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Ion Mobility Mass Spectrometry: Direct Isotope Abundance Analysis

Manuel J. Manard, Ph.D., Stephan Weeks, Ph.D., and Kevin Kyle, Ph.D.
National Security Technologies, LLC

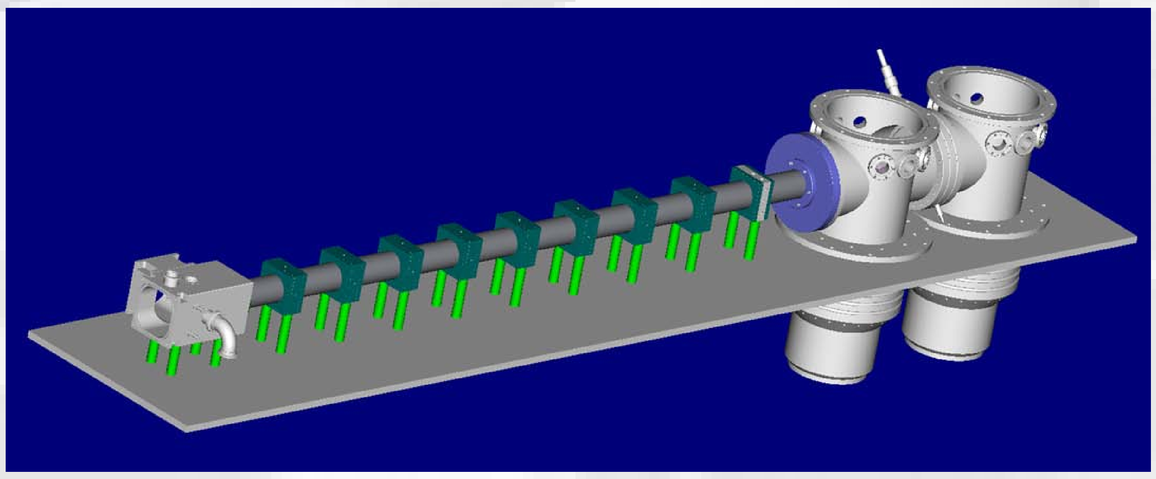
Goals and Objectives

The overall objective of this project is developing instrumentation and methods to produce near real-time isotope distributions with a modular mass spectrometric system that performs the required gas-phase chemistry and separations. The system couples a high-resolution ion mobility (IM) drift cell to the front end of a mass spectrometer (MS) allowing for chemical separation prior to isotope distribution analyses. This will yield isotope ratio measurement capabilities with minimal sample preparation.

Introduction

The nuclear forensics community is currently engaged in the analysis of illicit nuclear or radioactive material for the purposes of non-proliferations and attribution. One technique commonly employed for gathering nuclear forensics information is isotope analysis. At present, the state-of-the-art methodology for obtaining isotopic distributions is thermal ionization mass spectrometry (TIMS). Although TIMS is highly accurate at determining isotope distributions, the technique requires an elementally pure sample to perform the measurement. The required radiochemical separations give rise to sample preparation times that can be in excess of one to two weeks. Clearly, the nuclear forensics community is in need of instrumentation and methods that can expedite their decision making process in the event of a radiological release or nuclear detonation.

Accordingly, we are developing instrumentation that couples a high resolution IM drift cell to the front end of a MS. The IM cell provides a means of separating ions based upon their collision cross-section and mass-to-charge ratio (m/z). Two analytes with the same m/z, but with different collision cross-sections (shapes) would exit the cell at different times, essentially enabling the cell to function in a similar manner to a gas chromatography (GC) column. Thus, molecular and atomic isobaric interferences can be effectively removed from the ion beam. The mobility selected chemical species could then be introduced to a MS for high-resolution mass analysis to generate isotopic distributions of the target analytes. The outcome would be an IM/MS system capable of accurately measuring isotopic distributions while concurrently eliminating isobaric interferences and laboratory radiochemical sample preparation.



Current design of the IMMS instrumentation

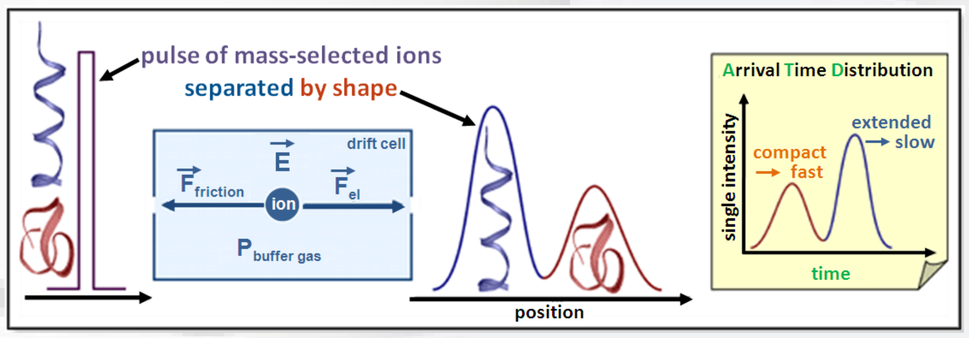
Methods

To obtain the mobility data, a pulse of ions are injected into the pressurized cell. The pressure in a cell is typically on the order of 5–10 Torr. The buffer gas is flowed through the cell so that a constant pressure can be maintained. A weak, homogeneous electric field is applied across the cell causing the ion packet to drift towards the exit orifice. The ion packet is rapidly thermalized by collision with the buffer gas. Ions exiting the cell are then selected and detected as a function of time in order to establish an arrival time distribution. The mobility of the ions K_o, is given by the equation below:

$$K_{\circ} = \left(l^2 \frac{273}{760T} \frac{p}{V} \frac{1}{t_a - t_{\circ}} \right)$$

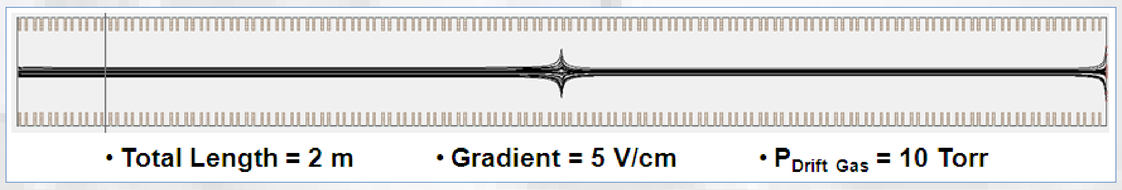
where l is the length of the drift cell, T is the temperature in Kelvin, p is the pressure of the buffer gas in Torr, V is the drift voltage, t_a is the arrival time of the ions acquired from the center of the ATD peak, and t_o is the time the ions spend outside of the cell. A plot of t_o versus p/V has a slope inversely proportional to K_o, which yields the collision cross-section of an ionic species.

Ion mobility drift cell principles of operation



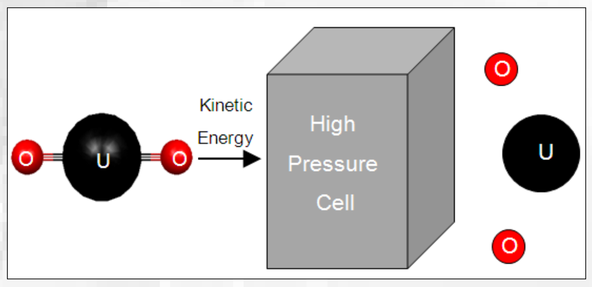
Results/Findings

We have used a commercially available software package (Simion 8) to simulate the trajectory of the ions in the drift tube. We have explored multiple experimental configurations to optimize the performance of the system.



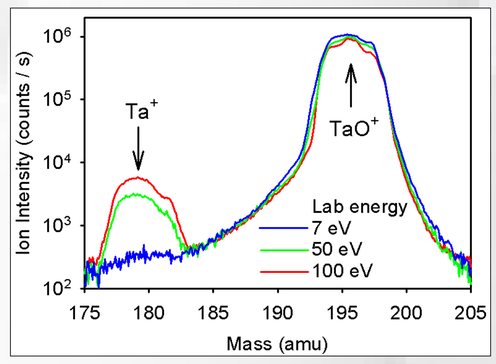
Simion 8 Drift Tube Simulation

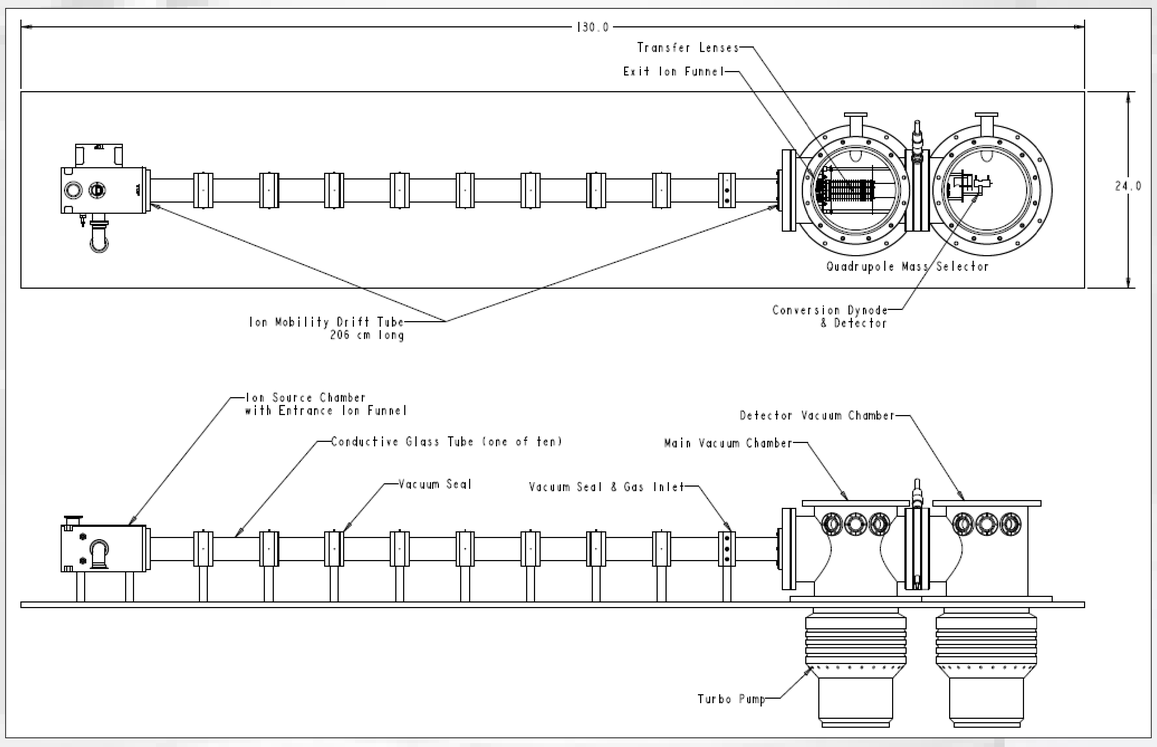
As part of a previous NA-22 project, we have demonstrated the capability of performing collision-induced dissociation (CID) of ions as a means of producing monoatomic metallic ions for mass spectrometric isotope analysis. If needed, CID can be utilized to remove molecular isobaric interferences from the system.



Schematic representation of CID principles

Mass spectra showing the formation of Ta^+ via CID of Ta^+O as a function of kinetic energy





Mechanical Drawing of IMMS Instrumentation (Preliminary)

Next Steps

The project will continue to move forward through the completion of the mechanical design of the system. Additionally, extensive research has been conducted to determine which type of ionization source would best be applied to the system. We have determined that radio frequency, glow discharge (rf-GD) sources would be a good fit for our application. The technique can be used to vaporize/ionize solid samples that are either electrically conductive or nonconductive and is highly efficient at generating relatively large amounts of atomic ions. Additionally, rf-GD has been successfully used to characterize nuclear and radioactively contaminated environmental samples with mass spectrometry.

Conclusions

An instrument that couples a high resolution IM drift cell to the front end of a MS is currently being designed and developed. When completed, the system will be capable of measuring isotope distributions for target analytes without the need for lengthy radiochemical separations prior to analysis. This is accomplished by utilizing the IM drift cell in a similar manner to a GC column to separate chemical species drifting through the cell based on their m/z ratio and their collision cross-section.

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POC: Charles Lohrstorfer, lohrstcf@nv.doe.gov 702-295-5688

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