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Development of a Chemical Ionization Ion Trap Mass Spectrometric Method for Trace Level Determination of Molecular Halogens

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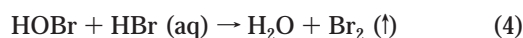
An ion trap mass spectrometric technique using negative ion chemical ionization has been developed for the quantitative determination of the molecular halogen species Br_2, Cl_2, and BrCl. The technique utilizes NO_2^- as a chemical ionization reagent in an electron-transfer reaction to form the corresponding molecular anions of the halogen species, lending excellent selectivity to the measurement. Reaction rate experiments performed in the ion trap yield a rate constant for $Br_2 + NO_2^- \rightarrow Br_2^- + NO_2$ of $(1.4 \pm 0.6) \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1}, determined relative to published data for $Cl_2 + NO_2^- \rightarrow Cl_2^- + NO_2$. This paper describes a mass spectrometer pinhole inlet design and cryogenic preconcentration system for detection of the molecular halogens at atmospherically relevant concentrations. Linear calibration curves were obtained for Cl_2 and Br_2 over 3 orders of magnitude and indicate limits of detection of 50 and 8 pmol for 3.8- and 5.1-L samples, respectively, corresponding to 220 and 50 parts per trillion (mole/mole). Quantitation is based on the total signal at m/z values of 70, 72, and 74 for Cl_2 and 158, 160, and 162 for Br_2. The effects of water vapor on the cryogenic preconcentration step are quatitatively assessed.

The importance of molecular halogen species in the Earth's troposphere has been discussed with recently increasing frequency. Chlorine concentrations as high as 150 parts per trillion (ppt) (mole of Cl_2/mole of air) have been measured off the east coast of North America.[1,2] Bromine and bromine chloride have been detected at significant concentrations near the frozen Arctic Ocean at Alert, Canada,[3,4] and are thought to play a role in the observed, sudden and total ozone destruction in the Arctic lower atmosphere at polar sunrise.[5]

In these ground level ozone depletion events, ozone concentrations fall from ~50 ppb (mol/mol of air) to sometimes less than 1 ppb.[5,6] The actual mechanism for ozone destruction is believed to be very similar to ozone destruction in the stratosphere, i.e., destruction by halogen atom initiated and catalyzed chain reactions. The bromine-catalyzed destruction of ozone is shown in reactions 1 and 2.[7]

$$Br + O_3 \rightarrow BrO + O_2 \qquad (1)$$

$$BrO + BrO \rightarrow O_2 + 2Br \qquad (2)$$
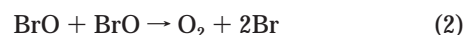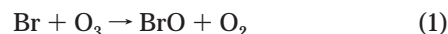
In the lower Artic troposphere, a Br atom branching chain reaction occurs, as first proposed by Fan and Jacob,[8] because HOBr, formed in reaction 3, deposits on the saline surface of ice or particles and oxidizes Br^- to Br_2 (reaction 4), which volitilizes, ulitmately releasing two Br atoms through photolysis (reaction 5) and giving rise to a "bromine explosion."

$$BrO + HO_2 \rightarrow HOBr + O_2 \qquad (3)$$

$$HOBr + HBr \ (aq) \rightarrow H_2O + Br_2 \ (\uparrow) \qquad (4)$$

$$Br_2 + h\nu \rightarrow 2Br \qquad (5)$$

Proof of this mechanism comes in part from detection of BrO, which is believed to be produced in the atmosphere solely by reaction 1.[9] This bromine explosion and the Br and BrO species produced are also thought to be important as oxidizers in the rapid depletion of Hg° during polar sunrise in the Arctic, where the resulting Hg^{2+} products deposit to the ocean and impact biota.[10] Ground level BrO has been observed not only in the Arctic[7] but at other mid-latitude inland lake sites as well,[11,12] indicating that

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tropospheric halogen chemistry may play a significant role in atmospheric oxidation chemistry even away from the Arctic.

Halogen atoms and radicals are potent oxidizers of a variety of species. For example, Cl atoms react with CH_4 ~16 times faster[13] than the dominant atmospheric oxidizer, OH. Emissions of Cl_2 may significantly impact the oxidizing characteristics of urban environments where it is emitted as a result of industrial processes such as polymer production and municipal water disinfection. For example, ~13 metric tons day^{-1} of Cl_2 are emitted[14] in Houston, TX.

Vertical profiles of ozone concentrations at Alert indicate the loss is mediated by chemical processes occurring at the earth's surface,[5] which in the Arctic is snow, ice, or open seawater. The source of the halogen atoms is thought to be molecular halogen species Br_2, Cl_2, and BrCl, produced from the chloride and bromide naturally present in seawater.[15] Measurements indicate concentrations of Br_2 and BrCl in the 10 ppt (mol/mol of air) range at Alert, Canada, within the Arctic Circle, while Cl_2 was not observed above the detection limit. The concentrations of these compounds have a strong anticorrelation with ozone concentrations, consistent with their involvement in the ozone depletion chemistry.[4] Laboratory evidence[16] shows that Br_2 can be produced on ice, in a process involving reaction 4.

Spatial resolution limitations of the molecular halogen data, however, do not allow for a thorough investigation of the sources of the molecular halogens on the surface in the Arctic. Questions still remain as to the roles different features of the snowpack play in the production of these photochemically active gases. For example, frost flowers[17] may be especially active emitters of halogens because of their high salt content and surface area. However, the environment that produces frost flowers, i.e., refrozen leads, is inhospitable. Portable instrumentation is needed to enable definitive exploration of molecular halogen sources. Elucidating the chemistry that produces molecular halogens in the Arctic will have implications concerning its formation at lower latitudes as well.

Previous analytical methods for the detection of atmospheric halogen species lacked the specificity to differentiate between molecular halogens and other halogen atom-containing species.[1,18] Foster et al.[3] used a triple quadropole mass spectrometer with atmospheric pressure chemical ionization to provide this specificity in the ability to quantify based on the signal at the mass-to-charge ratio of the molecular ion of the molecular anion. Selectivity for the molecular halogen was achieved by mass spectrometry/mass spectrometry, and the reported limits of detection for the technique were 0.2, 2, and 2 ppt for Br_2, BrCl, and Cl_2.

Ion trap mass spectrometry allows for a more portable analytical method and has been successfully miniaturized[19] to the point of field portability. Compared with other instruments (especially other types of mass spectrometers), ion traps are low power, low mass, and thus more capable of measuring molecular halogens in varying terrain (ice, water, snow).

The method discussed herein uses negative ion chemical ionization (CI) to provide selective ionization of the molecular halogens Br_2 and Cl_2. The ionization proceeds via an electron-transfer reaction between NO_2^- (CI reagent) and the analyte (reactions 6 and 7).

$$NO_2^- + Cl_2 \rightarrow NO_2 + Cl_2^- \qquad (6)$$

$$NO_2^- + Br_2 \rightarrow NO_2 + Br_2^- \qquad (7)$$
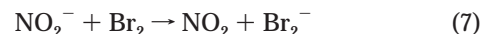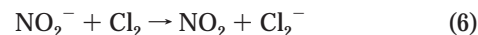
The specificity required for the detection of molecular halogens dictates that the halogen–halogen bond not be broken in the chemical ionization reaction. Thus, the enthalpy changes of reactions 6 and 7 must not be greater than the bond dissociation energy (BDE) of X_2^-. The enthalpy changes of electron-transfer reactions can be expressed as the difference in electron affinity (EA) between the neutral analogue of the reactant ion and that of the neutral reactant (eq I). The EA of NO_2 is reported[20] to be 2.3

$$\Delta H_{rxn\ 6/7} = EA(NO_2) - EA(X_2) \qquad (I)$$

eV. For reaction 6 involving Cl_2 with an electron affininity of 2.5 eV,[21] the enthalpy change is 0.2 eV, well below the 2.5-eV BDE[22] of Cl_2^-. Reaction 6 is well characterized[23] with a measured rate constant of 6.8×10^{-10} cm^3 molecule $^{-1}$ s^{-1}. The suitability for this chemical ionization scheme with respect to Br_2 was investigated. For molecular bromine, EA = 2.55 eV[21] and thus the enthalpy change for the chemical ionization reaction is only 0.25 eV, well below the 1.2-eV BDE[22] of Br_2^-. We conducted relative rate experiments to determine the rate constant for reaction 7 relative to that for reaction 6. The EA of BrCl is not documented in the literature, but we make the assertion that it most likely has a value between that of Cl_2 and Br_2. Moreover, gas-phase standards of BrCl are difficult to generate, so the remainder of the discussion will concentrate on Cl_2 and Br_2 under the assumption that the experimental conditions will apply equally well to the detection of BrCl.

Modern ion trap mass spectrometers do not typically have the sensitivity necessary to detect low ppt concentration levels by direct injection of ambient air. Preconcentration is often required to deliver the appropriate amount of analyte to the mass spectrometer. We report the development of a technique that uses cryogenic preconcentration of dried ambient air along with

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negative ion chemical ionization to achieve low ppt detection levels of atmospheric molecular halogens in an ion trap.

EXPERIMENTAL SECTION

All experiments were performed using a Finnigan GCQ Plus ion trap mass spectrometer. Nitromethane (Aldrich, 99+%) was ionized via electron impact ionization in an ion source external to the ion trap to produce NO_2^-, the CI reagent. Introduction of nitromethane to the vacuum chamber was controlled with a needle valve to a pressure in the vaccum chamber of $\sim 2 \times 10^{-5}$ Torr (uncorrected) as measured using an ion guage (Granville-Phillips). The halogen species were introduced into the ion trap with the ion trap bath gas, He (grade 99.999%, BOC Gases). Flow control of the bath gas into the vacuum chamber was accomplished with a 4 ± 1 μm pinhole (Lenox Laser) in a 6.5-mm-diameter, 1-mm-thick PTFE disk (Interplast, Inc.) held inline by PEAK fittings, machined in-house. Experiments confirmed that this flow restriction provided for the least loss of analyte (most importantly bromine) to surfaces. Bromine and chlorine permeation devices (VICI Metronics Inc.) kept at 30 °C in constant-temperature ovens (VICI) swept by He in the case of rate constant determinations, or dry, zero air in the case of gas-phase standard generation for the analytical method evaluation, provided sources of gas-phase molecular halogens. The permeation rates of these devices were determined by mass change over time and further confirmed by ion chromatography.[24] All gas lines used in these experiments were PFA Teflon.

Rate constant determination experiments were performed with a halogen/He flow rate of 0.1 mL/min through the PTFE pinhole for both the Cl_2/He and Br_2/He gas mixtures. Varying the flow rate of He (in the 5−50 mL/min range) past the halogen permeation devices gave halogen/He gas mixtures of varying halogen concentrations in the 0.1−6.0 ppm range. These dilute halogen mixtures were allowed to flow past the pinhole inlet of the ion trap with most of the mixture being vented and the relatively small 0.1 mL/min flow entering the mass spectrometer. The use of the same inlet for both Cl_2/He and Br_2/He mixtures assured the same bath gas pressure throughout the experiment. The partial pressure of each halogen species in the ion trap was controlled by varying the halogen concentration in the halogen/ He mixtures.

For each halogen/He mixture introduced into the ion trap, the halogen was allowed to react with the previously isolated NO_2^- for periods of 1, 3, 5, 7, and 9 ms before all ions accumulated in that time were ejected from the trap. This was accomplished using Finnigan's Xcalibur ion trap control software by creating an MS/ MS experiment with excitation periods of the aforementioned times without a dc voltage applied to the end caps of the trap. The abundance of NO_2^- ions in the trap was well in excess of the neutral halogen molecules in each experiment, evidenced by a linear increase in X_2^- signal and no decrease in NO_2^- signal over the reaction times used.

Application of this pinhole inlet/chemical ionization scheme to the detection of (near) ambient levels of molecular halogens required the use a preconcentration step that served to both preconcentrate the halogen analytes and remove the sample air
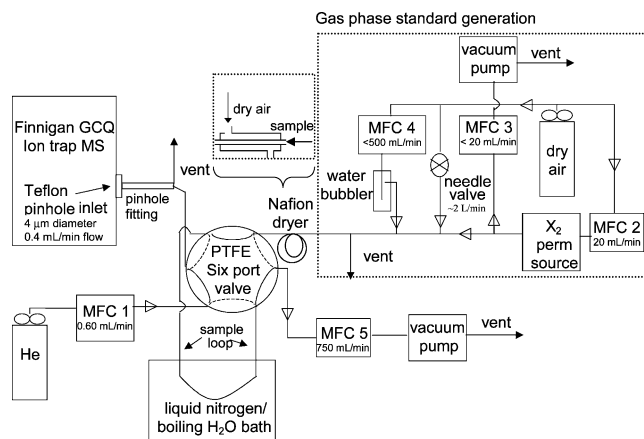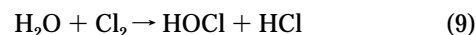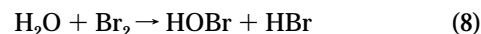
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**Figure 1.** Schematic diagram of ambient sampling instrument with cyrocooled trap. The gas-phase standard generation system used for calibration is also shown. MFC, mass flow controller.

matrix, as shown in Figure 1. Gas-phase halogen standards were drawn through a 15-cm-long segment of $^1/_{16}$-in.-o.d. PFA tubing immersed in liquid nitrogen (hereafter cryotrap) for a known period of time, usually ∼5 min. Under those conditions, the vapor pressure of Cl_2 and Br_2 is sufficiently low for quantitative collection of the halogen species in the PFA tubing. The cryotrap is then purged (at 77 K) with He at 0.6 mL/min to remove air, which would interfere with the mass analysis step in the ion trap under current instrument control conditions. Upon removal of the air, the cryotrap was rapidly heated to ∼90 °C to volatilize the halogens. The trapped halogens were transferred with the He flow to the PTFE pinhole, which for the analytical method evaluation experiments allowed He flow of 0.4 mL/min directly into the ion trap. A vent to the atmosphere allows the remainder to escape and keeps the sample line at atmospheric pressure. For these analyses of near-ambient concentrations, the CI reaction was performed inside the ion trap using the same trap control functions except for a fixed 30-ms reaction time.

Gas-phase standards were produced (Figure 1) by the dilution of Cl_2 and Br_2 outputs from the permeation devices with dry, zero air (BOC Gases). Flow through the temperature-controlled permeation device was controlled at 20.0 mL/min with a mass flow controller (MKS). A portion (1−19 mL/min) of this flow was then pumped away using another mass flow controller. The resulting difference flow was then diluted with 2 L/min of dry air flow to the final sample concentration.

As both Br_2 and Cl_2 are known to undergo hydrolysis in water (reactions 8 and 9), experiments were performed to determine the analyte signal as a function of absolute

$$H_2O + Br_2 \rightarrow HOBr + HBr \qquad (8)$$

$$H_2O + Cl_2 \rightarrow HOCl + HCl \qquad (9)$$

humidity. Humidified air was generated by bubbling dry air though deionized water at a rate of 10−450 mL/min. Humidity values were calculated based on dilution of 100% relative humidity air.

It was found that atmospherically relevant humidity levels resulted in a measurable decrease in signal for the molecular
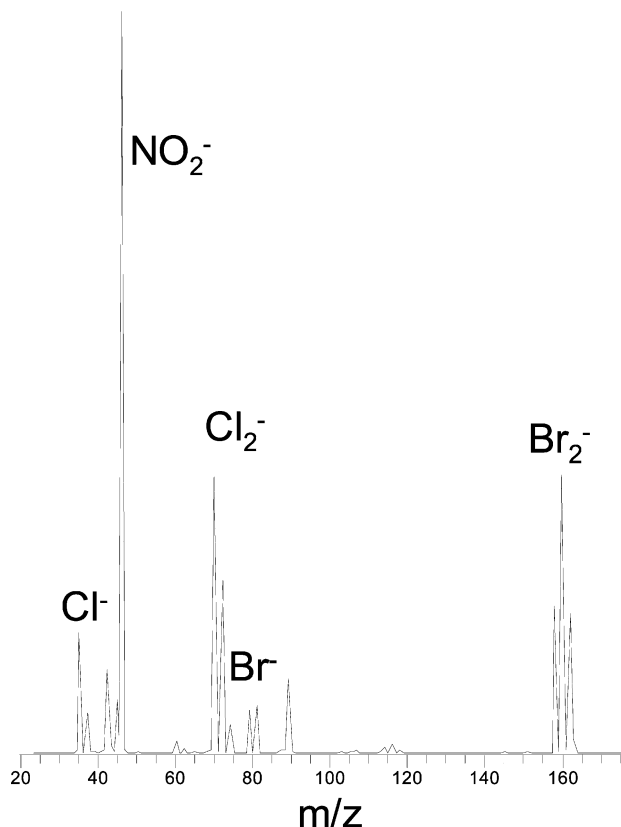
Figure 2. Mass spectrum of products of the NO_2^- + Br_2 and NO_2^- + Cl_2 reactions. The molecular halogen concentrations in the He bath gas are in an $[NO_2^-]$-depleting regime ($\sim$50 ppm) for illustrative purposes.

halogens; thus, it was necessary to dry the sample air. This was accomplished by using a Nafion dryer (Perma Pure). The dryer consisted of two concentric 3.6-m-long pieces of tubing. The inner tubing is a sulfonated polymer with high water permeability; the outer tubing is PFA Teflon. Sample flows through the inner tubing and countercurrent dry gas (in these experiments, air) flows outside the water-permeable polymer. We describe experiments in which we examine the halogen signal as a function of humidity with and without drying of the sample air.

RESULTS AND DISCUSSION

Ion Chemistry. Figure 2 shows a mass spectrum resulting from the chemical ionization of a mixture Br_2 and Cl_2 by NO_2^-. The CI reaction leads to molecular anion-to-atomic anion ratios of $\sim$5 for chlorine and $\sim$10 for bromine. Production of the halide ions likely results from X−X bond cleavage in a vibrationally excited X_2^-, perhaps made possible in part by superambient trap temperature in the non-temperature-controlled trap. However, the X_2^-/X^- signal ratios indicate relatively few halogen−halogen bonds are broken during the reaction, and as predicted by EA values, the NO_2^- + Br_2 ion molecule reaction is exothermic and proceeds under the conditions of the experiment.

Figure 3a shows a plot of the total (Cl_2^- + Cl^-) and (Br_2^- + Br^-) signal normalized by the NO_2^- signal as a function of reaction time in the ion trap that results from reactions 6 and 7. The rate constant for reaction 6 (k_6) is known[23] to be 6.8×10^{-10} cm^3 molecule^{-1} s^{-1}. The rate constant k_7 can be calculated relative to k_6. Both Br_2 and Cl_2 were added to the bath gas, and the conditions

were such that the reactions were pseudo first order with respect to the halogens so that $[NO_2^-]$ in the ion trap was not appreciably depleted over the course of the reaction. Equations II and III express the increase in halogen ion signal (accounting for some bond breakage and subsequent halide ion formation) normalized to $[NO_2^-]$ with time.

$$d[Cl_2^- + Cl^-]/[NO_2^-] = k_6[Cl_2]\,dt \qquad (II)$$

$$d[Br_2^- + Br^-]/[NO_2^-] = k_7[Br_2]\,dt \qquad (III)$$

Figure 3a shows the linear relationship between the NO_2^--normalized ion products of the reaction and time, as expected. The intercept for each curve represents the ion−molecule reaction products formed during the time from the beginning of the ion ejection scan until the time of detection of the ion product, plus any products formed during any additional time offsets that the instrument software adds. Data were obtained for several different values of $[Br_2/Cl_2]$ inside the ion trap. Equation IV expresses the linear relationship between the ratio of the slopes for data plotted as in Figure 3a and the halogen concentration ratios (i.e., for III/II).

$$\frac{d[Br_2^- + Br^-]/dt}{d[Cl_2^- + Cl^-]/dt} = \frac{k_7[Br_2]}{k_6[Cl_2]} \qquad (IV)$$

The plot of the ratio of the slopes versus the ratio of the halogen concentrations ($[Br_2/Cl_2]$ ranged from 0.3 to 4) in Figure 3b yields a slope $k_7/k_6 = 2.1 \pm 0.3$. Estimating an uncertainty of $\pm30\%$ in k_6 based on the flowing afterglow technique used in that determination yields a value of $(1.4 \pm 0.6) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} for k_7.

Collision rate coefficient calculations using the Su and Chesnavich method[25−27] yielded values of 9.6×10^{-10} cm^3 molecule^{-1} s^{-1} for reaction 6 and 1.1×10^{-9} cm^3 molecule^{-1} s^{-1} for reaction 7. The calculated collision rate is within the bounds of the uncertainty of our measured rate constant for reaction 7 and indicates that the reaction occurs effectively at the collision frequency.

Analytical Method Evaluation. Performing the CI reaction in the ion trap provides not only excellent molecular ion to atomic ion signal ratios for Br_2 and Cl_2 (typically 5−15) but also good signal-to-noise ratios for the mass-to-charge ratios of interest (m/z = 70, 72, and 74 for Cl_2 and m/z = 158, 160, and 162 for Br_2) and good selectivity for the detection of molecular halogens versus halogen-containing compounds. Panels a and b of Figure 4 show selected ion chronograms (ion signals vs time with no chromatography involved) for Cl_2 and Br_2, respectively. The chronograms represent sequential 30-ms reaction times between NO_2^- isolated in the ion trap and the injected halogen/He mixture from the cryotrap upon heating. Selected ion monitoring allows signal to be collected in the form of a peak and integrated for quantitation. The peak area normalized for NO_2^- signal is proportional to the number of moles of halogen injected. Peak widths are a function

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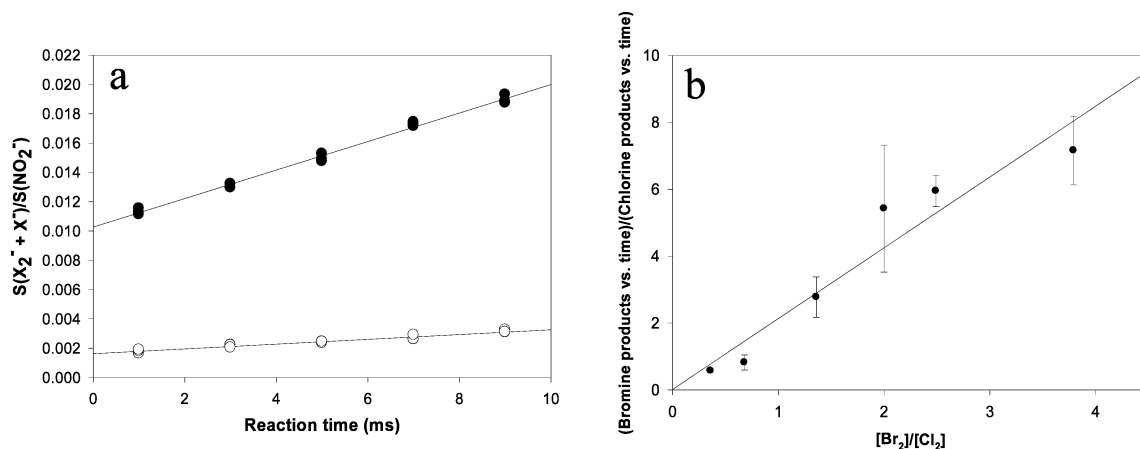
Figure 3. Relative rate constant determination data for $k_{Br_2 + NO_2^-}$ determination. (a) Plot of increase in signal with reaction time; open circles are Cl_2^- signal, closed circles Br_2^-. (b) Plot of relative reaction rate vs relative halogen concentration from multiple experiments. The slope is 2.1 ± 0.3.
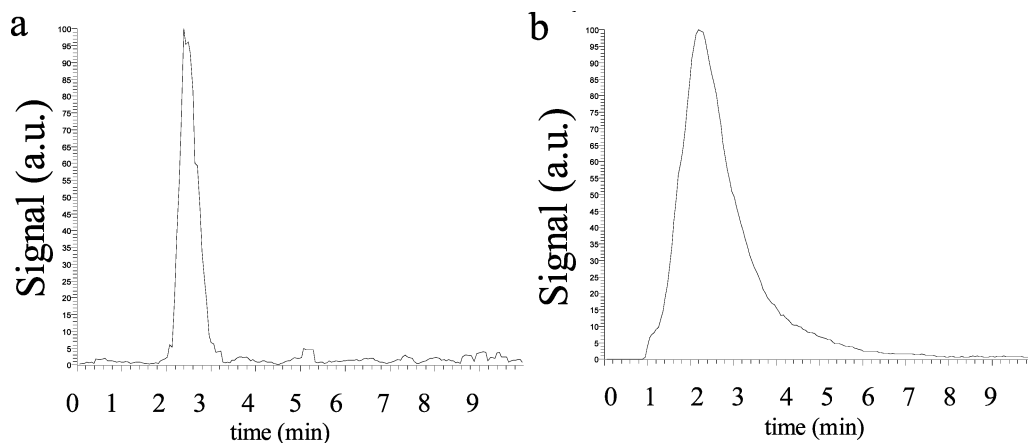

Figure 4. Selected ion chronograms. (a) Chronogram for Cl_2 is the sum of intensities at $m/z = 70$, 72, and 74. Injection of 5.15 L of 9.93 ppb Cl_2 occurred at 1.5 min. The signal is 5-point boxcar averaged. (b). Chronogram for Br_2 is the sum of intensities at $m/z = 158$, 160, and 162. Injection of 3.78 L of 14.2 ppb Br_2 was at 1.0 min. The signal is 15-point boxcar averaged.
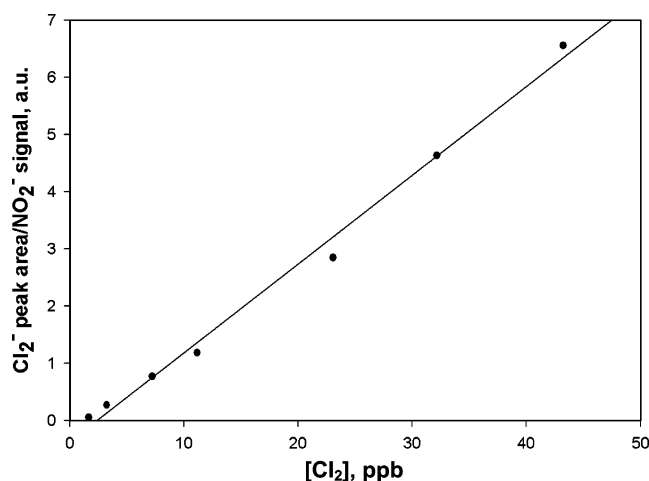

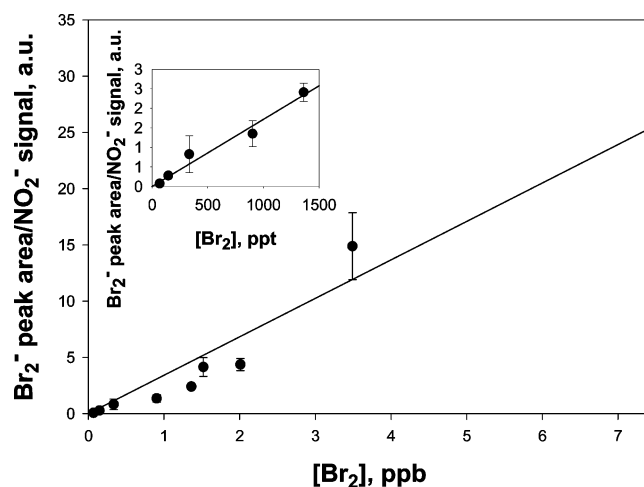**Figure 5.** Calibration curve for Cl_2. Injection of 5.15 L of Cl_2 in air.

Figure 6. Calibration curve for Br_2. Injection of 3.78 L of Br_2 in air.

of He flow rate through the cryotrap and, more importantly, reversible adsorption to the walls of the tubing between the cryotrap and the ion trap. The Cl_2 peak width is noticeably less than the width of the Br_2 peak, indicating that Br_2 molecules experience more reversible interactions with the walls. This is consistent with the lower vapor pressure and greater polarizability of bromine relative to chlorine.

Calibration curves obtained for Cl_2 and Br_2 with constant sampling times (i.e., cyrotrapping times) and constant flow rates through the cryotrap are shown in Figures 5 and 6, respectively. The method is linear over at least 3 orders of magnitude for both species. Nonlinearity at high concentrations (not shown) results from depletion of $[NO_2^-]$ over the course of the 30-ms reaction time in the trap. The relative 1σ precision of the method as
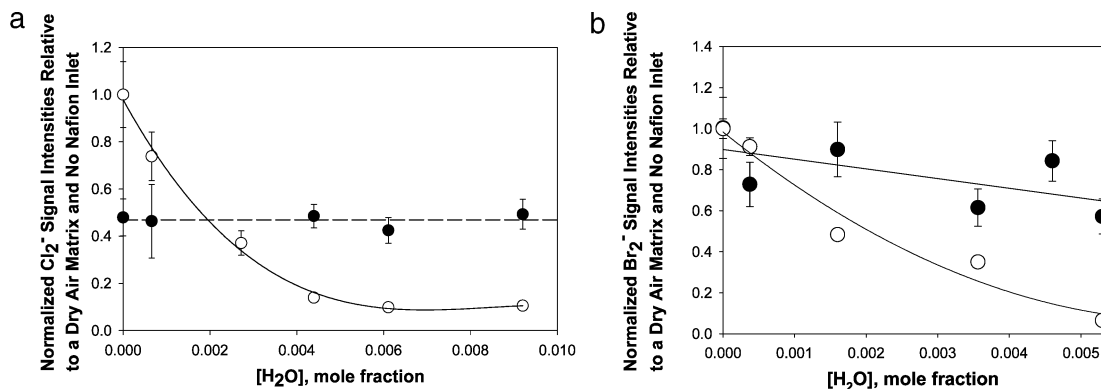
Figure 7. Effects of absolute humidity on Cl_2 and Br_2 signals. All data plotted relative to signal strength of analyte in a dry air matrix without the Nafion dryer in use. Open circles represent data taken without the Nafion dryer; closed circles are data from samples dried by the Nafion dryer: (a) 27 ppb Cl_2 signal; (b) 14 ppb Br_2 signal.

determined from replicate measurements of the same sample is 25% for 25 ppb Cl_2 ($n = 8$) and 20% for 14 ppb Br_2 ($n = 5$).

For ambient determination of Br_2 and Cl_2, low limits of detection are important. Blank samples were analyzed by integrating peak areas that resulted from the trapping and subsequent injection of dry, zero air over the same time span used for the integration of peaks that contain a known amount of halogen. These analyses indicate a LOD (defined as $3\sigma_{blank}$) of 50 ppt Br_2 and 220 ppt Cl_2 for sample volumes of ~4 L at flow rates through the cryotrap of ~1 L/min. Generation of a 70 ppt Br_2 standard yielded a S/N = 5, experimentally confirming the LOD. Since the method involves preconcentration, it is appropriate to express the LOD as the minimum amount (as opposed to concentration) of analyte needed to elicit a detectable signal. For 3.78 L of Br_2 at 50 ppt, the minimum detectable amount of substance is 8 pmol. These LODs can obviously be decreased by increasing the sample volume. For example, a sample volume of 60 L (1 h integrated sample) will yield LODs of 20 ppt for Cl_2 and 4 ppt for Br_2. However, this will decrease the temporal resolution of the data taken, an important aspect of atmospheric measurements since the atmospheric lifetimes of Cl_2 and Br_2 can be as short as 6 min and 20 s, respectively, and thus the concentrations can exhibit substantial temporal variability. Halogen molecular anion signal can also be increased by increasing $[NO_2^-]$ in the ion trap, although at high concentrations, space charge effects limit the magnitude of the potential benefit. Other ionization methods or the electron ionization of other nitro compounds may produce more NO_2^- ions. The upper limit of $[NO_2^-]$ in the ion trap was not investigated in this study. We note that although we have not specifically investigated detection of BrCl, we anticipate that the LOD will be comparable to that of Br_2.

Narrowing the chronogram peak would also lead to a lower LOD and can be achieved by reducing the amount of surface area between the cryotrap and the mass analyzer or by heating or chemically passivating these surfaces, leading to fewer reversible interactions between the analyte and the surfaces. Further specificity can be incorporated by using the mass spectrometry/mass spectrometry (MS/MS) capabilities of the ion trap, although the absence of chemical noise at the masses of the molecular anions indicates that MS/MS may not significantly impact the LOD.

As a major component of ambient air, the effect of water vapor on atmospheric measurement methods must be considered.

Panels a and b of Figure 7 illustrate the impact of water vapor on signal at several water vapor concentrations. Because of the anticipated impact of hydrolysis of the halogens (reactions 8 and 9), we employed a Nafion dryer to remove water vapor from humid samples before cryotrapping. A significant decrease in signal (Figure 7, open circles) was observed at high humidity levels without the Nafion dryer in place, i.e., when water vapor was being trapped as well as the analyte.

Reactions 8 and 9 have been characterized in solution[28,29] and have the potential to destroy the halogen analytes, most likely during the injection process. Less is known concerning the kinetics and thermodynamics of these reactions on the surface of ice or at the temperatures encountered in the cryotrap. It is possible, although not investigated experimentally, that these reactions account for the decrease in halogen signal. The drying accomplished by the Nafion system is significant enough to maintain a constant signal over the range of humidities studied and the humidities that one might expect in an Arctic environment. At 0 °C, the saturated vapor pressure of H_2O corresponds to a concentration of 0.006 (mole of water/mole of air). Thus, at 100% relative humdity, the technique is relatively free of water interferences for maximum temperatures expected in the Arctic. For summertime urban conditions, it might be necessary to more thoroughly dry the sample.

Although constant signal is observed with the Nafion dryer for Cl_2 over a range of water vapor concentrations, some signal loss relative to an inlet without the Nafion was observed. Very little chemical noise is observed in blank experiments using the Nafion dryer however, so the signal loss is perhaps irreversible interaction between the analyte and the Nafion. For Br_2, no significant loss of analyte through the dryer was observed. These experiments indicate that the method will be applicable to the atmospheric detection of low ppt Br_2 and Cl_2 concentrations at ambient humidities for sub-273 K conditions and that it is likely to be viable for BrCl determinations.

CONCLUSIONS

A method has been developed for the determination of atmospheric molecular halogen species using chemical ionization ion trap mass spectrometry with cryogenic preconcentration. The

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effectiveness of electron-transfer reactions between NO_2^- and Br_2 and Cl_2 was investigated, and a rate constant for the $NO_2^- + Br_2$ reaction was determined relative to the published value for $NO_2^- + Cl_2$. The chemical ionization scheme provides for good selectivity, and the preconcentration provides for low limits of detection when applied to ambient measurement conditions. The LOD may be improved by using longer sampling times, increasing $[NO_2^-]$ in the ion trap, and facilitating the flow of analyte from the cryotrap to the ion trap. By using a Nafion dryer at the inlet, the system has been shown to be relatively insensitive to water vapor interference. By incorporating the chemical ionization and pre-concentration schemes with an ion trap mass spectrometer, such a method can be employed to provide a relatively portable instrument capable of achieving good temporal and spatial resolution in ambient molecular halogen concentration determinations.