

Measurements of Nitrogen Reservoir Species Using Ion Drift-Chemical Ionization Mass Spectrometry (ID-CIMS) to Elucidate Nighttime Chemistry

Renyi Zhang

Department of Atmospheric Sciences

Texas A&M University

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1. Objectives

In this project, we have developed an ion drift-chemical ionization mass spectrometry (ID-CIMS) instrument, which is capable of providing online measurements of both VOCs and inorganic species. The method inherits the CIMS scheme yet with a controlled ion-molecule reaction time, hence extending the operation of PTR-MS for positive and negative reagent ions. This report consists of three sections: (1) description of the instrument configuration, (2) laboratory calibrations of VOCs and inorganic species (HNO_3 and N_2O_5), and (3) preliminary field measurements of nitrogen-containing compounds (N_2O_5 and HNO_3) in Houston.

2. Instrumentation Description

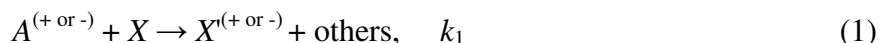
The ID-CIMS system consists of an ion source to produce positive or negative reagent ions, a drift tube where the ion-molecule reaction takes place, and a quadrupole mass spectrometer where the reagent ions are analyzed, as depicted schematically in Figure 1.

A flow tube was connected to the ID-CIMS system for laboratory measurements prior to the field campaign while an inlet was attached for field measurements during the field campaign. For the purpose of the calibrations conducted in our laboratory, the flow tube was a Pyrex tubing 70 cm in length and 2.25 cm ID. A coating of halocarbon wax was applied to the inner walls of the flow tube to reduce wall loss. The majority of the gases in the flow tube were diverted into a mechanical pump at the downstream end of the flow tube while only a small amount ($\sim 1\%$) of the total flow passed through a 1 mm pinhole into the drift tube region. The pressure in the flow tube was maintained at about 100 Torr. The inlet design is discussed in the field measurement section.

The ion source was a custom-made glow discharge device. For VOC detection, ambient air flowed through the discharge, and a positive voltage between 1 to 2 kV was applied to the electrode in the discharge producing H_3O^+ ions. For HNO_3 detection, nitrogen flowed through the discharge mixed with SF_6 at the ppm level, and a negative voltage (-2.5 to -5 kV) was applied to the electrode producing SF_6^- ions. For N_2O_5 detection nitrogen mixed with CF_3I at the ppm level passed through the discharge (-5 kV) creating I ions.

The drift tube was constructed of a 9.5 cm length Pyrex tube that contained a set of 10 stainless steel rings connected in series with 1 M Ω resistors between rings. The rings had an ID of 1.4 cm through which the flow passed. The chemical ionization reactions between the reagent ion and the neutral compound to be detected and quantified occurred in this region. A voltage was applied to the rings to enhance the ion flow. At the downstream end of the drift tube, the majority of the flow was diverted into a pump while a small portion of the flow passed through an aperture (0.2 mm) into the MS analyzer (Extrel QC-150). The aperture was slightly biased (0 to 10 V) for ion-tuning purposes, and the polarity was dependent on the polarity of the reagent ions produced. The pressure in the drift tube was regulated between 1 and 6 Torr. The sampled ions were focused with ion optics, analyzed with a quadrupole mass filter, and detected by an electron multiplier. The multiplier was connected with a preamplifier, which converted the raw signal into TTL pulses allowing them to be processed by a personal computer.

The principle that ID-CIMS utilizes is the detection of a neutral molecule X according to the ion-molecule reaction



where A is the reagent ion, X' is the product ion, and k_1 is the ion-molecule reaction rate constant. The abundance of the neutral species X in the drift tube can then be quantified from the equation

$$[X']_{\Delta t} = k_1 [A] [X] \Delta t \quad (2)$$

where

$$\Delta t = l/U_i \quad (3)$$

and l is the length of the drift tube and U_i is the total velocity of the reagent ion, determined from the ion drift velocity (U_i) and flow velocity (U_f) in the drift tube. The concentration of the neutral species in the flow tube, $[X_{ft}]$, can be expressed as

$$[X_{ft}] = P/\Delta P [X] \quad (4)$$

where P is pressure in the flow tube and ΔP is the pressure change in the drift tube due to addition of the gases from the flow tube. ΔP was determined by monitoring the pressure rise in the drift tube upon addition the gases from the flow tube. The ion drift velocity U_i is determined by the equation

$$U_i = uE \quad (5)$$

where u is the ionic mobility of the ion and E is the voltage gradient in the drift tube. The ionic mobility is determined by

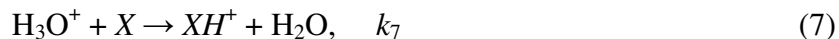
$$u = u_0(760/P) (T/273) \quad (6)$$

where P and T are the pressure and temperature within the drift tube and u_0 is the reduced ionic mobility taken from the literature.¹

If there is no mass-dependent discrimination in the MS detection efficiency, the concentrations of product ions and the reagent ions are proportional to their respective ion count signals measured by the mass spectrometer. Hence the concentration of X can be determined from the signal ratio of the product ion to the reagent ion according to equation (2). It has been suggested that no change in detection efficiency was measured in the mass range of 19 to 250 Dalton.² For the Δt term, the work by de Gouw et al. has shown that the reaction time can be calculated according to the ion drift velocity, which is in agreement with the measurement.³ Hence equations (2) and (4) allow for the quantification of the gas phase concentrations without the necessity of calibration, if the ion-molecule reaction rate constant for (1) is accurately obtained. The ion-molecule reaction rate constants can be determined experimentally or theoretically.^{2,4-7}

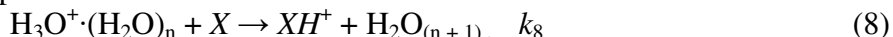
Recently, we have determined the proton transfer rate constants for a suite of atmospherically important VOCs using the average-dipole-orientation (ADO) theory according to their permanent dipole moment and polarizability calculated from ab initio calculations.⁷

For VOC detection, H_3O^+ is generally used as the reagent ion and the proton transfer reaction



occurs in the drift tube, an approach commonly referred to as PTR-MS.² The proton transfer reaction is very efficient for hydrocarbons and oxygenated VOCs with a proton affinity greater than that of water ($165.5 \text{ kcal mol}^{-1}$).⁷

If water clusters are present in the drift tube the reaction

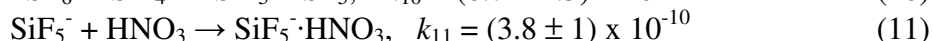
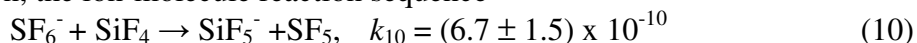


will occur in the drift tube when energetically allowed. If water clusters can be primarily limited to $n = 1$, the neutral species X can still be reliably quantified as

$$[\text{XH}^+] = (k_7 a [\text{H}_3\text{O}^+] + k_8 b [\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}]) [X] \Delta t \quad (9)$$

where k_7 and k_8 are the reaction rate constants for H_3O^+ and $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$ with X , respectively. The fractional percentage of the entire reagent ion signal is represented by a for H_3O^+ and b for $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$. For PTR-MS, E was kept sufficiently large so that $U_i \gg U_f$ in the drift tube and U_f was neglected. Within Δt , U_i must be modified to account for the fractional percentages of the different reagent ions. The ionic mobility of the two reagent ions is different and this affects U_i . The reduced ionic mobilities are 2.76 and 2.28 for H_3O^+ and $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$, respectively.¹ It has been experimentally determined that some hydrocarbons (such as aromatic hydrocarbons toluene and benzene) do not react with water clusters so equation (7) can be used to quantify these species regardless of the percentage of water cluster where H_3O^+ is used as the reagent ions.⁶ The method of employing PTR-MS to quantify atmospheric VOCs has been thoroughly discussed by Lindinger et al.² and de Gouw et al.,³ while the PTR-MS method to quantify products from hydrocarbon oxidation reactions has been described by Zhao et al.⁸

For HNO_3 detection, the ion-molecule reaction sequence

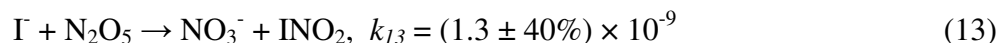


is used to produce the reagent ion.⁹ It has been suggested that a potential product of the reaction of SiF_5^- with HNO_3 is $\text{SiF}_4 \cdot \text{NO}_3^-$.⁹ However, we did not encounter a signal at this ion mass and on the basis of calibrations we believed that the impact of this potential ion-molecule reaction was minimal. It is likely though that this product ion formation is suppressed in the drift tube. HNO_3 is thus quantified using

$$[\text{HNO}_3] = [\text{SiF}_5^- \cdot \text{HNO}_3] / (k_{11} [\text{SiF}_5^-] \Delta t) \quad (12)$$

The voltage gradient E was kept small in this case so U_f and U_i must be added to obtain Δt . The reduced ionic mobility of SiF_5^- in N_2 has not been experimentally determined. We estimated its value on the basis of the literature value for SF_6^- in N_2 , assuming an exponential mass-dependent expression between the masses of the two respective ions. The literature value for the ionic mobility of SF_6^- in N_2 is $1.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,¹⁰ and we estimated a value of $2.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for SiF_5^- in N_2 .

For N_2O_5 detection, the ion molecule reaction sequence



was used to produce the product ion.¹⁰ N_2O_5 was thus quantified using

$$[\text{N}_2\text{O}_5] = [\text{NO}_3^-] / (k_{13} [\Gamma] \Delta t) \quad (14)$$

The Γ reagent ion reacts only with N_2O_5 and creates the product ion, NO_3^- , but its reaction with HNO_3 is much smaller.¹⁰

3. Laboratory Calibrations

To evaluate the application of the ID-CIMS technique for detection and quantification of organic and inorganic compounds, we first performed laboratory calibrations of the ID-CIMS method for isoprene, HNO_3 , and N_2O_5 .

Isoprene Calibration

The proton transfer reactions between H_3O^+ and the majority of VOC molecules generally proceed non-dissociately to produce the protonated molecules.² However, for the reaction between H_3O^+ and isoprene, our observation showed that other ionic products were formed, dependent on the E/N ratio where E is the electric gradient (V cm^{-1}) and N is the number concentration of the buffer gas (molecule cm^{-3}). A considerable peak at mass 39 was observed and a significant peak at mass 67 was also obtained at an E/N ratio larger than 140 Td ($1 \text{ Td} = 10^{17} \text{ V cm}^2 \text{ molecule}^{-1}$) when using air as the carrier gas. These two mass peaks increased when a higher E/N ratio was applied. This implies that there are three possible channels for the reaction between H_3O^+ and isoprene at high E/N ratios,



Hence a proper E/N ratio must be chosen in order to inhibit the dissociation of the protonated isoprene and assure the major channel for the desired proton transfer reaction. On the other hand, if the E/N ratio is too low, a significant amount of water ion cluster will be formed, which would complicate the interpretation of the mass spectra. In this experiment, we kept the E/N ratio at about 100 Td, which greatly prevented the protonated isoprene from being dissociated while the water clusters were effectively minimized. Figure 2 shows the spectra scan from 10 to 100 amu. The three peaks at mass 19, 37 and 69 correspond to H_3O^+ , $\text{H}_3\text{O} \cdot \text{H}_2\text{O}^+$, and protonated isoprene C_5H_9^+ , respectively. The $\text{H}_3\text{O} \cdot \text{H}_2\text{O}^+$ signal was about 10% of the H_3O^+ signal, while the water cluster $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_2$ had a much lower signal and was neglected along with all other higher order water clusters.

We conducted calibrations using volumetrically prepared samples of helium doped with 0.1% isoprene (Aldrich 99.5%).¹¹ For the ion-molecule reaction between H_3O^+ and isoprene, we used a value of $1.94 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.⁶ Using the ADO theory, we calculated a rate constant of $1.5 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reaction between $\text{H}_3\text{O} \cdot \text{H}_2\text{O}^+$ and isoprene. For isoprene calibration the pressures were about 100 and 3 Torr in the flow tube and drift tube, respectively. A carrier gas flow of about 26 SLPM (standard liters per minute) entered the flow tube, and a turbulent flow condition was effectively maintained.¹¹ A small isoprene sample flow (0-2 sccm, standard cubic centimeter per minute) was introduced into the flow tube. Air passed through the corona discharge and into the drift tube at 1 SLPM. As discussed above, the E/N

ratio potentially impacts the isoprene detection: a higher ratio produces less water clusters but significant fragment as it results in more ion kinetic energy which may be able to drive endothermic processes. For reagent ions that are supposed to form clusters, a higher E/N ratio may actually decrease detection sensitivity. For isoprene detection, the aperture plate was held at ground. Figure 3 shows an example of isoprene calibration. The horizontal axis corresponds to isoprene concentrations determined from the known volumetric mixing ratio of the gas standard in the flow reactor and the vertical axis represents those measured by the PTR-MS method according to equation (9). Using an E/N ratio of about 100 Td, an excellent agreement was achieved between the isoprene concentrations estimated from the known volumetric mixing ratio of the gas standard in the flow reactor and measured by the PTR-MS method. The correlation coefficient (R^2) in the isoprene calibration is within 99.9%. This comparison indicates that isoprene can be accurately quantified using equation (9). A detection limit of approximately 10 ppt (parts per trillion, 1 ppt corresponds to 2.46×10^7 molecule cm^{-3} at 298 K and one atm) was calculated with respect to isoprene for a unity ratio of signal to noise and one second integration time.

HNO₃ Calibration

For HNO₃ detection, the drift tube pressure was at about 3 Torr, and the flow tube was also maintained under the turbulent flow condition. Nitrogen doped with SF₆ at the ppm level was passed into the drift tube at a rate of 1.3 SLPM after passing through the discharge. A N₂ flow of 50 sccm doped with SiF₄ at the ppm level proceeded directly into the drift tube. A voltage gradient of 4.5 V/cm was applied in the drift tube and the aperture had a small voltage (-8 V) applied to it to assist in tuning. A spectrum of the reagent ion SiF₅⁻ and product ion SiF₅⁻·HNO₃ is shown in Figure 4 when a small (~ 1 sccm) flow of a 0.1% HNO₃ in helium sample was detected by the ID-CIMS apparatus. In our experiments, the residual signal due to SF₆⁻ was always much (by at least two orders of magnitude) smaller than that of the SiF₅⁻ reagent ions, and its effect on HNO₃ detection was negligible. Figure 5 shows the comparison between the HNO₃ concentration calculated using equation 12 (vertical axis) and that determined by the standard flow consideration knowing the mixing ratio of the HNO₃ sample (horizontal axis). The correlation coefficient in the HNO₃ calibration was within 99.8%, also indicating that HNO₃ can be reliably quantified using equation 12. A detection limit of approximately 10 ppt was estimated with respect to HNO₃ for a unity ratio of signal to noise and one second integration time.

N₂O₅ Calibration

N₂O₅ was synthesized in the laboratory. N₂O₅ was created in a glass reactor in which a flow of O₃ and NO₂ were mixed at atmospheric pressure. The reaction sequence is as follows.



N₂O₅ was collected in a trap maintained at -70° C where it precipitated as feather-like, white crystals.¹⁰

For N₂O₅ detection, the drift tube pressure was at about 2.2 Torr, and the flow tube was also maintained under the turbulent flow condition. Nitrogen doped with CF₃I at the ppm level was passed into the drift tube at a rate of 0.85 SLPM after passing through the discharge. A

voltage gradient of 2.9 V/cm was applied in the drift tube and the aperture had a small voltage (-2.6 V) applied to it to assist in tuning. A reagent ion count of 1.2 million was maintained. The N_2O_5 sample was kept at -35.5°C in order to keep a constant vapor pressure. The sample flow was varied between 0-3 sccm. The carrier gas flow into the inlet was maintained at 4.3 SLPM. Figure 6 shows a spectrum of the reagent ion I^- and the product ion NO_3^- while the sample flow was at 1.5 sccm. Figure 7 shows the comparison between the N_2O_5 concentration calculated using equation 14 (vertical axis) and that determined by the standard flow consideration knowing the mixing ratio of the N_2O_5 sample (horizontal axis). A detection sensitivity of about 10 ppt was estimated. It should be pointed out that unlike isoprene or HNO_3 the method of estimating N_2O_5 concentrations in our laboratory experiments might contain considerable uncertainty. A more reliable method for N_2O_5 calibration is needed for further studies.

4. Field Measurements and Field Calibrations

On August 17 2004 the ID-CIMS instrument was deployed to a field environment. The field site was surrounded by grass fields on all sides and was located behind Hambrick Middle School in the Aldine area of North Houston. There was a school parking lot located 50 meters North of the site. For the following 3 weeks, the ID-CIMS was housed in a 27' semi truck - trailer at this site. A hole was drilled in the side of the trailer for the inlet to pass through and another hole was drilled in the floor of the trailer for hoses, which connected to the rotary vane pumps located outside the trailer. A separate inlet was constructed for field measurements.

The inlet consisted of a 3' long 7/8" ID piece of PFA Teflon tubing which extended 2' outside of the trailer. The inlet hose connected to a Pyrex glass piece with a 90° bend. Two inches downstream from the bend the majority of the flow was diverted into a rotary vane pump (450 LPM) while a smaller amount (≈ 100 LPM) passed through a 1/8" pinhole constructed with Teflon sheet. The flow then proceeded through a 5" long 1" ID piece of Pyrex glass tubing at the end of which the majority of the flow was diverted into another rotary vane pump (450 LPM). The rest of the system setup was identical to that in the lab although flows and voltage tunings were changed. The inlet was surrounded by a conical rain shield. Pictures of the ID-CIMS instrument and the trailer and the inlet are shown in Figures 8 and 9, respectively.

Ambient Measurements of N_2O_5

The ID-CIMS was adapted to measure N_2O_5 . The ambient airflow entering the drift tube was 1 LPM and the drift tube pressure was 3.9 torr. The $\text{N}_2/\text{CF}_3\text{I}$ mixture passed through the discharge at 930 sccm. The discharge had a 5 kV applied to it. The voltage gradient in the drift tube was 1.6 V/cm and the voltage applied to the aperture was -4.5 V.

A representative nighttime concentration of N_2O_5 is shown in Figure 10 during the period of 23:00 to 1:00 am on September 2 2004. The measurements reveal a steady build-up in N_2O_5 , probably due to conversion from HNO_3 on sulfate aerosols. During the course of two hours the concentration of N_2O_5 increases from about 100 ppt to about 600 ppt. There was indication of a diurnal variation with regard to N_2O_5 . Limited daytime measurements of N_2O_5 show its concentrations were generally less than 300 ppt. To the best of our knowledge measurements of N_2O_5 in an urban environment have not been previously reported.

Ambient Measurements of HNO₃

In a field environment, the ability to quantify trace amounts of HNO₃ is hampered by an HNO₃ background. Desorption of HNO₃ from the walls of the drift tube is one source of this background.¹² A mixture of 0.2% ammonia in N₂ was added to the drift tube at a flow rate of 200 sccm to facilitate the heterogeneous reaction of NH₃ and HNO₃ producing NH₄NO₃, which has a lower vapor pressure than wall absorbed HNO₃. The addition of NH₃ lowered the background considerably and had no significant effect on the reagent ion signal. Using flows and tunings identical to those used when scanning only ambient air calibrations were conducted in the field environment using a permeation tube (VICI metronics). The permeation tube emitted 116 ng/min of HNO₃ at 40° C with a flow rate of 1 LPM. This flow joined with the ambient air flow (100 LPM) in the inlet immediately downstream of the first pinhole. The permeation tube flow was turned on and off during the calibration in the field.

HNO₃ was monitored for several 1-2 hour periods during the first two weeks of the field exercise. Due to the accumulation of heat in the trailer, longer periods could not be monitored. The drift tube pressure was 4 torr. An ammonia/N₂ mixture passed into the drift tube at 200 sccm. The N₂/SF₆ mixture passed through the corona discharge at 850 sccm, while the N₂/SiF₄ mixture entered the drift tube at 5 sccm. The ambient airflow entering the drift tube was 1 LPM. The voltage gradient in the drift tube was 5.8 V/cm while the voltage applied to the aperture was 8 V. The limited HNO₃ monitoring needs to be assessed further considering a combination of the background signal and possible HNO₃ loss in the sampling inlet, and we considered that the results were rather premature to be presented.

The field work was terminated prematurely due to an instrumentation failure. The turbo pump bearings failed and the system stopped functioning on 09/02/04. The cause of the turbo pump failure was likely attributed to a combination of several factors, including excessive heat inside of the trailer. Most of these issues will be remedied in the future with proper planning.

5 Summary

We have developed ion drift-chemical ionization mass spectrometry (ID-CIMS) instrumentation for in situ monitoring of organic and inorganic compounds in the atmosphere. Extensive evaluations and calibrations have been performed in the laboratory to prove the method and demonstrate its feasibility for atmospheric monitoring. Preliminary measurements of nitrogen containing compounds such as N₂O₅ and HNO₃ were conducted during a three-week period in the summer of 2004 at an Aldine site north of Houston.

This funded project demonstrates the great potential of the newly developed instrumentation for measuring nitrogen-containing compounds and lays the foundation for future field studies. These measurements provide critical insight into poorly understood nighttime chemistry, and will lead to a better understanding of modeling overnight and long range transport. The chemistry of nighttime nitrogen containing compounds and computer modeling are important SIP considerations in Houston/Galveston/Brazoria and other areas.

Future studies using ID-CIMS to measure nitrogen-containing compounds are planned for the TexAQS II 2005-2006 intensive, possibly at the Williams Tower and other locations.

One paper related to this project entitled “development of ion drift-chemical ionization mass spectrometry” has been published in *Analytical Chemistry*.¹³

References

- (1) Dotan, I.; Albritton, D.L.; Lindinger, W.; Pahl, M. *J. Chem. Phys.* 1976, *65*, 5028-5030.
- (2) Lindinger, W.; Hansel, A.; Jordan, A. *Int. J. Mass Spectrom.* 1998, *173*, 191-241.
- (3) de Gouw, J.; Warneke, C.; Karl, T.; Eerdekens, G.; van der Veen, C.; Fall, R. *Int. J. Mass Spectrom.* 2003, *223*, 365-382.
- (4) Su, T.; Bowers, M. T. *J. Chem. Phys.* 1973, *58*, 3027-3037.
- (5) Zhang, R.; Lei, W. *J. Chem. Phys.* 2000, *113*, 8574-8579
- (6) Warneke, C.; van der Veen, C.; Luxembourg, S.; de Gouw, J.A.; Kok, A. *Int. J. Mass Spectrom.* 2001, *207*, 167-182.
- (7) Zhao, J.; Zhang, R. *Atmos. Environ.* 2004, *38*, 2177-2185.
- (8) Zhao, J.; Zhang, R.; Fortner, E. C.; North, S. W. *J. Am. Chem. Soc.* 2004, *126*, 2686-2687.
- (9) Huey, G.L.; Lovejoy, E. R. *Int. J. Mass Spectrom.* 1996, *155*, 133-140.
- (10) Huey, G.L.; Hanson, D.R., Howard, C.J. *J. Phys. Chem.* 1995, *99*, 5001-5008
- (11) Zhang, R.; Suh, I.; Clinkenbeard, A. D.; Lei, W.; North, S. W. *J. Geophys. Res.* 2000, *105*, 24627-24635.
- (12) Huey, L. G.; Dunlea, E. J.; Lovejoy, E. R.; Hanson, D. R.; Norton, R. B.; Fehsenfeld, F. C.; Howard, C. J. *J. Geophys. Res.* 1998, *103*, 3355-3360.
- (13) Fortner, E. C.; Zhao, J.; Zhang, R. *Anal. Chem.* 2004, *76*, 5436-5440.

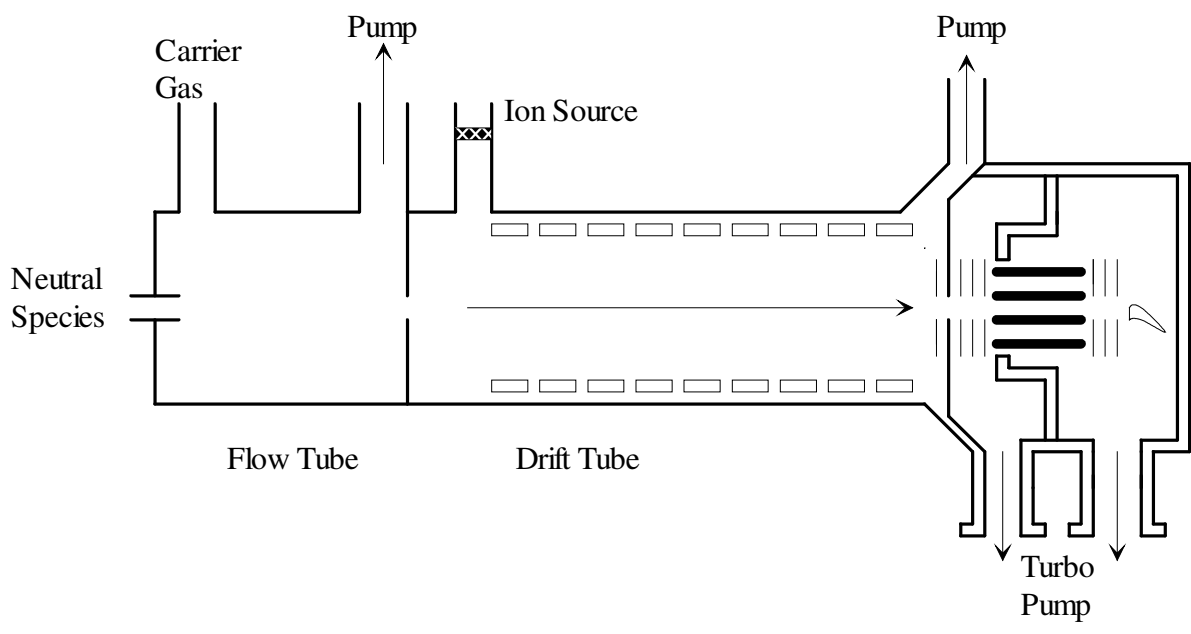


Figure 1. Schematic depiction of the ID-CIMS apparatus.

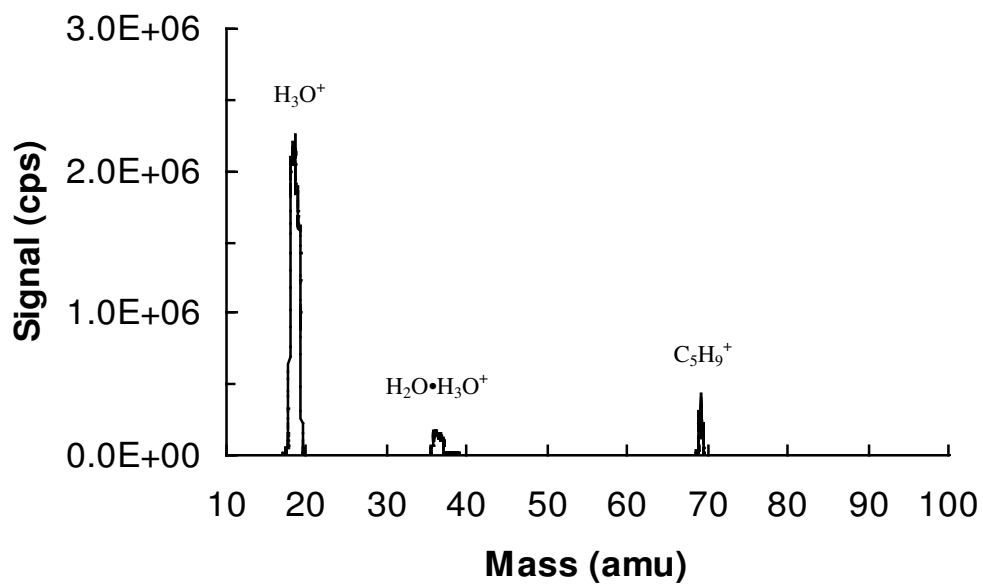


Figure 2. Spectral scan showing the H_3O^+ reagent ion, along a small $\text{H}_2\text{O}\cdot\text{H}_3\text{O}^+$ peak, and protonated isoprene C_5H_9^+ . The isoprene peak is multiplied by a factor of 20 for clarity.

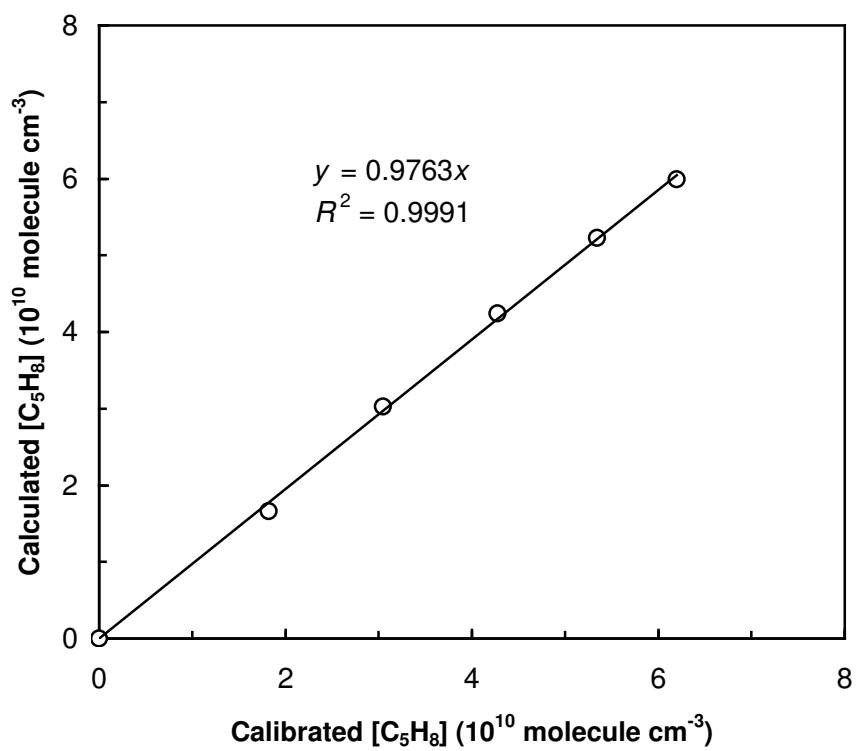


Figure 3. Comparison of isoprene concentrations calibrated from the known volumetric mixing ratio of the gas standard (horizontal axis) and calculated using equation (9) (vertical axis).

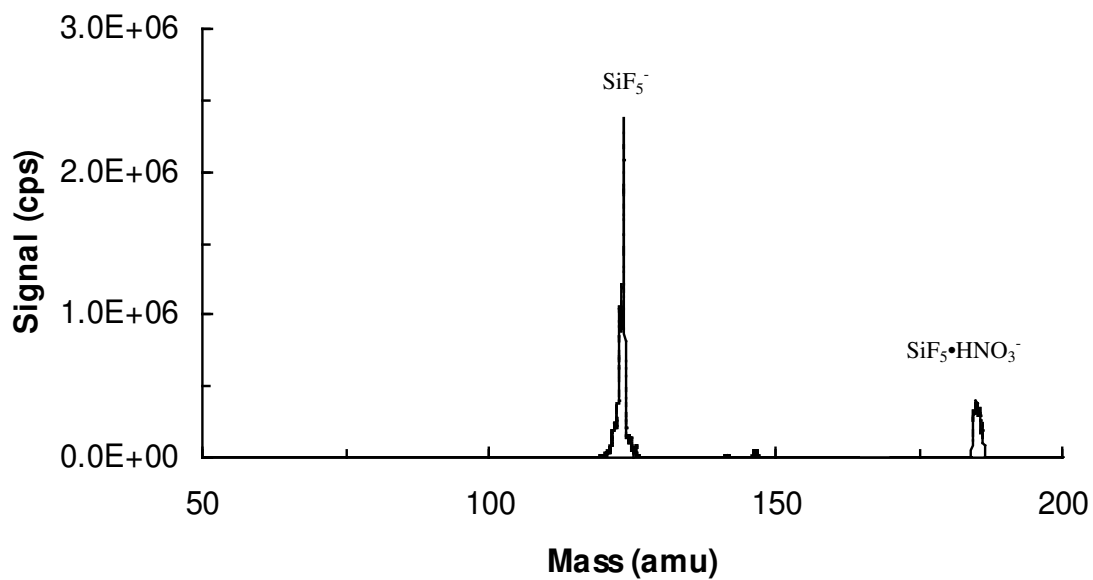


Figure 4. Spectral scan showing the reagent ion SiF_5^- and the product ion $\text{SiF}_5^- \cdot \text{HNO}_3$. The HNO_3 peak is multiplied by a factor of 100 for clarity. A small peak at 146 amu is due to the presence of SF_6^- .

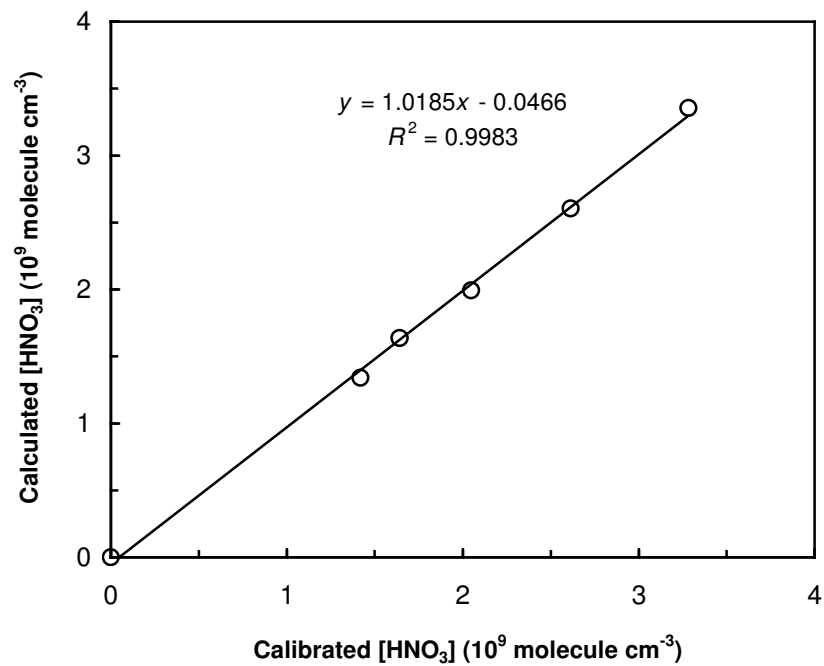


Figure 5. Comparison of HNO₃ concentrations calibrated from the known volumetric mixing ratio of the gas standard (horizontal axis) and calculated using equation 12 (vertical axis).

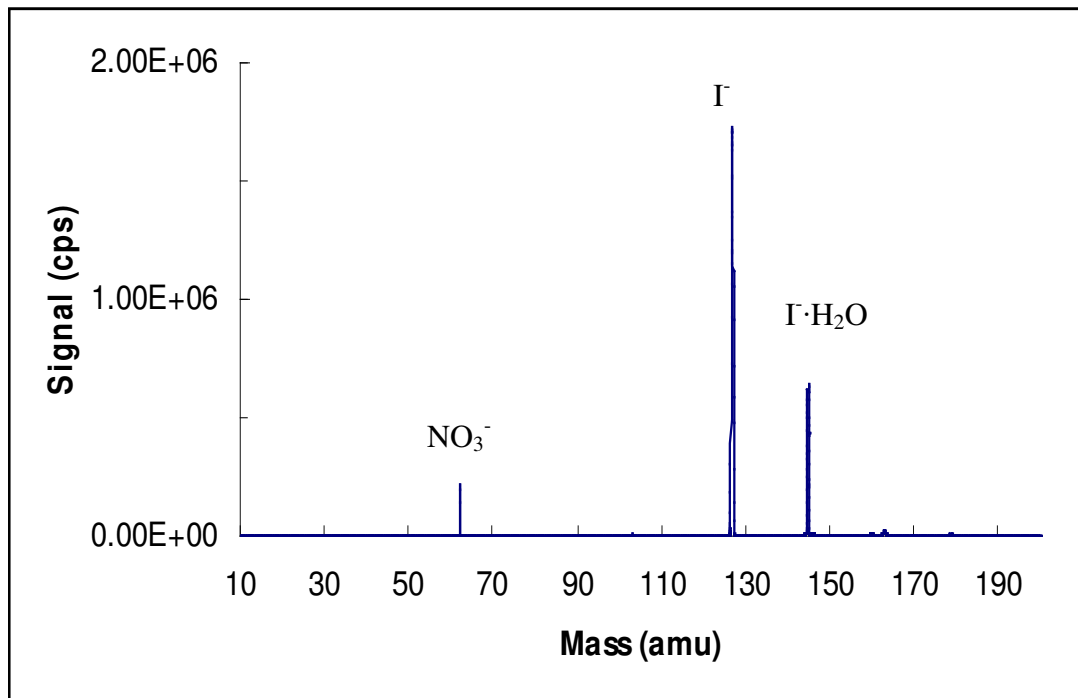


Figure 6. Spectral scan showing the reagent ion I^- and the product ion NO_3^- . The NO_3^- peak is multiplied by a factor of 1000 for clarity.

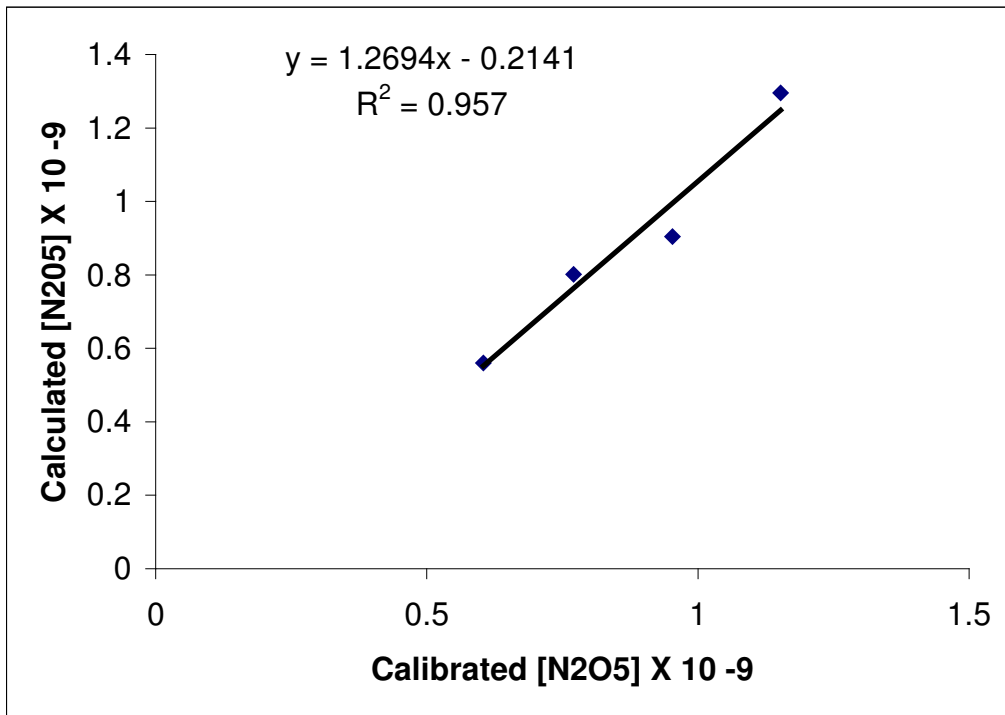


Figure 7. Comparison of N_2O_5 concentrations calibrated from the known volumetric mixing ratio of the gas standard (horizontal axis) and calculated using equation 14 (vertical axis).

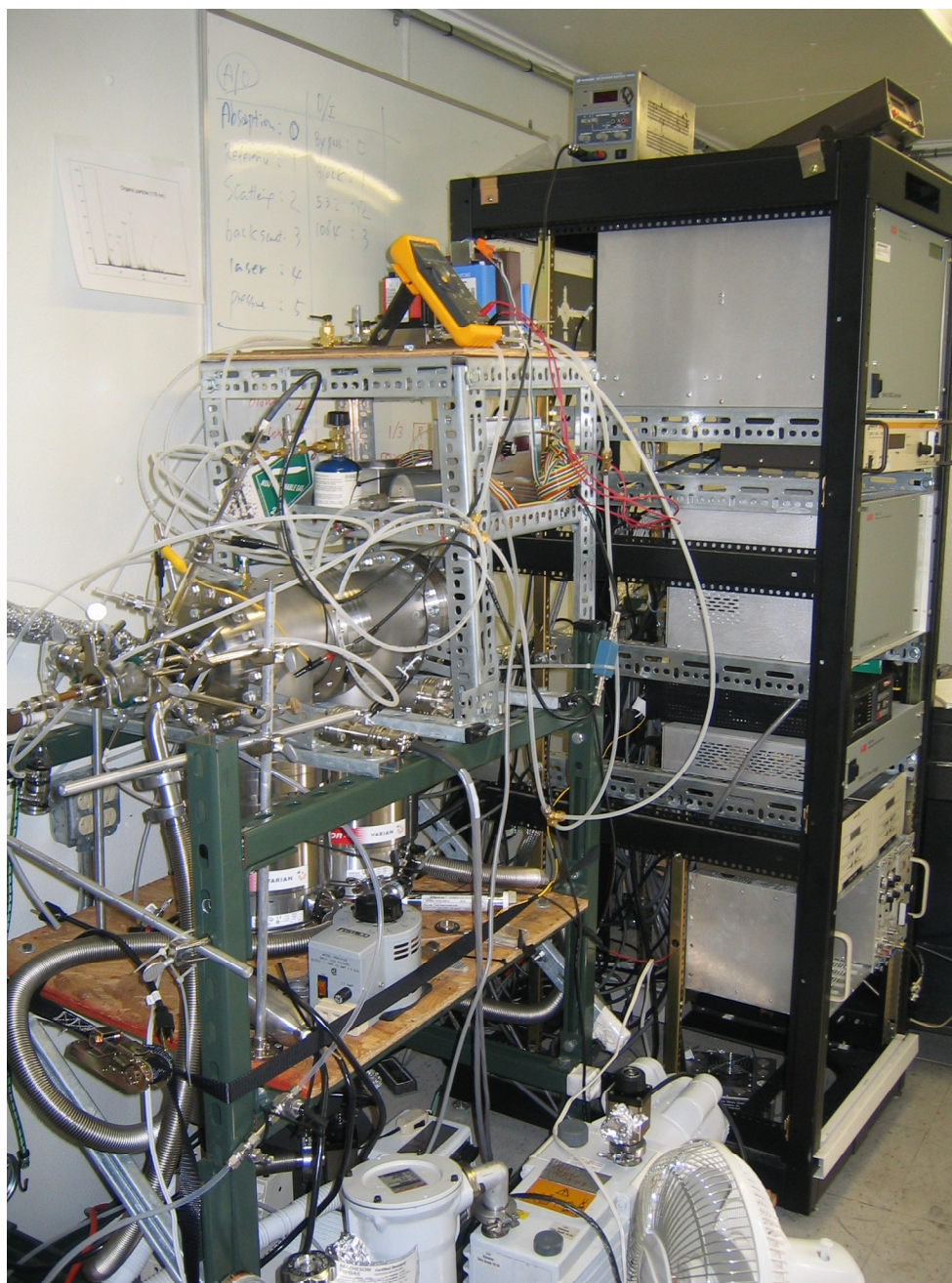


Figure 8. The ID-CIMS instrument deployed inside a trailer during the field study.



Figure 9. The outside of the trailer featuring the inlet for the ID-CIMS instrument. The inlet is a red conical device located in the center of the sidewall of the trailer.

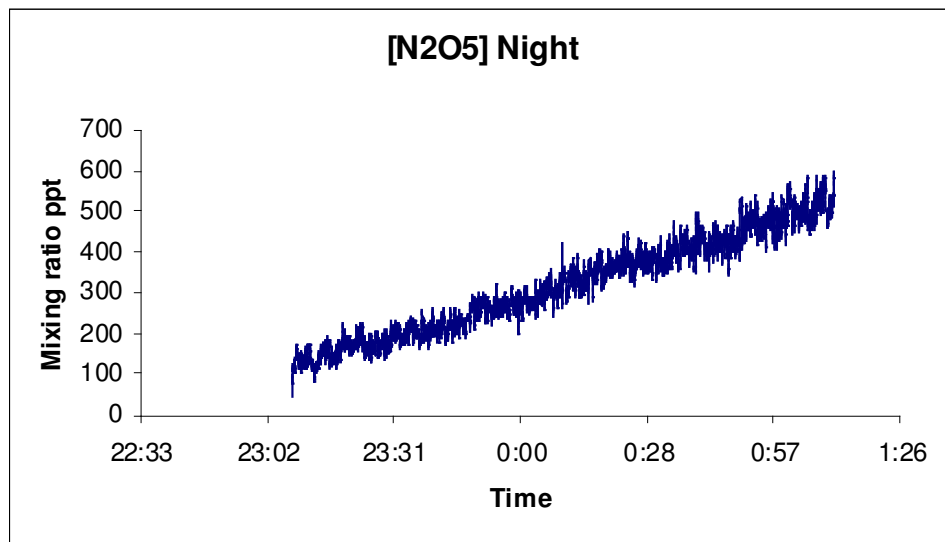


Figure 10. An example of nighttime measurements of N_2O_5 .