The Paper

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

- #📚 #quick-zeros
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- Brett B. Palm, Joel A. Thornton

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 5...

Annotations

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🟢 key findings

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This framework and associated terminology applies to any instrument and ionization technique that samples compounds susceptible to wall interactions.

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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).

- **Strategy for reducing wall interactions**

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The final design requirement was that the IMR was capable of operating at a constant IMR pressure on an aircraft platform

- **Final requirement was pressure controlling**

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To prevent any molecules coming from the drift tube wall being sampled, half of the drift tube flow was pumped out along the drift tube wall and away from the MS capillary. According to diffusion calculations, only 4 % of the analytes are predicted to encounter a wall in the drift region under laminar flow conditions, and a small fraction of those molecules would diffuse back to the center to be sampled, essentially removing the effects of the drift region walls.

- **pump out the molecules near the wall before the MS entrance**

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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.

🔵 atmospheric implications

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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 approximately 5–7◦ could be used.

- **what's this?**

Highlight (Page 4)

after the orifice. Given these considerations, as well as time constraints prior to a field campaign, we opted not to test a conical diffuser at this time.

- **Wanted to try a conical diffuser, but didn't.**
-

- **Future direction!**

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However, only modest total detected ion enhancements were measured when applying such electric fields.

- **tried an electric field to induce mixing? interesting.**

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in the moments just after t = t0, e.g., t = t1 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.

- **dynamic background signal and persistent background signal... good for a comparison slide**

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At t = t1, 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.

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At times equivalent to t = t2 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.

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After more time passes and t = t4 has been reached, the amount of analyte on the walls has been partially depleted since the wall system is now out of steady state. There is still a flux from the wall without a complementary flux to the wall to replenish the analyte. The flux from the wall is also lower at this time than at t = t3 because the concentration of analyte on the wall is lower. At a subsequent time long after t = t4, all of the analyte would eventually desorb from the walls, and the dynamic background signal from the inlet walls would reach zero

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As illustrated in Fig. 2a, this task is often made complicated by the fact that the ratio of the background signal to the background-subtracted signal can vary widely during measurements. The entire signal could be due to background signal (as at t = t3), due to gas-phase signal (t = t0), or some dynamic mix of the two (t = t1 and t = t2). Even when all signal is coming from the background, the magnitude of the background can also change (t = t4).

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As seen in the inset of Fig. 2b, the decay of the analyte signal occurs in two parts (or more). The first part is the rapid exponential decay as the volume of the inlet is cleared out of any remaining gas-phase analyte, and stability of flows is achieved. The next part, which applies when the analyte is of relatively lower volatility or higher Henry's law constant into wall-adsorbed water, is the typically slower exponential decay that accompanies desorption of the analyte from the walls. There may be multiple decay constants with varying timescales (e.g., as illustrated in Krechmer et al., 2018) if there are multiple types of wall surfaces (e.g., both Teflon and stainless steel in the same IMR) or voids with different residence times.

🟣 theoretical framework / equations

Highlight (Page 3)

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.

- **How pressure was controlled**

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As part of the process of designing the IMR with laminizers, fluid modeling simulations were performed to visualize the effects of turbulent vs. laminar flows. Two example cases are depicted in Fig. S1 in the Supplement.

- **Cool for the presentation**

Highlight (Page 8)

Any background measurement value taken at a later time, e.g., at t = t4 or at t t4 (a measure of the persistent background), would no longer represent the magnitude of the background at t = t2 and would underestimate the contribution of background signal to the total at the time the background measurement was initiated. This aspect is critical to the determination of so-called tails of measurements, e.g., when an aircraft platform is measuring in an analyte plume and then abruptly exits the plume to analyte-free air. The signal appears to decay as between t = t3 and t = t4 (and beyond) in Fig. 2b. The entirety of this signal is often due to background signal.

- **oooo!!**

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the data would be falsely reporting a nonzero concentration (i.e., tail) of the analyte after exiting the plume, which could lead to large errors in measurementmodel comparisons that would not be captured by simple uncertainties estimated by replicate calibrations.

🔴 instrument methods

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(Neuman et al., 2002; Crounse et al., 2006; Le Breton et al., 2012; Lee et al., 2018).

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We suggest practices for accounting for wall interactions, both in experimental measurements and when performing calibration measurements that will be later applied to experiments. #calibration , #background , #Fast-zeros , #IMR , #Zeros

- **boom.**

Highlight (Page 3)

n the commercially available lowpressure 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). 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.

- **Previous IMRs**

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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.

- **Because the pressure is lower, there's really no need for the "jet-induced" mixing. The diffusivity is so high that the mixing will occur anyway**

🟡 background / literature context

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and a measurement protocol to accurately capture the time dependence of analyte concentrations.

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The rates of flux of analyte molecules to and from these wall surfaces can depend on complex factors of water vapor concentration, coanalyte concentrations, etc. (Pagonis et al., 2017; Deming et al., 2019; Liu et al., 2019), leading to difficult interpretations of data that are often not consistent across different studies.

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

- **Background measurement is important, but not standardized**

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To examine and quantify the improvements made in this design, we start with a comprehensive discussion of the origin and meaning of wall effects.

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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.

- **no real perfect way to chose a bakcground**

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The effects of wall interactions in such an inlet are minor relative to the effects of wall interactions inside the IMR (as demonstrated in Fig. 2).

Image (Page 6)

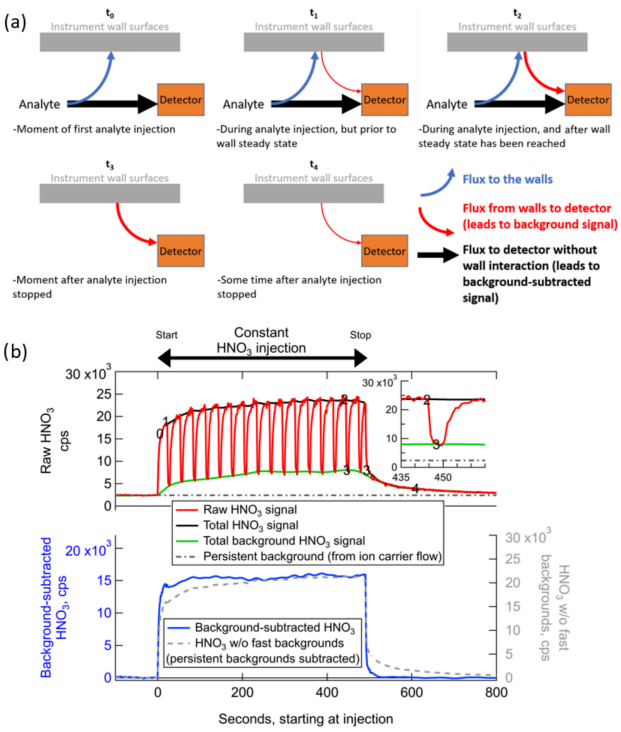

Figure 2. **(a)** Schematic illustrating how wall interactions affect the measurement of low-volatility or polar gases for several experimental conditions, and **(b)** example of the fast-zero method of background subtraction for the measurement of constant concentration of ~ 2 ppbv nitric acid from a permeation tube. The times corresponding to each panel in **(a)** are labeled on the time series in panel **(b)**. The bottom of panel **(b)** illustrates the benefits of performing frequent background signal subtractions as opposed to only subtracting the persistent background signal.

- **fast-zero method**

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As discussed further in Sect. 3.3, the amount of time required for the dynamic background signal to decay to 10 % of the original signal (i.e., to near zero) can range from less than 1 s to tens of minutes or more, depending on the volatility of the analyte as well as environmental conditions and surface types.

Highlight (Page 8)

he ideal way to determine the true concentration of the analyte in sampled air is to measure the amount of signal coming from the background sources at all points in time and subtract it from the total signal.

- **!!!!!! a main point. For a transition slide**

Highlight (Page 8)

Instead, a practical method for determination of background signal is to measure the instantaneous flux of analyte off the walls using high-frequency, short-duration injections of analyte-free gas (typically UHP N2) interspersed among the normal measurement of total signal and then interpolate

between these background measurements. This method is has been referred to as performing “fast zeros”.

- **!!!**

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The new IMR was shown to have delay times that were 3–10 times shorter than previous IMR versions. This translates to higher signal to noise of the background-subtracted signal (i.e., the signal that did not interact with walls), less influence from possible surface reactions, and easier interpretation of measured time series.

🟠 uncertainty & limitations

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Future low-pressure IMR designs could aim to further minimize wall effects in this region directly downstream of the variable orifice.

- **Future direction!**

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For recent aircraft measurements using this IMR, these 6 s background measurements were performed once per minute, striking a balance between minimizing background interpolation errors while maximizing the duty cycle of taking ambient measurements. One could imagine taking a 6 s background (or shorter, e.g., 4 s) as fast as every 20–30 s to capture extremely rapid changes in some specific circumstances, but information about the same temporal changes in backgroundsubtracted signal would be lost. Conversely, if the analyte concentrations are known to be relatively constant, e.g., in a laboratory experiment, then the intervals between background determinations could stretch much longer without leading to substantial interpolation errors.

- **considerations that must be made!**

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The distinction between background-subtracted ncps and background (including dynamic and persistent background) ncps, which add to total ncps, is necessary. As illustrated in Fig. 2b, when a constant concentration of HNO3 (approx. 2 ppbv) from a permeation tube was added into the inlet, neither the background counts per second nor the total counts per second were constant functions of the amount of HNO3 injected. The background-subtracted counts per second were constant, making

that value the only properly deterministic calibration constant that can be applied regardless of the relative amounts of background vs. backgroundsubtracted signals. Therefore, it is also recommended that the same background subtraction be performed on both calibration data and field/laboratory measurement data.

- **Woah... this is a really good point.**

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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.

- **another great point. Dont put the perm tube right up to the instrument.**

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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 is a quantification example!**

Highlight (Page 11)

In general, the delay times for the coaxial 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.

- **!!! results.**

🔘 questions / future work / unanswered

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But akin to Heisenberg’s uncertainty principle, one cannot precisely measure both the total signal and the background signal at the same time.

- **LOL. I was scared when I saw "Heisenberg" while skimming. Funny.**

Wow!

Highlight (Page 5)

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.

- **Main point here is that it is the IMR that leads to the most wall loss. The inlet tube is pretty high pressure and that limits the wall loss.**