

Interfacing Atmospheric Flow Tube to Ion Mobility Spectrometry

FY 2021 Final Report

September 2021

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Executive Summary

An atmospheric flow tube (AFT) provides extended ion-molecule reaction times of 2-3 seconds compared to milliseconds in typical mass spectrometers. This results in several orders of magnitude enhanced sensitivity allowing for vapor detection at the parts-per-quadrillion levels when an AFT is coupled to a mass spectrometer (MS). The goal of this project was to demonstrate the feasibility of integrating an AFT ionization source to a more portable ion mobility spectrometer (IMS).

This project was successful in integrating AFT to IMS, as shown in Figure ES.1. The PNNL team demonstrated measurable ion signal from an AFT-IMS with a Faraday plate detector. Reasonable ion signals were detectable at low flow rates approaching 1 m/s. This is close to the flow rates used with the AFT-MS, which has demonstrated parts-per-quadrillion vapor detection.

Vapor detection enables non-contact detection of a variety of illicit substances for various applications including cargo screening, mail sorting facilities, and checkpoints. With further improvements to enhance detection, AFT-IMS has the potential to allow ultra-trace vapor detection in a more portable device.

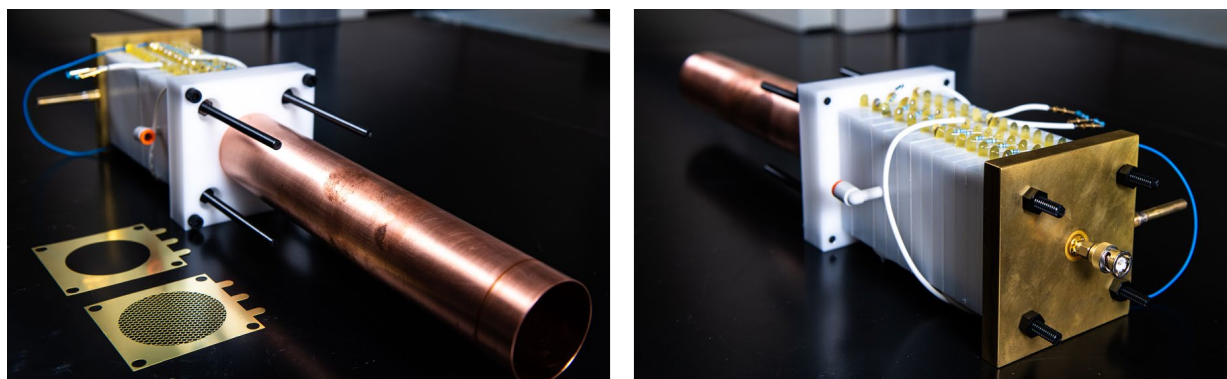


Figure ES.1. An atmospheric flow tube interfaced to an ion mobility spectrometer.

Acknowledgments

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Acronyms and Abbreviations

ADT	atmospheric drift tube
AFT	atmospheric flow tube
IMS	ion mobility spectrometry
MS	mass spectrometry
NG	nitroglycerin
PNNL	Pacific Northwest National Laboratory
ppq	parts per quadrillion

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1.0 Introduction

The detection and interdiction of explosives, illicit drugs, and other toxic chemicals is important for national security. Detection of these materials in the field (e.g., for airport security and border control) requires small, portable instruments that are robust and have minimal power requirements. The purpose of this project was to help develop a new generation of a field deployable detection technology with improved sensitivity and selectivity over current capabilities. Specifically, the project involved the integration of an atmospheric flow tube (AFT) with ion mobility spectrometry (IMS).

PNNL's atmospheric flow tube-mass spectrometer (AFT-MS) provides real-time detection and identification of airborne molecules of explosives, drugs, and other toxic chemicals at concentrations in the low parts per quadrillion (ppq) (5 publications, 4 patents, and an R&D 100 Gold Medal)¹⁻⁵. The mass spectrometer is large and not very portable. Interfacing the AFT with an IMS provides an option for a smaller footprint and possibly hand-held device with ultra-trace vapor detection. The AFT technology is based on atmospheric pressure chemical ionization mechanisms, as is current IMS technology. The AFT should theoretically be capable of interfacing with an IMS and provide similar detection enhancements as demonstrated with mass spectrometers. The PNNL team captured this concept in a patent; however, it had not been demonstrated. The objective of this effort was to demonstrate the feasibility of interfacing AFT with IMS to attract interest for commercialization and external funding.

The AFT provides extended ion-molecule reaction time (2-3 seconds instead of milliseconds in typical mass spectrometers), which enables several orders of magnitude enhanced sensitivity. This was achieved by moving the ion source away from the inlet of the mass spectrometer (~60 cm) as shown in Figure 1. A challenge resulting from the additional reaction time is that, due to ion diffusion, the ion density decreases as the time increases. This presents a difficulty for IMS, which uses a Faraday plate detector that is prone to high electronic noise and limits detection of low ion signals. The longer reaction times required for ppq sensitivity may result in undetectable ion signals. The key is to find an appropriate balance of ion reaction time and ion density, as well as to discover methods to improve ion signal, such as reducing detector noise (shielding) and increasing ion density at atmospheric pressure.

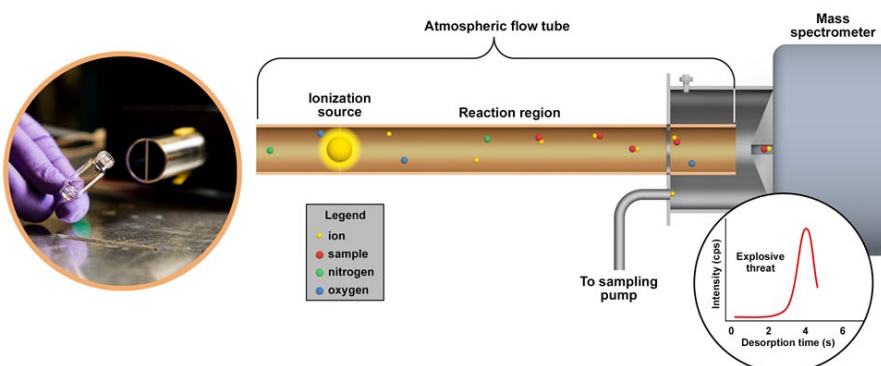


Figure 1. Operational diagram of an atmospheric flow tube-mass spectrometer.

A field portable device capable of detecting illicit substances is relevant to counter terrorism and non-proliferation needs and thus development of the AFT-IMS can have significant impact to national security applications.

The tasks outlined for this project were based on a sequential stepwise process to assess the feasibility of interfacing AFT to an IMS. The tasks were:

- Task 1: Demonstrate ion signal with respect to ion transit time in an AFT.
- Task 2: Evaluate signal with improvements in detector noise and ion density.
- Task 3: Assemble breadboard AFT-IMS.
- Task 4: Determine detection levels of the breadboard AFT-IMS.

2.0 Results

2.1 Demonstrate ion signal with respect to ion transit time

An AFT (2-inch diameter) was interfaced to a breadboard IMS to measure total ion current reaching a Faraday plate detector. The gating shutters in the IMS were “open” to allow the measurement of the total DC current reaching the detector. A corona discharge was used as an ionization source. The AFT-IMS components are shown in Figure 2 and the experimental setup is shown in Figure 3. An initial goal was to measure ion current as a function of ion residence time. Longer ion residence times provide more reaction time and thus increase sensitivity to analytes. However, the total ion current decreases with an increase in ion residence time, which reduces the measurable signal. The ion residence was controlled by either varying the flow rate on the flow tube or adjusting the voltage gradient across a drift tube.

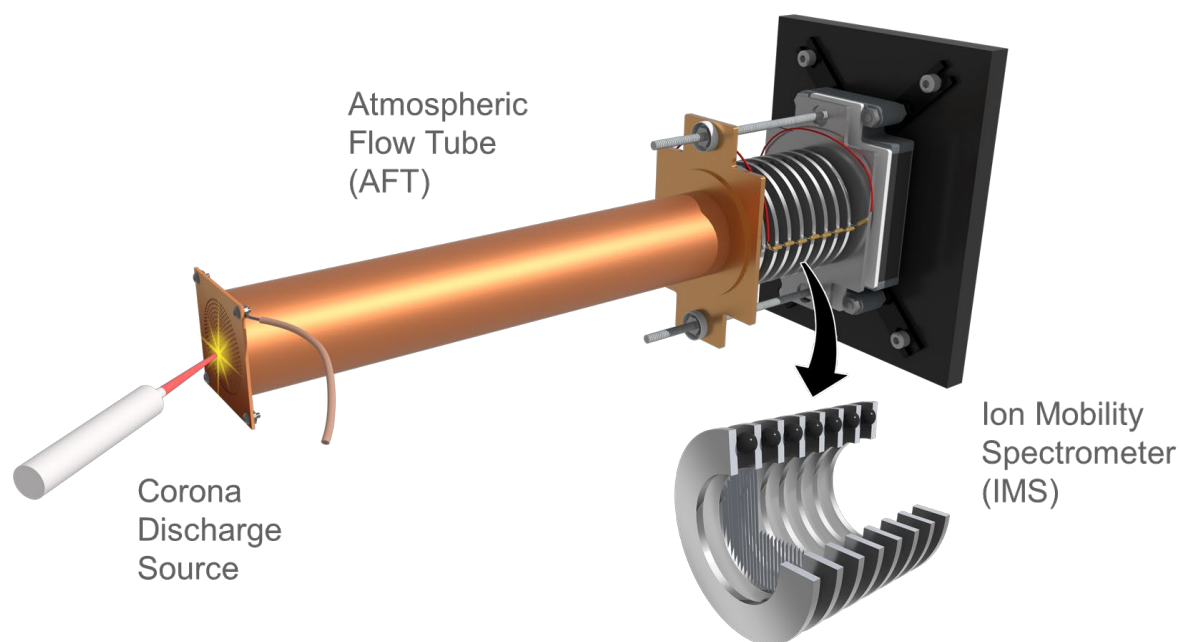


Figure 2. AFT-IMS components.

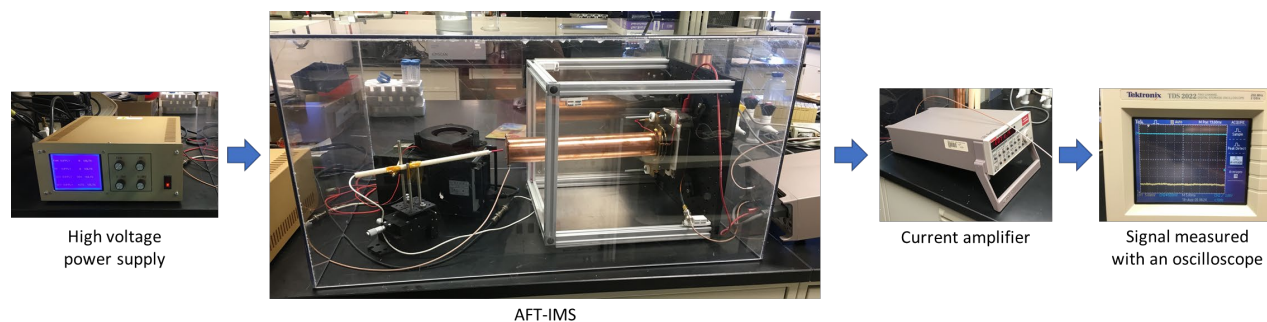


Figure 3. Experimental setup of AFT-IMS. A fan was used to create flow down the AFT.

Ion signal was measured with different flow velocities down the AFT. The computer fan voltage was adjusted and produced reproducible flow velocities. The corona discharge ion source voltage was set to -4200 V and the IMS cell voltage was set to -1000 V (monitoring negative polarity ions). The effect of flow down the tube is shown in Figure 4 with current amplifier set to 10^8 (left) or 10^9 (right). Ion signal was reproducible with higher flow velocities producing higher ion signals.

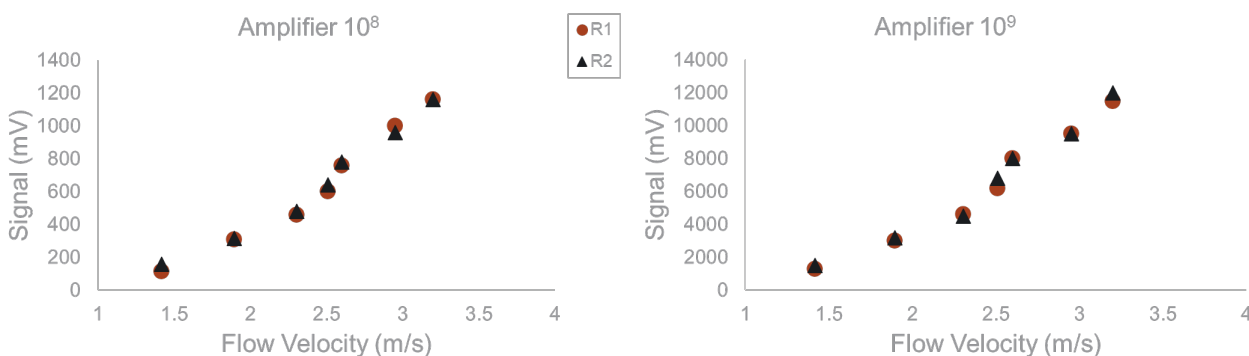


Figure 4. The effect of flow down the tube on ion signal for an AFT-IMS. The different symbols represent replicate measurements.

The effect of flow and cell voltage on ion signal was also investigated and the results are shown in Figure 5. In this case, the corona voltage was fixed at -4200 V and the IMS cell voltage was varied between 0 and -1000 V (monitoring negative polarity ions). The amplifier was set to 10^8 . Ion signal was reproducible. Higher cell voltage increased ion signal to a point depending on flow velocity, and then the ion signal plateaued at higher cell voltages.

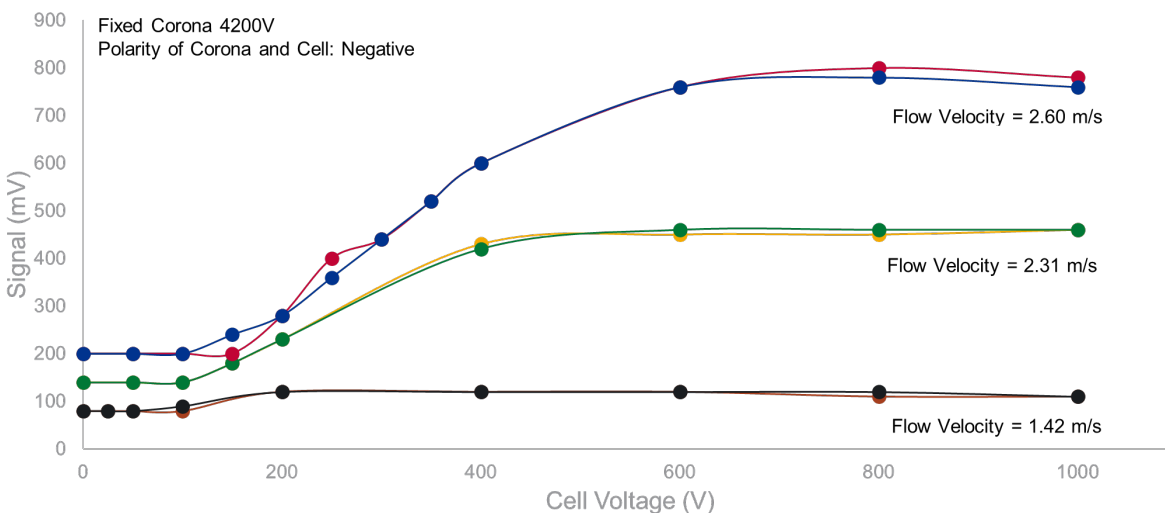


Figure 5. The effect of flow and cell voltage on ion signal.

As an alternative to air flow, voltage potential was used to move ions in an atmospheric drift tube-ion mobility spectrometer (ADT-IMS) setup as shown in Figure 6 and Figure 7.

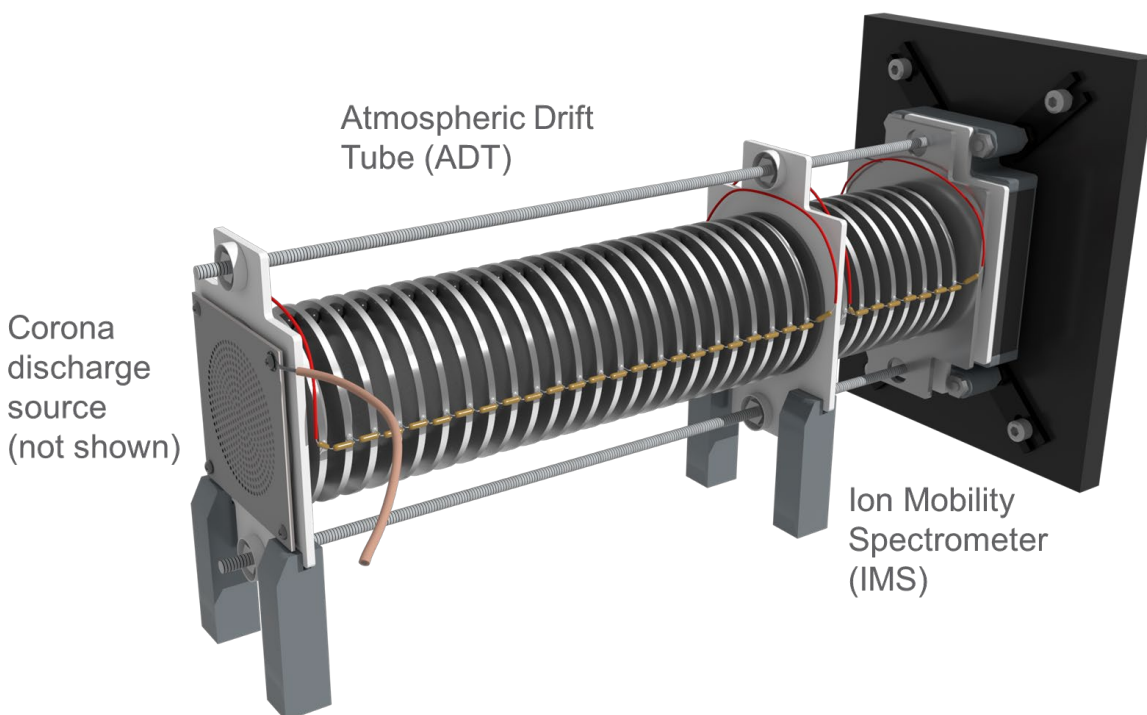


Figure 6. Components of an atmospheric drift tube-ion mobility spectrometer.

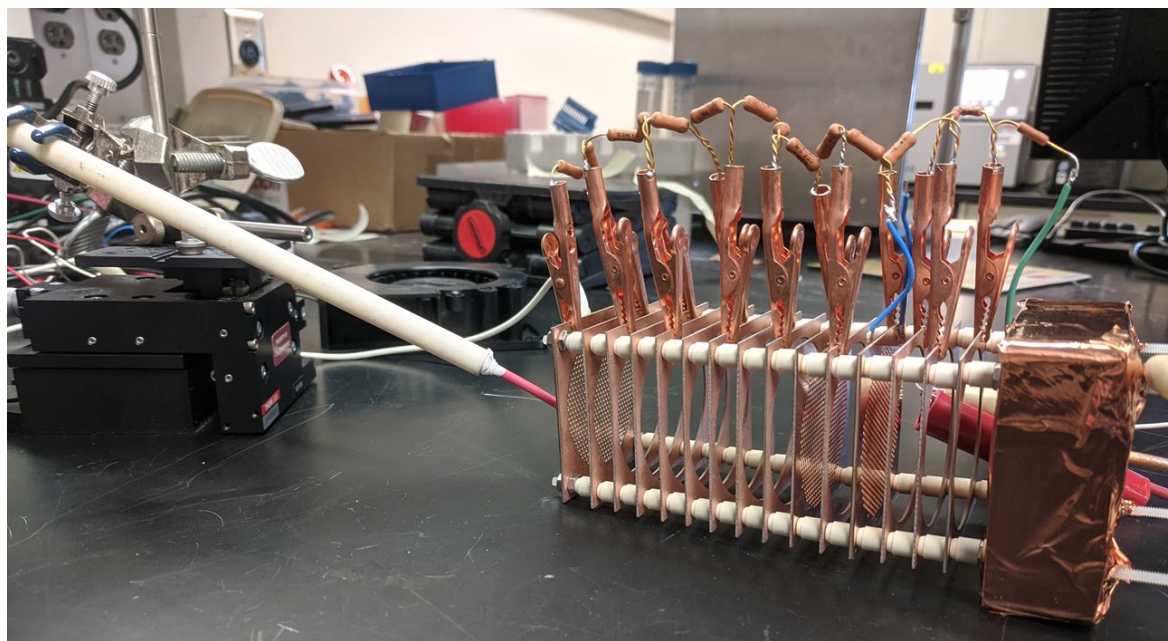


Figure 7. Experimental setup of ADT-IMS with a corona discharge source at the front end and a fan used for flow.

Ion signal was measured with different fan, cell, and corona voltages as shown in Figure 8. Cell and corona voltages were stepped together to maintain a difference of 3500 V. The fan was used to get a detectable ion signal. An ion signal above baseline was not observed without the fan. Placing an additional screen in front of the discharge at a higher electric potential negated

the need for the fan to produce a measurable signal. Increasing the cell and corona voltages resulted in increased ion signal.

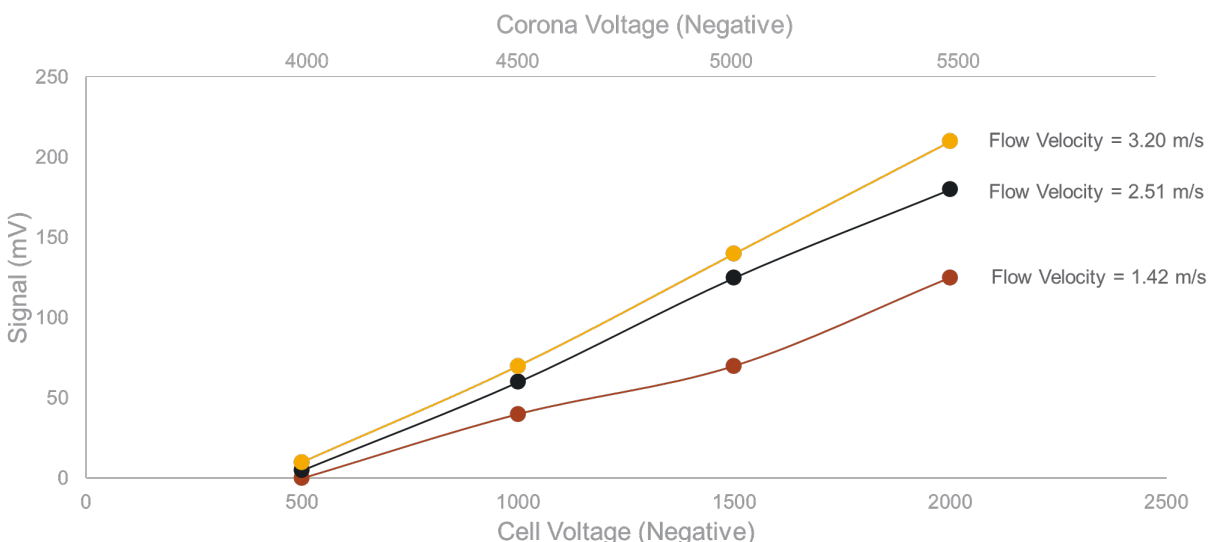


Figure 8. Ion signal measured with ADT-IMS with different fan, cell, and corona voltages.

Overall, the PNNL team demonstrated measurable ion signal from an AFT with a Faraday plate detector. Reasonable ion signals were detectable at low flow rates approaching 1 m/s. This is close to the flow rates used with the AFT-MS, which has demonstrated parts-per-quadrillion vapor detection.

2.2 Evaluate signal with improvements in detector noise

Once the preliminary device in Task 1 was characterized, efforts were made to increase ion signal. These efforts were directed toward reducing detector noise and increasing the original ion density at the ion source.

One of the ways evaluated to increase ion signal was by using both a positive and negative corona ion source. With the AFT-IMS flow at 2.5 m/s, negative ion signal was measured while changing cell voltage and using a dual corona setup to add both positive and negative ions as shown in Figure 9. With the current to voltage amplifier set to a gain of 10^9 , $1 \text{ V} = 6.24 \times 10^{10}$ ions/second. The comingling of positive and negative ions led to an enhanced negative ion signal, potentially due to increased ion density. The PNNL team captured this observation in a patent (U.S. Patent No. 11,043,370). These results are counterintuitive as one might expect ion recombination to cause loss of ion signal with the addition of counterions.

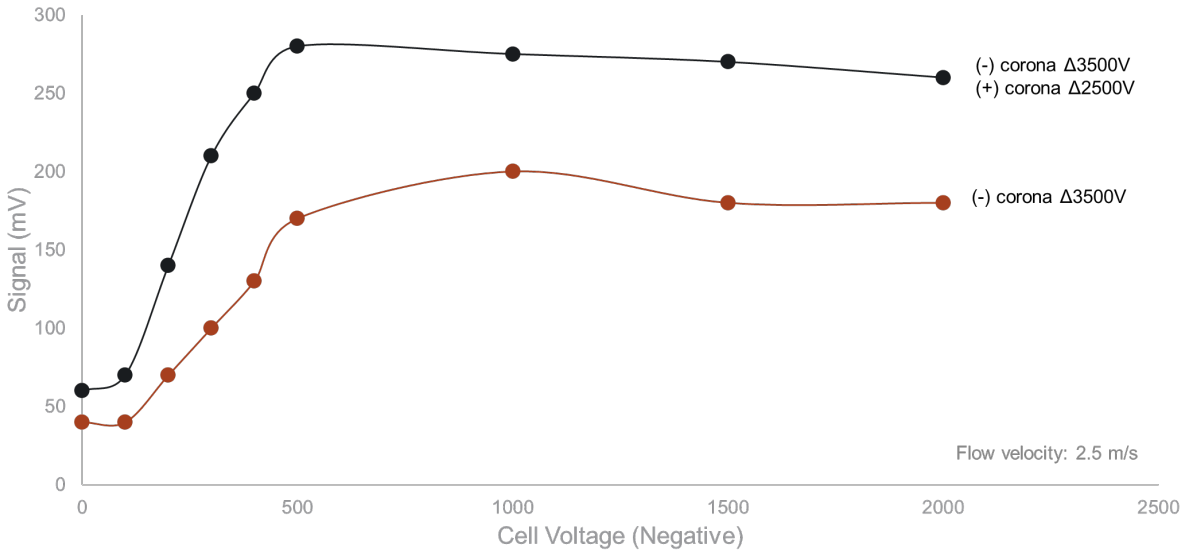


Figure 9. Negative ion signal measured at a range of cell voltages with AFT-IMS and dual corona sources (negative and positive).

2.3 Assemble breadboard IMS interfaced with an AFT

Another breadboard AFT-IMS was created with an enclosed IMS to better control and measure flow rates and ion reaction times as shown in Figure 10. An ion gating option was added to the IMS to produce ion mobility spectra. Parts were machined for the front-end of the AFT to house the corona sources and enable connection of a controlled flow.

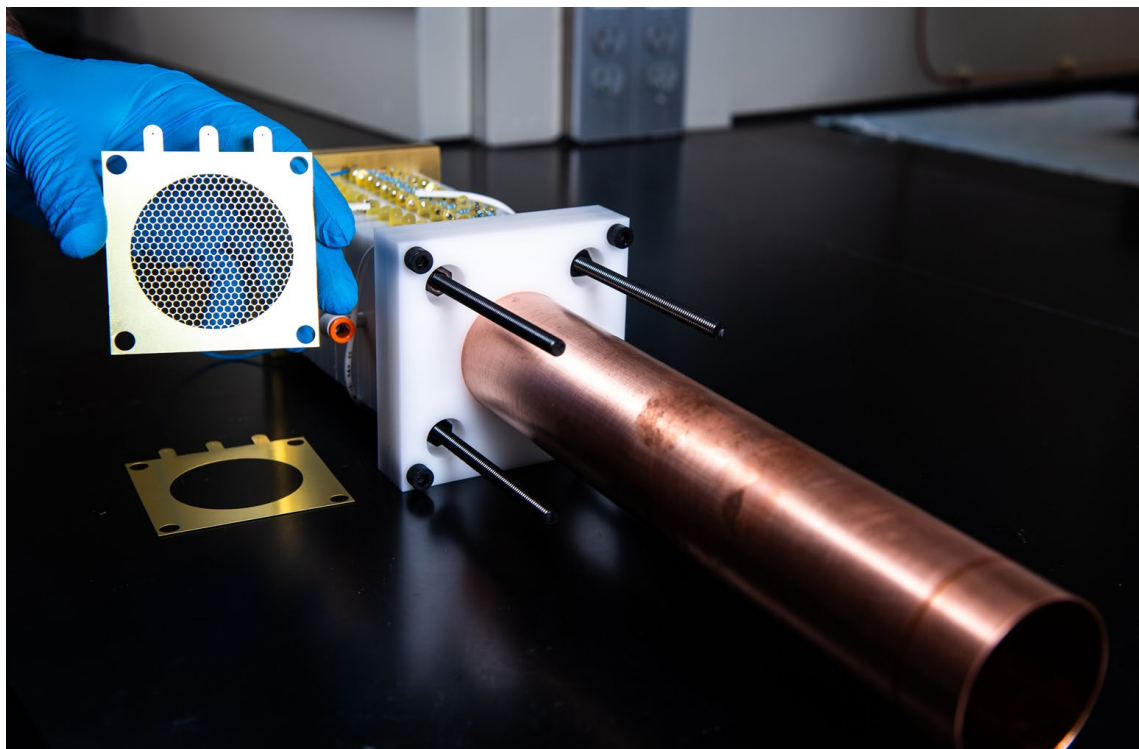


Figure 10. AFT interfaced to an enclosed IMS with improved ability to control and measure flow rates. As examples of the interior of the IMS, a ring and a screen are shown separately.

A new data acquisition setup enabled saving and reproduction of measured ion signal. Initial spectra demonstrating a peak with the AFT-IMS from negative ions in room air is shown in Figure 11.

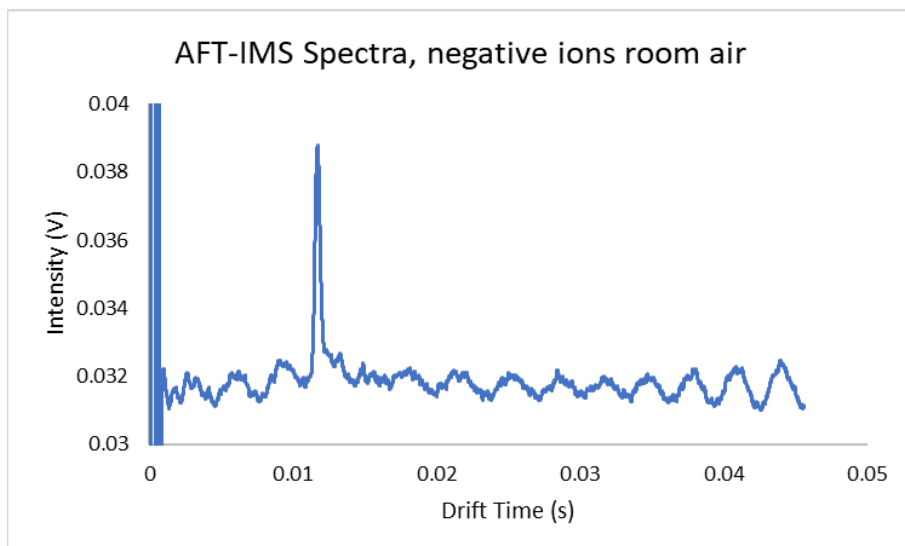


Figure 11. AFT-IMS spectra of a peak from negative ions in room air.

2.4 Determine vapor detection levels of the breadboard AFT-IMS

With successful integration of the AFT to an IMS, ion signal was measured for a representative chemical to assess initial detection levels. The detection of nitroglycerine (NG) is demonstrated with the AFT-IMS spectra in Figure 12. Future efforts could improve ion signal by decreasing ion loss and determining ways to further reduce detector noise.

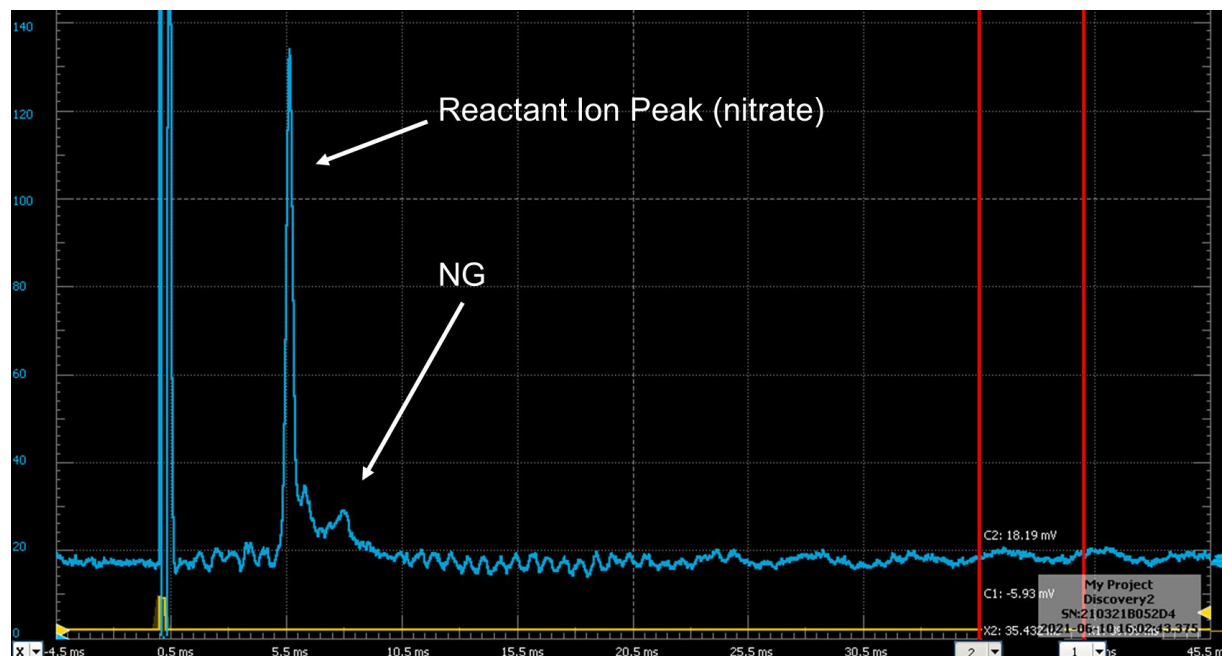


Figure 12. AFT-IMS spectra showing the nitrate reaction ion peak and a nitroglycerine (NG) peak.

3.0 Summary

This project was successful in integrating AFT to IMS. The PNNL team demonstrated measurable ion signal from an AFT-IMS with a Faraday plate detector. Reasonable ion signals were detectable at low flow rates approaching 1 m/s. This is close to the flow rates used with the AFT-MS, which has demonstrated parts-per-quadrillion vapor detection.

In evaluating the AFT-IMS, it was noted that ion signal was reproducible with higher flow velocities producing greater ion signals. Higher cell voltage increased ion signal to a point depending on flow velocity, and then the ion signal plateaued. A method to enhance ion signal involved using two corona sources, a negative and a positive ion source. When monitoring negative ions, for example, by introducing positive ions the ion signal noticeably increased.

A breadboard AFT-IMS was created with an enclosed IMS to better control and measure flow rates and ion reaction times. Further, the addition of an ion gate allowed for examination of both total ion current and ion peaks. Preliminary vapor detection of the chemical compound nitroglycerin was demonstrated, although the signal was lower than would be desired.

The remaining challenges to overcome are improving ion signal by decreasing ion loss and determining ways to further reduce detector noise. With further improvements to enhance detection, AFT-IMS has the potential to allow ultra-trace vapor detection in a smaller footprint and possibly hand-held device. Vapor detection enables non-contact detection of a variety of illicit substances for various applications including cargo screening, mail sorting facilities, and checkpoints. An ultimate goal would be to enhance detection capabilities in a more field deployable package.

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