source similar to the one described by Warneck and Zerbach [1992]. The PAN yield from this source was assumed to be 90 ±2% [Slusher et al. 2004]. The reaction sequence for the formation of PAN is:

$$CH_3COCH_3 + h\nu \rightarrow CH_3CO + CH_3 \tag{7}$$

$$CH_3CO + O_2 \rightarrow CH_3COO_2 \tag{8}$$

$$CH_3COO_2 + NO_2 \rightarrow CH_3COO_2NO_2 \tag{9}$$

A permeation tube similar to that described by Neuman et al. [2000] was used as the HNO_3 calibration source. The permeation rate was measured independently by ion chromatography, and was found to vary between 11.8 and 17.5 ng min^{-1} over the course of time (~4 mos.) that the perm tube was in operation, but was steady for each experiment. Though the flow rate of dry nitrogen into the permeation tube also varied

over the course of the experiment, it was consistent and continuous for each

measurement, and the variation should have little effect on the resulting nitric acid flow.

Sulfate aerosol for calibration was generated by running a 10^{-3}% by mass

ammonium sulfate solution (the dilution was made with deionized ~18MΩ water from a

Barnstead Nanopure Infinity ultrapure water system) through a Model 3075/3076

Constant Output Atomizer (TSI Inc., St. Paul, MN). Dry nitrogen at 35 psi is delivered to

the nebulizer, and the resulting flow of aerosol in nitrogen (at a total flow of 4 lpm) was

sent consecutively through a Model 3062 Diffusion Dryer (TSI Inc., St. Paul, MN), to

remove water, and a Model 3077 Aerosol Neutralizer (TSI Inc., St. Paul, MN), and was

added to a 0.8 lpm flow of nitrogen (to bring the total flow to 4 lpm). The aerosol
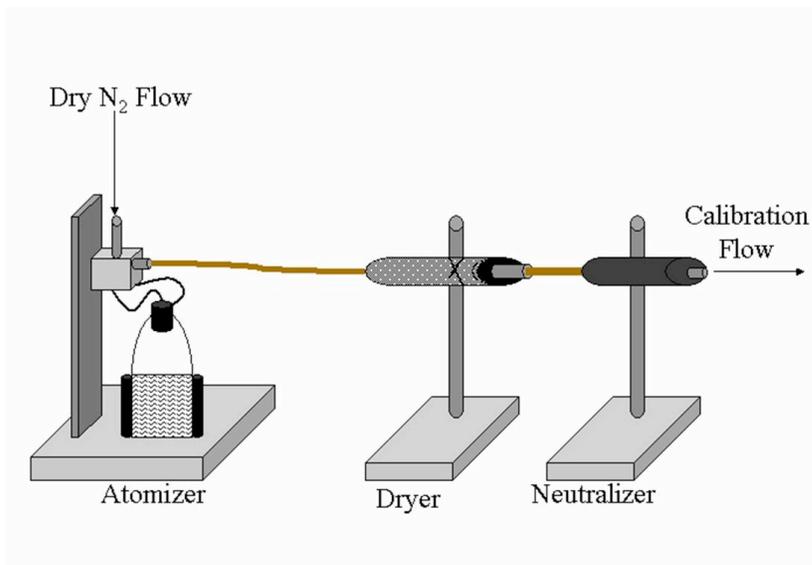
calibration setup can be seen in Figure 3.

Figure 3. Nebulizer setup.

The CIMS measurements of nitrate aerosol were taken from room and outdoor air

and compared to those of the particle-into-liquid sampler (PILS). The PILS makes

continuous measurements of ambient aerosol by drawing the aerosol into a supersaturated environment allowing the particles to grow into droplets, which are collected into a continuous liquid flow for analysis by ion chromatography. The PILS technique is described in further detail in Weber et al. [2001] and Orsini et al. [2003]. The instrument has a limit of detection of 10 ng m^{-3} for anions [Orsini et al. 2003]. Backgrounds during calibrations were determined by periodically disconnecting the calibration source and flowing only either dry nitrogen or zero air through the inlet. Backgrounds for ambient aerosol measurements were made using a HEPA capsulate filter (Gelman Sciences, Ann Arbor, Michigan).

3.1 Gas-phase PAN and Nitric Acid

The rate constant for the reaction of Br$^-$ with peroxy acetyl radicals was estimated relative to that of nitric acid. This was done by consecutively adding known amounts of nitric acid and then PAN to the CIMS and measuring the signal levels. The equations governing the production of product ion for PAN and HNO$_3$ (2, 3 and 5) are given below (10 and 11) using the assumption that little of the reagent ion is converted into the product. The ratio of these expressions for the reactions of Br$^-$ with nitric acid (5) and peroxy acetyl radicals (2 and 3) are given in (12):

$$[NO_3^-]/[Br^-] = k_5[HNO_3]t \qquad (10)$$

$$[CH_3CO_2^-]/[Br^-] = k_3[CH_3C(O)O_2]t \qquad (11)$$

$$[NO_3^-]/[CH_3CO_2^-] = (k_5/k_3)*([HNO_3]/[CH_3C(O)O_2]) \qquad (12)$$

This approach assumes that the Br$^-$ concentration and reaction time were the same for the PAN and nitric acid experiments. This was accomplished by performing the experiments back to back under the same conditions. It was also assumed that losses of nitric acid and peroxy acetyl radicals were approximately the same. The rate coefficient used for (5), k_5, was 7 x10^{-10} at 335 K [Davidson, et al., 1977] as mentioned above. This rate constant was found by Davidson, et al. to be highly insensitive to changes in temperature; a 90 K temperature change resulted in only a 10% change in the rate constant. The rate constant (k_3) for the reaction of Br$^-$ with peroxy acetyl radicals was found to be roughly 3x10^{-10}. The error associated with the calculation is ~±0.05, which is the 3σ deviation of the ratio of CH$_3$CO$_2^-$ to NO$_3^-$ derived from duplicate experiments.

The typical sensitivity of the CIMS to PAN (in dry synthetic air) was found to be ~ 6 Hz pptv^{-1}, as was determined by the addition of PAN from the photolytic calibration source described above. The ratio of the CIMS sensitivity for PAN to nitric acid was found to be approximately 0.33 (the sensitivity of the CIMS to nitric acid was ~ 18.8 pptv^{-1}) . A typical background measurement for PAN was 10 pptv, and for nitric acid was 895 pptv.

Because of the strong water dependence of the reaction of I$^-$ with peroxy acetyl radicals found by Slusher et al. [2004], the effect of humidity on the instrument's sensitivity to PAN was investigated for the reaction with Br$^-$. Humidified air was produced by passing a varying portion of the inlet flow through a water bubbler at a measured temperature (23°C) and atmospheric pressure, and assuming saturation. The PAN signal dropped considerably with the addition of water through the inlet, and was found to have the dependence shown in Figure 4. Even a relative humidity of 16% caused the PAN signal to drop by ~80%. The PAN signal continued to decrease with increasing relative humidity, but began to level off at ~50% RH. At the highest relative humidity (~83%) achieved, the raw PAN signal dropped by ~93%.
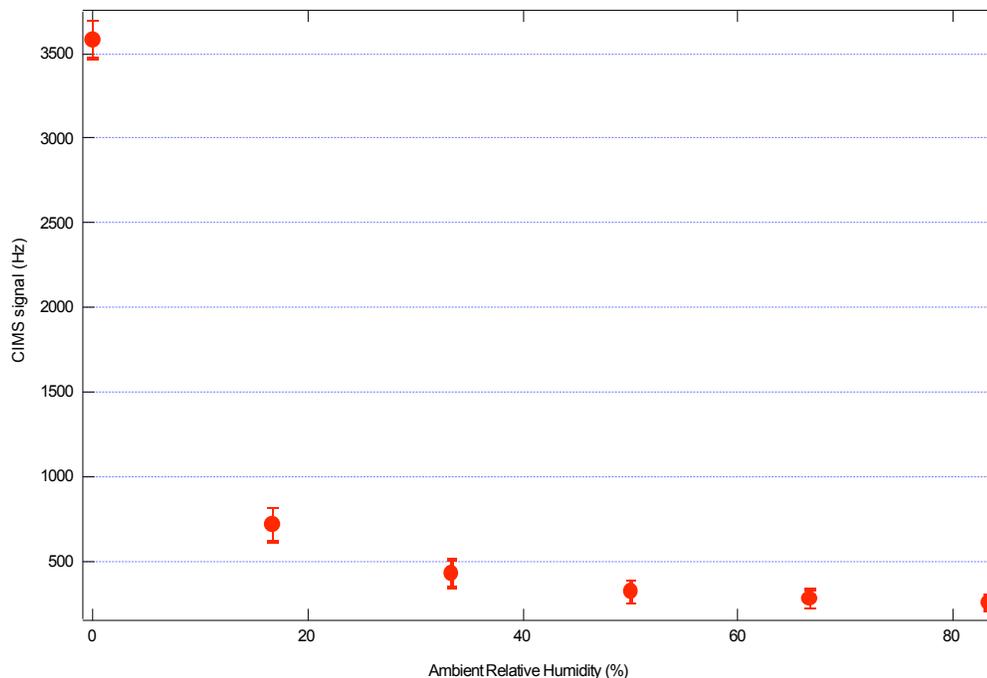
Figure 4. CIMS sensitivity to PAN as a function of humidity. Ambient pressure = 740 torr (9.87 x 10^4 Pa), ambient temperature = 23 °C. Flow tube pressure = 30 torr (4 kPa).

Detection limits for PAN and nitric acid were defined at a signal-to-noise ratio of three, where the noise is the standard deviation of the background measurement. The typical limit of detection for PAN in dry air was found to be 0.4 pptv for a 1-second integration period. The limit of detection for nitric acid was 13.8 pptv, which was much higher than that for PAN. The detection limit scales in proportion to the square root of the integration time as the variation in the background is essentially determined by counting statistics.

Mass spectra of both indoor and outdoor air were taken on August 7, 2005 to investigate the selectivity of the Br⁻ reagent ion for gas-phase species. Comparisons of the CIMS signal both filtered and unfiltered can be seen in Figures 5a and 5b, over a range of masses (10 to 200 amu). Figure 5a shows the comparison with a sampling of indoor air, while Figure 5b shows a sampling of outdoor air.
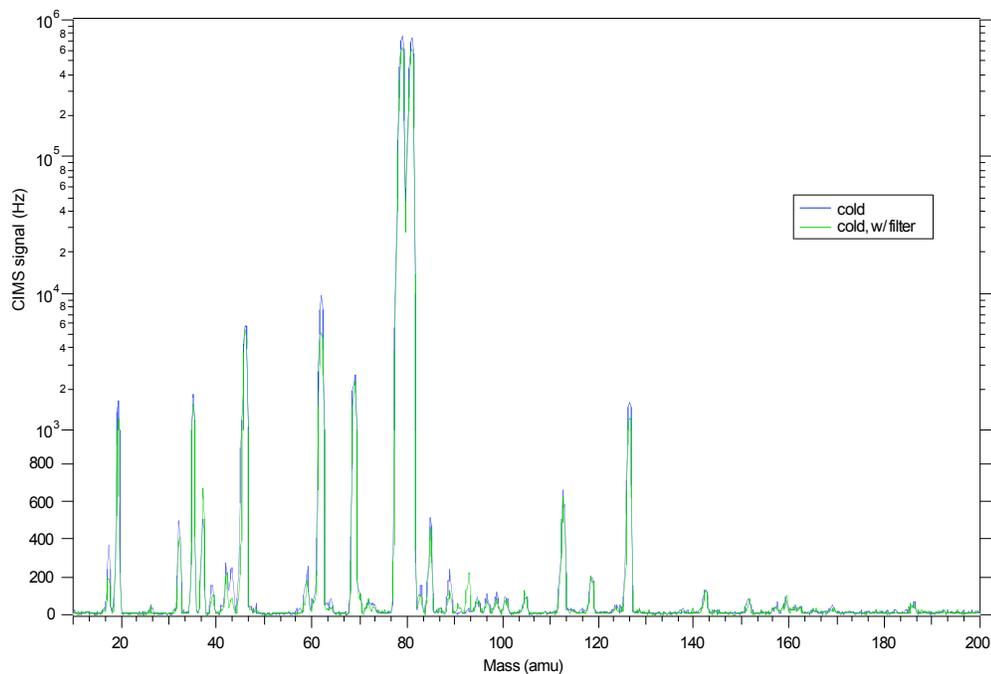
Figure 5a. Gas-phase mass spectrum of ambient indoor air using Br⁻. The plot is linear to 1000 Hz and logarithmic above in order to reduce noise. The peak at mass 62 amu corresponds to ~500 pptv of nitric acid (unfiltered).

Figure 5b. Gas-phase mass spectrum of ambient outdoor air in Atlanta, Ga on August 7, 2005 using Br⁻. The plot is linear to 1000 Hz and logarithmic above in order to reduce noise. The peak at mass 62 amu corresponds to ~350 pptv of nitric acid (unfiltered).
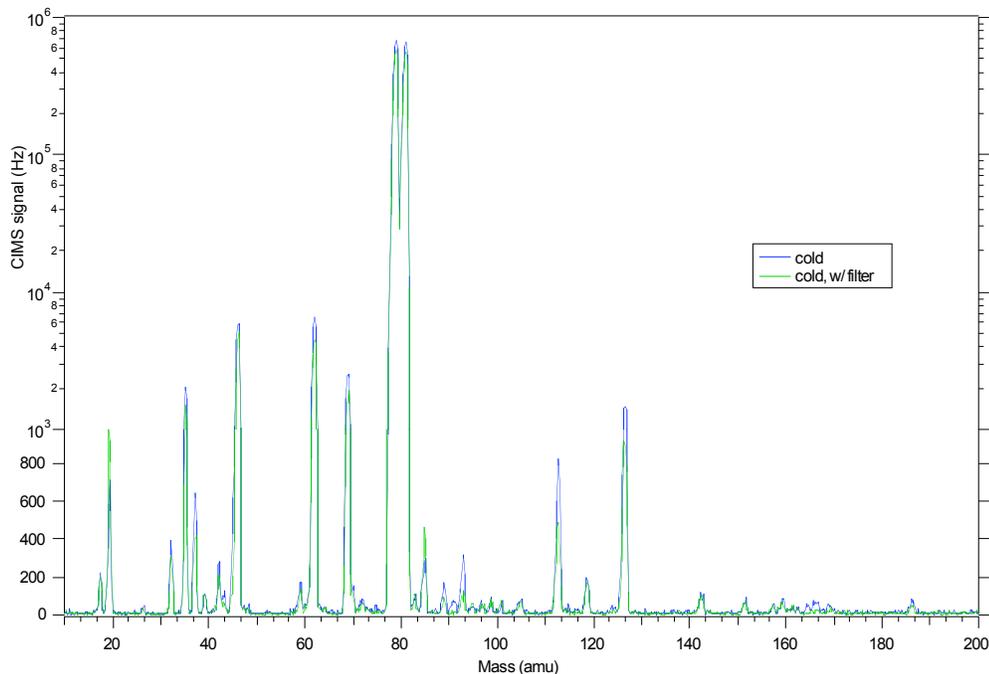
These gas phase comparisons were conducted with a cold, or room temperature (~25°C) inlet, and the filter used was a charcoal scrubber. Both mass spectra were found to be relatively clean, with a significant peak found at mass 62 (NO_3^-), as expected. A strong PAN signal was not observed, most likely due to water in the ambient air. Peaks at mass 69 (CF_3^-) and mass 113 ($CF_3CO_2^-$) are indicative of trifluoroacetic acid ($CF_3C(O)OH$) from Teflon used in the inlet. Other noticeable peaks were found at mass 35, mass 46 (NO_2^-), and mass 127. The peak at mass 35 is probably $OH^-\cdot(H_2O)$ and is due to water reactions. The NO_2^- detected at mass 46 is mostly likely due to the breakup of NO_3^- in the CDC. The peak at mass 127 is probably I^- and could be indicative of Br^- reacting with something in the air, perhaps CH_3I. The peaks at masses 79 and 81 are the two isotopes of the Br^- reagent ion. Using the filter did not result in significant differences in the mass spectra. The peak for nitric acid dropped by ~100 pptv, assuming a nitric acid sensitivity of ~20Hz pptv^{-1}, the typical sensitivity found for these experiments.

3.2 Sulfate and Nitrate Aerosol

In order to determine if the CIMS could detect aerosol sulfate, a 10^{-3}% ammonium sulfate solution was run through a nebulizer and into the CIMS system and heated over a range of temperatures to find the optimal inlet temperature. The temperature profile for the sulfate aerosol can be seen in Figure 6. The sulfate signal was found to peak at about 450°C.
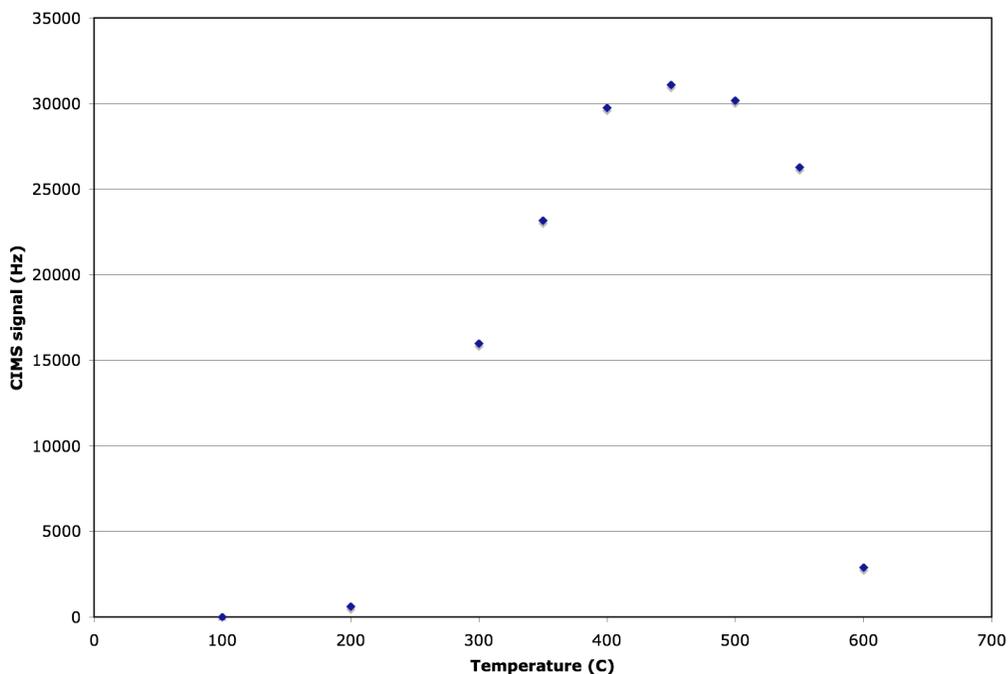
Figure 6. Temperature profile for ammonium sulfate calibration.

With 8 μg m^{-3} of ammonium sulfate aerosol coming out of the nebulizer at a rate of 3.2 slpm into a total inlet flow of 4 slpm, we found the sensitivity of the CIMS to sulfate to be 7000 Hz μg^{-1} m^{-3}. The limit of detection was ~3 ng m^{-3}, with an integration period of 1 second. A typical background measurement for ammonium sulfate was ~0.1 μg m^{-3}. The time response of the CIMS to ammonium sulfate addition can be seen in Figure 7.

Figure 7. Time response of CIMS to aerosol sulfate in ambient air. The sulfate level in the figure is ~1.75 μg m^{-3}. The standard deviation of the background is ~0.03 μg m^{-3}.
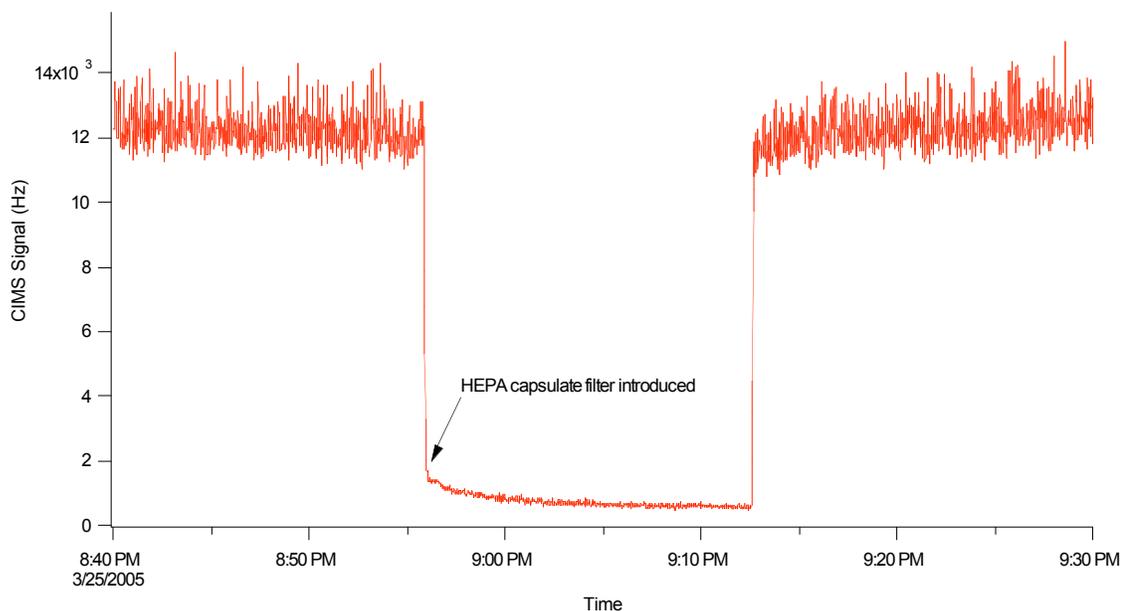
We also attempted to use a sodium sulfate solution to generate sulfate aerosol, however, the sodium sulfate was found to be involatile in the system due to its high boiling point.

In order to quantify the CIMS sulfate measurements, they were compared to sulfate measurements from the PILS instrument. The correlation between the CIMS and PILS sulfate aerosol measurements was determined by running the instruments concurrently on March 22-29, 2005. The correlation between the instruments was found to be robust as can be seen in a representative correlation from March 25, 2005 in Figure 8, with R^2 = 0.91 for 102 points, corresponding to the average of the CIMS measurements over the course of the PILS 90-second average (correlations ranged from 0.74 to 0.96 over 5 days, with an average of 97 points per correlation).
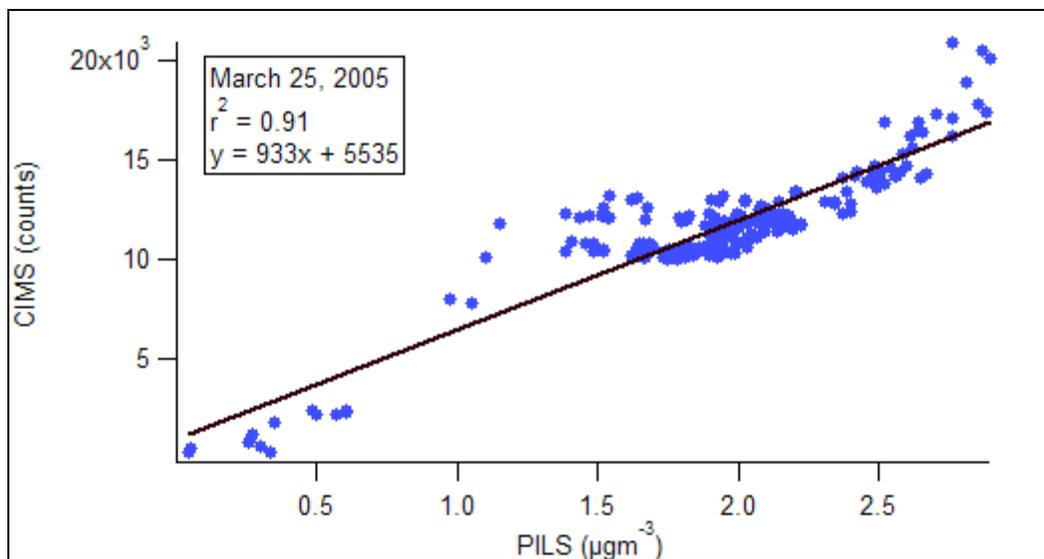
Figure 8. Correlation plot for sulfate aerosol measurements between CIMS and PILS sampled from ambient air. CIMS measurements were averaged over the PILS 90-second time interval.

The same nebulizer set-up used to determine the CIMS sensitivity was used for the correlation measurements.

In order to characterize the CIMS sensitivity to nitrate, the CIMS and PILS instruments were run concurrently on March 22-29, 2005. The procedure by which the PILS measures nitrate aerosol is similar to that described in *Orsini, et al*. [2002]. Both instruments sampled from the outdoor sample line described above. Outdoor air was sampled by both machines for 15 minutes, and backgrounds were taken every 5 minutes by running the outdoor air through a HEPA filter. The nitrate measurements of the two instruments were found to be very poorly correlated, with the best correlation being 0.36 (March 24, 2005, with approximately 109 points), as can be seen in Figure 9. This poor correlation may result from the highly variable nitrate background of the CIMS, which could be ameliorated by adding ammonia into the CIMS as described by Huey et al. [1998].
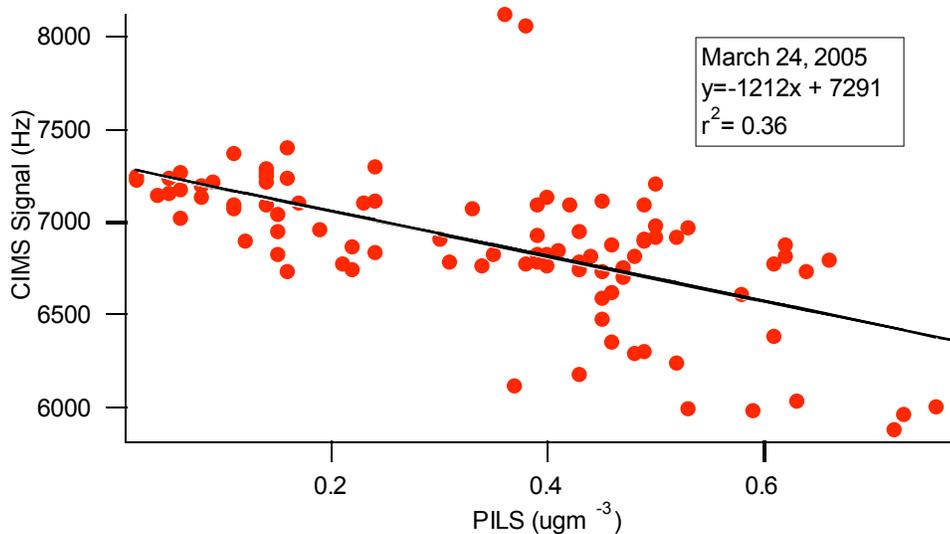
Figure 9. Correlation plot for nitrate aerosol measurements between CIMS and PILS sampled from ambient air. CIMS measurements were averaged over the PILS 90-second time interval.

Mass spectra of both indoor and outdoor air were also taken for aerosol phase measurements on August 7, 2005. Comparisons of the CIMS signal both filtered and unfiltered can be seen in Figures 10a and 10b, conducted over a range of masses (10 to 200 amu). Figure 10a shows the comparison with a sampling of indoor air, while Figure 10b shows a sampling of outdoor air.
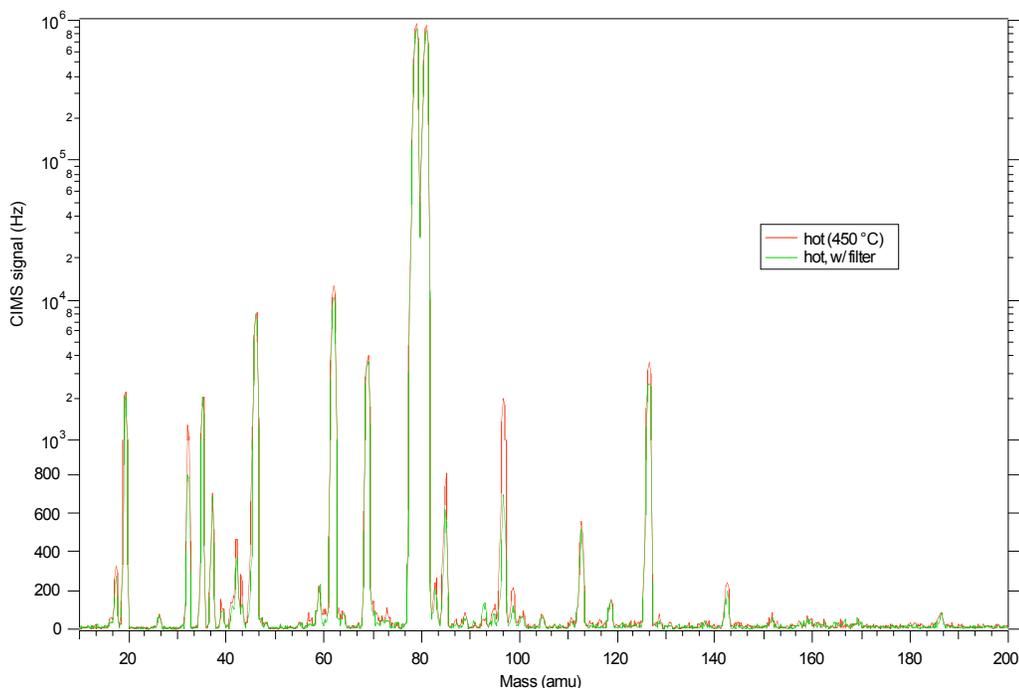
Figure 10a. Aerosol-phase mass spectrum of ambient indoor air using Br⁻. The plot is linear to 1000 Hz and logarithmic above in order to reduce noise. The peak at mass 97 corresponds to ~.25 µg m^{-3} (unfiltered).
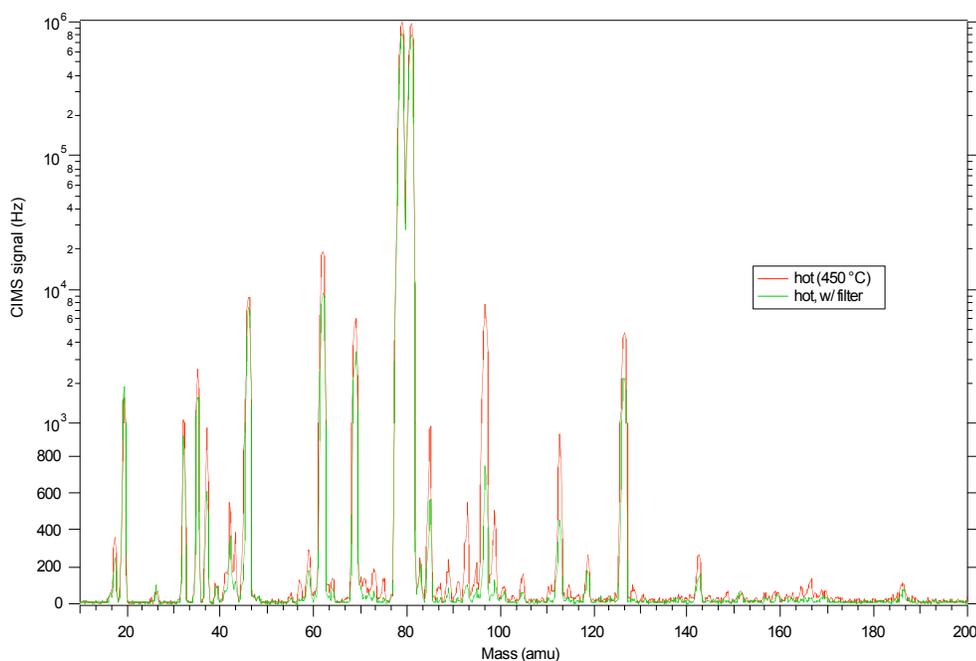
Figure 10b. Aerosol-phase mass spectrum of ambient outdoor air in Atlanta, Ga on August 7, 2005 using Br⁻. The plot is linear to 1000 Hz and logarithmic above in order to reduce noise. The peak at mass 97 corresponds to ~.82 µg m^{-3} (unfiltered).

These aerosol-phase comparisons were conducted with the inlet heated to ~450°C, and a charcoal scrubber was also used as the filter. As with the gas-phase mass spectra, the aerosol-phase mass spectra were also fairly clean, but the CIMS signal was higher across the spectrum than for the gas phase. A significant peak was seen at mass 97 (HSO_4^-), as expected, and was higher, by ~0.86 μg m^{-3}, for the outdoor sample. The same peaks at masses 35, 46, 69, 113, and 127 seen in the gas phase mass spectra were also seen here. The peak for nitrate at mass 62 was also seen, which is probably from a combination of gas-phase nitric acid and particulate nitrate. The sulfate peak was only peak that changed significantly when the air sample was filtered, dropping by ~0.14 μg m^{-3} for the indoor sample and ~0.7 μg m^{-3} for the outdoor sample.

Fast, sensitive and selective measurements of PAN and nitric acid can be achieved using the gas-phase CIMS set-up. The PAN signal was found to be greatly reduced by the addition of water to the inlet; this behavior is the opposite of that shown by I^- observed by Slusher et al. [2004], we speculate that this may be due to Br^- binding water more strongly than I^-.

$$Br^- + H_2O \rightarrow (Br^- \cdot H_2O) \qquad (\Delta_r G° = 30.5 \pm 3.3 \text{ kJ mol}^{-1}) \text{ [Lias 2005] (13)}$$

$$(Br^- + H_2O) + H_2O \rightarrow (Br^- \cdot 2H_2O) \quad (\Delta_r G° = 26.0 \pm 4.2 \text{ kJ mol}^{-1}) \text{ [Lias 2005] (14)}$$

$$I^- + H_2O \rightarrow (I^- \cdot H_2O) \qquad (\Delta_r G° = 23.0 \pm 1.0 \text{ kJ mol}^{-1}) \text{ [Lias 2005] (15)}$$

$$(I^- + H_2O) + H_2O \rightarrow (I^- \cdot 2H_2O) \qquad (\Delta_r G° = 17.0 \pm 2.0 \text{ kJ mol}^{-1}) \text{ [Lias 2005] (16)}$$

This leads to larger water clusters for Br^- than I^- at the same relative humidity. These larger water clusters (i.e. $Br^- \cdot (H_2O)_n$) may be effectively well solvated and less reactive than bare Br^-. The reduction in PAN signal with the addition of water means that this technique is most useful in drier environments. The technique could possibly be used for aircraft-based measurements at high altitudes or in polar regions. PAN measurements in more humid environments could be improved by the use of a selective membrane to remove water from the sampled air; however, the membrane would also remove soluble gases, which would prevent the possibility of simultaneous measurements of PAN and nitric acid.

Mass spectra taken for both the gas and aerosol phases were relatively clean, but showed strong peaks corresponding to nitrate and sulfate, respectively. Because Br^- is the conjugate base of a strong acid, it will only react with strong acids, which is

evidenced by the mass spectra in that not many peaks are found above 120 amu. Though there is some evidence of small amounts of organic acid, the spectra do not exhibit a large signal in a chemically complex urban environment.

We have also found that we can evaporate ammonium sulfate and can efficiently detect sulfuric acid with a low limit of detection and a fast time response. CIMS sulfate measurements agreed well with measurements by the PILS instrument, which offers hope of quantitative measurements of sulfate aerosol. Accurate nitrate measurements could not be achieved due either to an inability to volatize nitric acid in the ambient aerosol, or to the highly variable background. The addition of ammonia in future investigations might help stabilize the background to achieve better nitrate measurements.

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