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Design and construction of a chemical ionization mass spectrometer for ambient nitryl chloride analysis

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Design and construction of a chemical ionization mass spectrometer for ambient nitryl chloride analysis

Abstract
Ambient measurements of trace gas phase species in the Earth’s troposphere continue to present an interesting analytical challenge. Instruments must have sufficient sensitivity to monitor low concentrations without compromising the specificity necessary to distinguish the analyte of interest from a complex matrix. A chemical ionization mass spectrometer (CIMS) has been designed and constructed to satisfy these criteria.

Upon validation, the CIMS will assist in the elucidation of the complex chemistry in the troposphere resulting from the influence of urban pollution and marine environment. The CIMS is currently configured to operate in the negative ion mode and employs I- as the reagent ion for detection of nitryl chloride (ClNO2). Gas phase ClNO2 is thought to be a reservoir species for tropospheric chlorine atoms and was accordingly chosen as the first target analyte. The design and construction of the CIMS, the validation plan and potential future directions will be discussed in detail.

Keywords
Chemistry, Analytical, Atmospheric Chemistry

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DESIGN AND CONSTRUCTION OF A CHEMICAL IONIZATION MASS SPECTROMETER FOR AMBIENT NITRYL CHLORIDE ANALYSIS

BY

LEANNA CONWAY
B.S. Chemistry, University of Massachusetts Lowell, 2006

THESIS

Submitted to the University of New Hampshire

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the Requirements for the Degree of

Master of Science

in

Chemistry

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This thesis has been examined and approved.

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7/2/2009
Date
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ABSTRACT

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by

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University of New Hampshire, September, 2009

Ambient measurements of trace gas phase species in the Earth's troposphere continue to present an interesting analytical challenge. Instruments must have sufficient sensitivity to monitor low concentrations without compromising the specificity necessary to distinguish the analyte of interest from a complex matrix. A chemical ionization mass spectrometer (CIMS) has been designed and constructed to satisfy these criteria.

Upon validation, the CIMS will assist in the elucidation of the complex chemistry in the troposphere resulting from the influence of urban pollution and marine environment. The CIMS is currently configured to operate in the negative ion mode and employs I⁻ as the reagent ion for detection of nitryl chloride (CINO₂). Gas phase CINO₂ is thought to be a reservoir species for tropospheric chlorine atoms and was accordingly chosen as the first target analyte. The design and construction of the CIMS, the validation plan and potential future directions will be discussed in detail.
CHAPTER I

INTRODUCTION

The composition of the troposphere, the layer of the atmosphere closest to Earth (spanning approximately 10-12 km in altitude), is governed by its oxidative capacity; the ability to remove important trace gases such as volatile organic compounds (VOCs). VOCs comprise a large class of compounds which are significant pollutants hazardous to human health, detrimental to plant life and can cause damage to buildings and infrastructure. Additionally, the oxidation of VOCs produces radicals that are involved in NO\textsubscript{x} (NO + NO\textsubscript{2}) catalyzed reactions generating secondary pollutants, including ozone (O\textsubscript{3}), which is also known to be harmful to human and plant health.

The major driving components of the chemistry in the troposphere are hydroxyl radicals (OH\textsuperscript{-}), nitrate radicals (NO\textsubscript{3}\textsuperscript{-}) and O\textsubscript{3}, all of which remove VOCs from the atmosphere.\textsuperscript{1} The OH\textsuperscript{-} radical is formed during the day from the photolysis of O\textsubscript{3}; the NO\textsubscript{3}\textsuperscript{-} radical is present at night and formed by the reaction of nitrogen dioxide (NO\textsubscript{2}) and O\textsubscript{3}. Both radicals are highly reactive oxidants of VOCs. The primary pathway for OH\textsuperscript{-} and NO\textsubscript{3}\textsuperscript{-} radical reactions is hydrogen atom abstraction from a VOC to form an alkyl radical. The alkyl radical can rapidly combine with O\textsubscript{2} to generate a peroxy radical. Furthermore, O\textsubscript{3} itself is an oxidant of atmospheric constituents during both day and night by hydrogen abstraction.\textsuperscript{2}

At present, there is increasing evidence that the gaseous halogen species existing in the marine boundary layer can significantly affect the oxidative capacity of the
troposphere, such as HCl, ClNO₂, ClNO, and Cl₂. Halogen species are easily photolyzed, producing halogen radicals that, in many cases, are more reactive than OH· by two orders of magnitude.³ Sources of halogen species include both natural and anthropogenic processes. For example, the Earth’s crust contains halogen species that can be transported to the atmosphere through crustal dust.⁴ Anthropogenic sources such as fossil fuel combustion and biomass burning can also contribute to halogens in the troposphere.⁵ However, the dominant halogen source is the ocean; this is clearly demonstrated by the correlation of the sea salt tracers Na⁺ and Mg²⁺ with sea salt aerosol samples.⁶

There are several proposed mechanisms to explain the release of halogen species from sea salt aerosols produced from the ocean; however, the chemical and physical processes of how reactive halogen species are generated from unreactive sources are yet to be understood. In order to determine the extent and effects of halogen radical release in the troposphere, the potential source reactions must be better characterized. As a result, a recent principal research focus is the role of nitryl chloride (ClNO₂) and its contribution towards the production of chlorine radicals (Cl·) in the marine boundary layer.

1.1 Chloride Depletion

Measurements have shown that marine aerosols are depleted in chloride (Cl⁻) in comparison with seawater.⁶,⁷ This finding is unexpected as marine aerosols have a similar composition to seawater because they are mainly formed by wind or breaking waves. The depletion of Cl⁻ is typically represented through the ratio of Cl⁻ in the sea salt aerosol to the original abundance in sea water, termed an enrichment factor (EF), where a ratio less than one corresponds to a depletion. The depletion can also be
described by the Cl⁻ concentration relative to Na⁺ concentration within the sea salt aerosol. For example, for samples collected in the relatively polluted northern Atlantic Ocean, a median EF of aerosol particles was determined to be 0.66.⁶ Samples from less polluted regions transported over the northern Atlantic Ocean had an EF range of 0.80 – 0.95,⁶ showing that Cl⁻ depletion is at least partially a result of anthropogenic emissions and the subsequent chemical processing. Aerosol samples from the Gulf of Maine were determined to have an average Cl⁻:Na⁺ of 0.87,⁷ compared to the seawater ratio of 1.16.⁸ The deficiency was greatest in the summer and least in the fall, with ratios of 0.75 and 0.99, respectively, exhibiting a seasonal trend.⁷

The Cl⁻ depletion phenomenon was originally believed to be the result of the marine aerosols reacting with strong acids, such as nitric acid (HNO₃) or sulfuric acid (H₂SO₄), as in the following reactions:⁹

\[
HNO₃(g) + NaCl(aq) \rightarrow HCl(g) + NaNO₃(aq)
\]  

(1)

\[
H₂SO₄(g) + NaCl(aq) \rightarrow 2HCl(g) + Na₂SO₄(aq)
\]  

(2)

Upon acidification, hydrogen chloride (HCl) volatilizes leading to the reduced Cl⁻ concentration in sea salt aerosols.⁴,¹⁰⁻¹³ However, lab studies show that marine aerosols are depleted more than expected from acid displacement alone.¹⁴⁻¹⁶ In areas of the North Atlantic Ocean, acid reactions have only been shown to contribute 40% to the total depletion.¹⁷ Field studies have also shown that there is an abnormally high concentration of Cl⁻ within the troposphere in polluted coastal regions.¹²

A halogen generation mechanism in addition to acidification has also been proposed.¹⁸
However, the concentration of NO\textsubscript{2} in the troposphere, even in polluted regions, is sub ppb\textsuperscript{18} and the reaction time is slow compared to other reactions with NaCl\textsuperscript{10}, making this reaction relatively unimportant.

There are also many other suggested mechanisms for the production of Cl\textsuperscript{-} from photolyzed chlorine gas (Cl\textsubscript{2}) released from sea salt particles. Both experimental\textsuperscript{18} and modelling\textsuperscript{19} results suggest that OH\textsuperscript{-} radicals uptake onto sea salt aerosols and can undergo the following reactions:

\begin{align*}
   OH\textsubscript{aq}^- + Cl\textsubscript{aq}^- & \leftrightarrow HOCl\textsubscript{aq}^- \quad (4) \\
   HOCl\textsubscript{aq}^- + H^+\textsubscript{aq} & \rightarrow H_2O\textsubscript{aq} + Cl\textsubscript{aq}^- \quad (5) \\
   Cl\textsubscript{aq}^- + Cl\textsubscript{aq}^- & \rightarrow Cl_2^-\textsubscript{aq} \quad (6) \\
   2Cl_2^-\textsubscript{aq} & \rightarrow Cl_2\textsubscript{aq} + 2Cl\textsubscript{aq}^- \quad (7) \\
   Cl_2\textsubscript{aq}^- & \rightarrow Cl_2\textsubscript{g} \quad (8)
\end{align*}

In a recent field experiment, negative ion atmospheric pressure chemical ion with tandem mass spectrometry was used to measure Cl\textsubscript{2} along the west coast of the United States and ranged from <2.5 to 20 ppt\textsuperscript{20}. Using the same measurement technique, Cl\textsubscript{2} mixing ratios of up to 150 ppt were observed along the east coast\textsuperscript{21}. Work by Spicer et al. supports this mechanism as a potential Cl\textsubscript{2} source, but they also conclude that there must be another non-photolytic mechanism contributing to its production because of the observed Cl\textsubscript{2} build up at night\textsuperscript{21}.

The reaction of sea salt particles with chlorine nitrate (ClONO\textsubscript{2}) to produce Cl\textsubscript{2}\textsuperscript{18,<22} has also been proposed as in the following reaction:

\begin{equation}
   NaCl\textsubscript{aq}^- + 2NO\textsubscript{2(g)} \rightarrow NaNO\textsubscript{3(aq)} + ClNO\textsubscript{(g)} \quad (3)
\end{equation}
however, ClONO$_2$ is predominantly present in the stratosphere and is only found in the
troposphere at relatively low concentrations (5-6 ppt), indicating that other reactions to
produce chlorine products are more probable.

1.2 Importance of Nitryl Chloride in the Troposphere

A likely explanation for the conversion of chloride ions to chlorine radicals is the
reaction of dinitrogen pentoxide (N$_2$O$_5$) with sea salt aerosols. This reaction has been
shown in the laboratory to produce nitryl chloride (ClONO$_2$) which may then be
photolyzed to produce chlorine radicals. Even with low Cl$^-$ concentrations, this
reaction will proceed and is one to two orders of magnitude faster than the reaction of sea
salt with nitric acid. The following mechanism has been proposed for gas phase Cl$^-$
production via N$_2$O$_5$ reactions:

\[
NO_2^-(aq) + O_3(g) \rightarrow NO_3^-(aq) + O_2(g) \quad (10)
\]

\[
NO_2(g) + NO_3^-(g) \leftrightarrow N_2O_5(g) \quad (11)
\]

\[
N_2O_5(g) \leftrightarrow N_2O_5(aq) \quad (12)
\]

\[
N_2O_5(aq) \leftrightarrow NO_3^-(aq) + NO_2^+(aq) \quad (13)
\]

\[
NO_3^-(aq) + NO_2^+(aq) + Na^+Cl^-(aq) \rightarrow ClNO_2(g) + Na^+NO_3^-(aq) \quad (14)
\]

\[
ClNO_2(g) + h\nu \rightarrow Cl^-(g) + NO_2^+(g) \quad (15)
\]

The nitrate radical has a short photolysis lifetime (estimated at 5 s), therefore,
N$_2$O$_5$ can only be produced and taken up into sea salt aerosols at night. The resulting
ClONO$_2$ is photolyzed within an hour at sunrise. The production of halogen radicals,
particularly chlorine radicals, is important to study because it impacts the oxidative capacity of the marine boundary layer by reacting with ozone and VOCs.

In the marine boundary layer, halogen radicals can directly react with O\textsubscript{3} and remove it through the following catalytic destruction cycle:\textsuperscript{6,14,28,29}\textsuperscript{30}

\[ X\cdot(g) + O_3(g) \rightarrow XO\cdot(g) + O_2(g) \] \hspace{1cm} (16)

\[ XO\cdot(g) + HO_2\cdot(g) \rightarrow HOX(g) + O_2(g) \] \hspace{1cm} (17)

\[ HOX(g) + h\nu \rightarrow OH\cdot(g) + X\cdot(g) \] \hspace{1cm} (18)

where X represents a halogen, e.g., Cl, Br, or I. The halogen-oxide XO\cdot can also react with NO\textsubscript{2} to produce NO\textsubscript{3}\textsuperscript{−} and X, contributing further to ozone destruction stemming from NO\textsubscript{x} (NO and NO\textsubscript{2}) being a precursor for O\textsubscript{3} production. In contrast to depleting O\textsubscript{3}, the halogen radicals, Cl or Br, can also react with hydrocarbons, producing HX, which in the presence of NO\textsubscript{x} will react to generate more O\textsubscript{3}. This pathway results in the halogen radicals acting as an O\textsubscript{3} sink in areas with low NO\textsubscript{x} concentrations, whereas in areas with high NO\textsubscript{x} concentrations, the halogen radicals contribute to O\textsubscript{3} production as seen in Figure 1.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{The cycle on the left shows the reaction pathway of halogen radicals removing O\textsubscript{3} in areas with low NO\textsubscript{x}. The reaction on the right shows the reaction pathway of halogen radicals producing O\textsubscript{3} in areas of high NO\textsubscript{x}.}
\end{figure}
Chlorine (Cl) and bromine (Br) halogen species are the main driving components of the chemistry in the marine boundary layer. Fluorine (F) exists predominantly in the stratosphere, where F is highly reactive and forms the stable compound HF, and thus F does not transport to the troposphere. In contrast, Iodine (I) exists mainly in the troposphere; however, its low sea water concentration and low reactivity limits its impact on the oxidative capacity of the troposphere. Like Cl and Br, sea water is a major source of I; however, the concentrations of these species vary tremendously; sea water consists of 55.17% Cl\(^-\), 0.19% Br\(^-\), and only 0.00002% I\(^-\). Furthermore, I is less electronegative than Cl and Br and is thus less reactive. Although I is a contributor to the destruction of O\(_3\) as shown in the catalytic destruction cycle in Figure 1, I is not responsible for the oxidation of VOCs. In addition to the limited importance of I on the oxidative capacity of the marine boundary layer, evidence has shown that rather than a depletion of I\(^-\) in sea salt aerosols, as observed for Cl\(^-\) and Br\(^-\), they are instead enriched in I\(^-\). This increased enrichment factor, often by a factor of 1000,\(^1\) indicates that I species are not being readily released to the troposphere from sea salt aerosol.

The overall roles played by Cl\(^-\) and Br\(^-\) in the troposphere differ but are both equally important. The molar concentration of Cl\(^-\) is higher than Br\(^-\) in sea water with a ratio of 650:1,\(^2\) resulting in a much greater amount of Cl\(^-\) contributing to the chemistry in the troposphere. Also, at room temperature, Cl\(^-\) has a faster reaction time with most alkanes than does Br\(^-\).\(^3\) However, because of the high reactivity of Cl\(^-\), it becomes tied up in less reactive reservoir species, leaving behind Br\(^-\) to react with O\(_3\). In some cases at higher latitudes, Br\(^-\) has been seen to be more reactive than Cl\(^-\).\(^9\) Although both Cl\(^-\) and
Br⁻ are important oxidants in the troposphere, the focus of this research is on Cl, but the project has the potential to study Br in the future as well.

### 1.3 Indirect Techniques to Monitor CINO₂ and Cl⁻ Production:

Modeling techniques have been used to provide details about the mechanisms involving CINO₂, demonstrating its potential importance in tropospheric chemistry. Erickson et al. estimated the impact of two predominant intermediate precursors of Cl⁻ in the troposphere, HCl and CINO₂, produced after sea salt aerosol dechlorination. The concentration of HCl was determined to be in the range of 10 – 350 pptv whereas the concentration of CINO₂ was 1 – 20 pptv. The total yearly flux estimates for sea salt, HCl and CINO₂ is 1785 Tg/yr, 7.6 Tg/yr and 0.06 Tg/yr respectively. Although the involvement of CINO₂ is much smaller than that of HCl, this model does demonstrate the contribution of CINO₂ towards the production of Cl⁻ in the marine boundary layer.

To date, the concentration of chlorine radicals cannot be directly measured and can only be estimated through calculations and modeling techniques. Aldener et al. estimated the production of CINO₂ and subsequent Cl⁻ release based on ambient measurements of N₂O₅. This estimate was obtained by experimentally determining the concentration of N₂O₅, the abundance of sea salt in the specific area of analysis and the uptake coefficient of this compound on the sea salt. Cavity ring-down spectrometry (CRDS) was used to measure ambient concentrations of N₂O₅. The surface area of the sea salt aerosols was calculated by Behnke et al. from the aerosol size distributions which were determined by a differential mobility particle sizer. Modeling techniques determined the uptake coefficient for N₂O₅ to be ~0.03. The production rate of CINO₂ was determined to be as high as 3 x 10⁴ molecules cm⁻¹ s⁻¹, resulting in a Cl⁻
concentration of 45 pptv, assuming that all of the produced ClNO_2 was photolyzed. However, the concentration of the hydrocarbons measured did not decrease as would be expected if Cl\cdot was present to react with them.\textsuperscript{25}

Keene et al.\textsuperscript{6} used steady state calculations to approximate the Cl\cdot concentration in the Gulf of Maine using the following equation:

\[ [Cl\cdot] = \frac{(k_{HC_1} *[HCl]*[OH] + J_{CI} *[CI\cdot])/(k_{O_3} *[O_3] + \sum k_H *[HC])}{k_{HC_1} *[HCl]*[OH] + J_{CI} *[CI\cdot]} \]

(19)

where [Cl\cdot] represents chlorine species including Cl\_2, HOC\_1, Cl\_3, ClNO\_2, ClNO\_3, and BrCl, \( k_{HC_1} \) is the rate constant of the reaction of HCl and OH, \( k_{O_3} \) is the rate constant for the reaction of O\_3 and Cl\cdot, \( k_H \) is the specific rate constant of Cl\cdot with a particular hydrocarbon, \( J_{CI} \) is the photolysis rate for each chlorine species. \([HCl] \), \([O_3] \), and \([Cl\cdot] \) are measured values, while \([OH] \) was calculated. Finally, \([HC] \) represents the measured hydrocarbons that were the sinks Cl\cdot sinks. For this study, the Cl atom concentration was found to range from \(10^4 \) – \(10^5 \) cm\(^{-3}\) based on transport trajectories from relatively clean regions and polluted regions respectively. A similar study performed by Pszenny et al.,\textsuperscript{31} also in the Gulf of Maine, determined atomic chlorine concentrations using lifetime-variability relationships. This method uses a modeled OH concentration with an estimated \([OH\cdot]/[Cl\cdot] \) ratio based on reaction rates of both oxidants with nonmethane hydrocarbons in order to determine the atomic Cl concentration. Cl atom concentrations were determined by Pszenny et al. to be between \(2.2 \times 10^4 \) and \(5.6 \times 10^4 \) cm\(^{-3}\), falling in the range determined by Keene et al.

Pechtl et al.\textsuperscript{32} used a modeling technique to estimate the Cl\cdot concentration in the Gulf of Maine as well as to determine the impact of Cl\cdot oxidation for VOCs in the marine boundary layer. The range of concentrations determined by the model at noontime was
about $10^4$ cm$^{-3}$ for clean conditions and $10^5$ cm$^{-3}$ for polluted episodes, similar in magnitude to the values calculated by Pszenny et al. and Keene et al. Pechtl et al. used the ratios of hydrocarbon pairs for OH$^\cdot$ and Cl$^\cdot$ reactions to determine the impact of each on VOC oxidation. As expected, OH$^\cdot$ was found to be the dominant oxidant in the model for “clean” conditions; however, in polluted regions the oxidation by Cl$^\cdot$ was more significant regarding VOC oxidation. Moreover, a modeling technique involving the measured losses of hydrocarbons was used by Wingenter et al.$^{33}$ to estimate both the OH$^\cdot$ and Cl$^\cdot$ concentrations in the North Atlantic. Wingenter et al. used tetrachloroethene to distinguish the contributions from Cl$^\cdot$ and OH$^\cdot$ oxidation, a compound commonly used because its Cl$^\cdot$ rate constant is 200-300 times greater than that of OH$^\cdot$. At noontime, OH$^\cdot$ was calculated to be $2.6 \times 10^6$ cm$^{-3}$ and Cl$^\cdot$ to be $6.5 \times 10^4$ cm$^{-3}$, again similar to previously mentioned results.$^{33}$

The mixing ratio of ClNO$_2$ as well as its impact of produced Cl$^\cdot$ on marine boundary layer chemistry in Houston, Texas has been estimated through modeling studies. Simon et al.$^{35}$ estimated the ClNO$_2$ mixing ratio to be over 1 ppb and found that ClNO$_2$ increases the amount of reactive Cl$^\cdot$ by 20-40%, which contributed an increase in the marine boundary layer O$_3$ levels by up to 1 - 1.5 ppb. The O$_3$ increase was determined by incremental reactivities, involving a VOC and NO$_x$ mixture, where the total extra O$_3$ is divided by the excess VOC. The incremental reactivity model also depends on the NO$_x$/VOC ratio.

The production of ClNO$_2$ from the reaction of N$_2$O$_5$ with sea salt was first measured in the laboratory by Behnke et al.$^{24}$ In their laboratory experiments, NaCl aerosols were exposed to N$_2$O$_5$, which was produced by reacting NO$_2$ and O$_3$, in an
aerosol smog chamber to generate ClNO\textsubscript{2}. The resulting ClNO\textsubscript{2} was photolyzed to produce Cl\textsuperscript{+}, which was monitored by its reaction with other hydrocarbons within the chamber. The outcome of this experiment showed an average ClNO\textsubscript{2} percent yield of 65\% from the reaction of NaCl with N\textsubscript{2}O\textsubscript{5}.

1.4 Monitoring ClNO\textsubscript{2} with CIMS

Techniques such as ion chromatography and Fourier transform infrared spectroscopy (FTIR spectroscopy)\textsuperscript{12,18} have been used to characterize N\textsubscript{2}O\textsubscript{5} and ClNO\textsubscript{2} in ambient air.\textsuperscript{24,36} However, ion chromatography\textsuperscript{37} requires long integration times and FTIR spectroscopy only provides qualitative information. Trace gas analysis in complex matrices (e.g., the atmosphere) by ion chromatography is also difficult in that overlap will result between molecules with close separation characteristics. This analysis allows the monitoring of Cl\textsuperscript{+}, but cannot speciate ClNO\textsubscript{2}.\textsuperscript{6} FTIR has the similar disadvantage in that common constituents of the atmosphere, including water, will cause interference with the analyte molecules. The two techniques work in optimal lab conditions with high concentrations of precursors; however, the methods are not ideal in uncontrolled settings.\textsuperscript{38}

Ambient concentrations of ClNO\textsubscript{2} may be measured by chemical ionization mass spectrometry (CIMS). This method has a fast time response, is highly selective and, because of its low detection limit (on the order of magnitude of pptv), is sensitive to trace gas analysis. In the complex matrix of air, these characteristics are crucial to identify a gas that makes up less than 0.03\% of the troposphere.

Thornton et al.\textsuperscript{39,40} measured N\textsubscript{2}O\textsubscript{5} and ClNO\textsubscript{2} simultaneously using CIMS, where I\textsuperscript{-} reagent ions reacted with N\textsubscript{2}O\textsubscript{5} and ClNO\textsubscript{2} producing NO\textsubscript{3}\textsuperscript{-} and ICl\textsuperscript{-}.
respectively. The I⁻ reagent ions were produced by flowing methyl iodide (CH₃I) in nitrogen (N₂) over a radioactive polonium (²¹⁰Po) source. This reaction of N₂O₅ with NaCl resulted in an evident first-order loss of N₂O₅ as well as a first-order growth for ClNO₂.

Both N₂O₅ and ClNO₂ were also measured using CIMS by Leu et al.⁴¹ to determine the reaction probability of ClNO₂ with NaCl to be 4.5 x 10⁻⁴. The reagent ions were also I⁻; however, they were produced by the dissociative attachment by electrons of CF₃I. The electrons were generated by passing a current of 6-10 A through a tungsten, rhenium, or thoriated iridium filament. Helium (He) was used as the carrier gas in this system as opposed to nitrogen used by Thornton et al.⁴⁹

The in-situ detection of ambient ClNO₂ by CIMS was performed for the first time during the Texas Air Quality Study – Gulf of Mexico Atmospheric Composition and Climate Study (TexAQS/GoMACCS) in 2006 on a research vessel in the Gulf of Mexico. ClNO₂ was measured through the use of I⁻ reagent ions to produce ClNO₂I⁻, which was detected by CIMS and assumed to represent the concentration of ClNO₂. Corresponding N₂O₅ concentrations were determined by CRDS. This analysis showed a robust correlation between the mixing ratios of N₂O₅ and ClNO₂ at night, providing further evidence that the production of ClNO₂ is dependent upon N₂O₅. The mixing ratios detected for N₂O₅ and ClNO₂ were as high as 400-800 pptv and 800–1000 pptv, respectively, which are greater than estimated by previous models. The highest mixing ratios of ClNO₂ were also observed in the marine regions nearest to anthropogenic sources.⁴²,⁴³ Ambient N₂O₅ has also been monitored by CRDS during the daytime on the
east coast during the New England Air Quality Study – Intercontinental Transport and Chemical Transformation (NEAQS-ITCT) campaign of 2004, where a high mixing ratio of 4 pptv was observed.\textsuperscript{44} The nighttime measurements of N$_2$O$_5$ are two orders of magnitude greater than the daytime measurements of N$_2$O$_5$ because the formation of N$_2$O$_5$ is dependent upon NO$_3$, as shown in equation 11, which has an extremely fast photolysis rate.

Ambient ClNO$_2$ and N$_2$O$_5$ were first detected simultaneously using the CIMS described above in the Gulf of Mexico by Kercher et al.\textsuperscript{45} during the ICEALOT 2008 campaign; a cruise extending from Massachusetts, USA to Rekjavik, Iceland. The novel method was validated by analyzing samples side by side with the CRDS also used in the Gulf of Mexico, also resulted in a strong correlation between gases. During this campaign, N$_2$O$_5$ was measured to be in the range of 100 – 250 pptv, while ClNO$_2$ was between 150 – 200 pptv. A key change between the previous CIMS instrument (monitored only ClNO$_2$) to the current CIMS instrument (monitored both ClNO$_2$ and N$_2$O$_5$) was the application of a smaller field strength between ion lenses to improve the throughput of both ClNO$_2^-$ and N$_2$O$_5^-\Gamma$ clusters.

The production of ClNO$_2$ from the reaction of N$_2$O$_5$ and sea salt aerosols has been determined to contribute greatly to the amount of Cl· in the troposphere through photolysis. Roberts et al.\textsuperscript{46} was the first group to recognize that in addition to acting as a direct source, ClNO$_2$ may act as an intermediate to the production of Cl· in acidic marine aerosols. The following mechanism of ClNO$_2$ producing Cl$_2$ was proposed:

\begin{align}
O_3 + hv &\rightarrow O_2 + O(^1D) \\
O(^1D) + H_2O &\rightarrow 2OH
\end{align}
\[ N_2O_5(g) + aerosol \rightarrow NO_2^+(aq) + NO_3^-(aq) \]  

(22)

\[ NO_2^+(aq) + Cl^-(aq) \rightarrow ClNO_2(aq) \]  

(23)

\[ ClNO_2(aq) + H^+(aq) \rightarrow ClNO_2H^+(aq) \]  

(24)

\[ ClNO_2H^+(aq) + Cl^-(aq) \leftrightarrow Cl_2(g) + HNO_2(aq) \]  

(25)

In this reaction scheme, Cl\(_2\) will ultimately be photolyzed to produce Cl\(^+\). Evidence of the production of Cl\(_2\) from ClNO\(_2\) was demonstrated in the laboratory experiments by monitoring both ICINO\(_2\) and ICl\(_2\) by CIMS; a 60 - 100% conversion efficiency of ClNO\(_2\) to Cl\(_2\) was observed when exposed to a NaCl/oxalic acid mixture.\(^{46}\)

Ongoing research has clearly shown that Cl\(^+\) contributes to the oxidative capacity of the marine boundary layer and that a likely source is ClNO\(_2\). However, the exact production mechanism is currently still a subject of debate. By constructing a CIMS designed specifically for the analysis of ClNO\(_2\) at the University of New Hampshire, a better understanding of Cl in the atmosphere will be achieved.
CHAPTER II

DESIGN AND CONSTRUCTION OF A CHEMICAL IONIZATION MASS SPECTROMETER

The following chapter describes the construction of a chemical ionization mass spectrometer (CIMS) for atmospheric trace gas analysis from an existing electron-impact mass spectrometer (EIMS). The goal of this project was to salvage as many components as possible from the EIMS and any parts that needed to be custom made were to use the most cost effective and efficient means as possible. Using the pumps from the EIMS, with known pumping speeds, and desired pressure ranges obtained from the literature, a vacuum system was designed using components specifically calculated to allow for an exact pressure gradient and efficient transport of ions from the beginning source region where the product ions are generated, to the last chamber where the ions are mass filtered and detected.

2.1 Theory of EIMS and CIMS

A CIMS and EIMS are similar in that they both involve ionization of the sample followed by mass separation and detection, but they differ in ionization methods. EIMS involves the production of energetic electrons as the ionization agent, leaving the molecules in a highly excited state. The relaxation of the excited states results in extensive fragmentation, leading to complex spectra. CIMS relies on reaction with gaseous reagent ions, allowing for selective ionization producing well defined peaks. The EIMS method uses hard ionization, whereas CIMS uses a soft ionization technique.
The CIMS method is advantageous in that it is highly selective and results in reduced fragmentation of the molecules.

The EIMS that was located in the laboratory consisted of differentially pumped chambers with an electron impact quadrupole mass spectrometer as shown in Figure 2. The molecules to be analyzed were transported through the first chamber in a glass reaction tube that was evacuated by a roots blower pump. The next chamber in the system was separated from the first chamber through a pinhole. This second chamber was connected to a turbomolecular vacuum pump, with a pumping speed of 330 L s\(^{-1}\), and to the manifold where an ionization gauge was used to determine the pressure of the system. A skimmer cone acted as the divider between the second chamber and the third chamber. This third chamber contained the electron impact source, quadrupole mass filter and electron multiplier detector and was connected to another turbomolecular vacuum pump, with a pumping speed of 450 L s\(^{-1}\). All three chambers were connected to a manifold via angle valves to permit roughing of the chamber by the roots blower.

The CIMS was constructed similarly to the EIMS in that it consists of differentially pumped chambers, where the pressures are stepped down incrementally as shown by the schematic of the CIMS instrument in Figure 3. Each of these regions is divided using apertures as well. The pressure in each of these systems is important in that high-vacuum prevents collisions with neutral molecules that could interfere with the stability of trajectories, preventing the ions from reaching the detector, or result in unwanted ion-molecule reactions.
Figure 2. Schematic of the electron-impact mass spectrometer (EIMS). The instrument consists of 4 differentially pumped chambers where the last chamber contains the mass filter and the detector.

Figure 3. Schematic of a chemical ionization mass spectrometer (CIMS). The instrument consists of 4 differentially pumped chambers where the sample enters the first chamber where it is ionized and is focused through ion lenses to the last chamber where the ions are separated by m/z and detected.

2.2 Necessary Changes from EIMS to CIMS

The existing EIMS system was configured exclusively for detection of positive ions. In order to monitor negative ions, a new spectrometer was required that had the
capability of selecting polarity, allowing for the analysis of positive or negative ions. In October 2007, the Hiden mass spectrometer that was used in the EIMS was exchanged for the Extrel Max 300 quadrupole mass spectrometer to be used in the new CIMS. This mass spectrometer can monitor mass to charge ratios ranging between 0 and 300 amu of both positive and negative ions.

In addition to installing a different probe, the pressures required for the CIMS differ from those required for the EIMS system. The target pressures for the new system were based on the existing systems described in Thornton et al., Osthoff et al., and Huey. Calculations based on the gas kinetic theory provide the corresponding pinhole diameters necessary to achieve these values. The approach of Moore et al. is carried out through the following calculations, where pumping speed, conductance and throughput are contributing factors to the behavior of the vacuum system.

The throughput, Q, usually expressed in torr L s\(^{-1}\), is the mass rate of flow through the system. The throughput is related to pressure, P, and pumping speed, S, through the equation:

\[ Q = PS. \] (26)

The pumping speed, expressed in L s\(^{-1}\), is the volume rate of flow through an aperture. The ability of a tube to transmit gas, termed conductance, C, is related to the throughput as well as the change in pressure between regions. Conductance in a region of viscous flow (high pressure) is expressed in L s\(^{-1}\) through the equation:

\[ C = \frac{Q}{\Delta P} = 15d^2, \] (27)
where \( d \) is the diameter of the pinhole aperture in cm. The pinhole aperture is a hole in a stainless steel plate that acts as a partition between each region in the vacuum system.

Conductance in a molecular flow (low pressure) region is expressed through the equation,

\[
C = 3.7\left(\frac{T}{M}\right)^{1/2} \pi \left(\frac{d}{2}\right)^2,
\]

(28)

where \( T \) is the temperature and \( M \) is the molecular weight of the carrier gas. The temperature and atomic mass values are used to account for their impact on the mean free path of the molecules. In a region of viscous flow, intermolecular interactions govern the gas behavior, resulting in the gas flow being dependent upon pressure. However, molecular gas flow has a large mean free path and is thus independent of pressure and dependent on density.

The net pumping speed \( (S) \) is the actual rate of which a pump can evacuate the system through the tubing connecting the pump to the instrument. The net pumping speed is expressed through the equation:

\[
S = \frac{1}{\left(\frac{1}{S_p} + \frac{1}{C}\right)},
\]

(29)

where \( S_p \) is the pumping speed of the pump in L s\(^{-1}\) and \( C \) is the conductance of the manifold, also in L s\(^{-1}\). The conductance (L s\(^{-1}\)), of the manifold in a viscous flow regime for air at 20°C is determined through the equation:

\[
C = 180 \frac{d^4}{l} P_{av},
\]

(30)

where, \( d \) is the diameter of the tube in cm, \( l \) is the length of the tube in cm, and \( P_{av} \) is the average pressure in torr.
In molecular flow, the conductance of a straight cylindrical tube with air at 20°C, is expressed through the equation:

\[
C = 12 \frac{d^3}{l}, \tag{31}
\]

The conductance will decrease if there are bends in the tubing. The conductance of a tube with a 90° bend with air at 20 °C is expressed through the equation:

\[
C = \frac{12d^3}{l + \frac{4d}{3}}, \tag{32}
\]

In order to determine the net pumping speed of the entire manifold which consists of many connections with various dimensions, the total conductance in series is determined by:

\[
C_{series} = \left[ \frac{1}{C_1} + \frac{1}{C_2} + \frac{1}{C_3} + \ldots \right]^{-1}, \tag{33}
\]

with the original dimensions of the intermediate vacuum flange, the net pumping speed was only 0.800 L s\(^{-1}\), if it is assumed to be a viscous flow and 1.61 L s\(^{-1}\) if it were molecular flow. In parallel, conductance is additive when the components are in parallel, as shown by the equation:

\[
C_{parallel} = C_1 + C_2 + C_3 + \ldots, \tag{34}
\]

The equations for throughput, pumping speed and conductance were all used to establish the parameters of the instrument components. Specifically, through the use of equations 26 and 27, the dimensions of the pinhole apertures 1 and 2 and range of desired pressures for the source and declustering regions were determined. Pinhole 3 and the pressure in the mass spectrometer region were determined using equations 26 and 28.
The intermediate vacuum region is between a viscous and molecular flow and an estimate must be made using equations 26 – 28.

Furthermore, a voltage gradient had to be applied to the system to help drive the ions toward the detector and minimize losses within the instrument. This was not necessary in the EIMS because the source was located in the last vacuum chamber just ahead of the mass filter. The source in the CIMS however, is located in the highest pressure region of the system near the sample entrance.

This voltage gradient is achieved through a series of ion lenses as well as the application of voltages to the pinhole apertures. In-vacuum insulated wire and ultem 2300 screws were used to connect the lenses and pinhole plates to feedthroughs where a voltage is applied from several power supplies. The first two chambers in the system, the declustering region and the intermediate vacuum region, each contain a two element transmission lens. These lenses are stainless steel disks, with an opening in the center, that were cut to the desired dimensions. Within the declustering region, the lenses allow for water clusters to be dissociated. In the intermediate vacuum region, the lenses act to transmit the ions to the third chamber, where an Einzel lens stack will be located in front of the quadrupole mass spectrometer. The Einzel lens stack is a three-element lens, consisting of three stainless steel plates with holes in the center, that focuses the ions into the quadrupole without changing their overall energy. 50

The following sections provide a detailed description of the design and construction of each region of the CIMS. Unless otherwise stated, the machine work discussed was completed at the Space Science Machine Shop at the University of New Hampshire.
2.3 Source Region

The original design of the source region, as shown in Figure 4, consists of 0.635 cm (0.25") OD Teflon tubing as the sample inlet, connected to a stainless steel flow tube by a Swagelok fitting adapter and a needle valve to close off the flow. The sample is delivered through 0.635 cm OD Teflon tubing by a mass flow controller, calibrated for \( N_2 \) with a range of 5000 standard cubic centimeters per minute (sccm) (MKS Instruments, Model: 1179A53CS1BV) at a flow of 0.8 standard liters per minute (slpm). The flow tube is comprised of a stainless steel nipple and a modified stainless steel cross. The stainless steel nipple has an inner diameter of 3.66 cm and a length of 32 cm. The stainless steel reducer cross, shown in Figure 5, has a tube, which is in series with the nipple, with an inner diameter of 3.66 cm. This tube is crossed with a 1.27 cm outer diameter tube with a length of 6.35 cm.

![Figure 4. Original source region on the CIMS consisting of the sample inlet on the far right connected to \(^{210}\)Po source. This region is mounted to the rest of the CIMS instrument.](image)

The two ends of the smaller tube are attached to quick connect adapters. One is affixed to a stainless steel tee connecting to a pirani gauge (Edwards, APG100-XLC) to monitor the pressure and a feedthrough with four pins (Kurt J. Lesker Company, PN: EFT0044038) that supplies a voltage to the first pinhole plate. The pressure is
determined with a pirani gauge by a sensitive bridge that detects a change in resistivity. As the pressure decreases, filaments within the gauge will heat up, resulting in an increase in resistance.

The other quick connect adapter allows connection to a rotary vane mechanical pump (E2M18, BOC Edwards) with a pumping speed of 5.7 L s⁻¹, to maintain a pressure of 3.2 torr. On the connection to the pump, there is also a manual brass ball valve that is used to isolate vacuum volume from the pump and control gas flow to obtain the desired pressure. On the large tube, a boss with a ¼” NPT thread was made so the ²¹⁰Po source can screw in and was designed so it did not enter the tube. The boss was positioned at a 90° from both of the ends of the smaller tube to prevent the source from interfering with the quick connect adapters. The thread of the ²¹⁰Po source going into the tube, as well as 0.635 cm OD Teflon tubing leaving the ²¹⁰Po source, were sealed using Teflon tape. The 0.635 Teflon tubing continues from the ²¹⁰Po source to a plug valve, to allow the flow to be closed off, to a permeation oven, custom made by group member, Karl Haase, which contains a methyl iodide permeation device (VICI Metronics, PN: 1002004600U50).

Figure 5. The reducer cross in source region that contains the boss for connection to the ²¹⁰Po source and the connections to the pump, pressure gauge, and feedthroughs.
The N₂ carrier gas in this system is flowed through the Dynacalibrator, where the N₂ picks up trace amounts of methyl iodide (Figure 6). The permeation device has a length of 23.5 cm, with an active length of 20.0 cm and diameter of 0.98 cm. A constant temperature of 50 °C is used to maintain a constant vapor pressure allowing for equilibrium between the liquid and vapor phases. The vapor passes through the permeable membrane at a rate of 17,800 ng/min (+/- 15%). Over the active length of 20.0 cm, the net rate is 890 ng/min/cm (+/- 15%). With a total flow (sample and N₂/CH₃I flows) of 1 slpm at the given conditions, the resulting concentration of methyl iodide is 3.1 ppm as is determined from the following equation:

\[
C_{\text{onc}} = \frac{P_r \times \frac{24.46}{M}}{F_c},
\]

where \(C_{\text{onc}}\) is the concentration in ppm, \(P_r\) is the permeation rate in ng/min, \(M\) is the molecular weight of the calibration gas (CH₃I) in g mol\(^{-1}\), and \(F_c\) is the total flow of the calibration mixture in ccm. The constant 24.46 is the molar volume (L) at the given conditions.

**Figure 6.** Schematic of the permeation oven where N₂ flows into the oven where CH₃I\(_\text{l}(l)\) is heated to generate CH₃I\(_\text{g}(g)\) which then flows with the N₂ to the \(^{210}\text{Po}\) Source on the CIMS.

The diluted methyl iodide flow is delivered into the system by a mass flow controller, calibrated to N₂ with a range of 200 sccm, (MKS Instruments, Model:
1479A22CR1BM) at a flow rate of 0.2 slpm. The flow through the controller is determined by two resistive legs in a wheatstone bridge where a change in temperature between the two is directly related to a change in resistance. The change in temperature, and thus resistance, increases with increasing flow.

The methyl iodide mixture is then passed through a radioactive $^{210}$Po source (P-2031 Nuclecel Static Eliminator, NRD) to produce excess reagent ions, $I^-$. The $^{210}$Po within the source decays to $^{206}$Pb, emitting alpha particles that collide with $N_2$, removing an electron. This removed electron interacts with $CH_3I$, resulting in the negative reagent ion, $I^-$, as well as a methyl radical. This is shown in the following reactions:

$$^{210}Po \rightarrow^{206} Pb + \alpha \text{ particles}$$  \hspace{1cm} (36)

$$\alpha \text{ particles} + N_2 \rightarrow N_2^+ + e^-$$  \hspace{1cm} (37)

$$CH_3I + e^- \rightarrow I^- + CH_3.$$  \hspace{1cm} (38)

The purpose of the 32 cm long nipple connecting the sample inlet and the reducer cross with the source, is to obtain a proper entrance length, which is the distance required for fully developed flow velocity within the flow tube. It is necessary to achieve this state before any mixing of the sample and reagent ions occurs. This length ($l_e$), the minimum distance from the sample inlet to the source, was determined through the equation:\textsuperscript{52}

$$l_e = 0.115aR_e,$$  \hspace{1cm} (39)

where $a$ is the tube radius (1.83 cm) and $R_e$ is the Reynold's number. The Reynold's number is represented through the equation:\textsuperscript{52}

$$R_e = \frac{2av}{\mu},$$  \hspace{1cm} (40)
where \( v \) is the flow velocity in cm s\(^{-1}\) (330 cm s\(^{-1}\)), \( \rho \) is the gas density in g cm\(^{-3}\) (N\(_2\): 4.8 x 10\(^{-6}\) g cm\(^{-3}\)) and \( \mu \) is the absolute viscosity in poise (18 x 10\(^{-5}\) poise).\(^{53}\) N\(_2\) is used as it is the most predominant constituent of the troposphere. The flow velocity is determined by the equation:\(^{52}\)

\[
v = \frac{760}{P} \frac{T}{273.2} \frac{F}{\pi a^2},
\]

where \( P \) is the pressure in torr (3.2 torr), \( T \) is the temperature in Kelvin (298 K), and \( F \) is the flow rate in standard cubic centimeters per second (13 sccs). The gas density for nitrogen was determined using the ideal gas law at a pressure of 3.2 torr and temperature of 298 K. Through these calculations, the minimum distance required for parabolic flow was determined to be 6.8 cm and the entrance length in this instrument was made to be 34.8 cm. The entrance length is larger than necessary because the flow tube was designed to ensure flexibility in the distance based on the obtained pressure. The availability of parts was also a limiting factor.

The stainless steel nipple was welded to a KF40 weld connection to allow for attachment to the stainless steel reducer cross containing the \(^{210}\)Po source. The other end of the reducer cross was shortened and welded to a 0.95 cm thick stainless steel disk with a 10.2 cm diameter that acts as the mounting plate to the next chamber, the declustering region. It is attached by four 1.9 cm long 4-40 metal screws and sealed with a viton o-ring with an outer diameter of 8.57 cm and an inner diameter of 7.62 cm.

The mounting plate was originally 1.27 cm thick and was reduced to 0.95 cm to allow for a mixing length, distance from the source to the first pinhole, of 5.3 cm. The large tube was also originally 11.4 cm long and shortened on both sides to 7.5 cm to achieve this distance. Given the area of the flow tube and total flow rate of 1 slpm, 5.3
cm was chosen an ideal mixing length to allow for a reaction time of 13 ms, a value that lies in the range given in the literature of approximately 10 – 15 ms. The mixing length includes the distance from the center of the source to the end of the reducing cross, the stainless steel disk, as well as the 0.48 cm thick o-ring. The reaction time was determined by the equation:\(^{52}\)

\[
t = \frac{z}{\nu},
\]

where \(t\) is the reaction time, \(z\) is the flow tube length (5.3 cm), and \(\nu\) is the flow velocity (410 cm s\(^{-1}\)).

The original design of this region has since been modified several times in attempt to obtain signal. The modifications and recommended designs are discussed in the subsequent section 3.2.

2.4 Declustering Region

The next chamber of the instrument is the declustering region, which has a pressure drop from 3.2 torr to 1.4 torr, and is mounted to the source region. Within this region, energetic collisions occur, breaking apart the weakly bound cluster ions, such as \(\Gamma^-(\text{H}_2\text{O})_n\), resulting in simplified spectra \(^{49}\). The declustering region is a 15.2 cm (6") OD blank flange that was custom made by Kurt J. Lesker Company to have a thickness of 3.81 cm, as opposed to the standard thickness of 1.98 cm. The increase in size allows sufficient space for the lens stack, while the flange design maintains efficient space and allows for easy connection to the surrounding chambers.
Figure 7. The side of the declustering region facing high pressure region in the CIMS. Pinhole plate 1 with an aperture of 0.1 cm is shown in the top left and is attached in the inset shown on the flange. Three ports are shown that allow connection to a pump, pressure gauge, and feedthrough. The top lens of the ion lens stack is shown in the center.

A 9.68 cm diameter hole was bored through the flange to allow the transport of the sample from the source region to the intermediate vacuum region. On the side facing the source region, an indentation with a diameter of 7.0 cm and depth of 0.635 cm was made to allow room for the first pinhole plate. This indentation, as well as the top lens in the lens stack, is shown in Figure 7, displaying the side of the flange facing the high pressure side.
Figure 8. The side of the declustering region facing low pressure region in the CIMS. Pinhole plate 2 with an aperture of 0.5 cm is shown in the top right and is attached in the center of the flange. Three ports are shown that allow connection to a pump, pressure gauge, and feedthrough. The mounting plate of the ion lens stack is shown in the center.

The custom made pinhole plate (Extrel) is a 0.16 cm (1/16") thick stainless steel plate with an outer diameter of 6.50 cm and an aperture of 0.05 cm; this segregates the source region from the declustering region. The pinhole aperture on the side of the plate facing the low pressure side was beveled to allow for better transmission of the ions. The pinhole plate had three holes drilled to allow for attachment and electrical isolation by three 0.95 cm long, pan head, ultem 2300 screws. The pinhole plate was sealed to the flange by a viton o-ring with an outer diameter of 4.76 cm and an inner diameter of 4.44 cm. The space outside the indentation is for the connection to the source region, via the four screws described above.
On the side facing the intermediate region, an indentation with a diameter of 5.72 cm and a depth of 0.635 cm was made to allow for the lens stack mount. Once in place, the backside of the mount is approximately flush with the side of the flange. Figure 8 shows the side of the flange facing the low pressure region where the lens stack is shown screwed into the lens mount.

Figure 9 shows the lens stack located inside the bore of the declustering region. The lens stack was fabricated from 0.16 cm thick stainless steel plates cut into two equal sized circles with an outer diameter of 3.49 cm. A hole was made in each lens with a diameter of 0.6 cm. The lenses were mounted to the lens mount, which was a circle cut out of a 0.32 cm (2/16") thick stainless steel plate. The mount had an outer diameter of 5.7 cm and a hole in the center with a diameter of 1.7 cm. The two lenses and lens mount were electrically isolated using 0.95 cm long ceramic spacers and with 2.54 cm long, pan head, 4-40, ultem 2300 screws. With the aid of ion lenses, the ions will be transmitted to the next pinhole.

The second pinhole plate is mounted on the outside of the lens mounting plate facing the low pressure side, acting as a partition between the declustering region and intermediate vacuum region. This 0.16 cm thick plate was custom made by Extrel, with an outer diameter of 7.49 cm and a beveled aperture of 0.1 cm facing the low pressure region. The pinhole plate had three holes made where three 0.95 cm long, pan head, 4-40, ultem 2300 screws are used to hold the plate to the flange. The plate is sealed with a viton o-ring with an outer diameter of 6.35 cm and an inner diameter of 6.03 cm.
Figure 9: The ion lens stack that consists of two stainless steel plates with holes in the center to transmit ions in the CIMS. The lenses are separated using ceramic spacers and mounted on a stainless steel plate shown furthest to the right.

Three pockets with a diameter of 0.95 cm were machined in the side of the flange, where three KF16 flanges were welded on. One flange connects to a 4 pin feedthrough (Kurt J. Lesker Company, PN: EFT0044038) to allow for an applied voltage on the lens stack and pinhole plate, a second to a rotary vane mechanical vacuum pump (E2M12, BOC Edwards), with a pumping speed of 4.3 torr L s\(^{-1}\), to allow for a pressure of 1.4 torr and lastly, a pirani gauge (Edwards, APG-L-NW16) to monitor the pressure. The feedthrough is connected to the pinhole plates and lens stack by in-vacuum insulated wire and one ultem 2300 screw. A manual brass ball valve is also located between the declustering region and the mechanical pump to control the gas flow.

2.5 Intermediate Vacuum Region

The intermediate vacuum region is a double sided 15.2 cm OD conflat flange with an attached 6.35 cm OD tube and is maintained in mtorr range. This flange was used in the pre-existing EIMS as housing for the mass spectrometer. On the side that attaches to the declustering region (Figure 10) an indentation 0.48 cm deep with an outer diameter of
8.26 cm was made to allow space for the second pinhole plate that is mounted on the declustering flange, extending into the intermediate vacuum flange.

Figure 10. The side of the intermediate vacuum region facing the high pressure region in the CIMS. The back of the ion lens stack is shown in the center. One of the three ports allows connection to the feedthrough, and the other two allow connection to the pump.

The tube extending from the side of the flange facing the low pressure region (Figure 11) was shortened to 1.91 cm. An end cap for this tube was made from 0.32 cm thick stainless steel and welded on. A hole was bored in the center with an outer diameter of 1.27 cm. This end cap also serves as the mounting plate for the second lens stack and the last pinhole plate. The length of the tube was designed so that the last pinhole plate would be located 0.8 cm from the Einzel lens stack in the mass spectrometer region allowing for the two components to be as close as possible without any contact. This last pinhole plate is 0.16 cm thick, with an outer diameter of 5.99 cm and aperture of 0.2 cm. Like the other two pinhole apertures, this was beveled on the side
facing the low pressure region. The plate is mounted to the end cap using three 0.48 cm long, slotted flat head, ultem 2300 screws with a 2-56 thread size.

The second lens stack was designed much like the one described in the declustering region. Two stainless steel circles were cut from 0.16 cm thick stainless steel plates and a 0.6 cm wide hole bored in the middle. Instead of a separate mounting plate as in the declustering region, the lenses mounted to the end cap, as mentioned above. The lenses were electrically isolated using 0.95 cm long ceramic spacers and 2.22 cm long, pan head, 4-40, ultem 2300 screws. The plate is sealed to the end cap with a viton o-ring with an outer diameter of 3.81 cm and an inner diameter of 3.49 cm.

Figure 11. The side of the intermediate vacuum region facing the low pressure region of the CIMS. The third pinhole plate with an aperture of 0.2 cm is shown on the top right and is located on the end cap on the tube of this region. One of the three ports allows connection to the feedthrough, and the other two allow connection to the pump.
Similar to the declustering region, three 0.95 cm wide pockets were machined in the side of the flange, where three KF16 flanges were welded on to allow for connections to a four pin feedthrough (Kurt J. Lesker Company, PN: EFT0044038), another to a rotary vane mechanical vacuum pump, and the last to a pirani gauge. This chamber is maintained at an order of mtorr with the rotary vane mechanical vacuum pump (E2M40, BOC Edwards) with a pumping speed of 10 L s\(^{-1}\) that is also connected to a booster pump that allows for a total pumping speed of 66 L s\(^{-1}\). However, the small sized pocket connection resulted in the pump being choked, preventing a total pumping speed of 66 L s\(^{-1}\). Based on the calculations of pressures involving the pinhole diameters and pumping speeds using equations 26 – 28, a net pumping speed of 3.1 – 5.3 L s\(^{-1}\) can be reached in the intermediate vacuum region, which is in the transition region between viscous and molecular flow, and would still allow for the desired pressures. A flow rate of 3.1 L s\(^{-1}\) corresponds to the molecular flow regime, whereas 5.3 L s\(^{-1}\) is representative of viscous flow.

Additionally, with an added connection to one of the other KF16 ports that connected to the pirani gauge, a net pumping speed of 1.61 L s\(^{-1}\) could be achieved. Despite the improvement of the added second port, the net pumping speed was still too low to allow for a functioning vacuum system. To further improve the pumping speed, two of the three bores were widened to 1.27 cm and the tube on the inside of the knife edge, where the copper gasket is placed, was opened up resulting in a length of 4.5 cm. According to equations 29 – 34, the net pumping speed resulted in 5.4 L s\(^{-1}\), drastically reducing the choking effects of the pump allowing for manageable pressures in each region. While this region no longer has a pressure gauge, it is the intermediate vacuum
region and the exact pressure is not required as long as the two surrounding regions are accurately monitored.

2.6 Mass Spectrometer Region

The mass spectrometer region is the final region of the instrument where the quadrupole mass filter and electron multiplier detector are located. The pressure in this region is maintained at $2.6 \times 10^{-5}$ torr. The molecules pass through the last pinhole aperture from the intermediate vacuum region to the Einzel lens stack that is used to direct the ions to the quadrupole mass spectrometer, where they are separated by their mass to charge ratio. The quadrupole contains 19 mm rods and is powered by Extrel's 150-QC quadrupole power supply, QMS DC power supply and QMS controller (model 5221). The negative ions are detected by a continuous dynode electron multiplier and reported as a signal in counts s$^{-1}$.

This region consists of two stainless steel chambers acting as the housing, shown in Figure 12. The first chamber, where the Einzel lens stack and the front end of the mass filter is located, contains six connections: four 15.2 cm CF flanges and two 6.99 cm (2.75") CF flanges. A 15.2 cm CF flange connects directly to the intermediate vacuum flange and the one across from it connects to the next chamber. Another 15.2 cm CF flange positioned on the bottom of the chamber is attached to a turbomolecular pump (Pfeiffer, TPH 330) with a pumping speed of 330 L s$^{-1}$. Also off of this pump connection, a 6.99 cm CF flange is attached connecting to an ionization gauge (Duniway Stockroom Corp, T-100-N). The other 6.99 cm CF flange is on top of the chamber, where an eight pin feedthrough (Kurt J. Lesker Company, PN: EFT0084033) is attached. The last 15.2 cm CF flange is not needed and is closed off with a cold finger that was
used on the EIMS. The cold finger will not be used as a trap, but it is an ideal blank because it consumes a lot of space inside the chamber (without blocking the ion path) thus reducing the amount of volume that needs to be pumped down to the desired pressure. It is also convenient to have an opening on this side while inserting the quadrupole mass spectrometer into the system to allow for viewing. It is crucial to be careful that it does not get damaged against the housing and that all of the wires remain attached and electrically isolated, which can be difficult with the lack of excess space between the quadrupole and the housing.

![Image](image_url)

**Figure 12.** The region of the CIMS housing the mass spectrometer, consisting of two chambers, labeled 1 and 2. The ionization gauge is shown on the top of the CIMS and two turbomolecular pumps are shown on the bottom.

The second chamber, housing the back end of the mass filter and the detector, is a cross with four 15.2 cm CF flange connections. The flange across from the connection to the previously mentioned chamber connects to the flange base of the Extrel Max 300 quadrupole mass spectrometer. The quadrupole mass spectrometer is shown in Figure
13. A turbomolecular pump (Pfeiffer, TPH 450H) with a pumping speed of \(450 \text{ L s}^{-1}\), is attached to the flange on the bottom of the cross and an ionization gauge (MDC Vacuum Products Corp, PN: 432026) and is located on the top of the chamber through a 15.2 cm / 6.99 cm CF flange adapter. Although this region contains two ionization gauges, only one can be used at a time because they share the same controller. The ionization gauge on top of the second region will be the dominant gauge considering it is positioned closest to the detector. The ionization gauge determines the pressure by ionizing the gas molecules by electron impact. The positive ions produced are collected at an anode resulting in a current that is a function of the pressure.

![Figure 13](image)

**Figure 13.** The quadrupole mass spectrometer that contains an Einzel lens stack, a quadrupole mass filter and electron multiplier detector.

All CF connections in the mass spectrometer region are sealed with copper gaskets. The two turbomolecular pumps are backed with a rotary vane mechanical vacuum pump (RV5, BOC Edwards) with metal bellows as the connection. In between the turbomolecular pumps and the backing mechanical pump a solenoid valve is placed in order to ensure that the valve stays closed if power is lost to avoid back streaming from the pump into the system. A manual valve is also on the backing mechanical pump to close off the pump from the system manually. A pirani gauge (Edwards, APG-L-NW16) is next to the solenoid valve to ensure adequate backing pressure for the turbomolecular
pumps. Two other solenoid valves are used in the system for the same purpose; one between the pump and the bellows to the source region and one between the bellows to the declustering region and its pump. The roots blower pump also has a valve, but because of the size of the connection it is a manual bellows angle valve. In the case of a power outage while collecting data, this pump will not be automatically isolated from the vacuum system. While the connection is at an angle and is quite long (68 cm), autonomous operation should still be carried out with caution.

In order for the solenoid valves to close during a power outage and remain closed once power is restored, an optically isolated solid state relay (Omega Engineering Corp, SSR330AC10) is necessary. This is an electronic switch that is powered on when a voltage is applied to it and contains a feedthrough that allows the switch to remain closed once power goes out and then back on. The wire configuration of the solid state relay is shown in Appendix J. The two turbomolecular pumps are also connected to the solid state relay to ensure that they will not turn back on once power is restored in case the pressure of the system has returned to atmosphere.

This chapter specifically describes the design of the four individual chambers of the CIMS from the EIMS. The components used in each region are configured precisely to allow the production of negative product ions in the source region and the transport of the ions to the mass spectrometer region to be separated by mass to charge ratio (m/z) by the quadrupole and detected by the electron multiplier.
CHAPTER III

OPERATING THE INSTRUMENT

3.1 Establishing Positive Ion Signal

For the general purpose of this instrument, the electron impact (EI) source included with the mass spectrometer purchased from Extrel will not be used, as negative ions are used for the detection of ClNO₂. However, it was beneficial to begin with monitoring positive ions using the EI source to ensure the mass filter and detector were functioning properly.

The Merlin Automation program provided by Extrel was used to obtain the positive ion mass spectrum. A custom configuration file by Extrel, as well as a tune file, were provided. The configuration file (New Hampshire Configuration.cw) contains setup information for the baseboard, filament, optics, Q1 scan, multiplier, dynode, and the digital signal processor (DSP). No alterations were required for this file because it was accurately configured for this mass spectrometer. The tune file (counting spectrum.tw) contains controls for the system voltages, filaments, optics, quadrupole, dynode, multiplier, preamplifier, and scan parameters. Table 1 contains the original set points (labeled as is in the Merlin Automation program) in column 1 and the final set points necessary to obtain signal in column 2.
Table 1. Adjustments made to the original tune file to obtain positive ion signal

<table>
<thead>
<tr>
<th>CONTROL</th>
<th>ORIGINAL SET POINTS</th>
<th>FINAL SET POINTS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>System Voltages</strong></td>
<td>ON</td>
<td>ON</td>
</tr>
<tr>
<td><strong>Filaments</strong></td>
<td>ON</td>
<td>ON</td>
</tr>
<tr>
<td>eV</td>
<td>-100 V</td>
<td>-75 V</td>
</tr>
<tr>
<td>em_cmp</td>
<td>3 mA</td>
<td>3 mA</td>
</tr>
<tr>
<td>Filament limit</td>
<td>5 A</td>
<td>5 A</td>
</tr>
<tr>
<td>Emission meter</td>
<td>3 mA</td>
<td>3 mA</td>
</tr>
<tr>
<td>Fil V meter</td>
<td>5 V</td>
<td>5 V</td>
</tr>
<tr>
<td>Fil 1 meter</td>
<td>4 A</td>
<td>4 A</td>
</tr>
<tr>
<td><strong>Optics</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ion region</td>
<td>7 V</td>
<td>7 V</td>
</tr>
<tr>
<td>Extractor lens</td>
<td>-7 V</td>
<td>-7 V</td>
</tr>
<tr>
<td>Lens 1 &amp; 3</td>
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<td>-10 V</td>
</tr>
<tr>
<td>Lens 2</td>
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<td>-90 V</td>
</tr>
<tr>
<td>Entrance lens minimum</td>
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<td>-10 V</td>
</tr>
<tr>
<td>Entrance lens maximum</td>
<td>-80 V</td>
<td>-80 V</td>
</tr>
<tr>
<td>Exit</td>
<td>-200 V</td>
<td>-200 V</td>
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<tr>
<td><strong>Quadrupole 1</strong></td>
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<td></td>
</tr>
<tr>
<td>Q1 pole reverse</td>
<td>Normal</td>
<td>Normal</td>
</tr>
<tr>
<td>Q1 Delta Resolution</td>
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<td>0 %</td>
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<td><strong>Dynode On</strong></td>
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<td></td>
</tr>
<tr>
<td>Dynode voltage</td>
<td>5000 V</td>
<td>5000 V</td>
</tr>
<tr>
<td>Dynode polarity</td>
<td>Negative voltage</td>
<td>Negative voltage</td>
</tr>
<tr>
<td><strong>Multiplier: On</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Multiplier Voltage</td>
<td>1900 V</td>
<td>2700 V</td>
</tr>
<tr>
<td>Multiplier Polarity</td>
<td>Positive ions</td>
<td>Positive ions</td>
</tr>
<tr>
<td><strong>Preamp</strong></td>
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<td></td>
</tr>
<tr>
<td>Preamp 1 gain</td>
<td>$10^8$</td>
<td>$10^8$</td>
</tr>
<tr>
<td>Preamp 1 polarity</td>
<td>Normal</td>
<td>Normal</td>
</tr>
<tr>
<td>Preamp 1 bipolar</td>
<td>Unipolar</td>
<td>Unipolar</td>
</tr>
<tr>
<td>Preamp 2 gain</td>
<td>$10^8$</td>
<td>$10^8$</td>
</tr>
<tr>
<td>Preamp 2 polarity</td>
<td>Normal</td>
<td>Normal</td>
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<tr>
<td>Preamp 2 bipolar</td>
<td>Unipolar</td>
<td>Unipolar</td>
</tr>
<tr>
<td><strong>Scan Parameters</strong></td>
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<td></td>
</tr>
<tr>
<td>Samples per mass</td>
<td>31</td>
<td>31</td>
</tr>
<tr>
<td>Prescan</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Baseline</td>
<td>0.00 mv</td>
<td>0.00 mv</td>
</tr>
</tbody>
</table>
Table 2. Adjustments made to the scan method to obtain positive ion signal

<table>
<thead>
<tr>
<th>CONTROL</th>
<th>ORIGINAL SET POINTS</th>
<th>FINAL SET POINTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass range</td>
<td>10-35 amu</td>
<td>1-250 amu</td>
</tr>
<tr>
<td>Requested scan time</td>
<td>0.5 s</td>
<td>8.0 s</td>
</tr>
<tr>
<td>Actual scan time</td>
<td>0.50 s</td>
<td>4.75 s</td>
</tr>
<tr>
<td>SIM width</td>
<td>0.700 amu</td>
<td>0.700 amu</td>
</tr>
<tr>
<td>Microscan per scan</td>
<td>8</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 2 presents the changes made to the scan method that were required to obtain signal. The “mass range” was increased under the scan method from 10-35 amu to 1-250 amu for the mass spectrum in Figure 14 to generate an entire mass spectrum of the components in air with methyl iodide. The “requested scan time”, the time it takes to analyze all of the masses in the mass range, was increased from 0.5 s to 8.0 s, with the “actual scan” time being only 7.44 s. The resulting “microscan per scan” was 12 after the “scan time” and “mass range” were selected.

The critical change needed to obtain positive ion signal was to increase the multiplier voltage in the tune file. The voltage was originally set to 1900 V, as shown in Table 1. At this low voltage setting, only noise was generated and the instrument would periodically disconnect. By increasing the multiplier voltage to 2700 V, the noise decreased from thousands of counts per second (cps) to only hundreds of cps and continuous connectivity was obtained. However, the recommended range specified in the Extrel manual was 2200-2400 V for a new electron multiplier, with a maximum setting of 3000 V. It is not surprising that this final voltage is outside the specific voltage range considering the current electron multiplier had been at atmospheric pressure for approximately 1 year, consequently shortening the multipliers lifetime and resulting in the need for a higher voltage to operate properly. Another necessary adjustment was
made to the filament voltage from -100 eV to -75 eV, for ease of spectral comparison with those in the literature.

A positive ion spectrum for various flows of N₂ with CH₃I is shown in Figure 14. Table 3 lists the components of air represented by the m/z values in the spectrum and their corresponding intensities. The relative intensity of each fragment to the molecular ion N₂⁺ is also listed. The intensity of the fragment ions for both N⁺ and O⁺ are both larger than the intensities of N₂⁺ and O₂⁺ because of the high imparted ionization energy of -75 eV.

Table 4 provides the calculated concentration of CH₃I entering the QMS from the permeation oven at each flow rate as well as the corresponding intensities of the two primary masses, CH₃I⁺ and I⁺ at m/z 142 and 127 respectively. As the flow rate increases, the intensity of CH₃I⁺ and the fragment peak, I⁺, decreases. This trend is as expected because the higher flow rate dilutes the concentration of methyl iodide as described by equation 35 in section 2.3.
Figure 14. Positive mass spectrum of nitrogen with CH₃I in a carrier flow of N₂. The temperature on the permeation oven is held constant at 50°C while the N₂ flow is varied from 0.2-0.8 slpm. Inset shows expanded region between 120 – 150 amu to highlight peak at I⁺ 127 and CH₃I⁺ peak at 142.
Table 3. The positive ions detected by EI source and their corresponding m/z, average intensity and relative intensity to N$_2^+$.

<table>
<thead>
<tr>
<th>Ion</th>
<th>m/z</th>
<th>Average Intensity (cps)</th>
<th>Relative Intensity to N$_2^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2^+$</td>
<td>2</td>
<td>5.94E+03</td>
<td>6.48E-01</td>
</tr>
<tr>
<td>N$_2^+$</td>
<td>14</td>
<td>1.17E+04</td>
<td>1.28E+00</td>
</tr>
<tr>
<td>O$_2^+$</td>
<td>16</td>
<td>7.52E+03</td>
<td>8.20E-01</td>
</tr>
<tr>
<td>H$_2$O$^+$</td>
<td>18</td>
<td>5.05E+03</td>
<td>5.51E-01</td>
</tr>
<tr>
<td>Ar$^+$</td>
<td>20</td>
<td>1.42E+03</td>
<td>1.55E-01</td>
</tr>
<tr>
<td>N$_2$O$^+$</td>
<td>28</td>
<td>9.17E+03</td>
<td>1.00E+00</td>
</tr>
<tr>
<td>O$_2$N$^+$</td>
<td>32</td>
<td>3.58E+03</td>
<td>3.90E-01</td>
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<tr>
<td>Ar$^+$</td>
<td>40</td>
<td>5.98E+03</td>
<td>6.52E-01</td>
</tr>
<tr>
<td>CO$_2$O$^+$</td>
<td>44</td>
<td>5.23E+03</td>
<td>5.70E-01</td>
</tr>
</tbody>
</table>

Table 4. The varying flow rates and the corresponding CH$_3$I fragment intensities that are plotted in Figure 14. The calculated concentration of CH$_3$I entering the CIMS from the permeation oven is also shown in the second column.

<table>
<thead>
<tr>
<th>Flow Rate (slpm)</th>
<th>CH$_3$I Concentration (ppm)</th>
<th>Ion</th>
<th>m/z</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>15.3</td>
<td>CH$_3$I$^+$</td>
<td>142</td>
<td>4.27E+03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>I$^-$</td>
<td>127</td>
<td>1.85E+03</td>
</tr>
<tr>
<td>0.3</td>
<td>10.2</td>
<td>CH$_3$I$^+$</td>
<td>142</td>
<td>3.12E+03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>I$^-$</td>
<td>127</td>
<td>1.32E+03</td>
</tr>
<tr>
<td>0.4</td>
<td>7.67</td>
<td>CH$_3$I$^+$</td>
<td>142</td>
<td>2.52E+03</td>
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<tr>
<td></td>
<td></td>
<td>I$^-$</td>
<td>127</td>
<td>1.08E+03</td>
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<tr>
<td>0.5</td>
<td>6.13</td>
<td>CH$_3$I$^+$</td>
<td>142</td>
<td>2.16E+03</td>
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<tr>
<td></td>
<td></td>
<td>I$^-$</td>
<td>127</td>
<td>9.48E+02</td>
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<tr>
<td>0.6</td>
<td>5.11</td>
<td>CH$_3$I$^+$</td>
<td>142</td>
<td>1.94E+03</td>
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<td></td>
<td></td>
<td>I$^-$</td>
<td>127</td>
<td>8.65E+02</td>
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<tr>
<td>0.7</td>
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<td>1.83E+03</td>
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<tr>
<td></td>
<td></td>
<td>I$^-$</td>
<td>127</td>
<td>8.29E+02</td>
</tr>
<tr>
<td>0.8</td>
<td>3.83</td>
<td>CH$_3$I$^+$</td>
<td>142</td>
<td>1.79E+03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>I$^-$</td>
<td>127</td>
<td>8.05E+02</td>
</tr>
</tbody>
</table>

3.2 Establishing I$^-$ Signal

In order to obtain a negative ion spectrum after obtaining a positive ion spectrum, the polarity of the conversion dynode and electron multiplier needed to be reversed. This was done using the Merlin Automation software with the setting listed in Table 5. Other
necessary adjustments for negative ion mode included turning off the filaments of the EI source and adjusting the ion optics. The electron energy is controlled by the potential difference between the filament and ion region. The ion optic voltages were varied until the cleanest negative ion spectrum was obtained with a low noise intensity (100-500 cps range). The opposite voltage was used for the positive ion spectrum for the ion region, extractor lens and the three focusing lenses (Table 5). Other voltage values resulted in a noisy ion spectrum having an order of tens of thousands cps. The entrance lens and exit lens were also oppositely charged but needed to be increased close to the maximum value to maintain a flat base line without a slope. The high voltage also prevents co-generated positive ions. The scan method used for the positive ion analysis was the same as used for the negative ion analysis.

The specific voltages applied to each element of the system must be empirically determined. Based on previous studies, the voltage gradient stepped approximately -150 V at the source to -100 V and -25 V at the first and second pinholes, respectively, to a value of +5 V at the third pinhole. The voltage gradient must be large enough to transport the ions to the detector and incremented in such a way to allow passage through each lens and pinhole plate. Using several different power supplies with limited ranges, many voltage gradients were attempted with a typical pattern of approximately 20 V cm$^{-1}$ (e.g. each lens in a lens stack is about 1 cm apart, so the applied voltage was typically a difference of approximately 20 V). Voltage gradients across a wide range were attempted. Specifically, -300 to -80 V was applied to the first pinhole plate with the other plates as specified above.
The alignment of the lenses and pinhole plates were verified to ensure the transport of ions to the detector. This was performed by aiming a laser beam through the first pinhole plate (with the source region removed) and observing the light through the view port located on the back of the quadrupole mass spectrometer flange. The first iteration of lens alignment did not transmit the laser beam, indicating that the configuration of the lenses and pinholes were not aligned properly. In order to determine where the misalignment was occurring, the front pinhole plate, a likely cause considering its small aperture, was removed and again the laser beam was aimed through the system. With the first pinhole plate removed, the laser alignment beam was transmitted to the detector, denoting the first pinhole plate as the source of error.

A technique used to position the first pinhole properly involved a paper version (to scale) of the pinhole plate. While aiming the laser beam in the opposite direction, focusing through the ion lenses and last two pinhole plates (with the 15.2 cm OD flange attached to the cold finger removed to gain access into the instrument) to the paper pinhole plate, the point of the laser beam can be marked, indicating the exact location that the stainless steel pinhole plate needs to be positioned. It should be noted that it is necessary that each screw is uniformly tightened to maintain the alignment of the pinhole aperture.
Table 5. Attempted negative ion set points compared to the positive ion set points

<table>
<thead>
<tr>
<th>CONTROL</th>
<th>POSITIVE ION SET POINTS</th>
<th>NEGATIVE ION SET POINTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>System Voltages</td>
<td>ON</td>
<td>ON</td>
</tr>
<tr>
<td>Filaments</td>
<td>ON</td>
<td>OFF</td>
</tr>
<tr>
<td>eV</td>
<td>-75 V</td>
<td>0-200 V*</td>
</tr>
<tr>
<td>em cmp</td>
<td>3 mA</td>
<td>-</td>
</tr>
<tr>
<td>Filament limit</td>
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<td>-</td>
</tr>
<tr>
<td>Emission meter</td>
<td>3 mA</td>
<td>-</td>
</tr>
<tr>
<td>Fil V meter</td>
<td>5 V</td>
<td>-</td>
</tr>
<tr>
<td>Fil 1 meter</td>
<td>4 A</td>
<td>-</td>
</tr>
<tr>
<td>Optics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ion region</td>
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<td>-7 V</td>
</tr>
<tr>
<td>Extractor lens</td>
<td>-7 V</td>
<td>7 V</td>
</tr>
<tr>
<td>Lens 1 &amp; 3</td>
<td>-10 V</td>
<td>10 V</td>
</tr>
<tr>
<td>Lens 2</td>
<td>-90 V</td>
<td>90 V</td>
</tr>
<tr>
<td>Entrance lens minimum</td>
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<td>395 V</td>
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<tr>
<td>Entrance lens maximum</td>
<td>-80 V</td>
<td>395 V</td>
</tr>
<tr>
<td>Exit</td>
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<td>400 V</td>
</tr>
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<td>Quadrupole 1</td>
<td></td>
<td></td>
</tr>
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<td>Q1 pole reverse</td>
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<td>Normal</td>
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<td>0 %</td>
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<td>Dynode voltage</td>
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<td>5000 V</td>
</tr>
<tr>
<td>Dynode polarity</td>
<td>Negative voltage</td>
<td>Positive voltage</td>
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<tr>
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</tr>
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<td></td>
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</tr>
<tr>
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<td>$10^8$</td>
<td>$10^8$</td>
</tr>
<tr>
<td>Preamp 1 polarity</td>
<td>Normal</td>
<td>Normal</td>
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<tr>
<td>Preamp 1 bipolar</td>
<td>Unipolar</td>
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<tr>
<td>Preamp 2 polarity</td>
<td>Normal</td>
<td>Normal</td>
</tr>
<tr>
<td>Preamp 2 bipolar</td>
<td>Unipolar</td>
<td>Unipolar</td>
</tr>
<tr>
<td>Scan Parameters</td>
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<td>Samples per mass</td>
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<td>31</td>
</tr>
<tr>
<td>Prescan</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Baseline</td>
<td>0.00 mv</td>
<td>0.00 mv</td>
</tr>
</tbody>
</table>

* Range of values attempted individually
Attaining an I' signal has posed a significant challenge. After the range of voltage gradients attempted was unsuccessful and the proper alignment of lenses and pinhole plates was confirmed, the construction of the source region was modified. The original design places the source at a 90° to the first pinhole which could potentially result in a loss of ions to the walls. As shown in Figure 15, the source was oriented in-line with the first pinhole and the sample inlet was moved to the previous source location at the 90° angle. The source was also attached directly to the first pinhole plate; a design that would not be permanent because it does not incorporate the sample inlet to the system and was used solely to determine if distance was the only limiting factor in generating I' signal.

Figure 15. Modification of original source region in the CIMS where the $^{210}$Po source in-line with pinhole 1 and the sample inlet is where in the previous position of the $^{210}$Po source. A voltage is also applied to the source.
Next, a voltage gradient was applied to the source to help accelerate the ions to the first pinhole. The source was electrically isolated from the instrument by a small piece of 0.635 cm OD teflon tubing. The plastic housing over the live source was used to prevent electric shock.

A major disadvantage with the design exemplified in Figure 15 is the increased distance from the source to the first pinhole. Using a KF40 to ½" quick connect adapter and a ½" Swagelok to ¼" NPT fitting, the source was then placed directly onto the reducing cross as illustrated in Figure 16. This adapter, with the centering ring and pins removed, also acted to electrically isolate the source from the rest of the instrument. Next, the reducing cross was electrically isolated so that a voltage could be applied to that as well. This was done by replacing the stainless steel tube connections with the pressure gauge and feedthrough with 1.27 cm OD Teflon tubing. In addition, the metal screws holding the source plate to the instrument were replaced with ultem 2300 screws.

An oversight of the previous source region designs was the fact that there were no focusing aids from the source to the first pinhole that would prevent the ions from being directly pumped out. This was rectified by inserting a 17 cm x 1.27 cm OD stainless steel tube extending from the source to just slightly ahead of the first pinhole plate, using the two adapters, KF40 to ½” quick connect adapter and a ½” Swagelok to ¼” NPT fitting, as illustrated in Figure 17. A voltage was applied to the source and the stainless steel tube guided the ions to the first pinhole plate.
Figure 16. The modified source region in the CIMS where the $^{210}$Po source is in-line and closer to pinhole 1. A voltage is also applied to the $^{210}$Po source.

Figure 17. The modification of source region in the CIMS where stainless steel tube was attached to the $^{210}$Po source and inserted into the system to direct the ions to the first pinhole plate. A voltage is applied to the $^{210}$Po source as well.
Another modification that was made to the source region to obtain an I$^-$ signal is shown in Figure 18. This modification involved switching the positions of the source with the internal stainless steel tube described in Figure 17. This allows the source to be as close as possible to pinhole plate 1 inside of the source region. The mixture of N$_2$ with CH$_3$I flows through the stainless steel tubing to the source. Surrounding the stainless steel tube and source is a sheath flow of N$_2$. A voltage was applied to the stainless steel tube connected to the source as well.

**Figure 18.** The modified source region in the CIMS where the positions of the $^{210}$Po source and internal stainless steel tube illustrated in Figure 17 were switched. This places the $^{210}$Po source directly in front of the first pinhole plate. A voltage is applied to the stainless steel tube as well.
The design and assembly of a differentially pumped vacuum chamber that accommodates a variety of flow rates and maintains the necessary pressures to operate a mass spectrometer have been described in detail. Methyl iodide can be detected in this instrument in the positive ion mode; however, not currently in negative ion mode. The most probable location causing the difficulty is the source region, where ions are likely being lost to the surfaces or pump. An added difficulty is the limited number of power supplies, as well as the limited range of each power supply. This may be preventing us from attaining the exact voltage gradient necessary to transport the ions to the detector.
CHAPTER IV

FUTURE CONSIDERATIONS AND DIRECTION

4.1 Validation of CIMS

In order to validate the instrument, a proper calibration method needs to be determined for CINO2. This first involves the synthesis of CINO2 so that a known quantity can be delivered to the sample inlet of the CIMS. The synthesized CINO2 can be confirmed using FTIR spectroscopy. A calibration factor is determined that relates the CINO2 concentration to either the IC1 or CINO2 signal at 162 and 208, respectively. The concentration of CINO2 in future unknown samples will be determined from the experimentally determined calibration factor.

4.1.1 Design of CINO2 Synthesis Apparatus

The glass line apparatus in Figures 19 and 20 was specifically designed for the synthesis of CINO2. The design incorporated as many "ready made" parts as possible but also contained custom components made by Quark Glass (Vineland, NJ). From left to right in Figure 19, the apparatus begins with a high purity N2 cylinder with a regulator connected to 0.635 cm OD Teflon tubing that allows a small flow of N2, controlled by a flow controller, into the apparatus. A plug valve is placed in front of the regulator and a needle valve is placed between the flow controller and the apparatus. The 0.635 cm OD Teflon tubing connects to one neck of a three neck 500 mL round bottom flask (QIG-27-10) via a Teflon Ultratorr adapter. This neck of the round bottom flask consists of a 0.635 cm ID glass tube with a stopcock. The middle neck of this round bottom flask is
connected to the 125 mL separatory funnel (QFN-20-9), where the fuming H₂SO₄ and ClHO₃S are added by a 14/20 ground glass joint. The third neck, another 14/20 female ground glass connection, allows connection to an adapter containing a stopcock (QIG-4), where the gaseous ClNO₂ product flows to the next region of the apparatus. The green metal clip of the stopcock on this adapter was replaced with an o-ring seal to allow for a greater vacuum. This component was also modified such that the tube extending from the stopcock gradually decreases to 0.635 cm OD to allow connection by a ¼" Ultratorr union to the other half of the glass apparatus (0.635 cm OD glass tubing). The ability to separate the glassline is necessary for ease of transferring the final product from the synthesis apparatus to the CIMS.

![Diagram of apparatus](image)

**Figure 19.** The custom-made apparatus for the synthesis of ClNO₂. Gaseous ClNO₂ is formed in the reaction flask by the addition of ClSO₃H to HNO₃ and H₂SO₄ and flows to the cold trap (immersed in liquid nitrogen (LN₂)) before entering the CIMS. N₂ can also be used to purge the apparatus if the valves surrounding the cold trap are closed.

After this connection, the 0.635 cm OD glass tubing divides into two separate regions. One pathway is a bypass that leads directly to the pump. The other pathway leads to a vacuum trap where ClNO₂ is collected and stored. The 161 mL vacuum trap (QVA-11-1), acting as a cold trap, was modified so that the inner tube was shortened to
extend only halfway down the trap to allow sufficient space for solid ClNO₂ to be formed. These transfer lines consist of 0.635 cm OD glass tubing fused to a high vacuum valve (QVL-3-3). An Ultratorr union connects the end of the 0.635 cm OD glass tubing portion of the manifold to 0.635 cm OD Teflon tubing which leads to a rotary vane mechanical pump (E2M7, BOC Edwards). A plug valve permits isolation of the entire manifold from the pump.

Following the synthesis of ClNO₂, the manifold may be separated from the reaction flask and connected to the CIMS. A carrier flow of N₂ may be passed through the cold trap to deliver ClNO₂ to the instrument or a sample flow may be conveyed to the instrument through the bypass portion of the manifold.

4.1.2 ClNO₂ Synthesis Procedure

Several different methods of synthesizing ClNO₂ have been utilized in the past. One of the more commonly used methods employs N₂O₅. This procedure first
involves the synthesis of N$_2$O$_5$ before using it to produce ClNO$_2$. This method of ClNO$_2$

synthesis is similar to the mechanism occurring naturally in the atmosphere. As shown in

equations 10 – 11 in section 1.2, N$_2$O$_5$ is formed by the reaction of the NO$_3$ with NO$_2$. In

the laboratory this is achieved by reacting excess O$_3$ with a small flow of NO$_2$ to form

NO$_3$, which then reacts with more NO$_2$ to produce N$_2$O$_5$. N$_2$O$_5$ is trapped in a cold finger

that is maintained at 200 K with either dry ice, an ethanol slush bath or a chiller.

Analogous to the production process of ClNO$_2$ in the marine boundary layer, the

N$_2$O$_5$ is passed over either wetted NaCl salt crystals$^{42}$ or an aqueous NaCl solution to

produce ClNO$_2$. The solution can be either actual sea salt droplets or a solution

prepared from purchased NaCl crystals through nebulization. The decay of a known

calibration factor for ClNO$_2$ can then be determined by relating the ClNO$_2$ concentration
to either the ICl or ClNO$_2$I signal at 162 amu and 208 amu, respectively. However, this

procedure is based on the assumption that the N$_2$O$_5$/sea salt reaction proceeds with unity

yield.

A direct method of generating ClNO$_2$ would eliminate the need to assume a

product yield. Schweitzer et al.$^{55}$ synthesized ClNO$_2$ by adding chlorosulfonic acid

(ClHO$_3$S) drop wise to anhydrous nitric acid (HNO$_3$). After these two compounds are

mixed at room temperature, gaseous ClNO$_2$ is released and trapped at the liquid nitrogen

temperatures (63 – 77 K) $^{53}$ as a white solid. Upon warming to 200 K, the ClNO$_2$ may be

stored for several weeks as a green/yellow liquid.

The design of the aforementioned synthesis apparatus in section 4.1.1 was based

off of the procedure of Kaplan et al.$^{56}$ where ClNO$_2$ is synthesized directly using ClHO$_3$S

56
and HNO₃. The apparatus is set up in a well ventilated hood with minimal light to prevent the photochemical decomposition of the product ClNO₂. 66.2 mL of 90% fuming HNO₃ (Fisher Scientific, certified ACS plus, LOT 083160) is added to a 500 mL round bottom flask that is equipped with a stir bar. While vigorously stirring, 66.9 mL of 20% fuming sulfuric acid (H₂SO₄) (Mallinckrodt Chemicals, LOT HOTN60) is added dropwise from a 125 mL separatory funnel into the round bottom flask, that is cooled with dry ice to a temperature of 0 °C with the fuming HNO₃. Once the sulfuric acid has been added, 96.4 mL of 99% chlorosulfonic acid (Alfa Aesar, LOT A12S033) is added dropwise to the round bottom reaction flask through the separatory funnel over a course the 3 to 4 hours or at a rate that does not allow for brown fumes of nitrogen oxides to form above the reaction mixture. Gaseous ClNO₂ is evolved after each addition of ClHO₂S. The reaction flask is placed in dry ice to maintain a temperature of 193 K until all of the ClHO₂S has reacted. The dry ice is then removed and the product is stirred for 30 minutes, allowing the product to distill and be collected.

4.2 Discussion of Design and Construction of the CIMS

The goal in designing and constructing this instrument was to assemble a compact structure, while maintaining sensitivity and a low limit of detection. The current system design made use of components and materials that already existed in the lab. For components that were not available, the most practical, cost-efficient parts were purchased. The following is a discussion of changes that would be considered if money and availability of parts were not a consideration. Additionally, some suggestions are presented that were determined after designing and while constructing the instrument which may have allowed for improvements in the operation of the CIMS.
4.2.1 Source Region

The most recent configuration of the source region that was described in section 3.2 and is shown in Figure 18 still needs work to incorporate the sample inlet now that the internal stainless steel tube has been added. The port originally designed for the $^{210}$Po source connection will now be used as the sample inlet. The sample will flow to the system via 0.635 cm OD Teflon tubing. The Teflon tubing will connect to the source region through a tapped out ¼” swagelok to ¼” NPT adapter. After cutting a hole in the 1.27 cm OD stainless steel tubing connection to the source, the 0.635 cm OD Teflon tubing with sample will pass through the tapped out fitting and into the source region. This will then lead into the hole in the stainless steel tubing where the sample will react with the reagent ion.

4.2.2 Declustering Region

To reduce form factor of the system, the declustering region could have been designed similarly to the intermediate vacuum region. That is, instead of using a 3.81 cm thick flange, a typical 15.2 cm OD CF flange with a thickness of 1.98 cm could have been used that was attached to a tube, similar to the flange used in the current intermediate vacuum region. This design would allow for the declustering region to nest inside the intermediate vacuum region, minimizing both space and weight. The tube attached to the flange on the declustering region would need to have an outer diameter smaller than 8.26 cm in order to fit inside the intermediate vacuum region.

Another consideration is the idea of having an additional pair of ion lenses to better aid in transmission as described by Kercher et al. Each lens pair has a different
applied voltage, with each lens in the pair having an equal applied voltage. There is sufficient space within this flange for a second pair of lenses if the ceramic spacers used in the original lens stack are slightly shortened. The distance between lenses with the current configuration requires a voltage gradient between the two components to transmit the ions.

A better method of sealing the first pinhole plate, which acts as a partition between the source region and declustering region, would be beneficial. If the screws are not tightened exactly the same, which is difficult when one of the screws contains the wire to the filament, the source region will leak into the declustering region. Also once the system has been under vacuum for an extended period of time, one or more screws may loosen resulting in an uneven placement of the plate against the flange. Not only does this interfere with the pressure gradient, but the ion transmission is also affected. In order to adjust the pinhole plate, the system needs to be shut down and the front region has to be taken apart, consequently resulting in a great inconvenience and a large use of time. An easy solution is difficult because of the need to electrically isolate the pinhole plate from the declustering region.

4.2.3 Intermediate Vacuum Region

In the intermediate vacuum region, rather than the second set of ion lenses, an octupole ion guide, as used by Slusher et al.,\textsuperscript{57} would be a better option. While more expensive, this allows for an increased transmission of the ions to the mass spectrometer because only an RF voltage is applied. This results in a stable Y trajectory and unstable X trajectory, allowing the quadrupole to act as a low-pass mass filter only.
A major adjustment that could be made in the intermediate vacuum region is the pump's pump connections. The rotary vane mechanical pump with booster (E2M40, BOC Edwards) has a high pumping speed of 66 L s\(^{-1}\) but is limited by the small orifice to the intermediate vacuum region. Ideally, a larger orifice could be made, but is impossible with the current flange. Working with the current flange, another port connection to the pump could allow for a much higher pumping speed. Also, because the previous connection to the ion gauge is now being used as another connection to the pump, another port for the pressure gauge in this region would be beneficial.

Additionally, the large size of the pump will make it extremely difficult for this instrument to be moved easily if it were to be taken out of the lab and deployed in the field. A molecular drag pump would be better suited for this vacuum region; the pumping capacity is in between that of a turbomolecular pump and a rotary vane mechanical pump while being compact in size. The connection is the same as the current rotary vane mechanical pump so the same choking issue will most likely occur unless a change is made to the flange.

4.2.4 Mass Spectrometer Region

Ideally the two ion gauges, each located on one of the two chambers of the mass spectrometer housing, could be run simultaneously to obtain a more accurate measurement of the pressure between the two chambers during experiments.

If the eight pin power feedthrough (EFT0084033) used in this region needed replacement, a feedthrough having only one pin would be sufficient. The increased amount of pins has no negative effect on the system though and could always be used as spares if a pin ever gets damaged.
4.2.5 CIMS in the Literature

There are some distinct differences between CIMS instruments in the literature compared to the current CIMS described in this work. The variations mainly occur between the choice of buffer gas and reagent ions. Helium (He) has been used in many systems as the buffer gas;\(^\text{41,48}\) however, it is very difficult to pump He efficiently under high vacuum because of its low atomic weight. In addition, helium has a higher ionization energy than nitrogen, resulting in a more efficient removal of electrons from nitrogen during the ionization process in the source region. Argon is another potential buffer gas because of its low reactivity and has high molecular mass to allow for ideal pumping conditions; however, it is not commonly used because it is typically more expensive. The most important reason for the use of nitrogen over other buffer gases is when making ambient measurements, it is ideal to have a buffer gas that is characteristic of the sample; i.e. nitrogen, which is the predominant constituent of the troposphere.

Several reagent gases that have been used in CIMS systems include SF\(_6\)\(^\text{41}\) to generate SF\(_6^-\) ions, as well as CF\(_3\)I\(^\text{41,48}\) and CH\(_3\)I\(^\text{45,39,43}\) to generate I\(^-\) ions. SF\(_6^-\) is problematic in that it reacts with O\(_3\)\(^\text{48}\) While this reaction will not necessarily cause interferences, but when monitoring trace gases in ambient samples, an ideal reagent ion is one that will only react with the analyte of interest to reduce complexity. O\(_3\) exists in the troposphere at potentially high concentrations, resulting in the predominant signal being O\(_3\) rather than a trace gas such as CINO\(_2\). Also, because the potentially high O\(_3\) concentration, the amount of air sample entered into the CIMS would have to be limited
to prevent a depletion of the reagent ion signal, thus decreasing the sensitivity for ClNO$_2$ analysis.\textsuperscript{48} CH$_3$I is preferred over CF$_3$I because CH$_3$I does not cluster as strongly with I$^-$.\textsuperscript{57} While CH$_3$I seems to be the ideal choice for monitoring ClNO$_2$, other reagent gases may be used with this system to monitor other target molecules.

A quadrupole is the typical mass filter used in CIMS instruments. Quadrupoles have a large dynamic range and can function at a higher pressure than other mass analyzers. Their compact size allows for use in portable instruments and they are also low cost. Quadrupoles are also beneficial in CIMS instruments because of their ease of switching between positive and negative ions.

Other options for mass filters include ion trap and time-of-flight. Ion traps, like quadrupoles, are low cost, easily portable, and can analyze both positive and negative ions. Ion trap CIMS have been used to monitor halogen species,\textsuperscript{58} however, they cannot easily monitor trace levels. In order to monitor species on a pptv level, cryogenic pre-concentration of the ambient samples is required. Time of Flight CIMS has been used to monitor trace gases.\textsuperscript{59} This technique is low cost and has a high mass range. While high mass range is important for many analyses, for the case of this work, a mass range above 300 amu is unnecessary. The primary disadvantage of time of flight analyzers is the operating pressure requirement of $10^{-6}$ torr\textsuperscript{60} which is difficult to achieve in analyses with high flow rates.

\textbf{4.3 Future Work with the CIMS}

Upon validation of the CIMS for analysis of ClNO$_2$, experimentation can be performed to better understand the chemistry taking place in the troposphere. Durham, NH makes an ideal location to characterize these reactions because of its proximity to the
Gulf of Maine. This region is part of the area termed “the tailpipe of the United States” due to the fact that the pollution in areas throughout the continent will pass through New Hampshire then out to sea. This includes air from the western portion of the United States and from Canada, as well as polluted cities like New York City and Boston, resulting in the potential to measure both clean and polluted conditions. In addition to the chloride in sea salt aerosols as a source for ClNO₂, the sodium chloride (NaCl) used to salt the roads in the winter may also be a potential source that needs further analysis.

A further direction that may be pursued is the study of other possible intermediates of halogen species besides ClNO₂ alone. This idea stems from the recent work by Roberts et al.⁴⁶ where the reaction of ClNO₂ with NaCl was proven to produce Cl₂ under acidic conditions. This introduces another hypothesis of the reaction of ClNO₂ with sodium bromide (NaBr), also found in sea salt aerosols, to produce both Cl⁻ and Br⁻ as shown in Figure 21. This theory could be tested by flowing gaseous ClNO₂ over a sea salt solution and analyzing the product with the CIMS. Possible test solutions are listed in Table 6.

By monitoring the concentration of ambient ClNO₂ and studying other potential intermediates in such a dynamic location with CIMS, a better understanding of the halogen cycling in the marine boundary layer may be attained.
Table 6. Solutions to determine potential intermediates in the production of halogen species

<table>
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<th>Controls</th>
<th>Solution</th>
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<tr>
<td></td>
<td><strong>H₂O</strong></td>
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<tr>
<td></td>
<td><strong>H₂O + Acid (HNO₃, H₂SO₄)</strong></td>
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<tr>
<td></td>
<td>NaCl(aq)</td>
</tr>
<tr>
<td></td>
<td>NaCl(aq) + Acid (HNO₃, H₂SO₄)</td>
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<tr>
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<td></td>
<td>NaBr(aq) + Acid (HNO₃, H₂SO₄)</td>
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<tr>
<td>Is Br likely to be released in marine boundary layer?</td>
<td>Sea salt solution (600:1 Cl⁻:Br⁻)</td>
</tr>
<tr>
<td></td>
<td>Sea salt solution + Acid (HNO₃, H₂SO₄)</td>
</tr>
</tbody>
</table>

$$N₂O₅(g) \leftrightarrow N₂O₅(aq) \rightarrow NO_3^- (aq) + NO_2^+ (aq)$$

$$\begin{align*}
  & N₂O₅(g) \\
  & \Downarrow \text{Na}^+Cl^- \\
  & \text{ClNO}_2(g) \\
  & \xrightarrow{hv} \text{Cl}^- + NO_2^.
\end{align*}$$

Figure 21. Potential intermediates for the synthesis of Cl⁻ and potentially Br⁻ from the reaction of N₂O₅ with sea salt aerosols to form ClNO₂.
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35. Simon, H.; Kimura, Y.; McGaughey, G., Modeling the impact of ClNO₂ on ozone formation in the Houston area. *J Geophys Res-Atmos* 2009, 114, D00F03.


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CIMS START UP PROCEDURE

1) Turn on gauge controller
2) Close source region valve
3) Close declustering region valve
4) Close intermediate vacuum region valve
5) Turn all of the mechanical pumps
6) Open valve to backing pump (RV5)
7) Let vacuum chamber pump down until the pressures in source and declustering regions are on the order of hundreds of mTorr
8) Turn on cold water line to the turbomolecular pumps
9) Turn on each turbomolecular pump simultaneously
10) Once turbomolecular pumps have reached full speed, let vacuum chamber pump down until the pressures in source and declustering regions are on the order of tens of mTorr
11) Open the manual valve connecting the pump to the intermediate vacuum region
12) Open the ball valve connecting the pump to the declustering region
13) Open the ball valve connecting the pump to the source region
14) Turn on the permeation oven
15) Open the valve in between the permeation oven and flow controller
16) Open valve in between the sample inlet and flow controller
17) Turn on a small flow
18) Turn on the booster pump
19) Turn flows up to desired flow rate
APPENDIX B

CIMS SHUT DOWN PROCEDURE

1) Turn off voltages
2) Turn off Merlin power supplies
3) Turn off voltages supplied to the pinhole plates and lenses
4) Turn off permeation oven and wait for it to cool back to room temperature
5) Turn off the flows
6) Close valve in between the flow controller and the source
7) Close valve in between the flow controller and the sample inlet
8) Turn off booster pump
9) Close the manual bellows angle valve on the ED40 mech pump with booster
10) Close the two ball valves on the source and declustering regions to their corresponding mechanical pumps
11) Turn off ionization gauge both at the gauge controller as well as the power button on back of the ionization gauge power supply
12) Turn off both turbomolecular pumps simultaneously
13) Allow time for both turbomolecular pumps to wind down completely
14) Close the manual valve in between the backing mechanical pump and the turbomolecular pump
15) Vent the system with liquid N₂ at the entrance (Allow sufficient time to fill the entire system)
16) While liquid N₂ is still in place, individually open each mechanical pump to the source region, the declustering region and the intermediate vacuum region to vent and then close
17) Open the manual valve between turbomolecular pumps and the backing mechanical pump to vent and then re-close.
18) Close entrance valve and remove liquid N₂.
19) Turn off gauge controller
APPENDIX C

SOURCE REGION

Drawn by John Levasseur
Space Science Center Machine Shop
University of New Hampshire
APPENDIX D

BOSS FOR $^{210}$PO IN SOURCE REGION

Drawn by John Levasseur
Space Science Center Machine Shop
University of New Hampshire
APPENDIX E

DECLUSTERING REGION FLANGE

Drawn by John Levasseur
Space Science Center Machine Shop
University of New Hampshire

Weldment Connector Adapter
Rev. JHL 1-27-09
APPENDIX F

INTERMEDIATE VACUUM FLANGE: FRONT VIEW

Drawn by John Levasseur
Space Science Center Machine Shop
University of New Hampshire

Weldment Connector Adapter
JHL 11-27-07
APPENDIX G

INTERMEDIATE VACUUM FLANGE: SIDE VIEW

Drawn by John Levasseur
Space Science Center Machine Shop
University of New Hampshire
APPENDIX H

INTERMEDIATE VACUUM END CAP

Drawn by John Levasseur
Space Science Center Machine Shop
University of New Hampshire
APPENDIX I

HOLES FOR PINHOLE PLATE ATTACHMENT (PINHOLES 1, 2, 3)

Drawn by John Levasseur
Space Science Center Machine Shop
University of New Hampshire

Pin Hole Plates

JHL 11-27-07
APPENDIX J

SCHEMATIC OF SOLID STATE RELAY

The wire configuration of the solid state relay, where the colored lines represent different wires and the points of connection to the solid state relay: 1, 2, 3, 4 are the four points labeled on the solid state relay in each of the four corners.

An image of the solid state relay and switch mounted to the rack of the CIMS.