

Response to reviewer comments on “Performance of a new co-axial ion-molecule reaction region for low-pressure chemical ionization mass spectrometry with reduced instrument wall interactions”

Brett B. Palm, Xiaoxi Liu, Jose L. Jimenez, Joel A. Thornton

We thank the reviewers for their comments on our paper. To facilitate the review process, we have copied the reviewer comments in black text. Our responses are in regular blue font. We have responded to all the referee comments and made alterations to our paper (**shown in bold text**).

Anonymous Referee #1

Received and published: 16 August 2019

“Performance of a new co-axial ion-molecule reaction region for low-pressure chemical ionization mass spectrometry with reduced instrument wall interactions” by Palm et al. describes a new CIMS inlet and methods for determining sensitivities and wall losses that can be applied to other CIMS inlet designs. As the authors state, characterizing instrument performance to “sticky” compounds is very important as instruments become more and more capable of their measurement. The article is a pleasure to read, and I have only a few editorial suggestions. Otherwise I recommend publication in AMT.

Minor suggestions:

33: is “relatively” necessary in this sentence (if so, relative to what?)

We have removed the word “relatively” from the sentence, as it is not needed.

181 and 224: I recommend “at the inlet to the IMR” rather than “at the start of the IMR” . . . in the latter the use of “start” seems not quite appropriate.

As we are defining the word “inlet” as referring to the sampling tube, we would prefer not to use the same word when referencing the IMR. Instead, we have changed the text at line 181 from “at the start of the IMR” to **“into the IMR”**, and at line 224 from “to the start of the IMR” to **“to the IMR”**.

184: I recommend modifying this sentence to “The flow coming out of both the sample flow laminizer and ion flow laminizer exit in the same plane . . .” (that is, the flows are not co-planar).

We have modified the text as suggested.

244: I recommend “applies mainly to analyte. . .”

We have modified the text as suggested.

249: Is “theoretical” necessary in this sentence?

We thank the reviewer for their question, but we believe the word “theoretical” helps to make clear to the reader that we are introducing a framework of concepts that can be applied to other experimental data, rather than just specifically to the data presented in Fig. 2.

273: This sentence (to me) is awkward as it suggests surfaces compete for surfaces . . . Maybe change to: "Surfaces can also be modified by other analyte molecules, the latter essentially competing for surface sites."

We have modified the text to read **"Surfaces can also be modified by other analyte molecules, which essentially act in competition for surface sites."**

316: The reference to Fig. 3 is not correct, but I also think (since this is actually out of sequence) that the whole parenthetical comment can be eliminated (I don't see how reference to the figure is helpful).

We have deleted the text "(shaded box in Fig. 3)". To further ensure that the figures are referenced in the correct order, we have changed the text at line 338 from "As illustrated in Fig. 4 and discussed more in Sect. 3.3,..." to **"As discussed further in Sect. 3.3,..."**. We have also corrected an error by changing the reference in line 385 from "Fig. 4b" to **"Fig. 2b"**.

377: correct: "intercation"

We have changed the text from "intercation" to **"interaction"**.

441: It may be helpful to note here that there are many studies performed using laminar flow reactors (aka "flow tubes") that, according to this analysis, could be operated in steady state.

We have modified the text to read **"For laboratory measurements, these conditions may be achieved if special care is taken (e.g., flow tubes, oxidation flow reactors, or chambers operated in reproducible steady-state modes)."**

478: Is this sentence necessary? I doubt the reader will forget that the inlet was just described.

We have deleted the sentence as suggested.

494: Similarly, the sentence that starts "Further details of the experimental setup. . ." does not seem necessary.

We have modified the text from "Further details of the experimental setup can be found in Sect. 4.1 and in related work (Krechmer et al., 2017; Liu et al., 2019)." to **"Further details of the experimental setup can be found in related work (Krechmer et al., 2017; Liu et al., 2019)."**

501: In the sentence: "This way, the surface effects of water vapor on the IMR surfaces were probed." Is the second "surface" needed?

We have removed the first instance of "surface" from this sentence.

Response to reviewer comments on “Performance of a new co-axial ion-molecule reaction region for low-pressure chemical ionization mass spectrometry with reduced instrument wall interactions”

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Anonymous Referee #2

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CIMS has been widely used to measure trace gases. One of the most important artifacts for measuring low volatile gases is the inlet wall effects. The present work designed a low pressure IMR (I- as reagent ion) to reduce the wall impact. Also this study introduces a conceptual framework for considering instrument wall interactions and a measurement protocol to accurately capture the time-dependence of target compound concentrations. The manuscript is well written. I suggest acceptance of this manuscript on AMT.

We thank the reviewer for their comments.

Performance of a new co-axial ion-molecule reaction region for low-pressure chemical ionization mass spectrometry with reduced instrument wall interactions

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Abstract

Chemical ionization mass spectrometry (CIMS) techniques have become prominent methods for sampling trace gases of relatively low volatility. Such gases are often referred to as being “sticky,” i.e. having measurement artifacts due to interactions between analyte molecules and instrument walls, given their tendency to interact with wall surfaces via absorption or adsorption processes. These surface interactions can impact the precision, accuracy, and detection limits of the measurements. We introduce a low-pressure ion-molecule reaction (IMR) region primarily built for performing iodide-adduct ionization, though other adduct ionization schemes could be employed. The design goals were to improve upon previous low-pressure IMR versions by reducing impacts of wall interactions at low pressure while maintaining sufficient ion-molecule reaction times. Chamber measurements demonstrate that the IMR delay times (i.e., magnitude of wall interactions) for a range of organic molecules spanning five orders of magnitude in volatility are 3 to 10 times lower in the new IMR compared to previous versions. Despite these improvements, wall interactions are still present and need to be understood. To that end, we also introduce a conceptual framework for considering instrument wall interactions and a measurement protocol to accurately capture the time-dependence of analyte concentrations. This protocol uses short-duration, high-frequency measurements of the total background (i.e., fast zeros) during ambient measurements as well as during calibration factor determinations. This framework and associated terminology applies to any instrument and ionization technique that samples compounds susceptible to wall interactions.

1 Introduction

Trace gases in the atmosphere are drivers of the chemistry that determines air quality and climate effects (Seinfeld and Pandis, 2006), as well as oxidant budgets and oxidation pathways (e.g., Crutzen, 1979; Di Carlo et al., 2004) and secondary organic aerosol (SOA) formation (Shrivastava et al., 2017). Trace organic compounds are particularly complex, spanning more than 15 orders of magnitude in volatility (Donahue et al., 2012; Hunter et al., 2017; Isaacman-VanWertz et al., 2018). Large gaps remain in our knowledge of the chemistry and impacts of trace organic gases, in particular the ~~relatively~~ lower volatility compounds (Goldstein and Galbally, 2007). The ability to measure and quantify such lower volatility gases is an evolving analytical measurement challenge, but remains a limiting factor in our ability to test important theories governing, e.g., organic gas-particle partitioning, oxidation mechanisms, SOA formation, vertical distributions, and dry deposition.

Many of the recent advances in knowledge of atmospheric trace gases, particularly the lower volatility compounds in the gas phase, have been due to the application and development of advanced instrumentation (Mohr et al., 2013; Ehn et al., 2014; Isaacman et al., 2014; Krechmer et al., 2016a; Peng et al., 2016; Yuan et al., 2017). One of these major advances has been the development of field-deployable mass spectrometers, combined with the development of specialized inlets allowing the application of various chemical ionization methods to atmospheric compounds (Ehn et al., 2014; Lee et al., 2014; Krechmer et al., 2016a). In chemical ionization, analyte molecules are imparted an electrical charge either by charge transfer from or clustering with a reagent ion, processes which are relatively low energy and typically induce little fragmentation of the analyte molecules. A variety of reagent ions with the ability to ionize different subsets of analyte molecules have been used, including H_3O^+ , acetate, iodide (I^-), nitrate (NO_3^-), ammonium (NH_4^+), and others (e.g., Jokinen et al., 2012; Yatavelli et al., 2014; Zaytsev et al., 2019). Iodide-adduct ionization in particular has been used for both gas and particle composition measurements, and is sensitive to a wide range of inorganic and organic molecules (e.g., Huey et al., 1995; Le Breton et al., 2012; Lopez-Hilfiker et al., 2013; Mohr et al., 2013; Lee et al., 2014; Veres et al., 2015; Gaston et al., 2016; Lee et al., 2016).

One impediment to the measurement of lower volatility gases is the influence of inlet tubing and other experimental apparatus surfaces. Several recent experiments have probed the effects of Teflon chamber walls

on experimental processes (Matsunaga and Ziemann, 2010; Krechmer et al., 2016b; Krechmer et al., 2017; Huang et al., 2018). A variety of organic and inorganic gases have been shown to reversibly absorb into Teflon (and other polymer) tubing or reversibly adsorb onto the surface of a variety of solid materials including stainless steel (~~Pagonis et al., 2017; Deming et al., 2019; Liu et al., 2019~~)(Pagonis et al., 2017; Deming et al., 2019; Liu et al., 2019). Current CIMS instrumentation typically requires the use of such materials in the design of the inlet tubing as well as the ion-molecule reaction (IMR) region where chemical ionization occurs, which allows for wall interactions to occur. The rates of flux of analyte molecules to and from these wall surfaces can depend on complex factors of water vapor concentration, co-analyte concentrations, etc. (~~Pagonis et al., 2017; Deming et al., 2019; Liu et al., 2019~~)(Pagonis et al., 2017; Deming et al., 2019; Liu et al., 2019), leading to difficult interpretations of data that is often not consistent across different studies.

Past CIMS IMR versions have employed different designs, typically constructed from varying fractions of stainless steel and several types of Teflon (Eisele and Tanner, 1993; Jokinen et al., 2012; Lee et al., 2014; Zhao et al., 2017; Lee et al., 2018). Some IMR designs, such as the NO_3^- CIMS, can operate at ambient pressure with an IMR design that essentially eliminates wall interactions (e.g., Krechmer et al., 2015). However, the NO_3^- reagent ion is sensitive only to a narrow subset of highly-oxidized molecules with which it has clustering strengths greater than its cluster with HNO_3 . The I^- CIMS technique is sensitive to a much broader range of analyte molecules, making it a powerful technique for studying atmospheric chemistry. But, I^- can also cluster with one or more water molecules, causing the sensitivity of I^- toward other analyte molecules to be dependent on water vapor concentrations in the IMR. To reduce this water vapor dependence, the IMR is typically operated at low pressure (~2-200 Torr) to reduce the partial pressure of water vapor. For aircraft I^- CIMS measurements, a low-pressure IMR has also been desired in order to allow pressure control systems to maintain constant pressure in the ionization region with changing pressure/altitude, thus maintaining constant sensitivity to clustering (Neuman et al., 2002; Crounse et al., 2006; Le Breton et al., 2012; Lee et al., 2018). In order to operate at low pressure, the I^- CIMS must sample through an orifice, necessitating wall interactions in the IMR. Accounting for the flux of analyte from the IMR walls is a challenge of particular importance to aircraft measurements, where ambient concentrations can change rapidly on the edges of spatially narrow plumes from point or regional sources such as power plants, biomass burning, or urban areas. Background measurement and subtraction from

81 the total observed signal is typical (Neuman et al., 2002; e.g., Crounse et al., 2006; Veres et al., 2008; Lee et al.,
82 2018), however a uniform standard method for background subtraction does not exist, and methods applied by
83 different research groups vary widely.

84 In this work, we present a new design of a co-axial, low pressure IMR to minimize wall interactions,
85 incorporating knowledge acquired in the operation and analysis of past IMR designs. A detailed consideration of
86 the process of sampling through an instrument inlet is presented, explaining how the measured signal is
87 influenced by wall interactions. We suggest practices for accounting for wall interactions, both in experimental
88 measurements and when performing calibration measurements that will be later applied to experiments.
89 Finally, this new IMR design was characterized by measuring the magnitude of wall interactions of several
90 organic compounds spanning a wide range of volatility. Both the new IMR design considerations and the
91 broader discussion of wall interactions will be applicable to a broader community of analytical atmospheric
92 chemistry.

93 **2 Co-axial low-pressure IMR design**

94 **2.1 I⁻ CIMS method**

95 Iodide-adduct chemical ionization has been described in detail in previous studies (Huey et al., 1995;
96 Lee et al., 2014; Lee et al., 2018). Briefly, I⁻ anions are produced by passing methyl iodide (CH₃I) in nitrogen
97 through alpha particles from a polonium-210 radioactive sealed source. The anions form adducts by colliding
98 with neutral analytes inside an IMR, and the clusters are subsequently sampled by a high-resolution time-of-
99 flight mass spectrometer (HR-ToF-MS; ToFwerk AG, Thun, Switzerland). This spectrometer provides a nominal
100 mass resolving power ($m/\Delta m$) of approximately 5000 with pptv level detection limits for most compounds.

101 **2.2 IMR description**

102 Many different IMR designs have been employed in past CIMS measurements, each with advantages
103 and disadvantages. The primary function of any IMR region in a CIMS is to facilitate the process of imparting an
104 electrical charge onto analyte molecules in the sample air, whereupon they can be manipulated and analyzed
105 inside the mass spectrometer. Depending on which reagent ion is chosen and which analyte molecules are
106 targeted, the IMR will have different design requirements. Recent interest in identifying and quantifying a broad
107 range of reactive and/or low volatility compounds presents substantial challenges for CIMS instruments with

low-pressure ionization regions, including but certainly not limited to the I^- CIMS used in this work. The effects of IMR wall interactions can be a substantial impediment to making accurate and easily interpretable measurements of compounds that react on or reversibly partition to reactor walls.

Herein we describe the design of a new co-axial IMR, illustrated in the schematic in Fig. 1. This design aimed to improve upon that most recently employed by the Thornton research group during the WINTER 2015 research flights, which has been described in detail in Lee et al. (2018). That version was itself a design built to improve upon the characteristics of previous versions of the IMR including the model available commercially from Aerodyne Research Inc. with the mass spectrometer (Kercher et al., 2009; Bertram et al., 2011; Lee et al., 2014). In the commercially available low-pressure IMR, the analyte flow and ion flow are mixed via turbulence inside a region constructed out of stainless steel. In addition to the increased wall interactions that result from turbulence, stainless steel has been shown to suffer from enhanced wall effects for many compounds (~~Deming et al., 2019; Liu et al., 2019~~)(Deming et al., 2019; Liu et al., 2019). The WINTER IMR made improvements by decreasing the wall surface area and residence time of the turbulent region, and also by constructing two of the three walls of the cylindrical IMR region out of machined PTFE Teflon (Lee et al., 2018). However, the third wall remained stainless steel, and turbulence remained an issue.

The main goals of our improved IMR design were to reduce wall effects while maintaining sufficient residence time for clustering (i.e., maintain sufficient sensitivity). The initial strategies were to remove as many wall surfaces as possible, and have any necessary wall surfaces be constructed from materials such as perfluoroalkoxy (PFA) Teflon which have been shown to have the weakest interactions with many analytes (~~Pagonis et al., 2017; Deming et al., 2019; Liu et al., 2019~~)(Pagonis et al., 2017; Deming et al., 2019; Liu et al., 2019). To minimize wall effects further, we aimed to inject the sample flow into a co-axial sheath of ion flow, creating a larger distance between analyte and surfaces. This design feature was similar to what has been used in some previous IMR designs, in particular for the NO_3^- reagent ion (Eisele and Tanner, 1993; Jokinen et al., 2012; Massoli et al., 2018). Furthermore, we aimed to pump the flow out of the IMR in a similar manner to how it was injected, pumping a sheath flow radially outside of a sample flow. Any analyte that desorbed from a wall surface would be more likely pumped out in the sheath flow and not sampled into the MS.

The final design requirement was that the IMR was capable of operating at a constant IMR pressure on an aircraft platform, where ambient pressure can span the range from ~200-760 Torr. Ion-molecule reaction rates scale with total analyte number density, and ion-molecule cluster stability will depend on total pressure as well as H₂O partial pressure (Lee et al., 2014; Iyer et al., 2016; Lopez-Hilfiker et al., 2016). Thus, maintaining constant pressure (and temperature) can minimize changes in instrument response with large changes in altitude. This feature was added to the WINTER version of the IMR by incorporating a variable orifice on the upstream side of the IMR (Lee et al., 2018), and it is also included in this new co-axial IMR. As long as the pressure downstream of the orifice remains roughly less than half of the pressure of ambient air upstream, critical flow is achieved in the orifice (i.e., the speed of the air through the orifice is approximately the speed of sound). The mass flow through the orifice is then only a function of upstream pressure. As upstream pressure changes with altitude, the variable orifice can be opened or closed via computer control to maintain constant mass flow into the IMR. As the pumps maintain constant mass flow out of the IMR, the pressure inside the IMR remains constant at ~70 Torr downstream inside the IMR where I⁺ is introduced and ionization occurs.

The benefits of constant reduced pressure, e.g. stable instrument response and reduced effects of water vapor on ionization efficiency, come with enhanced wall interactions which can contribute potentially large and often poorly understood artifacts to the measurement. The pressure drop between ambient pressure and ~70 Torr leads to a high velocity jet expansion, which induces turbulent mixing. The jet-induced turbulence ensured mixing of reagent ions and sample flows in previous IMR designs, but also enhanced contact of the sample flow with IMR surfaces. Moreover, the low pressure leads to an order of magnitude larger diffusivity compared to ambient pressure, such that even in the absence of jet induced turbulence, gases in the sample flow will randomly reach the walls of the IMR more efficiently than at typical ambient pressures. Consistent with these ideas, it has been previously shown that the low pressure IMR is the main source of instrument memory and reactive trace gas losses, not the ~0.5 m long sampling inlet at ambient pressure with fast (~10-20 slpm) flow rates typically used (Lee et al., 2018).

Given the above considerations, the first design challenge was to slow the sample flow rate down by expanding the flow cross section while limiting turbulent mixing of analyte molecules to wall surfaces. In order to expand the flow without causing turbulence, an expansion cone/diffuser with an angle of less than

161 approximately 5–7 degrees could be used. Fluid dynamics simulations have shown that this method can prevent
162 flow separation that leads to turbulence in expansions, though possibly not for the Reynold's numbers of less
163 than 2000 in this IMR (Sparrow et al., 2009, and references therein). This cone angle would require a length of
164 more than 13 cm. Diffusion calculations suggest that one third of the analyte would contact the diffuser wall
165 surface under laminar conditions, which still requires getting the flow laminar after the orifice. Given these
166 considerations, as well as time constraints prior to a field campaign, we opted not to test a conical diffuser at
167 this time. Instead, the jet of air exiting the orifice was allowed to expand immediately into a fluorinated
168 ethylene propylene (FEP) Teflon-lined cylinder with 1.2 cm diameter and 1 cm length, after which it passed
169 through a parallel cluster of 3.175 mm OD, 1.5875 mm ID (0.125 inch OD, 0.0625 inch ID) PFA Teflon tubes with
170 a length of 1.5 cm. Turbulence was limited to the 1.2 cm diameter cylinder, and then the subsequent tubing
171 cluster acted to develop laminar flow. As a rough approximation, turbulent flow can be converted to laminar
172 flow by passing through a tube with an entrance length that is 10 times its diameter (Çengel and Cimbala,
173 2014). This concept guided our design specifications. When the sample air exits the laminizer element, the flow
174 has slowed down and become much less turbulent, mitigating the effects of walls downstream of that point.
175 Since having an orifice upstream of the IMR effectively necessitates having some region of turbulence in contact
176 with walls, this design strategy was aimed at limiting the residence time and amount of wall surface area in the
177 region of the IMR that encountered turbulent sample gas. Future low-pressure IMR designs could aim to further
178 minimize wall effects in this region directly downstream of the variable orifice.

179 While the sample gas enters the IMR through the orifice, the I⁻ anions are concurrently injected into a
180 region of the IMR concentric with and outside of the sample flow laminizing element. The anions are produced
181 by flowing dry N₂ over a permeation tube containing methyl iodide and then through a Po-210 radioactive
182 sealed source, producing I⁻. The ion flow experiences some turbulence when injected ~~at the start of~~into the IMR,
183 and then passes through a parallel cluster of 6.35 mm OD, 3.175 mm ID (0.25 inch OD, 0.125 inch ID) PFA Teflon
184 tubes with a length of 1.27 cm (0.5 inch) that act as a laminizer element. The flow coming out of both the
185 sample flow laminizer and ion flow laminizer ~~are~~exit in the same plane and can be arranged to have
186 approximately the same velocity in the axial direction. In this work, this was achieved by maintaining a constant
187 2 slpm sample flow and 3 slpm ionizer flow. As part of the process of designing the IMR with laminizers, fluid

188 modeling simulations were performed to visualize the effects of turbulent vs. laminar flows. Two example cases
189 are depicted in Fig. S1.

190 The exit of the laminizers marks the start of the drift region in the IMR where interactions of analyte
191 with I^- anions occur. Within the 3.49 cm (1.375 inch) ID, 3.81 cm (1.5 inch) long drift region, the I^- anions and
192 analyte flows mix together via diffusion, possibly aided by some residual turbulence. The design also includes
193 some exposed stainless steel surfaces on the drift region wall and at the exit of the sample flow laminizer and
194 entrance of sample pump flow tube, as far from the main sample flow as possible to limit wall interactions.
195 These surfaces can be used to apply an electric field inside the IMR to attempt to enhance the mixing of ions
196 into the sample flow. However, only modest total detected ion enhancements were measured when applying
197 such electric fields. We hypothesize that the relatively high diffusivity at 70 Torr, as well as any residual
198 turbulence, were dominating the flow mixing instead of the electric field forces in this particular design.
199 Because of the only modest gains and in the interest of simplicity, all exposed metal surfaces were grounded
200 together and electric fields were not employed during the measurements discussed herein.

201 Because the analyte molecules enter the drift region in the center, they would have to diffuse all the
202 way across the ion flow to reach a wall surface. In order to be sampled after encountering a wall, they would
203 also have to diffuse all the way back across the ion flow to the capillary into the mass spectrometer. To prevent
204 any molecules coming from the drift tube wall being sampled, half of the drift tube flow was pumped out along
205 the drift tube wall and away from the MS capillary. According to diffusion calculations, only 4% of the analyte
206 are predicted to encounter a wall in the drift region under laminar flow conditions, and a small fraction of those
207 molecules would diffuse back to the center to be sampled, essentially removing the effects of the drift region
208 walls. The other half of the drift region flow was pumped through an FEP Teflon-lined sample tube with ID of
209 2.18 cm (0.86 inch) and length of 5.08 cm (2.0 inch) and past the MS capillary, where it was sub-sampled into
210 the mass spectrometer.

211 Limiting the interaction between analyte and wall surfaces also limits the possibility of the analyte
212 undergoing chemical reactions on surfaces. To examine and quantify the improvements made in this design, we
213 start with a comprehensive discussion of the origin and meaning of wall effects. Although wall interactions are
214 not the only source of instrumental background signals, for semi-volatile and low volatility compounds they are

often the dominant source of residual non-ambient signal. The concept of background signal will be examined using laboratory measurements, and further discussed in the context of ambient measurements and instrument response calibrations. The improvements will be assessed by comparing laboratory measurements made with this IMR to previous measurements from other IMRs and instruments.

3 The effects of instrument wall surfaces

3.1 Measuring and subtracting instrument background signal

In order to properly evaluate the new IMR design, we must first introduce a common framework that can be used to describe how inlet tube and IMR wall interactions originate, what their effects are, and how they can be understood. The CIMS experimental setup will be defined here as comprised of two parts: the sampling tube (i.e., inlet) which transports the analyte from the sampling location (outside of aircraft, inside chamber, etc.) to the start of the IMR; and the IMR, where ionization occurs prior to entering the MS. The IMR is defined as part of the instrument. The background signal is typically measured by flooding the sampling tube and/or IMR with clean air or ultra-high-purity nitrogen (UHP N₂). Subtracting the resulting “background signal” from the total signal measured while sampling ambient air is a common practice in atmospheric mass spectrometry. However, the exact definition and quantification procedure of the ‘background’ can vary across different experimental configurations and analysis goals. The processes that lead to the background signal can also be dynamic and controlled by multiple factors.

The background signal can originate from molecules coming from either the sampling tube or the IMR. In many cases, the sampling tube can be designed such that its background effects are small relative to the IMR effects, e.g., by pulling a large flow through the inlet and subsampling into the IMR, thus minimizing inlet residence time and also diluting the flux from the walls into a large flow volume. Sampling at ambient pressure in the sample tube also minimizes diffusivity to and from the walls. The IMR walls have been shown to be the dominant source of background signal in previous field measurement setups (Lee et al., 2018), so this discussion will focus mainly on IMR background signal. The details and concepts discussed here of background signal sources and how to quantify them are not specific to the I⁻ CIMS IMR, but can be adapted to other IMRs and ionization types as well as for sampling tubes. The concepts involved are illustrated in Fig. 2a and demonstrated using laboratory measurements in Fig. 2b, where a constant gas-phase concentration of nitric acid (HNO₃) was

242 injected into a short polytetrafluoroethylene (PTFE) Teflon inlet tube (~20 cm length, 0.75" diameter, 20 slpm
243 flow rate) and subsampled into the IMR in the sample flow for a specified amount of time. The effects of wall
244 interactions in such an inlet are minor relative to the effects of wall interactions inside the IMR (as
245 demonstrated in Fig. 2). The schematic in Fig. 2a and the following discussion applies mainly ~~for~~to analyte
246 molecules that partition reversibly to the walls (or to thin films of water adsorbed on the walls, as is the case for
247 HNO₃; Liu et al., 2019), and for wall surfaces that allow for absorption such as Teflon varieties. Adsorbing
248 surfaces such as stainless steel, and irreversible loss of analytes such as many radical species, will be discussed
249 as exceptions.

250 At the theoretical time $t=t_0$ in Fig. 2, consider an IMR that has never previously sampled a specific
251 analyte molecule in the sample flow. Prior to t_0 , there will be no signal at all from this analyte entering in the
252 sample flow, and the only signal corresponding to that analyte will be defined here as the persistent
253 background, due to electronic noise and other baseline signal sources such as the ion source or carrier flows. In
254 the specific case of HNO₃ in the Fig. 2b example, a substantial persistent background exists due to a source in
255 the ion flow from the Po-210 ionizer. Most analytes will not have such a persistent background. At $t=t_0$, the
256 analyte has entered the IMR and experienced one of the following two fates: 1) traveled directly from outside
257 of the IMR to the detector in the gas phase without interacting with a wall surface (which may include bouncing
258 off of a wall surface without interacting), or 2) absorbing in (or adsorbing on) a wall surface, where it remains
259 for some amount of time longer than the residence time of the IMR before desorbing and being sampled to the
260 detector. The fraction of analyte that follows each of these two paths will be a function of instrument design
261 (i.e., what fraction of sampled air collides with a wall surface through turbulence or diffusion) and as a function
262 of the uptake and partitioning coefficients of each analyte on each wall surface type. The uptake coefficients
263 themselves will be a function of the exact environmental conditions of the wall surfaces at the time of collision.
264 These environmental conditions can modify the wall surfaces and change how gases are taken up into/on
265 surfaces or change how they desorb from the surfaces.

266 The most influential surface modifier is often water. The analyte can behave differently depending on
267 whether it encounters a bare Teflon or stainless steel surface under completely dry conditions, a surface coated
268 in a monolayer of water under low RH conditions, or a surface coated with a thick layer of water that causes an

aqueous diffusion limitation to the analyte interacting with the actual surface. Liu et al. (2019) demonstrated that some polar compounds partition to walls as a function of their Henry's Law constants during humidified conditions. This IMR design has the ability to add water vapor directly downstream of the variable orifice as in Lee et al. (2018). This maintains a relatively narrow range of water vapor concentrations in the IMR regardless of the sample air humidity, keeping the environmental conditions (and uptake/partitioning coefficients) in the IMR roughly constant. Surfaces can also be modified by other analyte molecules, which essentially ~~acting~~act in competition for surface sites. This behavior has been observed for materials such as stainless steel that are dominated by adsorption to a limited number of surface sites ~~(Deming et al., 2019).~~(Deming et al., 2019). While absorbing materials such as Teflon have been shown to be modified by water, they appear to be insensitive to the amount of other analytes absorbed in the surface ~~(Pagonis et al., 2017; Deming et al., 2019; Liu et al., 2019)~~(Pagonis et al., 2017; Deming et al., 2019; Liu et al., 2019), at least at analyte concentrations relevant to the atmosphere and typical laboratory chamber experiments.

As soon as there are analyte molecules ad/absorbed on surfaces, there will be a flux of that analyte from the surface back into the sample/ion flow. The flux from the surface will be a function of the amount of analyte on the surface, as well as the environmental conditions such as temperature, humidity, and history (see above). Therefore, in the moments just after $t=t_0$, e.g. $t=t_1$ in Fig. 2, there will be a flux of analyte from the walls. We define this flux as the source for the dynamic background signal, which is separate from the persistent background signal. Any analyte that is entering the IMR at this time will continue to split between reaching the detector directly or absorbing into the walls first, at the same fractional rates. These fractional rates will be constant as long as the environmental conditions remain constant, and the rates will not be a function of the flux of that analyte coming off of the wall. At $t=t_1$, the total flux into the IMR is greater than the total flux to the detector, and there is a net flux to the wall surfaces. As more analyte continues to enter the inlet and ad/absorb on the walls, the flux of analyte from the wall will continue to grow until a time comparable to $t=t_2$ in Fig. 2. Any analyte that partitions irreversibly to the walls or desorbs as a different compound due to surface reaction would appear to have no flux from the walls and no dynamic background signal. Only the fraction of such an analyte that did not interact with the walls would be detected, potentially at much lower sensitivities than expected from ionization efficiency considerations (Lopez-Hilfiker et al., 2016).

At times equivalent to $t=t_2$ in Fig. 2, the flux of reversibly-partitioning analyte from the wall has grown to be equal to the rate of ad/absorption of the analyte to the wall. The wall system is now in steady state. The amount of analyte arriving at the detector is now equal to the sum of the analyte that did not interact with walls and the analyte that entered the IMR at some earlier time, interacted with a wall, and then desorbed to reach the detector. Because the flux from the walls is equal to the flux to the walls, the total flux to the detector is equal to the total flux of analyte that is entering the IMR at that time. That is, the total signal is the same as it would be if the analyte were introduced into an IMR completely absent of wall interactions. This condition is only true when the incoming analyte concentration and environmental conditions have remained constant for long enough to establish wall steady state. As shown in Fig. 2b, the only signal that stays constant during a constant concentration injection with wall interactions is the background-subtracted signal. The background signal and thus also the total detected signal change over time and are both non-deterministically related to the analyte concentration entering the inlet. This concept is critical for the time-dependent quantification of analyte in the sampled air, and is also important for the determination and interpretation of calibration factors, as discussed later in Sect. 3.2.2.

The ratio of the background-subtracted signal to the background signal will remain constant after time $t=t_2$, as long as the environmental conditions in the IMR remain constant. However, the ratio will not be the same for all analytes. For analytes which are more volatile (or less soluble in water), interact with the wall surfaces less strongly, and desorb more rapidly, the background signal may be negligible relative to the background-subtracted signal (and the background-subtracted signal will be essentially equal to total signal). For analytes which are less volatile (more soluble), interact strongly with surfaces, and desorb slowly, the background signal may become a large majority of the total signal at the detector and the background-subtracted signal may reach a detection limit. The IMR geometry and design will largely determine which compounds qualify as 'more' and 'less' volatile on this relative scale. For instance, the NO_3^- CIMS (~~shaded box in Fig. 3~~) and the cross-flow ion source (Zhao et al., 2010; Zhao et al., 2017) which operate with laminar flows at atmospheric pressure in the IMR thereby minimizing turbulence and diffusion to walls, both employ geometries that prevent sampling of any analyte that encountered a wall surface in the ionization region, leading to an IMR

322 background signal flux that is essentially negligible. Atmospheric pressure sampling, which as noted above is
323 ultimately the source of such benefits, may not be suitable for an aircraft platform as discussed above.

324 Continuing our description of the evolution of wall interactions, consider that the source of the analyte
325 into the IMR is completely removed immediately following $t=t_2$. For instance, this could represent the injection
326 of analyte-free air during a background measurement, or a scenario where the sampled air transitions rapidly
327 from high concentrations of the analyte in a plume to very low concentrations outside of a plume. There will be
328 a short transition period, corresponding to the residence time distribution of air in the IMR downstream of
329 where analyte-free air is injected (approximately 100 ms on average in the IMR described herein) plus any time
330 for switching flows outside the ionization region (potentially several seconds), when the analyte-laden air is
331 replaced with analyte-free air in the IMR. The flux of analyte to the detector without wall interactions and the
332 flux of analyte to the walls both drop to zero at this point, which is specified as $t=t_3$. There remains essentially
333 the same amount of analyte adsorbed on the walls at $t=t_3$ as at $t=t_2$ immediately prior, so the flux from the
334 wall to the detector continues to provide the same dynamic background signal.

335 After more time passes and $t=t_4$ has been reached, the amount of analyte on the walls has been
336 partially depleted since the wall system is now out of steady state. There is still a flux from the wall without a
337 complementary flux to the wall to replenish the analyte. The flux from the wall is also lower at this time than at
338 $t=t_3$ because the concentration of analyte on the wall is lower. At a subsequent time long after $t=t_4$, all of the
339 analyte would eventually desorb from the walls, and the dynamic background signal from the inlet walls would
340 reach zero, equivalent to a time $t<t_0$. As ~~illustrated in Fig. 4 and~~ discussed ~~more~~further in Sect. 3.3, the amount
341 of time required for the dynamic background signal to decay to 10% of the original signal (i.e., to near zero) can
342 range from less than 1 s to tens of min or more, depending on the volatility of the analyte as well as
343 environmental conditions and surface types. For some analytes (including HNO_3 in the iodide anion source
344 discussed here), there can be other persistent sources of background signal coming from the tubing and carrier
345 gas related to the ion source. The persistent background is present at all times from $t<t_0$ to $t>t_4$, and can be
346 quantified by injecting analyte-free air for sufficient time to completely deplete the dynamic background signal
347 of interest here. The persistent background is also included in the signal measured during clean-air injections at
348 $t=t_3$.

349 The main goal of measuring and subtracting the background signal in an instrument is to ascertain the
350 concentration of the analyte present in sampled air at the time of sampling with high temporal/spatial
351 resolution, removing the instrumental artifacts related to the background signal caused by wall interactions. As
352 illustrated in Fig. 2a, this task is often made complicated by the fact that the ratio of the background signal to
353 the background-subtracted signal can vary widely during measurements. The entire signal could be due to
354 background signal (as at $t=t_3$), due to gas phase signal ($t=t_0$), or some dynamic mix of the two ($t=t_1$ and $t=t_2$).
355 Even when all signal is coming from the background, the magnitude of the background can also change ($t=t_4$).

356 Given these fluctuating factors combined with a potentially rapidly changing sampling environment due
357 to a moving aircraft platform or rapidly shifting air masses with different source characteristics, the ideal way to
358 determine the true concentration of the analyte in sampled air is to measure the amount of signal coming from
359 the background sources at all points in time and subtract it from the total signal. But akin to Heisenberg's
360 uncertainty principle, one cannot precisely measure both the total signal and the background signal at the same
361 time. Instead, a practical method for determination of background signal is to measure the instantaneous flux
362 of analyte off the walls using high-frequency, short-duration injections of analyte-free gas (typically UHP N_2)
363 interspersed among the normal measurement of total signal, and then interpolate between these background
364 measurements. This method is has been referred to as performing 'fast zeros'. Upon injection of analyte-free
365 gas, the measurement transitions from representing the total signal (equivalent to $t=t_1$, t_2 , or t_3 , depending on
366 whether wall steady state has been achieved) to a measurement of just the sum of dynamic and persistent
367 background signals (equivalent to $t=t_3$).

368 As seen in the inset of Fig. 2b, the decay of the analyte signal occurs in two parts (or more). The first
369 part is the rapid exponential decay as the volume of the inlet is cleared out of any remaining gas-phase analyte,
370 and stability of flows is achieved, etc. The next part, which applies when the analyte is of relatively lower
371 volatility or higher Henry's Law constant into wall-adsorbed water, is the typically slower exponential decay that
372 accompanies desorption of the analyte from the walls. There may be multiple decay constants with varying time
373 scales (e.g., as illustrated in Krechmer et al., 2018) if there are multiple types of wall surfaces (e.g., both Teflon
374 and stainless steel in the same IMR) or voids with different residence times. To know the background value at
375 the time when the background measurement was initiated ($t=t_2$), one needs to know the magnitude at which

376 the slower exponential decay begins, i.e. the signal value at $t=t_3$ shown in the inset of Fig. 2b. The background
377 determined at successive times of $t=t_3$ are then interpolated to estimate the background at all points in time.
378 Such periodic background determinations would also inherently account for any changes in the environmental
379 conditions that would change the analyte uptake coefficient and thus the ratio of the flux to the walls vs the flux
380 to the detector without wall ~~intercation~~interaction, such as an aircraft platform flying through varying ambient
381 H₂O concentrations. In other words, as long as the background signal can be determined at a given time, it does
382 not matter when those particular analyte molecules that led to background signal entered the IMR.

383 Any background measurement value taken at a later time, e.g., at $t=t_4$ or at $t \gg t_4$ (a measure of the
384 persistent background), would no longer represent the magnitude of the background at $t=t_2$ and would
385 underestimate the contribution of background signal to the total at the time the background measurement was
386 initiated. This aspect is critical to the determination of so-called tails of measurements, e.g., when an aircraft
387 platform is measuring in an analyte plume and then abruptly exits the plume to analyte-free air. The signal
388 appears to decay as between $t=t_3$ and $t=t_4$ (and beyond) in Fig. ~~4b~~2b. The entirety of this signal is often due to
389 background signal. If this background signal is not subtracted as described herein, the data would be falsely
390 reporting a non-zero concentration (i.e., tail) of the analyte after exiting the plume, which could lead to large
391 errors in measurement-model comparisons that would not be captured by simple uncertainties estimated by
392 replicate calibrations. Note that when calculating the integral of signal across a plume pass, the same integrated
393 concentration can be found whether or not the background signal subtraction method is used, provided that a
394 self-consistent calibration value is applied (see Sect. 3.2).

395 With the IMR described in this work as well as previous versions, it was found that a ‘fast zero’
396 background measurement of 6 s duration was sufficient to pass through the fast exponential decay (which
397 typically lasts ~ 2 s) and capture $t=t_3$ at the start of the slow exponential decay of analyte. The frequency at
398 which the background measurement needs to be taken depends on the application. For measurement of rapidly
399 changing analyte concentrations, the background needs to be determined as rapidly as possible to minimize
400 errors in interpolation of the background. For recent aircraft measurements using this IMR, these 6 s
401 background measurements were performed once per minute, striking a balance between minimizing
402 background interpolation errors while maximizing the duty cycle of taking ambient measurements. One could

403 imagine taking a 6 s background (or shorter, e.g., 4 s) as fast as every 20-30 seconds to capture extremely rapid
404 changes in some specific circumstances, but information about the same temporal changes in background-
405 subtracted signal would be lost. Conversely if the analyte concentrations are known to be relatively constant,
406 e.g., in a laboratory experiment, then the intervals between background determinations could stretch much
407 longer without leading to substantial interpolation errors. Linear interpolation can be the simplest method,
408 however other methods could be used depending on specific circumstances. For instance, a relative-
409 concentration-dependent interpolation may better describe the background signal for a case where a plume
410 with large concentration gradient was entered and/or exited between background determinations.

411 **3.2 Wall Interactions and Calibration of Instrument Response**

412 The previous section discussed accounting for dynamic background signals in the context of
413 determining accurate gas-phase concentrations in laboratory or field experiments. Also important is to account
414 for the background signal during instrument response calibrations. When calibrating, a known amount of an
415 analyte is injected into the instrument, and the amount of raw signal measured per unit analyte is determined.
416 This raw signal has to be normalized to a constant number of reagent ions, given that the total number of ions
417 created by an ion source (and thus clusters formed and signal measured) can change with time. Therefore, a
418 calibration value for this I⁻ CIMS typically has units of counts per second per 1×10^6 total reagent ion count
419 (TRIC) per ppt of analyte, also called normalized counts per second (ncps) per ppt of analyte. When the raw
420 signal in units of ncps is divided by the calibration value, a concentration in units of ppt is derived. The
421 calibration value for each analyte must also be determined as a function of the amount of water vapor in the
422 IMR.

423 However, in light of the earlier discussion of background signal, considering the signal as units of ncps is
424 not enough information. The distinction between background-subtracted ncps and background (including
425 dynamic and persistent background) ncps, which add to total ncps, is necessary. As illustrated in Fig. 2b, when a
426 constant concentration of HNO₃ (approx. 2 ppbv) from a permeation tube was added into the inlet, neither the
427 background counts per second nor the total counts per second were constant functions of the amount of HNO₃
428 injected. The background-subtracted counts per second were constant, making that value the only properly
429 deterministic calibration constant that can be applied regardless of the relative amounts of background vs.

background-subtracted signals. Therefore, it is also recommended that the same background subtraction be performed on both calibration data and field/laboratory measurement data. Also, care should be taken to ensure that wall steady state is achieved in any tubing that is used to transfer a calibration gas from its source to the IMR, such as in the PFA Teflon tubing between the HNO₃ permeation tube and the IMR used in this work. This ensures that the flux of HNO₃ coming out of that transfer line is the same as the calibrated flux out of the permeation device.

If background measurements are not performed or are not possible in a certain configuration, an alternative method may be used in specific circumstances. The calibration constant could be measured as the total ncps ppt⁻¹ during a time equivalent to t=t₂, when wall steady state has been achieved. This calibration constant represents the total (background-subtracted plus background) amount of signal that a given incoming gas-phase concentration will generate. It applies only at wall steady state, only when environmental conditions (e.g, RH) are the same as during calibration, and only in a given inlet configuration. Therefore, the calibration can only be applied to data that has not been background subtracted, and it will only be accurate when wall steady state has been achieved and environmental conditions are the same as during calibration. For laboratory measurements, these conditions may be achieved if special care is taken- (e.g., flow tubes, oxidation flow reactors, or chambers operated in reproducible steady-state modes). However, dynamic conditions in field studies likely preclude this calibration method from being a routinely viable option for analytes with substantial background signal. The integral of signal across a plume would still be accurate (i.e., mass balance is achieved in the IMR), but the real concentration would be underestimated at the start of the plume, and overestimated in the tail of the plume, provided that there are no signal tails from previous plumes still desorbing from surfaces. If sufficient background measurements were taken during a measurement period, but the calibration constant applied to that data was calculated using the total signal, the calibration constant can be retroactively converted to units of background-subtracted ncps ppt⁻¹ by finding a suitable time when wall steady state was achieved during the measurement period. The ratio of background-subtracted signal to total signal during wall steady state can be derived and multiplied by the total signal calibration constant to obtain the background-subtracted calibration constant, using the following equation:

$$\frac{\text{Background-subtracted ncps}}{\text{ppt}} = \frac{\text{Total ncps}}{\text{ppt}} \times \frac{(\text{Background-subtracted ncps})_{ss}}{(\text{Total ncps})_{ss}}, \quad (1)$$

where the subscript ss implies the value at wall steady state. Lastly, it will be important to keep this relationship between background-subtracted and total calibration constants in mind when comparing experimentally derived sensitivities to theoretically calculated sensitivities (as in, e.g., Iyer et al., 2016; Lopez-Hilfiker et al., 2016; Sekimoto et al., 2017). The theoretical calculations will be estimating the total signal per amount of analyte, without regard to wall effects.

In summary, the accuracy of a calibration constant will depend on how the wall interactions for an analyte are quantified during calibration and ambient measurements. For sticky compounds with substantial wall interactions, systematic biases in instrument response, and thus reported concentrations, can easily approach a factor of 2 (or much more in signal ‘tails’) without a self-consistent accounting of wall induced backgrounds during calibrations and measurements.

4 Quantifying IMR delay times

4.1 Chamber measurement methods

The wall interactions in the IMR designed in this work were characterized through a series of experiments, including extensive tests performed in the University of Colorado Environmental Chamber Facility in Boulder, CO. The chamber contained a 20 m³ FEP Teflon bag operated in batch mode. The experimental method used in this work has been described in more detail in similar experiments designed to characterize wall interactions in various types of tubing, Teflon bags, and other instrument inlets (Krechmer et al., 2017; Liu et al., 2019). Briefly, a series of 1-alkanol compounds (C₆, C₈, C₉, C₁₀, and C₁₂) were injected into the dark chamber along with methyl nitrite and NO at room temperature. UV blacklights were turned on for 10 s to photolyze methyl nitrite, producing OH radicals through subsequent chemistry (Atkinson et al., 1981). Rapid oxidation of the 1-alkanol compounds until the OH radicals were depleted led to quasi-stable ppt-level concentrations of a range of oxidation products, including hydroxynitrates (HN), dihydroxynitrates (DHN), and dihydroxycarbonyls (DHC) as listed in Table S1. The volatilities of these compounds were estimated using the SIMPOL method (Pankow and Asher, 2008) as in Liu et al., (2019). Chamber air was sampled into the IMR through a 0.75” OD, approximately 8” long PTFE tube. The sample flow through this inlet and into the IMR was 2 slpm, and the ion flow into the IMR was 3 slpm, for a total flow of 5slpm at a constant ~70 Torr in the IMR. ~~Further detail about the IMR can be found in Sect. 3.1.~~

4.2 IMR delay times vs. previous designs

The main goal of updating the IMR design as described in Sect. 3.1 was to reduce the measurement artifacts due to interactions between analytes and IMR wall surfaces. As described in detail in Sect. 3.2 above, a reduction in wall-induced artifacts leads to improved spatial/temporal accuracy of the measurements, reduced impacts of possible surface chemistry artifacts, and more easily interpretable data. In this section, we describe the measurements used to quantify the improvement achieved in the new design.

In past experiments, wall interactions occurring in lengths of tubing or in IMRs have been quantified using the amount of time required for a signal to decay to 10% of the maximum total signal after wall steady state had been achieved and the signal source was removed (~~Neuman et al., 1999; Veres et al., 2008; Pagonis et al., 2017; Deming et al., 2019; Liu et al., 2019~~)(Neuman et al., 1999; Veres et al., 2008; Pagonis et al., 2017; Deming et al., 2019; Liu et al., 2019). When the ambient source of the compound is removed, the background-subtracted signal rapidly decays and all of the remaining signal is due to molecules evaporating or desorbing from the wall surfaces.

To systematically test delay times in the updated IMR design, we employed the recently developed method of sampling a range of HN, DHN, and DHC oxidation products spanning more than five orders of magnitude in volatility. Further details of the experimental setup can be found ~~in Sect. 4.1 and~~ in related work (Krechmer et al., 2017; Liu et al., 2019). These compounds were allowed to equilibrate with the chamber walls, and sampling from the chamber then provided a constant source of these compounds. Chamber air was sampled through the co-axial IMR into the CIMS until IMR wall steady state was achieved for all compounds. At this point, UHP N₂ was injected into the variable orifice upstream of the IMR, removing the source of analyte and starting the measurement of delay times. While the chamber air was dry for all experiments, measurements were performed with and without adding an estimated 1-2 x 10¹⁶ molec cm⁻³ water vapor directly to the IMR. This way, the ~~surface~~ effects of water vapor on the IMR surfaces were probed.

The delay time measurement for one compound, a C₉H₁₉NO₅ DHN with an estimated C* of 14.6 µg m⁻³ (which would typically be categorized as a semivolatile organic compound or SVOC), is shown in Fig. 3. Fast zero measurements (6 s every 1 min) of the background signal were taken prior to the start of the delay time measurement, illustrating that wall steady state was reached and that approximately 48% of the total signal

was due to the background in the IMR. In other words, half of those analyte molecules that entered the IMR had interactions with a wall surface prior to desorbing and being sampled at the detector. Once the delay time measurement started, the signal due to molecules that did not interact with walls rapidly decayed (within several seconds) followed by the slower decay of the background signal. The amount of time required for the total signal to drop to within 10% of the persistent background level (which for this compound was essentially equal to the baseline noise) was measured to be 356 s, or 5.9 min. This DHN is an example of a compound that would require the fast zero method of background determination in order to achieve temporal/spatial resolution when sampling variable concentrations such as plumes. Delay times were also determined for the range of other compounds present in the chamber for both a dry and humidified IMR.

Liu et al. 2019 compiled delay times for the IMRs of several instruments, including a quadrupole proton transfer reaction MS (q-PTRMS; Pagonis et al., 2017), a Vocus inlet coupled with a time-of-flight MS (Krechmer et al., 2018), an I⁻ CIMS using the commercially available IMR (Aerodyne, Inc.) operated at dry conditions by the Jimenez group, and a custom design similar to the commercially available IMR operated under humidified conditions by the Ziemann group. The I⁻ CIMS instruments were tested using the same method and analytes as in this work, while the delay times for the q-PTRMS and Vocus instruments were measured using a similar method involving a series of ketones at equilibrium with the walls in a chamber (Pagonis et al., 2017; Deming et al., 2019)(Pagonis et al., 2017; Deming et al., 2019). Figure 4 illustrates the delay times measured here in context with the previous results.

In general, the delay times for the co-axial IMR described herein were approximately an order of magnitude shorter than for the stainless steel IMR under dry conditions, and approximately 5 times shorter than the similar but humidified stainless steel IMR. The effects of humidity in an IMR appear to depend both on the material of the IMR as well as the type of analyte. In stainless steel IMRs, increased humidity led to uniformly shorter delay times for all analytes. However, in our new IMR, humidity led to slightly longer delay times for DHN and no change for HN. These results illustrate how the interaction between an analyte and a surface can be determined by a complex combination of factors, including the surface type, surface modifications, and functional groups and properties of the analyte.

For both the dry and humidified stainless steel IMRs, results indicated that delay times started trending back towards shorter values at the lowest measured C^* values. This trend is in contrast to the results from the co-axial IMR. Liu et al. (2019) attributed this to irreversible loss of the analyte to the walls, which would decrease the background signal relative to background-subtracted signal. It may be the case that this irreversible loss for species of $C^* < 100 \mu\text{g m}^{-3}$ is unique to those stainless steel IMR surfaces and doesn't occur on the PFA and FEP Teflon surfaces in the co-axial IMR. However, it may also be the case that those lowest volatility compounds had not yet achieved wall steady state with the inlet tubes and stainless steel IMR walls. This would have led to an artificially low amount of background signal relative to background-subtracted signal, causing underestimates of delay times. Successively lower C^* compounds would be further away from steady state for the sampling time prior to the start of the delay measurement, leading to successively more underestimated delay times. If one assumes the linear relationship (in log-log space) observed in the co-axial IMR and for $C^* > 100 \mu\text{g m}^{-3}$ in the stainless steel IMRs would hold for the lower C^* compounds, the delay times in the stainless steel IMRs would reach on order of ~ 1000 minutes at most, which would become an implausible amount of time to wait for wall steady state to be reached (and for all of the background to decay during the delay measurement) during a batch mode chamber experiment. Also, it would be extremely difficult to ascertain when wall steady state was achieved due to the slow rate of increase of the background signal.

At first glance, extrapolation of results would indicate that the Vocus and q-PTRMS instruments would have one or several orders of magnitude longer respective delay times for the same HN, DHN, and DHC compounds compared with our new IMR. The Vocus and q-PTRMS instruments are designed primarily for H_3O^+ ionization chemistry, typically to target a much more volatile set of analyte compounds compared with I^- ionization. They also typically operate with an IMR pressure in the range of 2 Torr, which will greatly enhance the rates of diffusion to the walls compared with the ~ 70 Torr I^- CIMS IMRs. Both our new IMR and the Vocus have delay times spanning from a second to greater than several minutes over their respective volatility ranges of interest. However, these results indicate that a Vocus-type design would not perform as well for I^- ionization without modifications.

The IMR used in Lee et al. (2018), which employed the same variable orifice with an H_2O vapor addition port but with turbulent mixing of ions and analyte, was not tested on the CU chamber. However, laboratory

564 experiments indicate that the delay time for HNO_3 under similar humidified conditions in the Lee et al. (2018)
565 IMR was approximately a factor of three longer than in this new IMR (see Fig. S2), providing a measure of the
566 improvements between that design and the one presented herein.

567 **5 Conclusions**

568 The effects of wall interactions in mass spectrometer inlets and IMRs have been a persistent but
569 sometimes nebulous concern for as long as researchers have been sampling gases, particularly the lower
570 volatility and soluble ones often referred to as “sticky” gases. As the importance of such gases to atmospheric
571 processes like new particle formation/growth and SOA formation continues to be discovered, so does the need
572 for higher precision and accuracy of the measurements. Recent research has begun to focus on analyte-surface
573 interactions, including absorption and adsorption processes and how they can affect measurements in IMRs and
574 in sample tubing. In this work, we introduced a new IMR design with the goal of reducing IMR wall interactions.
575 This design was informed by the concepts in this and prior research. It sought to minimize wall interactions by
576 limiting both turbulent and diffusive mixing to the walls, and by choosing wall surfaces that interact least with
577 the analyte molecules. The new IMR was shown to have delay times that were 3–10 times shorter than previous
578 IMR versions. This translates to higher signal-to-noise of the background-subtracted signal (i.e., the signal that
579 did not interact with walls), less influence from possible surface reactions, and easier interpretation of
580 measured time series.

581 Since there are a large number of factors affecting wall interactions, many of which are poorly
582 understood, there has been little ability for researchers across different platforms to apply a uniform treatment
583 to wall effects. Here, we aimed to provide a common framework of concepts with which the wall interactions in
584 all instrumental systems could be described and treated. In this framework, the total signal measured at the
585 detector for a given analyte can be described as originating from the sum of the following two pathways: 1)
586 some fraction of the molecules do not interact with IMR wall surfaces, and are sampled with a time response
587 equal to the average residence time in the IMR, and 2) the remaining fraction of molecules interact with the
588 IMR walls via adsorption/absorption, and are sampled with a delayed time response longer than the average
589 IMR residence time. We demonstrated a method of using fast zeroing to separate the signal into these parts,
590 namely the background-subtracted signal and the dynamic plus persistent background signals. The background-

591 subtracted signal is the only part that is a constant function of, and deterministic of, the concentration of
592 analyte entering the IMR as a function of time, and is thus an essential quantity for accurately capturing time-
593 dependence of analyte concentrations. This framework could be adapted to other inlet and instrument
594 configurations. A consistent manner of calibration was also presented.

595 This IMR design and the characterization of wall interactions represents an improvement over previous
596 low-pressure CIMS techniques used in atmospheric chemistry. Future work could build upon this design, for
597 instance by further decreasing wall interactions. One could also imagine a case where the walls are
598 modified/treated with a method similar to that in Roscioli et al. (2016), but in such a way as to make the walls
599 an irreversible sink for a particular analyte, thereby eliminating the background signal and making the total
600 signal equal to the background-subtracted signal. However, finding a modification technique that would work
601 for the entire range of diverse analyte molecules to which iodide-adduct ionization is sensitive could prove
602 challenging.

603 To facilitate comparisons and merging of data sets from different instruments, we also encourage the
604 users of all CIMS techniques to adopt the methods for calibration and background subtraction discussed herein
605 when sampling analytes that suffer from wall interactions, and encourage the reporting of all relevant sampling
606 and calibration method details in the publication of such research.

607 **Data Availability**

608 All data is available upon request to the authors.

609 **Author Contributions**

610 BBP and JAT designed, assembled, and tested the IMR, and determined the framework of wall interactions. BBP,
611 XL and JLJ conducted the characterization experiments at the CU Environmental Chamber facility and
612 participated in the analysis of the data. BBP wrote the manuscript. All authors contributed to revisions of the
613 manuscript.

614 **Competing Interests**

615 The authors declare that they have no conflict of interest.

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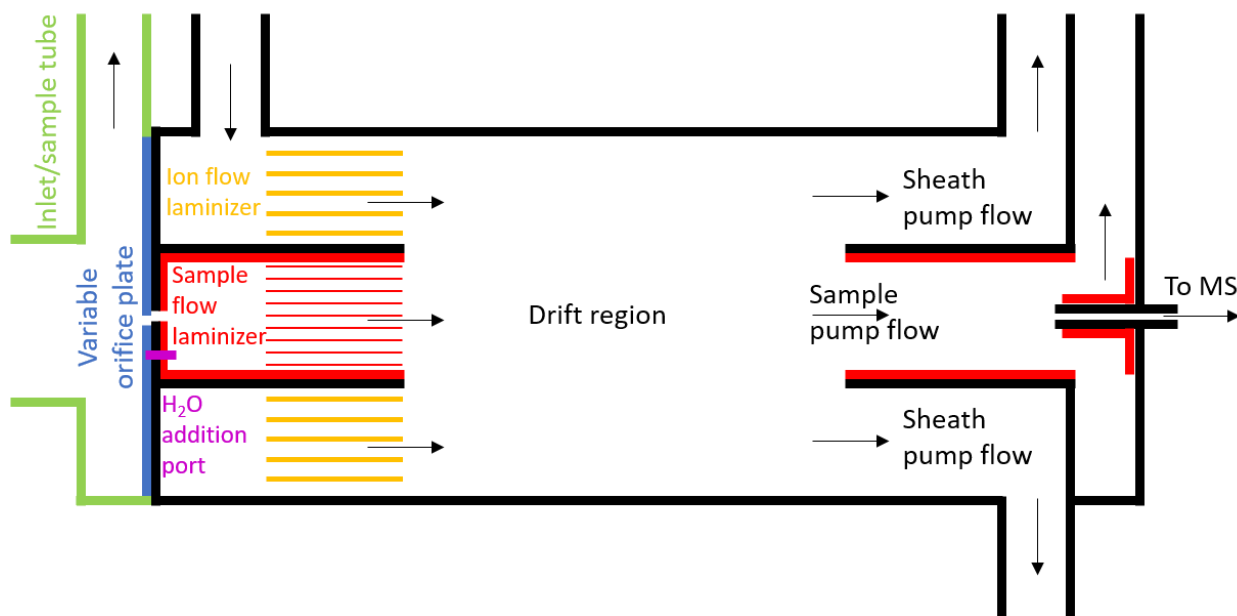
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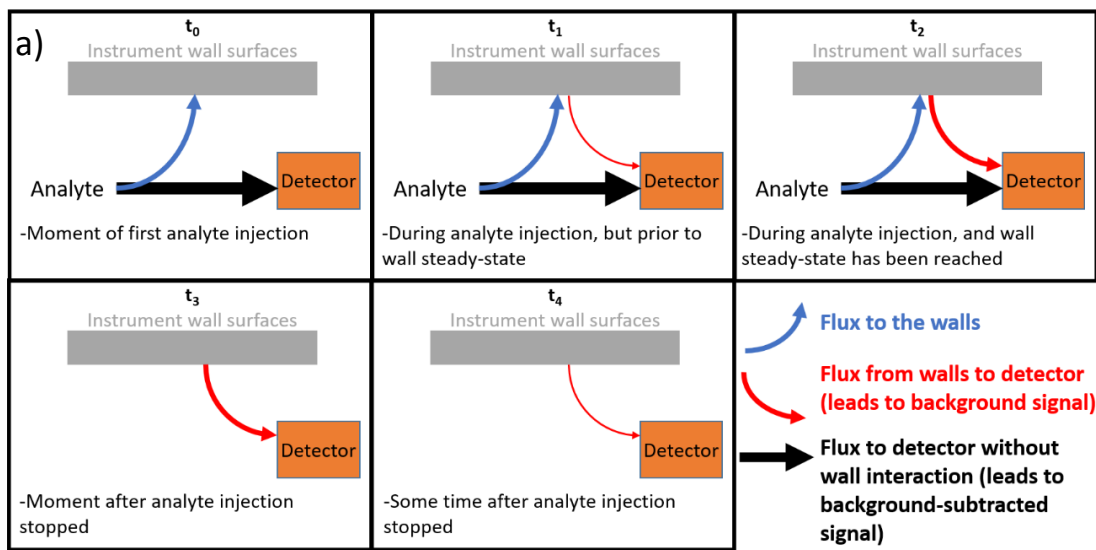


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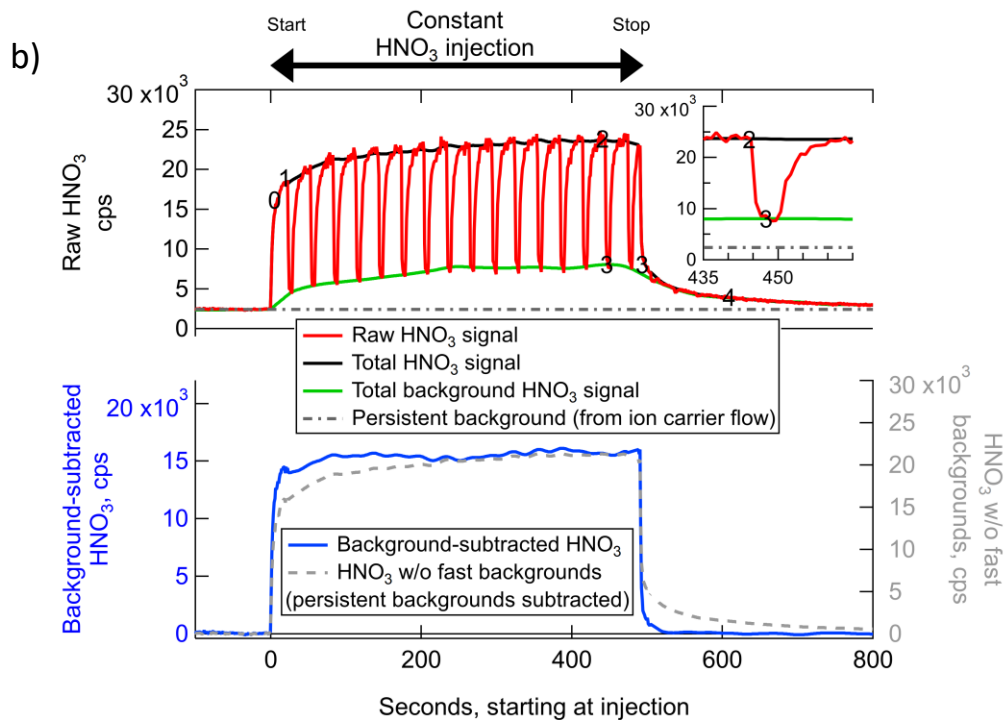
816 **Figure 1.** Schematic of the new, co-axial, low-pressure IMR design for CIMS. This is a two-dimensional cross
817 section of the cylindrical IMR along the axis of flow, and it is not to exact scale. Black lines represent stainless
818 steel surfaces, green and blue lines represent PTFE Teflon, and red/yellow lines represent FEP or PFA Teflon.
819 Constant mass flow into the IMR is controlled using a variable orifice. Water vapor can be added through a port
820 in the orifice plate, in order to keep the environmental conditions in the IMR more constant. The sample flow
821 and ion flow are passed through laminizer elements to limit the effects of turbulent diffusion to the IMR walls.
822 Ion-molecule adducts are formed via diffusive mixing in the drift region. The ability to enhance the mixing of
823 ions into the sample flow by applying an electric field between the drift region wall and the exit of the sample
824 flow laminizer was also included (not shown), but led to only modest enhancement and was not used in the
825 measurements presented herein. A mirrored pumping scheme also prevents turbulence and limits the effects of
826 wall interactions. Adducts are sampled through a capillary into the time-of-flight mass spectrometer.

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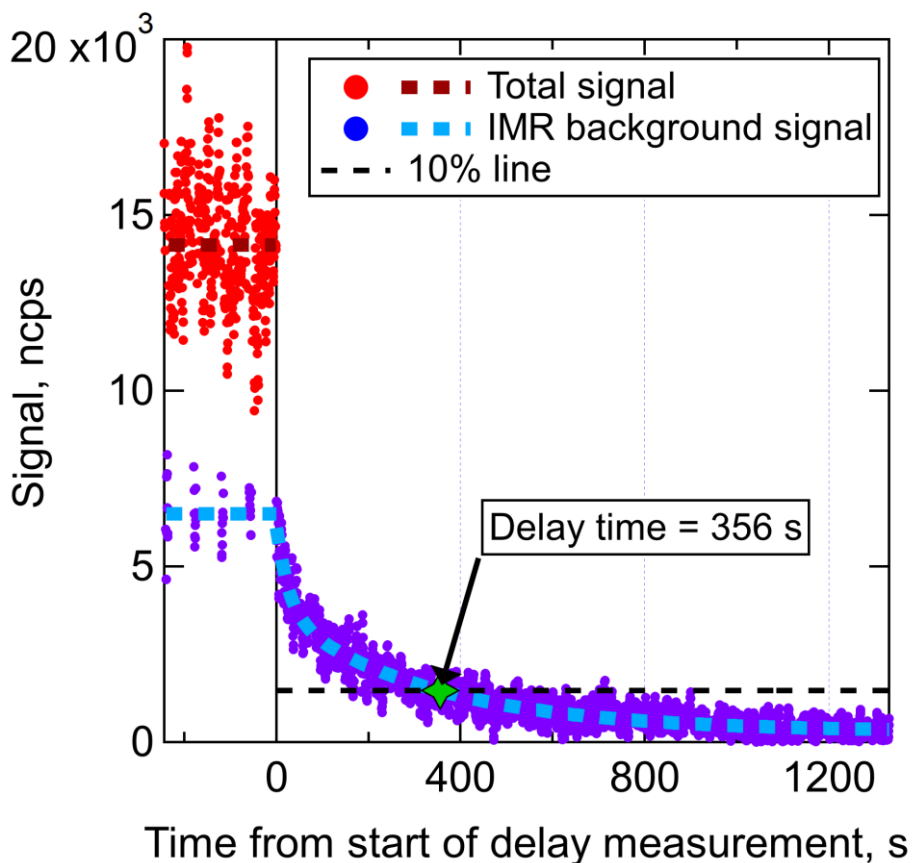


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830 **Figure 2.** a) Schematic illustrating how wall interactions affect the measurement of low volatility or polar gases
 831 for several experimental conditions, and b) example of the fast zero method of background subtraction for the
 832 measurement of constant concentration of ~2 ppbv nitric acid from a permeation tube. The times
 833 corresponding to each panel in a) are labeled on the time series in panel b). The bottom of panel b) illustrates

834 the benefits of performing frequent background signal subtractions as opposed to only subtracting the
835 persistent background signal.



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837 **Figure 3.** Delay time measurement of a DHN ($C_9H_{19}NO_5$) in an I⁻ CIMS with the new IMR. Prior to the start of the
838 delay measurement, wall steady state had been achieved. The total signal is equal to the background-
839 subtracted signal plus the background signal. Regular background measurements were performed for 6 s of
840 each 1 min, illustrating that approximately half of the $C_9H_{19}NO_5$ that entered the IMR was interacting with the
841 walls prior to desorbing and being sampled. The delay time for this DHN, defined as the time required for the
842 signal to return to 10% of the original value, was determined to be 356 s.

843

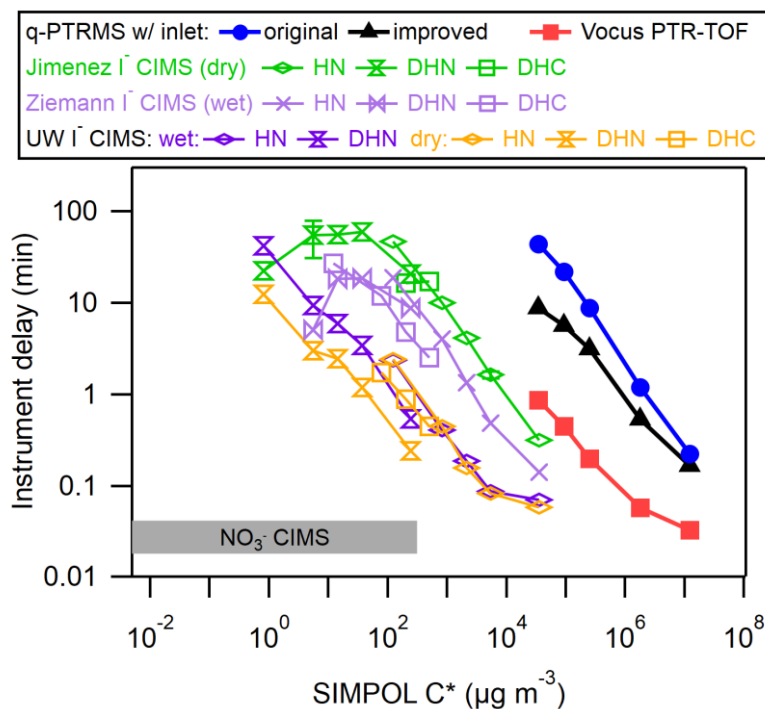


Figure 4. Delay times for a variety of organic molecules as a function of saturation vapor concentration (C^* , $\mu\text{g m}^{-3}$), compared with previous IMR designs including a q-PTRMS, Vocus PTR-TOF-MS, and several I⁻ CIMS instruments with different IMRs. The delay time in a nitrate (NO_3^-) CIMS is also shown for comparison. The organic molecules are described in Table S1.