Analysis of Gas Phase Halogen Compounds Using Atmospheric Pressure Ionization-Mass Spectrometry

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I. INTRODUCTION

Environmental chamber studies involve numerous chemical compounds with a variety of physical properties that make it difficult to identify all of them with a single analytical technique. Mass spectrometry is unique in its ability to detect most compounds, and is a valuable component for environmental chamber studies because of this characteristic. We show here that atmospheric pressure ionization-mass spectrometry (API-MS) in the negative ion mode is a highly sensitive and selective technique ideal for measuring halogen compounds such as HOCl, Cl_2, and Br_2 both in laboratory systems and in air. This presentation will focus on the quantitative analysis of HOCl with API-MS [*Foster et al.*, 1999].

Field studies show elevated bromine measurements correlated with surface-level O_3 depletion in the Arctic spring [*Barrie et al.*, 1988]. In order to explain these observations, a very large or recyclable source of gaseous bromine must be identified [*McConnell et al.*, 1992; *Vogt et al.*, 1996]. Sea-salt aerosol and ice contain bromide ions, and are a potential source of gaseous bromine compounds. Hypochlorous acid (HOCl) is a potential intermediate in halogen activation involving deliquesced sea-salt aerosol and sea-salt ice [*Sander and Crutzen*, 1996; *Vogt et al.*, 1996; *Abbatt and Nowak*, 1997; *Chu and Chu*, 1999]

$$HOCl + Br^- \rightarrow\rightarrow BrCl, Br_2 \qquad (1)$$

Existing measurement techniques fail to distinguish HOCl from other chlorine compounds [*Keene et al.*, 1993; *Pszenny et al.*, 1993; *Impey et al.*, 1997a; *Impey et al.*, 1997b]. Chlorine (Cl_2 and HOCl) compounds other than HCl have been identified separate from HCl and organic chlorine in mist chamber studies conducted at mid-latitudes [*Keene et al.*, 1993; *Pszenny et al.*, 1993]. Other studies have been performed wherein photolabile chlorine compounds in the Arctic were photolyzed to produce chlorine radicals, which were reacted with propene to produce the measured compound chloroacetone [*Impey et al.*, 1997b]. This technique was used to measure up to 100 ppt of photolyzable chlorine as Cl_2 (200 ppt Cl radicals) in the high Arctic.

Atmospheric pressure (chemical) ionization-mass spectrometry is a highly sensitive and selective technique which has been used for specific measurements of inoganics [*Spicer et al.*, 1998] and for the identification of organics [*Kwok et al.*, 1995; *Kwok et al.*, 1996a; *Kwok et al.*, 1996b] in air. For example Cl_2 has been measured in the negative ion mode using air as the chemical ionization reagent (*CIR*) gas. Here, O_2 acts as the *CIR* ion by accepting an electron in the corona discharge. In the ionization of Cl_2, electron transfer can occur between O_2^- and Cl_2 forming the Cl_2^- ion observed at m/z = 70, 72, and 74 [*Spicer et al.*, 1998; *Caldwell et al.*, 1999]. This technique is not only selective, but sensitive as well. Spicer et al. have reported a detection limit of Cl_2 using air as the *CIR* gas of ~16 ppt in ambient air [*Spicer et al.*, 1998].

Chemical ionization is a soft ionization technique wherein ion-neutral adduct formation is possible. For example, to detect HONO in ambient air, Spicer *et al*. created Cl^- *CIR* ions by using chloroform as the *CIR* reagent gas. The ion-neutral adduct $(HONO\bullet Cl)^-$, was formed and used to selectively monitor HONO in air. The estimated detection limit in this study was 0.5 ppb, illustrating that sensitive measurements of ion-neutral adducts can be achieved with API-MS [*Spicer et al.*, 1993].

The instruments used in these studies employed tandem quadrupoles which were used to further enhance the selectivity of chemical ionization produced ions. Q1 scans were used to measure a range of m/z ratios with a single quadrupole to survey ions. Multiple reaction monitoring (MRM) scans measured the signal intensity for parent-daughter ion pairs. This is a highly selective technique used for quantitative analysis.

Here we present techniques for quantitative measurements of HOCl with API-MS using air as the *CIR* gas for field and laboratory studies. We also explore the effects of alternative *CIR* gases, such as bromoform ($CHBr_3$), on the selectivity and sensitivity of HOCl measurements with API-MS. A detailed discussion of this work will be presented elsewhere [*Foster et al.*, 1999]. A summary is presented below.

II. EXPERIMENTAL

A schematic of the experimental apparatus is presented in Figure 1.

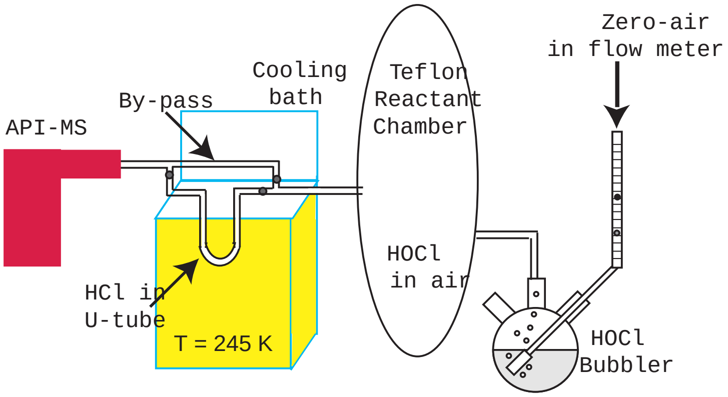

FIGURE 1: Schematic representation of the experimental apparatus used for the heterogeneous titration of HOCl.

Samples in 35-55 L Teflon reaction chambers were flowed into to the API-MS at an estimated flow rate of 1 L min^{-1}. The apparatus included a glass U-tube which was submerged in a cooling bath and equipped with a by-pass. Samples were monitored directly by the API-MS through the by-pass, or diverted through the U-tube.

Experiments were performed to determine the effects of H_2O vapor and acids on the *CIR* ions in air. Dry air samples were prepared by filling an evacuated Teflon reaction chamber with dry zero-air. Humid air samples were prepared by bubbling the zero-air through room temperature ultra-pure water and into a Teflon reaction chamber. The relative humidity of the air was measured as 84% using a humidity and temperature transmitter. Concentrated HCl samples (~300 ppm) were prepared by flowing zero-air through the U-tube containing 37% HCl cooled to 273 K in a cooling bath.

HOCl samples were synthesized by adding sodium hypochlorite (NaOCl) dropwise to anhydrous magnesium sulfate ($MgSO_4$) dissolved in ultra-pure water. The product was vacuum distilled to minimize impurities. Cl_2O and HCl impurities were determined to be < 1% for each species by electron-impact time-of-flight mass spectrometry [*Caldwell et al.*, 1999]. Molecular chlorine impurities were reduced in the experiment by bubbling the HOCl solution rapidly prior to HOCl sample preparation in each experiment. Hypochlorous acid samples were prepared by bubbling zero-air through the HOCl solution into a 35 L Telfon reaction chamber. Further dilution was achieved by adding additional zero-air.

To calibrate HOCl, heterogeneous titration of HOCl with HCl was performed to produce gaseous Cl_2 [*Abbatt and Molina*, 1992; *Chu et al.*, 1993; *Hanson and Ravishankara*, 1993; *Donaldson et al.*, 1997; *Caldwell et al.*, 1999].

$$HOCl + HCl \rightarrow Cl_2 + H_2O \qquad (2)$$

First, HOCl samples were flowed directly to the API-MS through the U-tube by-pass. Next, the HOCl was diverted through the U-tube, which contained a thin layer of dilute HCl and was submerged in a 245 K cooling bath. Throughout, MRM signal intensities for select parent/daughter ion pairs were used to monitor HOCl and Cl_2. The Cl_2 signals were calibrated with known concentrations of pure Cl_2 gas. Calibration of the HOCl was performed by plotting the HOCl signal intensity as a function of calibrated Cl_2 produced in reaction 2.

III. RESULTS and DISCUSSION

A. Effects of H_2O and acids on the CIR ions in air

When air is used as the *CIR* gas, H_2O and acids effect the *CIR* ions. A comparison of the observed ions in dry air, humid air, and air with ~300 ppm of HCl vapor is presented in Figure 2.

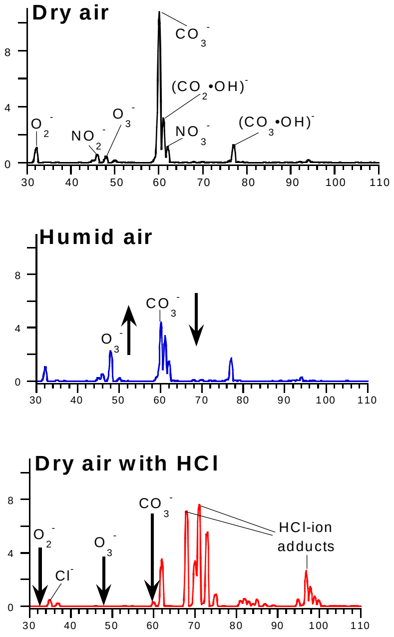

FIGURE 2: Q1 scans of (a) dry air, (b) humid air (84% RH) and (c) dry air with HCl vapor (~300 ppm).

Figure 2a shows the Q1 spectra of dry air. The ions labeled in Figure 2a have been assigned in previous work [*Kotasek*, 1981]. In humid air, the signal intensity of O_3^- rises while the CO_3^- signal intensity decreases as shown in Figure 2b. Previous studies have shown water vapor produces OH^- in chemical ionization sources [*Vogt.*, 1969; *Spinks and Woods*, 1990]. Because OH has a larger electron affinity than O_3 [*Lias et al.*, 1988], electron transfer is expected to produce an increase in the O_3^- signal intensity in humid air where OH^- concentrations are high:

$$OH^- + O_3 \rightarrow O_3^- + OH \qquad (3)$$

The ozone anion can react with CO_2 to produce CO_3^- [*Fehsenfeld and Ferguson*, 1974]:

$$O_3^- + CO_2 \rightarrow O_2 + CO_3^-. \qquad (4)$$

However, the rate of reaction 4 is slower with ≥ 2 waters of hydration, which can explain the observed decrease in CO_3^- in humid air despite the observed O_3^- increase [*Fehsenfeld and Ferguson*, 1974].

Chemical ionization reagent ions are severely decreased by the concentrated acid vapor in Figure 2c. The signal intensities of O_2^-, O_3^-, and CO_3^- are all below the detection limit in Figure 2c. However, the NO_3^- signal intensity remains high. The relative gas phase acidities of ion neutrals for the ions present in the corona discharge (i.e. HO_2, HOH, HNO_3) compared to gas phase acidities of acids added to the corona discharge can be used to predict if proton transfer will occur [*Dzidic et al.*, 1974; *Yamdagni and Kebarle*, 1973; *Lias et al.*, 1988]. For example, the gaseous acid strength of HCl > HO_2 [*Lias et al.*, 1988], so

$$HCl + O_2^- \rightarrow HO_2 + Cl^- \qquad (5)$$

which can explain the observed decrease in O_2^- signal intensity in Figure 2c.

B. HOCl titration using air as the ion source

Figure 3a shows the Q1 spectra of HOCl using air as the *CIR* gas.

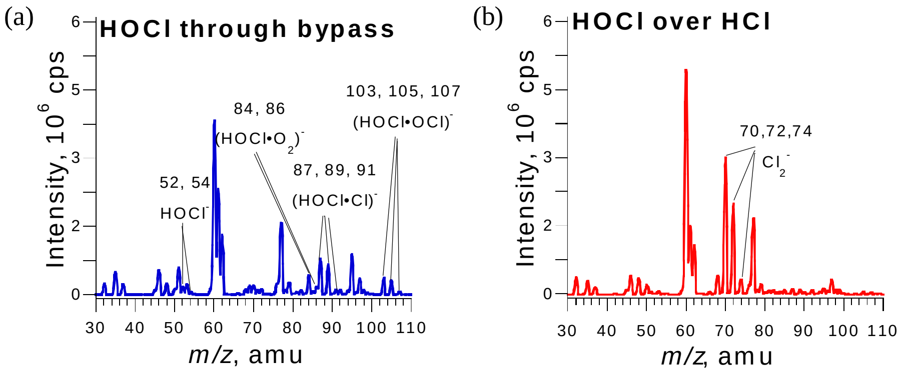

FIGURE 3: Q1 scans of (a) air containing ~700 ppb HOCl and (b) products of the HOCl titration with HCl using air as the *CIR* gas.

Parent peaks (*m/z* = 52, 54) are small in this spectra. The strongest non-background signals are assigned to HOCl-ion adducts labeled in Figure 3a including $(HOCl{\bullet}O_2)^-$. Unlike the HCl sample in Figure 2c, HOCl deprotonation is not found because the acid strengths of HCl and HO_2 are greater than that of HOCl [*Lias et al.*, 1988]. Hypochlorous acid was successfully titrated by flowing HOCl over the HCl filled U-tube. Figure 3b shows the HOCl-ion adducts have nearly vanished during titration with HCl. These signals have been replaced by intense Cl_2 signals which appear at *m/z* = 70, 72, and 74.

In MRM experiments, the calibrated $^{35,37}Cl_2$ (72/35) titration product is used to determine the HOCl concentration, which is monitored using the ion pair 84/35 assigned to $(HO^{35}Cl{\bullet}O_2)^-$. HOCl concentration plotted as a function of $(HO^{35}Cl{\bullet}O_2)^-$ signal intensity at 84/35 is linear for concentrations up to 500 ppb. At higher concentrations, non-linear results are observed. These non-linear results are attributed to the effects of acid and water vapor described in Section III A.

C. HOCl titration using bromoform as the CIR gas

Figure 4 shows the heterogeneous titration of HOCl with HCl using bromoform as the *CIR* gas.

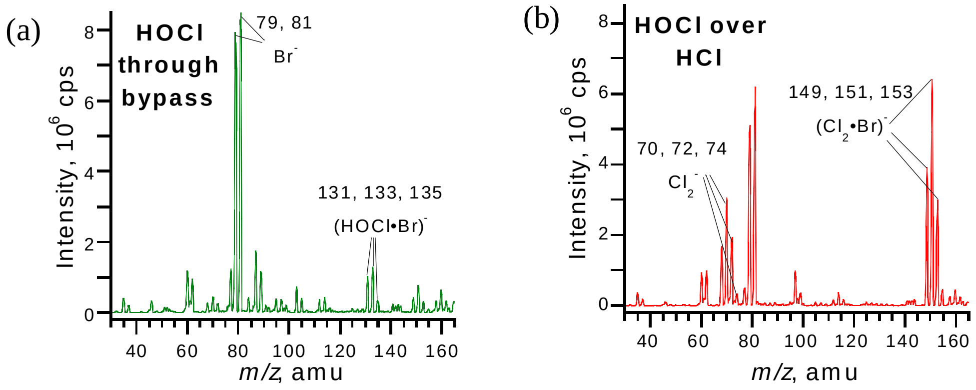

FIGURE 4: Q1 scans of (a) air containing 340 ppb HOCl, and (b) products of the heterogeneous HOCl titration with HCl using bromoform as the *CIR* gas.

Here, strong signal intensities for the *CIR* ion Br^- are observed at *m/z* = 79 and 81. A new $(HOCl{\bullet}Br)^-$ adduct is also observed at *m/z* = 131, 133, 135 and is used to calibrate HOCl in these experiments [*Caldwell et al.*, 1999]. In this experiment Cl_2 is observed not only as Cl_2^-, but also as the $(Cl_2{\bullet}Br)^-$ adduct at *m/z* = 149, 151, 153. Figure 4 shows HOCl is readily titrated by the condensed phase HCl to from the Cl_2 titration product when bromoform is used as the *CIR* gas.

In MRM experiments using bromoform as the *CIR* gas, the calibrated $(^{35,35}Cl_2{\bullet}^{79}Br)^-$ (149/35) titration product is used to determine the HOCl concentration, which is monitored using the ion pair 131/79 assigned to $(HO^{35}Cl{\bullet}^{79}Br)^-$. This technique yields an estimated detection limit of 0.9 ppb, lower than the 3 ppb detection limit measured using air as the *CIR* gas. Additionally, non-linear results were not observed for concentrations up to 960 ppb monitored in this experiment, which indicate that the effects of water vapor and acids are minimized here.

IV. SUMMARY AND ATMOSPHERIC IMPLICATIONS

In summary:

- Water vapor and acids affect the *CIR* ions in air.
- In air, HOCl concentrations > 500 ppb could not be measured because of the effects of water vapor and acids on the *CIR* ions.
- In bromoform, HOCl concentrations > 960 ppb were measured, and complexities due to water and acid vapor concentrations were not observed.
- Initial detection limits were 3 ppb in air and 0.9 ppb in bromoform.

The atmospheric implications of this work are that both methods can be used to measure HOCl in the laboratory, however, when air is the *CIR* gas, care must be taken to insure *CIR* ions are not severely depleted by H_2O and acid vapor during quantitative measurements. Secondly, with an order of magnitude gain in sensitivity, it will be possible to measure ambient HOCl concentrations. It is possible to gain an order of magnitude sensitivity by increasing the dwell time in the MRM experiments from 0.5 s to

50 s. Similar techniques can be developed to perform selective and sensitive measurements of other halogen compound in air as well.

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