

## Evaluation of a New Vocus Reagent-Ion Source and Focusing Ion-Molecule Reactor for use in Proton-Transfer-Reaction Mass Spectrometry

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### Abstract

We evaluate the performance of a new chemical ionization source called Vocus, consisting of a discharge reagent-ion source and focusing ion-molecule reactor (FIMR) for use in proton-transfer-reaction time-of-flight mass spectrometry (PTR-TOF) measurements of volatile organic compounds (VOCs) in air. The reagent ion source uses a low-pressure discharge. The FIMR consists of a glass tube with a resistive coating, mounted inside a radio-frequency (RF) quadrupole. The axial electric field is used to enhance ion collision energies and limit cluster ion formation. The RF field focuses ions to the central axis of the reactor and improves the detection efficiency of product ions. Ion trajectory calculations demonstrate the mass-dependent focusing of ions and enhancement of the ion collision energy by the RF field, in particular for the lighter ions. Product ion signals are increased by a factor of 10 when the RF field is applied (5,000-18,000 cps ppbv<sup>-1</sup>), improving measurement precision and detection limits while operating at very similar reaction conditions as traditional PTR instruments. Due to the high water mixing ratio in the FIMR, we observe no dependence of the sensitivity on ambient sample humidity. In this work, the Vocus is interfaced to a TOF mass analyzer with a mass resolving power up to 14,000, which allows clear separation of isobaric ions, observed at nearly every nominal mass when measuring ambient air. Measurement response times are determined for a range of ketones with saturation vapor concentrations down to  $5 \times 10^4 \mu\text{g m}^{-3}$  and compare favorably with previously published results for a PTR-MS instrument.

## 1. Introduction

Proton-transfer-reaction mass spectrometry (PTR-MS) is a valuable tool for measurements of volatile organic compounds in air<sup>1</sup>. In PTR-MS,  $\text{H}_3\text{O}^+$  ions are produced in a discharge ion source and ionize trace gases in the sample air by proton-transfer reactions in a drift tube reactor. The reagent and product ions are then detected with a mass spectrometer. The collision energy in a traditional PTR-MS is enhanced using a linear electric field, which is used to suppress cluster ion formation with water molecules and simplify the ion chemistry. The PTR-MS technique allows measurements of a broad range of trace gases including most volatile organic compounds (VOCs) in air with high sensitivity (parts-per-trillion by volume) and fast time response ( $>1$  Hz)<sup>1-4</sup>.

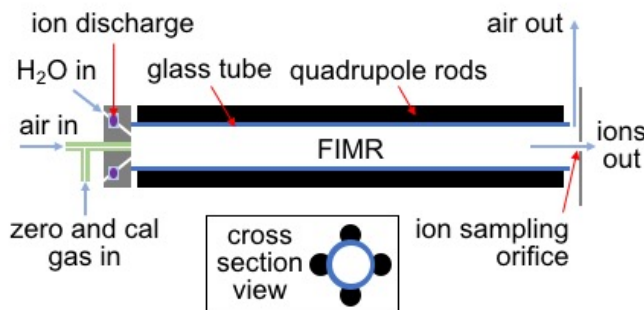
Since its invention, the PTR-MS technique has been improved in many significant ways. The original PTR-MS instruments used quadrupole mass analyzers, which were often used in selected-ion mode to improve measurement precision at the cost of comprehensiveness. Subsequent designs used time-of-flight (TOF) mass analyzers, which overcame the need to pre-select the masses of interest before a measurement<sup>5-7</sup>. TOF mass analyzers with higher mass resolving power allowed the separation of isobaric ions, which significantly improved the analytical detail obtained<sup>8</sup>. Interfaces with quadrupole ion guides were used to improve the product-ion detection efficiency and lower the detection limits<sup>9,10</sup>.

Up until recently, the design of the reactor was relatively unchanged from the first PTR-MS instruments. In most instruments, a homogeneous electric field along the axial direction is used to enhance the ion kinetic energy and suppress cluster-ion formation. An added advantage is that the electric field transports the ions down the reactor, which reduces the need for large sample air flows and pumps. A disadvantage is that the reaction times are very short ( $\sim 100$   $\mu\text{s}$ ), which limits the net product ion formation. In the transverse direction, ions scatter and diffuse away from the central axis of the reactor. As the ion sampling orifice at the end of the reactor is small compared to the size of the ion beam, the detection efficiency of product ions is relatively low. Two recent instrument developments were aimed at overcoming these issues. First, ion funnels were introduced to collimate ions at the end of the reactor and improve detection efficiency<sup>11,12</sup>. A more radical redesign of the reactor was implemented in the PTR3 instrument, which is operated at a higher pressure (50-80 mbar), uses a tri-pole to enhance the ion kinetic energy, and relies on a large sampling flow to transport ions down the reactor, thereby allowing for much longer reaction times and more efficient product ion formation<sup>13</sup>.

Here, we evaluate the performance of a new reagent-ion source and focusing ion-molecule reactor, the so-called Vocus, developed by TOFWERK for use in PTR-MS. The Vocus uses a quadrupole RF field in the reactor to collimate ions onto the central axis and improve the detection efficiency, while maintaining approximately similar collision conditions used in conventional drift tubes. We describe the general design of the Vocus and evaluate the performance of an instrument that combines a Vocus with a time-of-flight mass spectrometer (TOFWERK Vocus 2R PTR-TOF; hereafter Vocus 2R). The operating principle of the Vocus is investigated using ion-trajectory calculations and laboratory characterization. We compare the performance of the Vocus 2R with a  $\text{H}_3\text{O}^+$  ToF-CIMS instrument built at NOAA<sup>10</sup>, which uses a conventional drift tube and standard ion source but is otherwise very similar to the Vocus 2R. Finally, we investigate the response time of the system, which uses a short PEEK tube to introduce sample air into the reactor with important advantages over previously used inlets<sup>14</sup>.

## 2. Instrument Description

A schematic drawing of the Vocus is shown in Figure 1. Reagent ions are produced in a discharge ion source. The focusing ion-molecule reactor (FIMR) is composed of a glass tube with four quadrupole rods mounted radially on the outside. More detailed descriptions of the individual components follow below.



**Figure 1:** Design of the Vocus consisting of a discharge reagent-ion source and a focusing ion-molecule reactor (FIMR).

### 2.1 Reagent ion source

The reagent-ion source consists of two conical surfaces between which a plasma is produced. The design is different from the hollow-cathode ion sources used in most PTR-MS instruments. Water vapor from a reservoir flows at 20-30 sccm ( $\text{cm}^3 \text{min}^{-1}$  at  $10^5 \text{ Pa}$  and  $273.15 \text{ K}$ ) in between the surfaces, all of which enters the FIMR. A voltage of  $\sim 450 \text{ V}$  discharges across the water vapor and the discharge current is regulated to  $\sim 1.5\text{-}2.0 \text{ mA}$ , i.e. the smallest value that still gives a stable ion signal. The discharge takes place in a ring around the central axis and ions enter the FIMR through a ring offset from the central axis. Photons generated by the discharge cannot directly enter the reactor. The water flow is optimized to yield the best reagent-ion signal distribution.

### 2.2 The focusing ion-molecule reactor

Sample air enters the FIMR through a short (10 mm) PEEK tube with an internal diameter of 0.18 mm that acts as a pressure restriction similar to a critical orifice. The FIMR was operated at pressures of 1.0-1.5 mbar in this work. At these pressures, the sample flow is approximately 100 sccm. A larger diameter inlet tube allows a larger flow of air (e.g. 5 LPM) to be drawn to the entrance of the Vocus to reduce inlet wall losses and sampling delays. Only 100 sccm of this flow is sampled into the FIMR and the remainder is directed to the sample pump. Also orthogonal to the flow direction is a small port through which calibration and/or VOC-free air can be injected. This allows for fast and frequent calibrations and zeroing of the instrument while not perturbing the inlet line or sampling conditions (Figure S1).

The FIMR consists of a 10 cm long glass tube with an outside diameter of 13 mm and a glass thickness of 1.5 mm. The tube has a resistive coating on the inside surface, which forms a more homogeneous electric field than a stacked ring-electrode approach<sup>15</sup>. A DC voltage across the ends of the glass tube (typically  $\sim 500 \text{ V}$  in this work) establishes the axial electric field in the

reactor. Resistive glass tubes have been used previously as a reactor in other PTR-MS instruments<sup>16,17</sup> but with key differences to the approach used here. The Vocus uses four rods (6 mm diameter) mounted radially on the outside of the resistive glass tube, which are used to establish a quadrupole RF field inside to collimate ions into a narrow beam. At the end of the FIMR, ions are sampled into the TOF mass analyzer through a 2 mm diameter pinhole. The RF frequency is 1.3-1.6 MHz and is operated with an amplitude up to 600 Vpp.

The FIMR is pumped by a mechanical pump (430 L min<sup>-1</sup> at 1 mbar), which is also used to back the turbo pump (Pfeiffer Split Flow 270) used for the differentially pumped interface and the TOF mass analyzer. The reactor pressure is controlled by a valve between the reactor and mechanical pump. The pressure of the drift tube remains stable enough over time for laboratory or ground site measurements without intervention (Figure S2). A pressure controller is added for applications where sample pressure changes are significant.

### 2.3 Interface and time-of-flight mass analyzer

In the Vocus 2R, the FIMR is coupled to an API-TOF mass spectrometer<sup>18,19</sup> with two important changes: (i) the API-TOF is operated without the small segmented quadrupole that serves as an intermediate pressure stage in higher pressure chemical ionization systems, and (ii) the Vocus 2R employs a mass analyzer from TOFWERK with a longer TOF tube (nominal resolution 10,000 FWHM). Ions from the FIMR travel first into a big segmented quadrupole (BSQ) ion guide operated at  $7 \times 10^{-3}$  mbar to focus the ion beam before entering the primary beam (PB) region, and finally into the time-of-flight chamber held at  $1 \times 10^{-6}$  mbar. The TOF was configured to measure a mass-to-charge range of ~1-500 Th (16 kHz extraction frequency) for the experiments described herein.

### 2.4 Ion trajectory calculations

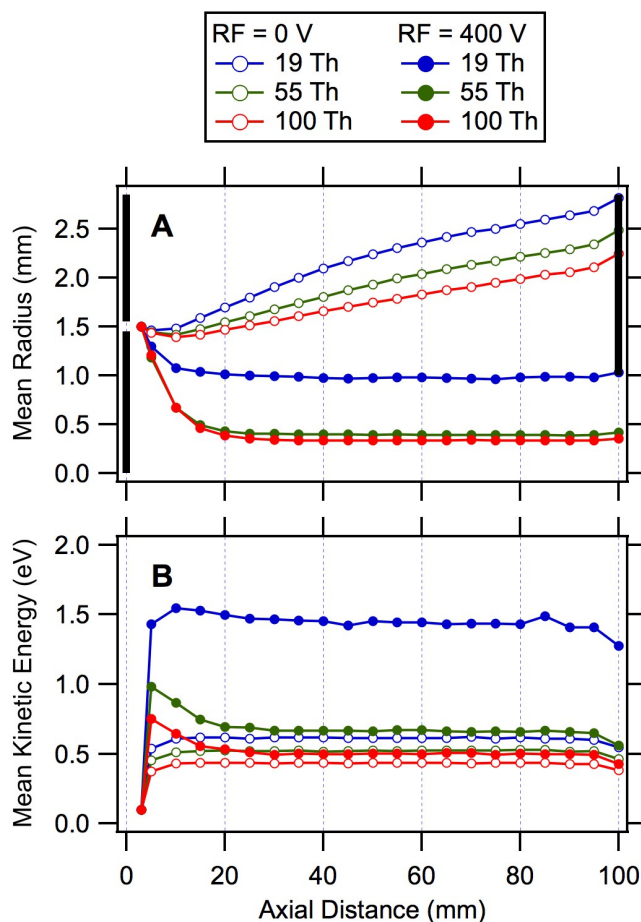
While the RF field adds a time-varying electric field, this field is zero along the central axis where the ion density is highest, and the average collision conditions are mostly dictated by the axial DC field as in conventional drift tubes. The average ion velocity  $v_{ion}$  in the axial direction is given by:

$$v_{ion} = K \times E = K_0 \times (p_0/p) \times (T/T_0) \times E = K_0 \times N_0 \times E/N \quad (1)$$

where  $K$  is the ion mobility,  $E$  the electric field strength and  $N$  the number density of gas in the FIMR. The reduced electric field strength,  $E/N$ , is a quantity describing the velocity and collision energy of the ions. The ion mobility under standard conditions ( $p_0 = 1.013 \times 10^5$  Pa,  $T_0 = 273.15$  K and  $N_0 = 2.69 \times 10^{19}$  cm<sup>-3</sup>), or reduced ion mobility  $K_0$ , has been reported as 2.76 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for H<sub>3</sub>O<sup>+</sup> ions in nitrogen<sup>20</sup>. Using  $K_0$  and the operating conditions in the FIMR ( $p = 1.25$  mbar,  $T = 298$  K and  $E = 50$  V cm<sup>-1</sup>), the residence time of ions is calculated to be 82 μs, which allows for ~120 cycles of the RF field before ions exit the reactor.

At a pressure of 1.25 mbar, the ion collision frequency of H<sub>3</sub>O<sup>+</sup> reagent ions is around 28 MHz (assuming a collision rate coefficient with N<sub>2</sub> of  $9 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>)<sup>21</sup>. This is a higher frequency than that of the RF (1.5 MHz) and therefore the reagent ions will undergo many collisions during each RF cycle. It is therefore expected that the collision energy of the

ions will vary at the frequency of the RF field, and that cluster formation and fragmentation can occur on each RF cycle.



**Figure 2:** Results of trajectory calculations by SIMION for  $\text{H}_3\text{O}^+$  (19 Th),  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_2$  (55 Th) and product ions at 100 Th. Panel (A) shows the mean radius of the trajectories with and without the RF voltage as a function of the axial distance. The black, vertical lines show the geometry of the annual ion source and the sampling orifice of the Vocus. Panel (B) shows the mean kinetic energy of the modeled ions with and without the RF voltage.

Electric fields and ion trajectories in the FIMR were simulated using the software package SIMION (Scientific Instrument Services Inc.) and results are presented in Figure 2. A total of 10,000 trajectories were calculated in each case, with the Trajectory Quality parameter, which determines the time step and convergence of the calculations, set to 100. A smaller number of trajectories (1,000) were also run at a higher Trajectory Quality parameter of 300 and gave very similar results. The pressure in the Vocus was set to 1.25 mbar. The axial electric field was set to  $50 \text{ V cm}^{-1}$  and simulations were run with and without a radial RF voltage (frequency 1.65 MHz; amplitude 400 Vpp) to show the focusing effect. The effects of collisions were simulated using a hard-sphere collision model. Hard-sphere collision cross sections for the  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$  cluster ions were estimated from their ion mobilities<sup>20</sup> ( $\text{H}_3\text{O}^+$   $47.6 \text{ \AA}^2$ ,  $\text{H}_3\text{O}^+(\text{H}_2\text{O})$

60.6 Å<sup>2</sup>, H<sub>3</sub>O<sup>+</sup>(H<sub>2</sub>O)<sub>2</sub> 64.7 Å<sup>2</sup>). For product ions at 100 Th, we used a collision cross section of 98 Å<sup>2</sup> by extrapolation from the previous values.

Figure 2 shows the mean radial positions of ions of three different mass-to-charge values (19, 55, and 100 Th) with and without the RF voltage (RF amplitude equals 0 or 400 V). Ions are injected into the FIMR as a ring with a radius of 1.5 mm around the central axis, so all trajectories and their means start at that radius. Figure 2A shows that without the RF voltage, the ions spread out radially with the lighter ions forming a wider beam than heavier ions. A large part of the ion beam will not be sampled by the 2 mm pinhole. Figure 2A shows that with an RF amplitude of 400 V, the mean ion trajectories are collimated towards the central axis. The focusing is the least efficient for the H<sub>3</sub>O<sup>+</sup> ions, but the mean radius of the beam is still ~1 mm, which is the same as the size of the sampling orifice. Figure S3 illustrates the radial distribution of ions at the end of the FIMR with and without an RF amplitude of 400 V. Table S1 summarizes the fraction of the ion trajectories in the simulation that pass through the sampling orifice. The focusing effect of the RF field enhances the ion transmission by a factor of 7 to 9, which results in transmission efficiencies ranging from 54% for H<sub>3</sub>O<sup>+</sup> to 99% for ions with a mass-to-charge of 100 Th. An added advantage of the RF field is that the residence time of the H<sub>3</sub>O<sup>+</sup> reagent ions in the FIMR becomes 39% longer (Table S1). We attribute this to the higher average collision energy, which leads to a larger loss of ion velocity in the axial direction. Combined with the more efficient transmission of product ions, an overall increase in the product ion signals of more than an order of magnitude is achieved.

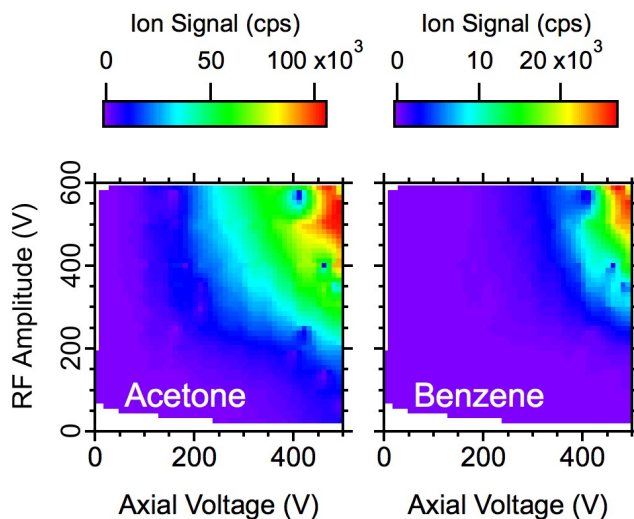
Figure 2 also shows the average ion kinetic energies of the three different ions with and without an RF field. Without the RF field, all ions reach a constant average kinetic energy after about ~10 mm of travel (Figure 2B). The kinetic energies are similar for the different ions, with the H<sub>3</sub>O<sup>+</sup> ions reaching the highest mean energy. With an RF amplitude of 400 V, the ion kinetic energy is enhanced (Figure 2B). While the electric field along the central axis is only determined by the axial voltage, the time-varying electric field in the radial direction adds to the axial component of the electric field. As a result, the average ion kinetic energy increases with the radial distance. The H<sub>3</sub>O<sup>+</sup> ions move on average further from the central axis, and their enhancement in kinetic energy is larger than for the heavier ions. This illustrates a beneficial feature of the FIMR: the H<sub>3</sub>O<sup>+</sup> ions are more efficiently heated than heavier ions by the RF field, which prevents the formation of water cluster ions, so that proton transfer from H<sub>3</sub>O<sup>+</sup> is favored over switching reactions with H<sub>3</sub>O<sup>+</sup>(H<sub>2</sub>O). The product ions are better collimated to the central axis, where their kinetic energy is less enhanced by the RF field. This limits the fragmentation of product ions.

### 3. Results and Discussion

#### 3.1 Reagent ions and Instrument Response

Due to the focusing effect of the RF fields, the signal intensities for the  $\text{H}_3\text{O}^+$  and  $\text{H}_3\text{O}^+(\text{H}_2\text{O})$  reagent ions are very high in the Vocus 2R and would quickly degrade the microchannel plate detector. To prevent this, the BSQ is set up as a high-pass band filter, whereby ions  $<35$  Th are detected at a much-reduced efficiency. As a result, the actual distribution of  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$  reagent ions in the FIMR is not the same as the measured distribution, which complicates the interpretation of the ion chemistry and the normalization of the measured signals to the changing reagent ion signals.

To illustrate the response of the Vocus 2R with regard to different VOCs, Figure 3 shows the product ion signals for acetone and benzene as a function of the axial voltage and RF amplitude. It is seen that the signals increase with both the axial voltage and RF amplitude. The RF fields enhance the ion detection efficiencies as shown above. A higher axial voltage reduces the residence time of ions in the FIMR and therefore limits the loss of ions by radial diffusion. In addition, the axial voltage determines the mean collision energy and therefore degree of  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$  cluster ion formation. While acetone reacts efficiently with all  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$  cluster ions, benzene has been shown to only react with  $\text{H}_3\text{O}^+$  ions<sup>2</sup>. This explains why the acetone signal is observed over a broader range in axial voltages.



**Figure 3:** Product ion signals for acetone and benzene as a function of axial voltage and RF amplitude. Data were binned into  $50 \times 50$  matrices and interpolated using Voronoi polygons.

The FIMR is operated at a relatively high value of  $E/N$  ( $148 \times 10^{-17} \text{ V cm}^2 = 148$  Townsend) at a pressure of 1.25 mbar and electric field of  $45 \text{ V cm}^{-1}$ . This is higher than the typical values of 100-120 Townsend used in PTR-MS<sup>2</sup>. Part of the reason that a higher value of  $E/N$  is needed to de-cluster the reagent ions is the high mixing ratio of water in the FIMR (~20%). Also, the addition of this lighter gas to the sample flow lowers the collision energy and effectively decreases the mobility in the  $\text{N}_2\text{-O}_2\text{-H}_2\text{O}$  mixture<sup>22</sup>, which even further lowers the ion velocity and collision energy. At these values of  $E/N$ , the  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$  reagent ion distribution is

dominated by  $\text{H}_3\text{O}^+$  ions<sup>2</sup> (Figure S4). Fragmentation of product ions is not strongly enhanced by the RF field (Figure S5). Based on the count rate of acetone product ions (102,000 cps) at their sampled mixing ratio of 10 ppbv, the  $\text{H}_3\text{O}^+$  count rate can be calculated to be  $\sim 10^9$  cps. This is much higher than the measured count rate due to the mass discrimination effect of the BSQ. Other ions such as  $\text{NO}^+$  and  $\text{O}_2^+$  have typically 1 and 3 orders of magnitude lower signals than  $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ .

### 3.2 Sensitivity

The Vocus 2R was deployed in the field during the PICAB campaign (PTR-MS Intercomparison campaign at CABauw) that was conducted in 2017 in the framework of ACTRIS (European Research Infrastructure for the observation of Aerosol, Clouds, and Trace gases). A comparison of the different PTR-MS measurements involved will be presented elsewhere. Here, we focus on the results of the calibration measurements.

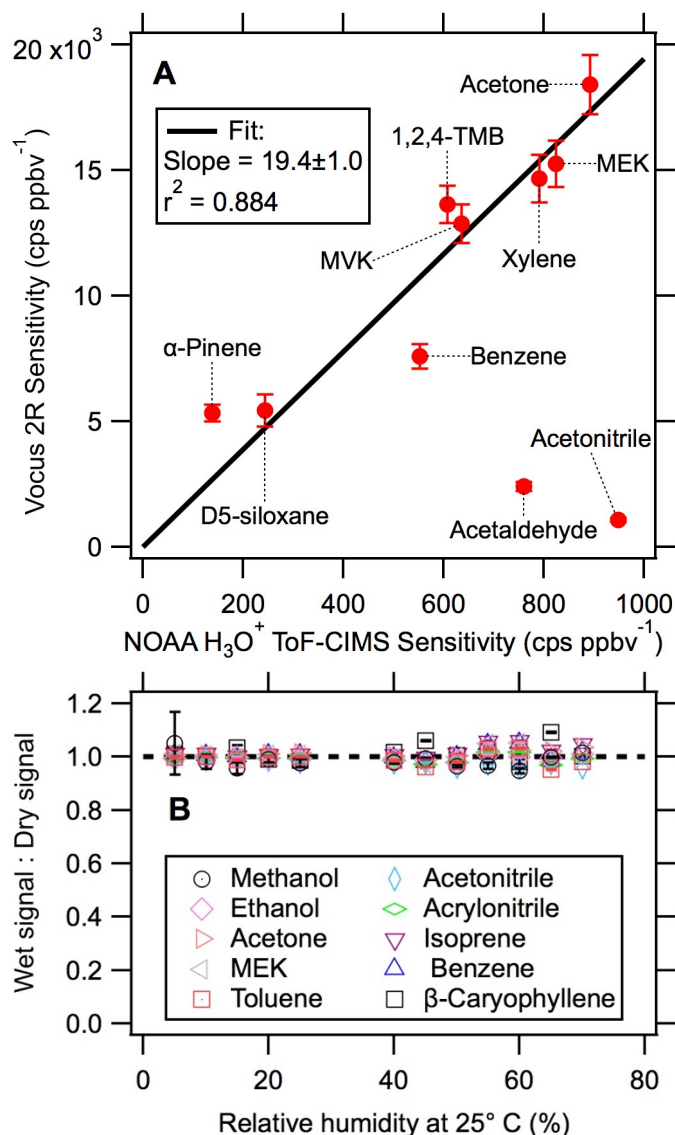
Automated gas-phase calibrations of the Vocus 2R instrument were performed every two hours by injecting a measured concentration of gas-phase standard from a prepared cylinder (Apel-Riemer Environmental). The gas calibrant was diluted into VOC-free air produced by flowing ambient air through a hydrocarbon trap (VICI). The results of 24 h of calibrations for several atmospheric VOCs are summarized in Table S2 and are compared in Figure 4A with published values from the NOAA  $\text{H}_3\text{O}^+$  ToF-CIMS instrument<sup>23-25</sup>. The sensitivities of the two instruments correlate well with each other ( $r^2=0.884$ ), with the exception of acetonitrile and acetaldehyde, which are partially cut off by the BSQ. The slope of a linear regression fit through these data points (excluding acetonitrile and acetaldehyde) shows that the Vocus 2R is  $\sim 19$  times more sensitive than the  $\text{H}_3\text{O}^+$  ToF-CIMS instrument. These two instruments differ in two important ways: (i) a conventional drift tube reactor in the  $\text{H}_3\text{O}^+$  ToF-CIMS vs. the FIMR in the Vocus 2R, and (ii) a TOFWERK HTOF mass analyzer in the  $\text{H}_3\text{O}^+$  ToF-CIMS vs. a TOFWERK LTOF mass analyzer in the Vocus 2R. The enhancement in sensitivity is very similar to the enhancement calculated from ion trajectories in SIMION. Acetaldehyde is detected about 3 times more sensitively, and acetonitrile has about the same sensitivity as the  $\text{H}_3\text{O}^+$  ToF-CIMS instrument at these BSQ settings. Depending on the mass spectral region of interest, these sensitivities can be improved by adjusting the bandpass window of the BSQ. The Vocus 2R sensitivities are at the upper end of the range for PTR-MS instruments as summarized elsewhere<sup>4,10</sup> and similar to the sensitivities of the PTR3 for oxygenated VOCs<sup>13</sup>.

The Vocus 2R sensitivities for acetone and benzene were the same within a factor of 2-3 (Table S2). This confirms that  $\text{H}_3\text{O}^+$  ions are the dominant reagent ions in the Vocus 2R, as benzene and other hydrocarbons do not react as efficiently with  $\text{H}_3\text{O}^+(\text{H}_2\text{O})$  ions<sup>2</sup>.

In contrast with conventional PTR sources<sup>2</sup>, the Vocus does not show a sensitivity dependence on the humidity of the sample air (Figure 4B). This is due to the large mixing ratio of water vapor in the FIMR ( $\sim 20\%$  by volume). Therefore, the humidity of the sample air has only a very small effect on ion-molecule reactions in the Vocus and thereby the sensitivity.

A specific advantage of PTR-MS is that the sensitivities for different VOCs can be calculated from the kinetics of the proton-transfer reactions<sup>23,26,27</sup>. We note here that the same is true for the Vocus 2R: Figure S6 shows the correlation between the sensitivities from Figure 4A and their proton-transfer rate coefficients. More work is needed to study the sensitivity of the Vocus 2R given the time-varying effect of the RF field on the collision energy.





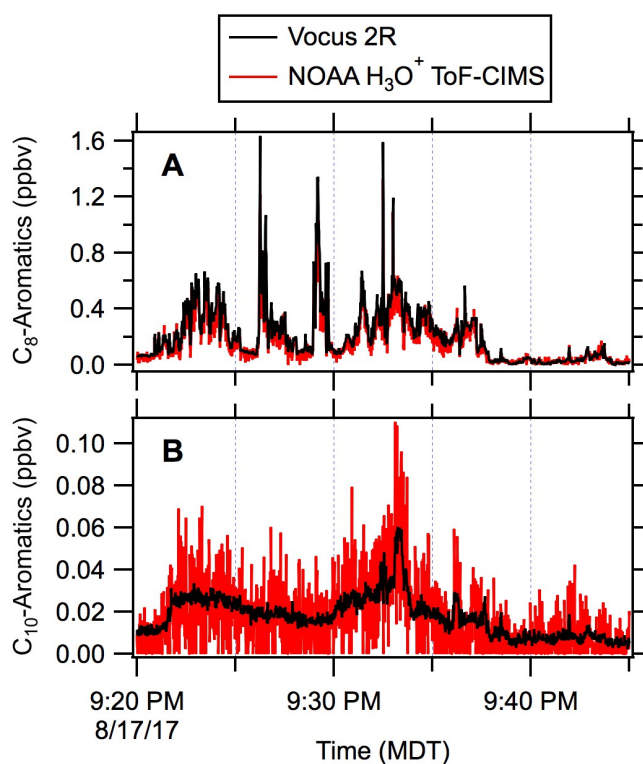
**Figure 4:** (A) Comparison of sensitivities between the Vocus 2R and the NOAA H<sub>3</sub>O<sup>+</sup> ToF-CIMS. Vocus sensitivities were determined during the ACTRIS-PICAB field campaign and represent an average over 24 hours (12 separate calibrations). Error bars represent the 1σ standard deviation. Sensitivities are reported for a 25 kHz extraction frequency. Sensitivities for the H<sub>3</sub>O<sup>+</sup> ToF-CIMS for o-xylene<sup>23</sup>, D5-siloxane<sup>25</sup>, and other compounds<sup>24</sup> were taken from the literature. (B) Humidity dependence of the Vocus 2R product ion signals from a separate experiment.

### 3.3 Measurement Comparison

In August 2017, the Vocus 2R performance was characterized in a series of tests in the NOAA laboratories. Measurements of ambient air were made in parallel with the NOAA H<sub>3</sub>O<sup>+</sup> ToF-CIMS<sup>10</sup>. Figure 5 shows a comparison of measurements of different aromatics in ambient air made by the two instruments. Both instruments were calibrated using the same standard mixture containing toluene, o-xylene and 1,2,4-trimethylbenzene. The sensitivity of the H<sub>3</sub>O<sup>+</sup>

ToF-CIMS to  $C_{10}$  aromatics was calculated from the kinetic rate constant, and the VOCUS 2R sensitivity to  $C_{10}$  aromatics is estimated based on the comparison. Both instruments measured at the same time resolution (1 Hz saved spectra).

Figure 5 shows that the VOCUS 2R and  $H_3O^+$  ToF CIMS show all of the same features for  $C_8$ - and  $C_{10}$ -aromatics, but the VOCUS 2R measures with much higher precision due to its higher sensitivity. During the measurement period, the  $C_8$ -aromatics had enhancements above 1 ppbv and the two instruments agree well for these high signals. Mixing ratios of  $C_{10}$ -aromatics were generally below 100 pptv. The precision of the  $C_{10}$ -aromatics measurements was estimated from a brief period when there was no discernable structure in the signal. The  $1\sigma$ -noise in the Vocus 2R data was 1.2 pptv and the  $1\sigma$ -noise in the  $H_3O^+$  ToF-CIMS data was 5.9 pptv. This improvement in precision by a factor of  $\sim 5$  is as expected from the enhancement in sensitivity<sup>4</sup>.



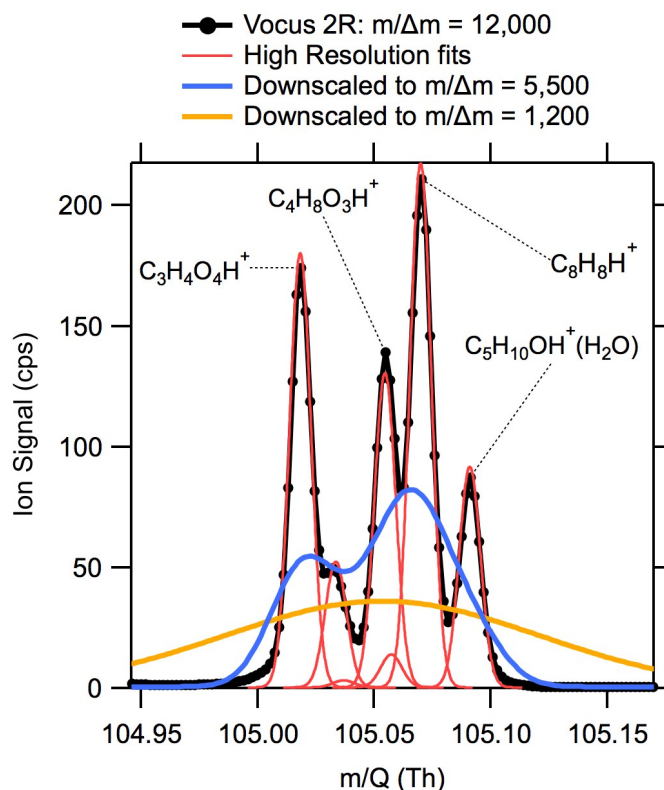
**Figure 5:** Comparison of measured time series of (A)  $C_8$ -aromatics and (B)  $C_{10}$ -aromatics in Boulder by the Vocus 2R and NOAA  $H_3O^+$  ToF-CIMS instruments. Both instruments acquired data at 1 Hz and are compared on the same time base here (i.e. not smoothed). The Vocus 2R was not equipped with a catalytic converter for the determination of background mixing ratios. Instead a constant value was subtracted from each time series for the purpose of this comparison.

### 3.4 Mass spectral resolution

Figure 6 shows a 2-Hz mass spectrum obtained during the ACTRIS-PICAB campaign at 105 Th. The full mass spectrum is provided in Figure S7. With a mass resolution  $m/\Delta m = 12,000$ , the Vocus 2R resolved 5 peaks. Previous work has attributed the signal at 105 Th to styrene, which is indeed the largest peak ( $C_8H_8H^+$ ). In photochemically aged air masses, peroxy

isobutyryl nitrate or PiBN can also contribute to the signal as protonated peroxybutyric acid<sup>28</sup> ( $C_4H_8O_3H^+$ ), which is the third largest peak in the spectrum. The other two peaks are possibly malonic acid ( $C_3H_4O_4H^+$ ) and the water cluster of  $C_5$ -carbonyls ( $C_5H_{10}OH^+(H_2O)$ ). Malonic acid may not have been identified previously due to its low volatility, which prevents it from passing efficiently through inlet tubing<sup>14</sup>.

At a theoretical mass resolving power  $m/\Delta m = 5,500$  and  $1,200$ , the instrument would only detect two and one peak(s), respectively, as illustrated in Figure 6. This shows the higher mass-resolving power of the Vocus 2R allows smaller signals to be quantified with higher precision, in addition to the higher measurement sensitivity.

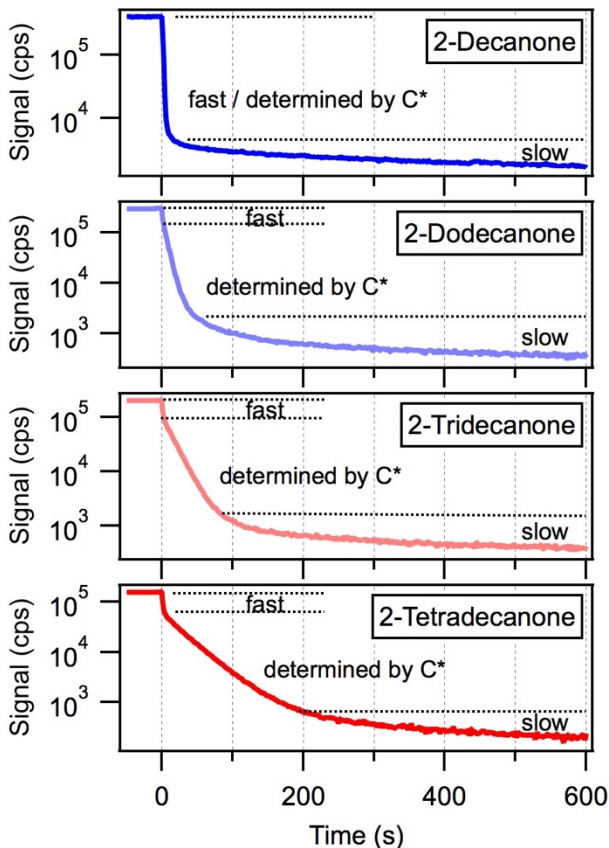


**Figure 6:** A mass spectrum of ambient air from one 2-Hz saved spectrum (24 September 2017, 18:48:34 UTC) at  $m/Q = 105$  Th. With a mass resolving power  $m/\Delta m = 12,000$ , 5 peaks were resolved in the deconvolution. The same mass spectrum was then down-sampled to lower resolving powers of 5,500 and 1,200.

### 3.5 Inlet design and time response

Instrument response times were determined from experiments with an  $8\text{ m}^3$  environmental chamber following procedures described previously<sup>14</sup>. Several ketones with varying vapor pressures were added to the chamber and allowed to equilibrate between the gas phase and the FEP chamber walls. Mixing ratios were approximately 20 ppbv and less for the compounds with lower saturation vapor concentration<sup>29</sup>  $C^*$  that partition to the walls. The Vocus 2R was set up to sample from the chamber. After all ketones had reached a constant product ion signal, the inlet was abruptly removed from the critical orifice and the decrease in signal recorded (Figure

7). The decrease in signal versus time can be described by a double or triple exponential. The first 40-60% of the signal decreased within ~1 sec for all compounds, which is attributed to the rapid clearing of the volume of the FIMR with laboratory air (marked as “fast” decrease in Figure 7).



**Figure 7:** Decrease in the signal for four ketones after abruptly stopping the sampling from an environmental chamber equilibrated with these compounds. For 2-dodecanone through 2-tetradecanone, three phases can be distinguished in the time response. For 2-decanone, the fast decrease due to volume clearing and the decrease determined by C\* occur at the approximate same rate and cannot be distinguished from each other.

The next fraction of the signal showed a slower decrease on a time scale of seconds to a minute that was different for each compound. We attribute this decrease (marked as “determined by C\*” in Figure 7) as the partitioning of ketones from the walls of the inlet and FIMR to the sample air, which was previously shown<sup>14</sup> to be mostly determined by C\*. In Figure S8 we compare the measurement delay times resulting from this effect with those from an earlier study with a PTR-MS instrument equipped with a pressure-controlled inlet. Importantly, these delay times in the Vocus 2R are about an order of magnitude shorter than those obtained with the quadrupole PTR-MS.

The remaining fraction of the signal decreased at the same rate for all compounds (marked as “slow” in Figure 7). A potential explanation is the slow mixing out of sample gas

trapped in dead spaces in the instrument. For all compounds, this slow decrease of the signal only concerns a very small fraction of the signal.

In summary, overall measurement response times in the Vocus 2R are better than 1 sec for compounds with  $C^* > 10^6 \mu\text{g m}^{-3}$ . Below  $10^6 \mu\text{g m}^{-3}$ , a fraction of the signal decreases within ~1 sec and another fraction decreases more slowly. At a lower  $C^*$  than used in these experiments, one can expect that the decrease determined by  $C^*$  becomes so slow that it is not important on the time scale of most measurements, making the effective response time on the order of seconds. This effect has been observed for chamber wall losses<sup>30</sup>, but needs to be verified for the Vocus 2R in future work.

#### **4. Conclusion**

The design of the new Vocus annular ion source and focusing ion-molecule reactor for use in PTR-MS is described. Trajectory calculations and calibrations show that the use of RF fields improves the detection efficiency of ions produced from reactions between  $\text{H}_3\text{O}^+$  reagent ions and VOCs by about an order of magnitude. The instrument sensitivity shows virtually no dependence on ambient humidity. The Vocus is coupled to a TOF mass analyzer with a longer time-of-flight region, thereby achieving a mass resolving power of 14,000. The time response of the Vocus 2R instrument is characterized. At least ~50% of the signal decreases within seconds, whereas the remaining fraction decreases more slowly depending on the saturation vapor concentrations  $C^*$  of the measured compounds.

The new Vocus chemical ionization source combined with the 2R time-of-flight mass analyzer allows fast measurements of VOCs at single pptv levels, with a higher mass resolution and shorter response times than previously demonstrated. Historically an important application of PTR-MS has been the measurements of atmospheric VOCs. The Vocus 2R will allow measurements of many more atmospheric VOCs, which will improve the quantitative separation of different emission sources. The Vocus 2R will allow measurements of VOC reaction products and intermediates, which are present in small concentrations and often difficult to measure because of partitioning to instrument surfaces.

Finally, this work demonstrated the use of  $\text{H}_3\text{O}^+$  as the reagent ion, but we note that the Vocus chemical ionization source can also be operated with other ions, which can further expand its capabilities.

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## Conflict of Interest Disclosure

Felipe Lopez-Hilfiker, Manuel Hutterli, Carsten Stoerner, Joel Kimmel, Katrin Fuhrer and Marc Gonin are employees of TOFWERK, which has developed and commercialized the Vocus PTR-TOF. Jordan Krechmer, John Jayne, Joel Kimmel and Douglas Worsnop are employees of Aerodyne Research Inc., which has partnered with TOFWERK to develop and commercialize atmospheric chemistry research applications of the Vocus PTR-TOF. Joost de Gouw worked as a part-time consultant for Aerodyne Research Inc. during this project.

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