

Development of Ion Drift-Chemical Ionization Mass Spectrometry

Edward C. Fortner, Jun Zhao, and Renyi Zhang*

Department of Atmospheric Sciences, Texas A&M University, College Station, Texas 77843

An ion drift-chemical ionization mass spectrometry (ID-CIMS) technique has been developed to detect and quantify trace gases, including volatile organic compounds and inorganic species. The trace species are chemically ionized into positive or negative product ions with a well-controlled ion–molecule reaction time. The ID-CIMS method allows for quantification of the trace gases without the necessity of performing calibrations with authentic standards for the trace gases. Demonstrations of the ability of ID-CIMS to accurately quantify isoprene and HNO₃ in a laboratory setting are presented. The results illustrate that the ID-CIMS technique facilitates detection and quantification of organic and inorganic species in laboratory kinetic investigations and field measurements.

Chemical ionization mass spectrometry (CIMS) has been widely employed in atmospheric chemistry research, including laboratory kinetic investigations and field trace gas measurements.^{1–6} In the CIMS method, a neutral species is ionized by a reagent ion to yield a product ion, which is analyzed by a quadrupole mass analyzer for species identification and abundance determination.

One type of CIMS applications involves proton-transfer reaction mass spectrometry (PTR-MS), which was developed originally by Lindinger and co-workers for on-line quantification of volatile organic compounds (VOCs) in air.⁵ There is a wide variety of sources of VOCs to the Earth's atmosphere ranging from natural to anthropogenic in origin. Many questions exist concerning the ultimate fate of these compounds in the atmosphere. Understanding the VOC loss processes is critical to resolving the atmospheric budget of organic carbon.⁷ The photooxidation of VOCs also plays a key role in the processes of tropospheric ozone and secondary organic aerosol generation.^{8,9} These two major air pollutants have

detrimental health effects and have adverse consequences to the Earth's climate. In the PTR-MS method, proton-transfer reactions with hydronium ions (H₃O⁺) are employed to ionize VOCs, and the resulting protonated product ion is then detected by mass spectrometry.^{5,6} VOCs directly emitted from natural and anthropogenic sources as well as their oxidation products can be quantified simultaneously by PTR-MS. Some desirable features offered by PTR-MS that differentiate it from the traditional GC/MS include a fast-time response on the order of seconds or less, a lack of air sample preconcentration and chromatography, and the ability to perform unmanned on-line measurements over extended time periods.^{5,6} A recent experimental study has also demonstrated the application of the PTR-MS method in quantifying product yields of hydrocarbon oxidation reactions.⁸ This method allows product yield measurements without the necessity of calibration and hence is advantageous because of the general difficulty to obtain the authentic standards for many products of hydrocarbon reactions. In particular, recent advances have been made in quantum-chemical calculations to investigate the oxidation mechanism of VOCs.^{10–15} The PTR-MS application of measuring product yields without calibration using authentic standards offers a great potential for validation of the theoretical predictions, which could have a profound impact on elucidation the VOC chemistry in the atmosphere.

The CIMS method has also been widely used in atmospheric monitoring of inorganic species.^{4,16,17} For example, nitric acid is a critical member of the NO_y (NO, NO₂, NO₃, HNO₂, HNO₃, HNO₄, peroxyacetyl nitrate, and organic and inorganic nitrates) family that is created in the troposphere predominantly by the association of OH with NO₂. The transformation of NO_x (NO + NO₂) to HNO₃ is the primary scavenging method of NO_x from the atmosphere. Due to the fundamental role that NO_x plays in the production and destruction of O₃ in the atmosphere, it is critical that the magnitude of this transformation is understood in order to resolve the global ozone budget. Huey and co-workers originally developed a selective and high-sensitivity CIMS method for in situ

* Corresponding author. E-mail: zhang@ariel.tamu.edu.

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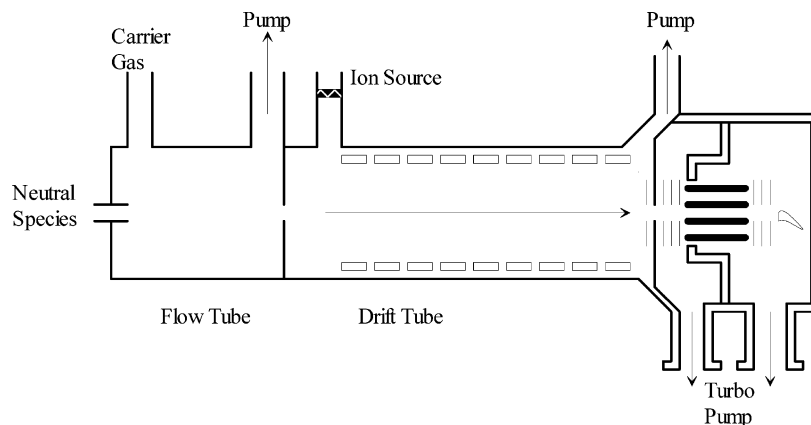


Figure 1. Schematic depiction of the ID-CIMS apparatus.

measurements of HNO_3 .^{4,17} It has been shown that this method allows for detection of HNO_3 with a time resolution on the order of a few seconds and a detection sensitivity of the order of parts-per-trillion (ppt) levels.^{4,16,17}

In this paper, we describe the development of an ion drift-chemical ionization mass spectrometry (ID-CIMS) instrument, which is capable of providing on-line 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. A description of the instrument configuration follows. The methodology used to quantify VOCs and inorganic species will be presented, and the differences between the two detection schemes will be detailed. The results of laboratory calibrations of isoprene and HNO_3 will then be presented.

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.

In the current configuration, a flow tube is connected to the ID-CIMS for laboratory measurements and calibrations, and an inlet will be needed for its use in the field. 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 i.d. A coating of halocarbon wax was applied to the inner walls of the flow tube to reduce wall loss. The majority of the gas in the flow tube was 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 opening into the drift tube region. The pressure in the flow tube was maintained at ~ 100 Torr.

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 and 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 (-5 kV) was applied to the electrode producing SF_6^- ions.

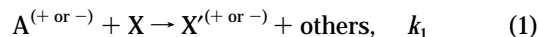
The drift tube was constructed of a 9.5-cm-length Pyrex tube that contained a set of 10 stainless steel rings connected in series with 1-M Ω resistors between rings. The rings had an i.d. of

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 (0–10 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 4 Torr.

The sampled ions were focused with an 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.

METHODOLOGY

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

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

where

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

and l is the length of the drift tube and U_t 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, $[\text{X}_f]$, can be expressed as

$$[\text{X}_f] = P/\Delta P[\text{X}] \quad (4)$$

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 of 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 respectively the pressure and temperature within the drift tube and u_0 is the reduced ionic mobility taken from the literature.¹⁸

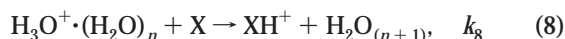
If there is no mass-dependent discrimination in the MS detection efficiency, the concentrations of product ions and the reagent ions are proportional to their respective ion count signals measured by the mass spectrometer. Hence, the concentration of X can be determined from the signal ratio of the product ion to the reagent ion according to eq 2. It has been suggested that no change in detection efficiency was measured in the mass range of 19–250 Da.⁵ 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.⁶ Hence, eqs 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 eq 1 is accurately obtained. The ion–molecule reaction rate constants can be determined experimentally or theoretically.^{5,19–22} 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.²²

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.⁵ The proton-transfer reaction is very efficient for hydrocarbons and oxygenated VOCs with a proton affinity greater than that of water (165.5 kcal mol⁻¹).²²

If water clusters are present in the drift tube the reaction



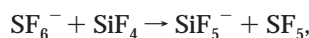
will occur in the drift tube when energetically allowed. If water clusters can be primarily limited to $n = 1$, the neutral species X can still be reliably quantified as

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

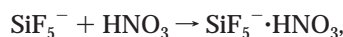
where k_7 and k_8 are the reaction rate constants for H_3O^+ and $\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O}$.

H_2O 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 $U_i \gg U_t$ in the drift tube and U_t 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 cm² V⁻¹ s⁻¹ for H_3O^+ and $\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O}$, respectively.¹⁸ It has been experimentally determined that some hydrocarbons (such as aromatic hydrocarbons toluene and benzene) do not react with water clusters so eq 7 can be used to quantify these species regardless of the percentage of water cluster where H_3O^+ is used as the reagent ions.²¹ The method of employing PTR-MS to quantify atmospheric VOCs has been thoroughly discussed by Lindinger et al.⁵ and de Gouw et al.,⁶ 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



$$k_{10} = (6.7 \pm 1.5) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (10)$$



$$k_{11} = (3.8 \pm 1) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (11)$$

is used to produce the reagent ion.¹⁷ It has been suggested that a potential product of the reaction of SiF_5^- with HNO_3 is $\text{SiF}_4 \cdot \text{NO}_3^-$.¹⁷ 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_t 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 cm² V⁻¹ s⁻¹,²³ and we estimated a value of 2.0 cm² V⁻¹ s⁻¹ for SiF_5^- in N_2 .

RESULTS AND DISCUSSION

To demonstrate the application of the ID-CIMS technique for detection and quantification of organic and inorganic compounds, we performed experimental evaluations of the ID-CIMS method for isoprene and HNO_3 .

The proton-transfer reactions between H_3O^+ and the majority of VOC molecules generally proceed nondissociately to produce the protonated molecules.⁵ 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

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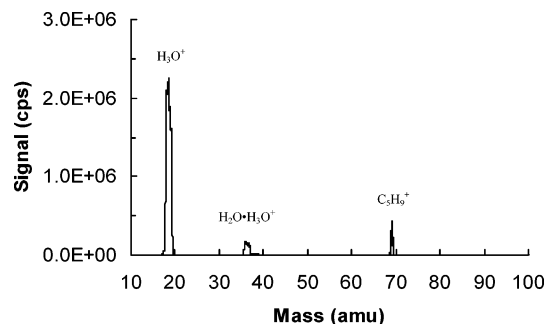
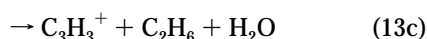
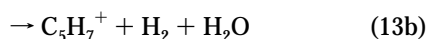
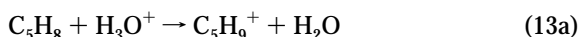


Figure 2. Spectral scan showing the H_3O^+ reagent ion, along a small $\text{H}_2\text{O}\cdot\text{H}_3\text{O}^+$ peak, and protonated isoprene C_5H_9^+ . The isoprene peak is multiplied by a factor of 20 for clarity.

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 ensure 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 $\sim 100 \text{ Td}$, which greatly prevented the protonated isoprene from being dissociated while the water clusters were effectively minimized. Figure 2 shows the spectral 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 $\sim 10\%$ 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%).²⁴ For the ion–molecule reaction between H_3O^+ and isoprene, we used a value of $1.94 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.²¹ 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 ~ 26 standard liters per minute (SLPM) entered the flow tube, and a turbulent flow condition was effectively maintained.²⁴ A small isoprene sample flow (0–2 standard cubic centimeters per minute, sccm) was introduced into the flow tube. Air passed through the corona discharge and into the drift tube at 1 SLPM. As discussed above,

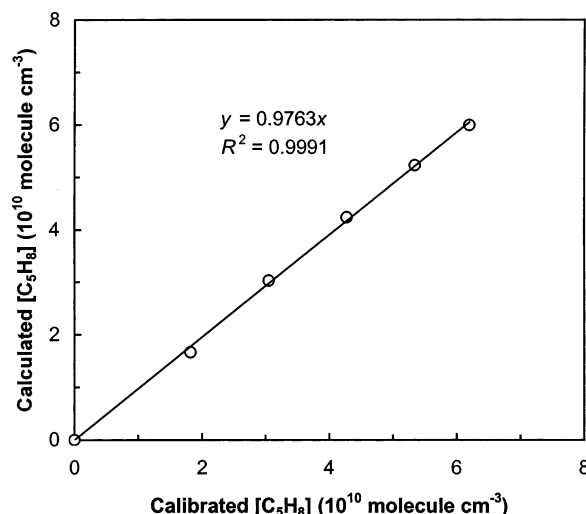


Figure 3. Comparison of isoprene concentrations calibrated from the known volumetric mixing ratio of the gas standard (horizontal axis) and calculated using eq 9 (vertical axis).

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 eq 9. Using an E/N ratio of $\sim 100 \text{ Td}$, 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 eq 9. A detection limit of $\sim 10 \text{ ppt}$ (1 ppt corresponds to $2.45 \times 10^7 \text{ molecule cm}^{-3}$ at 298 K and 1 atm) was calculated with respect to isoprene for a unity ratio of signal-to-noise and 1-s integration time.

For HNO_3 detection, the drift tube pressure was at $\sim 3 \text{ Torr}$, and the flow tube was maintained under the turbulent flow condition. Nitrogen doped with SF_6 at the ppm level was passed into the drift tube at a rate of 1.3 SLPM after passing through the discharge. A N_2 flow of 50 sccm doped with SiF_4 at the ppm level proceeded directly into the drift tube. A voltage gradient of 4.5 V cm^{-1} 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 SiF_5^- and product ion $\text{SiF}_5^-\cdot\text{HNO}_3$ is shown in Figure 4 when a small ($\sim 1 \text{ sccm}$) flow of a 0.1% HNO_3 in helium sample was detected by the ID-CIMS apparatus. In our experiments, the residual signal due to SF_6^- was always much (by at least 2 orders of magnitude) smaller than that the SiF_5^- reagent ions, and its effect on HNO_3 detection was negligible. Figure 5 shows the comparison between the HNO_3 concentration calculated using eq 12 (vertical axis) and that determined by the standard flow consideration knowing the mixing ratio of the HNO_3 sample (horizontal axis). The correlation coefficient in the HNO_3 calibration was within 99.8%, indicating that HNO_3 can be reliably

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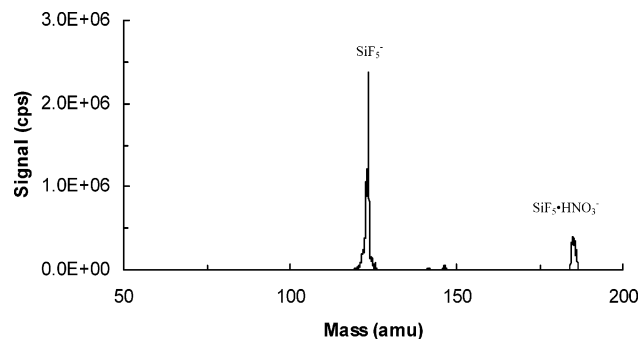


Figure 4. Spectral scan showing the reagent ion SiF_5^- and the product ion $\text{SiF}_5\cdot\text{HNO}_3$. The HNO_3 peak is multiplied by a factor of 100 for clarity. A small peak at 146 amu is due to the presence of SF_6^- .

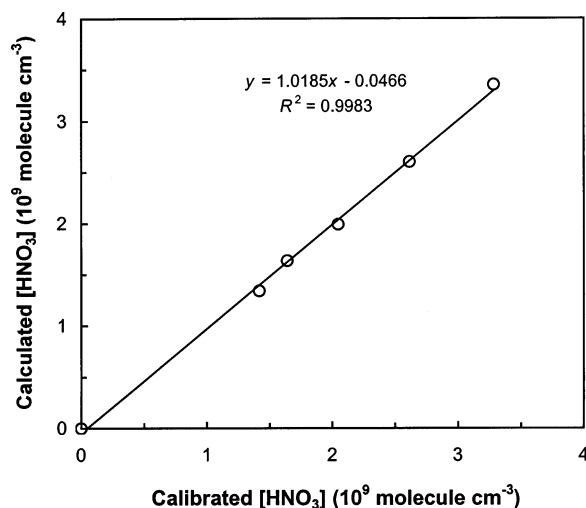


Figure 5. Comparison of HNO_3 concentrations calibrated from the known volumetric mixing ratio of the gas standard (horizontal axis) and calculated using eq 12 (vertical axis).

quantified using eq 12. A detection limit of ~ 10 ppt was estimated with respect to HNO_3 for a unity ratio of signal-to-noise and 1-s integration time.

We have also conducted calibrations of several other organic (such as toluene) and inorganic (such as NO_2) compounds that were not featured in this paper. For example, NO_2 was detected as NO_2^- using the SF_6^- reagent ion. The calculated concentrations consistently corresponded to the calibrated values with the correlation coefficient within 99%. It is worth noting that while the calibrations show the ability of the ID-CIMS instrument to

detect the desired product ions in our laboratory experiments several parameters will likely change in a field environment. It should be expected that variables such as the percentage of water clusters and the reagent ion signal intensity would likely be affected by the changes, potentially impacting the performance of the instrument under ambient conditions.

CONCLUSION

The PTR-MS method, which allows for a controlled ion-molecule reaction with the hydronium ion within the drift tube, has been previously demonstrated for allowing on-line detection of atmospherically important VOCs with high detection sensitivity and fast-responding time.^{5,6,21,25} This method, however, is limited to detection of organic compounds whose proton affinity is larger than of water. On the other hand, the conventional CIMS approach does not employ a well-controlled ion-molecule reaction time.¹⁷ We have demonstrated in this paper the application of ID-CIMS, which expands the operation of PTR-MS to allow for the use of both negative and positive reagent ions. The trace species are chemically ionized into positive or negative product ions with a well-controlled ion-molecule reaction time; quantifying the trace species is possible, provided that the rate constants for the ion-molecule reaction are known. Our recent work showed that ion-molecule reaction rate constants can be reliably determined using theoretical approaches.²²

The laboratory experiments presented in this work show the capability of ID-CIMS to execute on-line measurements of organic and inorganic compounds, as exemplified for isoprene and HNO_3 . Our results demonstrate that the ID-CIMS method allows for accurate quantification of trace gases without the necessity of performing calibrations with authentic standards. Hence, the ID-CIMS technique facilitates detection and quantification of organic and inorganic species in laboratory kinetic studies and field measurements. Future work will focus on designing such a system to allow for implementation of ID-CIMS in a field environment.

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