

SIMION-Related ASMS 2014 Posters/Presentations

Effect of Extraction Electric Field on Radial Ion Confinement in a Linear Quadrupole Ion Trap Equipped with Angled-Wire Extraction Electrodes

Mon 648 - Steve C. Beu¹; Yu Chen²; Christopher L. Hendrickson²; Nathan K. Kaiser²; Alan G. Marshall^{2,3}; ¹S C Beu Consulting, Austin, TX; ²National High Magnetic Field Laboratory, Tallahassee, FL; ³Dept. of Chem. and Biochem., Florida State Univ., Tallahassee, FL

A Real Dual-Source System for Triple Quadrupole Mass Spectrometer

Mon 664 - Gang Li; Gangqiang Li; , Hang Zhou, CHINA

The Aerolens: An Evaluation Study based on Computational Methods and Mass Spectrometric Tests

Mon 668 - Dimitris Papanastasiou¹; Diamantis Kounadis¹; Alexander Lekkas¹; Athanasios Zacharos²; Ioannis Nikolos²; Ioannis Orfanopoulos¹; Emmanuel Raptakis¹; ¹Fasmatech, Athens, GREECE; ²Technical University of Crete, Chania, Greece

The after-life for radially ejected ions in the linear ion trap.

Mon 673 - Viatcheslav V. Kovtoun; Thermo Fisher Scientific, San Jose, CA

Simulations of Ion Motion in Toroidal Ion Traps

Mon 687 - Jessica M. Higgs; Daniel E. Austin; Brigham Young University, Provo, UT

A mass analyser utilising a toroidal DC electrostatic field: A theoretical approach

Mon 688 - Will Johnson; Swansea University, Swansea, UNITED KINGDOM

Study of the Impact of Gas Flow in a Microscale Ion Trap Operated at High Pressure

Mon 693 - Bruno Coupier; Dmitriy Chernookiy; Sorin Mitran; J. Michael Ramsey; UNC Chapel Hill, Chapel Hill, NC

Optimization of the Cylindrical Ion Trap Geometry Using Mesh Endcaps

Mon 694 - Dmitriy Chernookiy; Bruno Coupier; J. Michael Ramsey; University of North Carolina at Chapel Hill, Chapel Hill, NC

Improved Electrostatic Ion Trap for Charge Detection Mass Spectrometry

Mon 698 - Deven Shinholt; Martin Jarrold; IU Chemistry Dept., Bloomington, IN

Toroidal Multipole Expansion for the Design of Circular Ion Traps

Mon 696 - Steve Lammert¹; Ed Lee¹; Joe Oliphant¹; Randy Waite¹; Daniel Austin²; Dennis Tolley²; Karl Warnick²; ¹Torion Technologies, Inc, American Fork, UT; ²Brigham Young University, Provo, UT

Theory and application of instantaneous frequency in FTMS

Mon 700 - Oleg Yu. Tsybin¹; Anton N. Kozhinov²; Konstantin O. Nagornov²; Yury O. Tsybin²; ¹Saint-Petersburg State Polytechnical University, Saint-Petersburg, Russia; ²Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

Accurate Simulation of Image Charge Effects in Cylindrical and Harmonized FT-ICR Cells via Particle-in-Cell Method

Mon 703 - Joshua Driver²; Jon Amster¹; Andriy Kharchenko¹; Ron M.A. Heeren³; ¹University of Georgia, Athens, GA; ²Univ of Georgia, Athens, GA; ³FOM Institute AMOLF, Amsterdam, NETHERLANDS

Miniaturized Planar Electrode Linear Ion Trap (LIT) Mass Analyzer

Mon 706 - Ailin Li; Brett J. Hansen; Andrew T. Powell; Yuan Tian; Aaron R. Hawkins; Daniel E. Austin; Brigham Young University, Provo, UT

How far can ion trap miniaturization go? Space-charge limits and scaling parameters for very small cylindrical ion traps (CITs)

Mon 707 - Yuan Tian; Daniel Austin; Brigham Young University, Provo, UT

Understanding the Impact of Space Charge Upon the Sensitivity of Atmospheric Ion Sampling

Tue 374 - Charles Jolliffe; Serguei Savtchenko; Reza Javahery; IONICS Mass Spec Group, Inc., Bolton, CANADA

Development of a Hybrid Ion Mobility Spectrometry/Time-of-Flight Mass Spectrometer with Printed Circuit Board Technology

Tue 714 - Ian K. Webb; Tsung-Chi Chen; Xinyu Zhang; Sandilya V. B. Garimella; Randolph V. Norheim; Gordon A. Anderson; Yehia M. Ibrahim; Keqi Tang; Richard D. Smith; Pacific Northwest National Laboratory, Richland, WA

Simulation Driven Design and Development of Structures for Lossless Ion Manipulations

Tue 716 - Sandilya V.B. Garimella; Ian K. Webb; Yehia M. Ibrahim ; Aleksey V. Tolmachev; Keqi Tang; Gordon A. Anderson; Richard D. Smith; *Pacific Northwest National Laboratory, Richland, WA*

Investigation of Gas- and Ion-Dynamics in Heated Glass and Metal Inlet Capillaries: Work in progress

Tue 732 - David Mueller; Yessica Brachthaeuser; Valerie Derpmann; Sebastian Klopotowski; Markus Langner; Christine Polaczek; Hendrik Kersten; Walter Wissdorf; Thorsten Benter; *University of Wuppertal, Wuppertal, GERMANY*

Fundamental ion-molecule reaction studies at elevated ion temperatures and analytical application of an ion activation stage ('ion tunnel')

Tue 733 - Sonja Klee; Albrecht Brockhaus; Marco Thinius; Walter Wissdorf; Thorsten Benter; *University of Wuppertal, Wuppertal, GERMANY*

An efficient ion funnel operated at 100 mbar background pressure

Tue 736 - Sascha Albrecht¹; Jochen Barthel¹; Armin Afchine¹; Fred Stroh¹; Thorsten Benter²; ¹*Forschungszentrum Jülich GmbH, Jülich, GERMANY*; ²*University of Wuppertal, Wuppertal, GERMANY*

A Microfabricated Ionizer for High Pressure Mass Spectrometry

Tue 738 - Craig Cavanaugh¹; Kenion Blakeman¹; Tina Stacy¹; Stanley Pau²; J Michael Ramsey¹; ¹*University of North Carolina, Chapel Hill, NC*; ²*University of Arizona, Tuscon, AZ*

Experimental Validation of an Analytical Model for Trapped Ion Mobility Spectrometry

Wed 686 - Melvin A. Park¹; Karsten Michelmann²; Joshua Silveira¹; Mark Ridgeway¹; ¹*Bruker Daltonics, Inc., Billerica, MA*; ²*Bruker Daltonik GmbH, Bremen, GERMANY*

Technical Advances and Theoretical Performance Assessment of a Spatially Multiplexed Ion Mobility-Mass Spectrometer

Wed 688 - Katrina L. Leaptrot; Jody C. May; John A. Mclean; *Vanderbilt University, Nashville, TN*

Improving Ion Mobility Measurement Sensitivity by Utilizing Helium in an Ion Funnel Trap

Wed 698 - Yehia Ibrahim; Sandilya Garimella; Aleksey Tolmachev; Erin Baker; Richard D. Smith; *Pacific Northwest National Laboratory, Richland, WA*

Effect of Electrode Geometry on FAIMS Gas Flow Focusing and Lateral Diffusion

Wed 762 - Jean-Jacques Dunyach; Satendra Prasad; Michael Belford; *Thermo Fisher Scientific, San Jose, CA*

Characterization of surface induced dissociation in a multi-reflecting TOF - TOF mass spectrometer

Thu 690 - Aleksey Vorobyev; Andrey Trufanov; Sergey Kirillov; Anatoly Verenchikov; *MSC-CG, Bar, MONTENEGRO*

Investigation of the Influence of Laser Spot Size and Ion Trajectory to Mass Resolving Power of Dual-Polarity Time-of-Flight Mass Spectrometer

Thu 742 - Yi-Hong Cai; Yin-Hung Lai; Hsun Lee; Yi-Sheng Wang; *Genomics Research Center, Academia Sinica, Taipei, TAIWAN*

3D SIMULATION OF QUADRUPOLE MASS FILTERS WITH OFFSET AND TILTED RODS

Thu 747 - David Langridge; *Waters, Wilmslow, UK*

Optimizing Ion Optical Rail for Coupling a Drift Tube to a Mass Spectrometer

Thu 759 - Alex Mordehai; Nathan Sanders; Ruwan Kurulugama; Mark Werlich; *Agilent Technologies, Santa Clara, CA*

Rectangular Ion Funnel (RIF): Conceptualization and Analytical Performance of a New ESI-MS Interface for Structures for Lossless Ion Manipulations (SLIM)

Thu Room 307-308 - Tsung-Chi Chen; Ian Webb; Marques Harrer; Spencer Prost; Sandilya Garimella; Xinyu Zhang; Jonathan Cox; Randy Norheim; Brian Lamarche; Erin Baker; Aleksey Tolmachev; Gordon Anderson; Keqi Tang; Yehia Ibrahim; Richard D. Smith; *Pacific Northwest National Laboratory, Richland, WA*

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ABSTRACTS

3D SIMULATION OF QUADRUPOLE MASS FILTERS WITH OFFSET AND TILTED RODS

Thu 747 - David Langridge; Waters, Wilmslow, UK

Introduction

The performance of a quadrupole mass filter depends on the accuracy to which it is manufactured. Defects in the machining or positioning of the rods will introduce non-quadrupole components into the electric field which result in poor peak shapes and reduced resolution / transmission.

Prior calculations of imperfectly constructed quadrupole mass filters have generally been performed in 2D. While 2D simulations are computationally less demanding they rely on an approximation to the initial ion beam distribution, and cannot correctly model the fields at the entrance and exit of the quadrupole. Furthermore there are mechanical imperfections that are impossible to simulate in 2D, for example a rod with an axial tilt.

Methods

SIMION 8.1 (with surface enhancement) was used to simulate a 3D system comprising a stacked ring ion guide, a differential aperture and a quadrupole mass filter with pre-filters. The ion guide is at an elevated pressure relative to the quadrupole and a hard-sphere collision model was used for the interaction with the buffer gas. Gas flow through the differential aperture was calculated using the DSMC method. An ensemble of ions is run at a range of RF/DC values to generate a mass spectrum. Due to the reduced symmetry of systems with tilted rods memory constraints prevent simulation of the ion guide and rods. In this case ion properties are recorded in the prefilter and used as the initial ion distribution.

Preliminary Results/Abstract

A variety of systems with imperfections have been modelled in SIMION. Generally the imperfections were limited to a single change to a single rod to simplify the analysis of the effects. Imperfections include a vertical or horizontal positional offset of the rod, an axial tilt, or a change in the rod cross-section.

Initial 2D calculations were performed with comparable results to those in the literature. For example in the case of an offset rod the effects on the peak are strongly dependent on the polarity of the resolving DC applied to the offset rod.

3D calculations were then performed for the various imperfect systems. Comparison of the 3D results to the 2D results shows qualitative agreement in some respects, for example shifts in the peak position and the significant difference in peak distortion seen depending on the polarity of the resolving DC applied to an offset rod. However as with 3D calculations of perfect quadrupoles we see qualitative and quantitative differences between the 2D and 3D results, demonstrating the requirement for 3D simulation of these systems.

Calculation of the multipole components of the electric field within the quadrupole allow the effect on the field of a given imperfection to be characterised. We observe that the magnitude of the additional multipole components varies linearly with the degree of imperfection. Analysis of the multipole components of the field allows the effects on the peak to be interpreted in terms of the additional field components that are introduced.

Novel Aspect

3D simulation of the performance of imperfectly constructed quadrupole mass filters, including offset and tilted rods.

A Microfabricated Ionizer for High Pressure Mass Spectrometry

Tue 738 - [Craig Cavanaugh](#)¹; Kenion Blakeman¹; Tina Stacy¹; Stanley Pau²; J Michael Ramsey¹; ¹University of North Carolina, Chapel Hill, NC,²University of Arizona, Tuscon, AZ

Introduction

Handheld mass spectrometry promises rapid, in-field chemical analysis. Ion trap based high pressure mass spectrometry (HPMS) combined with current advances in vacuum pumps, electronics, and energy storage can potentially fulfill this promise. At HPMS pressures, which we define as the 1 Torr regime, the mean free path drops to approximately 10^2 ?m. An electron impact ionization source based upon a thermionic emitter is impacted by the mean free path because a large source-to-trap spacing is required to

insulate the trap from the hot filament. To circumvent the spacing and the large power draw of a thermionic source, a silicon-based, low-power, field emission microionizer capable of operating in close proximity to the ion trap was developed and characterized.

Methods

The microionizer is based upon semiconductor fabrication techniques. A layer of silicon nitride (< 2 μm) was deposited on a highly-doped silicon wafer, followed by a thin layer of highly-doped polysilicon (< 1 μm). Device geometry was defined by photolithography, while etching was performed through a combination of wet chemistry and deep reactive ion etching. The ionizer is mounted on a printed circuit board for incorporation into the cylindrical ion trap (CIT) electrode stack. A source-to-trap spacing of fewer than 500 μm was obtained with this set-up. The microionizer was tested in a custom, differential pressure mass spectrometer utilizing a miniature CIT ($r_0 < 500 \mu\text{m}$) for analysis and electron multiplier for detection.

Preliminary Results/Abstract

The microionizer is a field emission electron source designed to be compatible with the buffer gas including helium, nitrogen, and air. Microionizers with varying silicon doping, anode thicknesses, and geometric arrangements were studied. After fabrication, the feature morphologies were examined using scanning electron microscopy. Data including electron current density and mass spectra were recorded at the microionizer positioned approximately 1 cm from the ion trap, replacing a standard electron impact ionization source in our instrument. The microionizer was powered using short voltage pulses (< 1 ms) during the ionization period of mass analysis and required minimal power draw (< 100 mW). Electron current density was monitored using a Faraday cup detector in each buffer gas of interest from 1 mTorr to 1000 mTorr. Mass spectra of several analytes including xenon, toluene, and mesitylene were recorded at the traditional source-to-trap spacing. The ion source - trap geometry was also modeled using Simion v8.1 and compared to experimental results. Electrical contact and mechanical support of the microionizer was reengineered to decrease the source-to-trap distance to less than 500 μm . Initial mass spectra with the ion trap mounted microionizer in helium buffer gas have been positive and efforts are underway to gather data in air buffer gas.

Novel Aspect

The microionizer provides electron impact ionization with an unprecedented combination of low power consumption, pressure tolerance, and small form factor.

A Real Dual-Source System for Triple Quadrupole Mass Spectrometer

Mon 664 - [Gang Li](#); Gangqiang Li; , Hang Zhou, CHINA

Introduction

A conventional triple quadrupole mass spectrometer is usually combined with either an electrospray ionization (ESI) or an electron impact (EI) ionization source to form an instrument for specific application. When equipped with ESI, a triple quadrupole mass spectrometer can be coupled with a liquid chromatography or capillary electrophoresis (LC-MS and CE-MS, respectively) for analyzing samples in liquid phase. When equipped with EI, the triple quadrupole mass spectrometer can be used directly for analyzing gas phase samples or coupled to a gas chromatography to form a GC-MS system. Commercial triple quadrupole mass spectrometers are readily come with an ESI or an EI source, but not both in one instrument.

Methods

In this paper, we present a dual-source system for triple quadrupole mass spectrometer. In this system, the triple quadrupole mass spectrometer is coupled with an ESI ion source as well as an EI ion source, and the ESI and EI can be operated alternatively. To enable such operation, the EI source is arranged in-line with triple quadrupole while the ESI source is mounted off-axially. This arrangement has additional advantage to block neutral species which usually are produced by electrospray ionization from entering the quadrupole mass filter. Since the ESI and EI are operated under different pressures, a gate valve has been installed and differential pumping is implemented.

Preliminary Results/Abstract

When operated in ESI mode, the gate valve is opened to receive ions from the spray source. While during the EI operation, the gate valve is closed to ensure sufficient vacuum required by EI. To select ion beams from either ESI or EI, a set of novel transfer ion optics is designed, built and installed upstream of the triple quadrupole spectrometer. The ion optics comprises of a deflection component to bend ion beam 90 degree during the ESI operation. During the EI operation, a different set of voltages is applied to the deflection component so it will transfer ion beam axially. After passing through the focusing lens and before entering quadrupole mass filter, the ion beam will be transferred by an ion guide device, such as hexapole or octopole ion guide. Ion trajectory simulations had been handled by using SIMION8 and the results showed that this ion optics are capable of transmitting nearly 100% ions from ESI and EI source to the transfer guide and quadrupole mass filter.

Novel Aspect

By using dual-source arrangement, it is possible to build a hybrid instrument which has the performance of LC-MS and GC-MS.

A mass analyser utilising a toroidal DC electrostatic field: A theoretical approach

Mon 688 - Will Johnson; Swansea University, Swansea, UNITED KINGDOM

Introduction

A toroidal electrostatic analyser is described which utilises the unique focal properties of a spherical field. Its design is based on strong symmetry considerations whereby ions are trapped in cyclic motion within a 360° electrostatic sector and detected using image current detection. Detected frequencies are used to calculate very precise mass-to-charge ratios (m/z) of ions. The analyser may find applications in portable mass spectrometers, or as a new low cost design arising from a unique and simple fabrication. Properties such as low DC voltages and minimal size, combined with high sensitivity and mass resolution suggests that the device has very strong potential for a new class of mass measurement instrumentation.

Methods

Two approaches have been taken to investigate the properties of a spherical field for mass analysis. Firstly a program has been written in C# to calculate the transfer matrix for a 360° spherical field to a third order approximation. The matrix elements define aberrations according to initial beam conditions such as width, height, angular dispersion, fractional energy and mass dispersion.

Secondly a computational model has been developed in conjunction with SIMION 8.1 to simulate the motion of ions within a spherical field. The Shockley-Ramo theorem was used to calculate the charge induced on detection electrodes with respect to time. Time domain current is converted to frequency domain via fast Fourier transforms using a script written in the statistical computing package R.

Preliminary Results/Abstract

It has been demonstrated via the transfer matrix method that the analyser provides near perfect stigmatic and chromatic focussing every 360 degrees. To a first order approximation the frequency of an ion within the field is dependent upon only fractional energy dispersion and mass dispersion. Isochronous focussing is maintained through ensuring total ion beam energy is constant, thus the fractional energy dispersion of the beam is zero. As such, a 'nine-fold focussing' system is obtained where frequency is dependent upon only m/z . To a third order approximation, higher order terms in the transfer matrix are small but over time periods of ~0.1 s cause the orbit to deteriorate; creating a drift in detected frequency over time. This is well defined theoretically and may be accounted for during signal processing in a working device.

The SIMION approach has been used to verify results from the transfer matrix method. In order to characterise the analyser several properties have been investigated. Smaller optic axis radii provide smaller path lengths and therefore higher frequencies. Similarly larger DC potentials require greater initial ion energies for circular motion, thus higher frequencies are detected. Higher frequencies provide increased resolving power and subsequently improved mass accuracy.

Angular dispersion in axial and radial directions as well as initial beam height have significantly smaller effects (~3 orders of magnitude) than variance in initial ion energies on measured frequency. The resolving power ($m/\Delta m$ 50%) of the analyser (5cm radius) has been simulated to 16,000 (primary harmonic) for a mass of 500 u, a transient of 0.1 seconds, beam energy 2.142KeV and initial beam width of 0.2 mm.

The spherical electrostatic field may be generated from a unique surface electrode design that greatly simplifies manufacture. The uniform potential distribution between spherical concentric electrodes can be maintained using a resistive surface.

Novel Aspect

Unique focal properties in a spherical electrostatic field are used to analyse frequency dependent mass to charge ratios of ions.

Accurate Simulation of Image Charge Effects in Cylindrical and Harmonized FT-ICR Cells via Particle-in-Cell Method

Mon 703 - Joshua Driver²; Jon Amster¹; Andriy Kharchenko¹; Ron M.A. Heeren³; ¹University of Georgia, Athens, GA; ²Univ of Georgia, Athens, GA; ³FOM Institute AMOLF, Amsterdam, NETHERLANDS

Introduction

Multi-particle simulation is a useful approach for studying ion motion in an FTICR analyzer cell. A current trend in cell design is static or dynamic harmonization of the trapping potential aimed to increase ion cloud coherence and thus, mass resolution. As a result,

smaller effects, such as space charge and image charge can be more important factors in mass accuracy. Previously, particle-in-cell simulations have implemented image charge on the rectilinear boundaries of the PIC grid. Although this works well for cubic cells, this force is not accurate for cylindrical cells. Here we present a new method to take image charge effects on the inner surface of cylindrical cells into account and report observed dependencies in several popular ICR cell designs.

Methods

For accurate simulation of ion trajectories we used the 3-dimensional particle in cell approach. This method was modified to utilize a charge collocation method for determining the force due to image charge. Electric fields from different analyzer cell geometries were imported from SIMION models. Matlab was used to construct an array of image charge points which modeled the position of the image charge on the analyzer cell electrodes. Analysis of ion trajectories was performed with Partvis and AWE software. Simulations were performed using GPU resources at the University of Georgia's z-cluster supercomputer.

Preliminary Results/Abstract

This work is focused on understanding image charge interactions in several ICR analyzer cell geometries. By simulating monoisotopic clusters of Cs⁺ ions, we are able to observe the effects of image charge without interference from space charge. We have implemented a charge collocation based method to determine the force due to image charge on cylindrical electrodes inside the PIC workspace. Until recently, this has been impractical due to the high computational cost associated with this method. To offset this cost we have made use of massively parallel ad-hoc processors (Graphics Processing Units). Image charge interactions have been explored in several popular ICR cell geometries and under a range of initial conditions. We have also examined image charge interactions in a perfect 3D hyperbolic trapping field to aide in understanding how various imperfections in the trapping field affect image charge interactions. The differences in the way these interactions affect the ion motion in different trapping fields suggest potential ways to minimize this adverse effect. Another advantage to this method is that we can now translate the transient directly from these image charge points, giving us the ability to see how different electrode shapes can affect the observed frequencies as well.

Novel Aspect

Comparing image charge effects on simulated ion frequencies in cylindrical and harmonized ICR analyzer cells.

An efficient ion funnel operated at 100 mbar background pressure

Tue 736 - Sascha Albrecht¹; Jochen Barthel¹; Armin Afchine¹; Fred Stroh¹; Thorsten Benter²; ¹Forschungszentrum Jülich GmbH, Jülich, GERMANY; ²University of Wuppertal, Wuppertal, GERMANY

Introduction

Ion funnels are known to work properly at pressures below 30 mbar. We demonstrate the scaling parameters for an operation at pressures of 100 mbar and higher. Additional simulations of the ion funnel at 100 mbar, including the fluid dynamics, electrostatic fields and the resulting ion trajectories, are presented. The results of the calculation and the simulation are validated by experimental data, e. g. the transmission of the ion funnel at 100 mbar. Further properties of the ion funnel are discussed, which are used to drive the ion funnel under optimal conditions.

Methods

A ToFwerk HTOF time of flight analyzer was fitted with a custom high throughput differential pumping stage consisting of an ion transfer capillary sampling at AP, followed by two ion funnels, a transfer quadrupole and a single electrostatic lens. The background pressure of the ion funnels is controlled by butterfly valves. Properties as for example the flow through the ion funnel are controlled for optimal transmission. Ions are generated by a dielectric barrier discharge ion source or by laser ionization of toluene molecules.

Preliminary Results/Abstract

Initial experiments at 5 mbar background pressure have revealed relevant properties of the ion funnel. It is demonstrated that the gas flow velocity in the ion funnel potentially decreases the ion transmission. For an operation of the ion funnel at 100 mbar several parameters of the device need to be scaled for operation at higher pressure: The effective field strength operating on the ions is reduced as pressure increases, so the distance between the electrodes has been decreased accordingly. The reduced electrode distance results in field gradients that are strong enough to counteract the fluid dynamic forces. The frequency of the RF field is increased linear with the molecular collision rate. So the effective potential of the RF field is not damped by collisions.

Simulations using SIMION/SDS in combination with fluid dynamical simulations using Ansys CFX are presented. This simulation includes the effects of the reduced field strength and the collision frequency. The simulation results show that the ion funnel works properly at 100 mbar background pressure.

Measurements with this device at up-to 100 mbar were performed and compared to the simulation results.

Novel Aspect

The performance of an ion funnel operated at 100 mbar background pressure is demonstrated.

Characterization of surface induced dissociation in a multi-reflecting TOF - TOF mass spectrometer

Thu 690 - [Aleksey Vorobyev](#); Andrey Trufanov; Sergey Kirillov; Anatoly Verenchikov; MSC-CG, Bar, MONTENEGRO

Introduction

The concept described in [1] suggests tandem mass spectrometry analysis for all parent ions with a high duty cycle (up to 30%) and with a high resolution at both mass spectrometric stages. Implementation of surface induced dissociation (SID) technique in the concept requires fundamental knowledge about the process. It was known that: SID efficiency improves by coating of collision surfaces with a dielectric; dissociation rates are within us timescale. The goal of this study is to measure absolute efficiency of precursor-to-product conversion and product ion kinetic energy. These values are crucial for a mass spectrometer design and may reveal novel insights into ion-surface interactions.

1. A. Verenchikov et. al. Tandem time-of-flight mass spectrometry with non-uniform sampling, WO2013192161A2

Methods

Ions formed in an atmospheric pressure chemical ionization source and accumulated in a linear ion trap were injected into a multi-reflecting (MR) time of flight (TOF) analyzer with 12m ion path. MR-TOF provides ~2000 resolution for ion packets up to 5E+6 ions at 10-20 eV kinetic energy spread. Precursor ions were selected using a two deflector scheme. Further, ions were decelerated to hit a stainless steel surface with an energy varied from 0 to 50 eV. The surface was covered with a fluorinated vacuum oil - Krytox (DuPont) or Fomblin (Sigma-Aldrich). Produced fragment ions were accelerated toward a bi-polar detector (Photonis) placed 20 cm away from SID surface. SIMION 8.1 model was used for data interpretation.

Preliminary Results/Abstract

SID technique requires narrow energy distribution of precursor ions. 10 to 20 eV precursor ion energy distribution width limits the resolution of the first mass spectrometric stage at a value of about 2000. In agreement with literature data, SID has a similar to collision induced dissociation fragmentation pattern. A stainless steel surface has low efficiency of precursor to fragment conversion - typically 2-4%. Covering of the surface with the Krytox vacuum oil results in 10 fold increase in the conversion efficiency. Heavier ions were found to have higher conversion efficiency: acetone (+1) - 10%; phthalate fragment ion (+1, 149Th) - 15%; reserpine (+1) - 33%. Therefore, we expect about 40% conversion efficiency for peptide size samples. Surprisingly, the mean kinetic energy of fragment ions was found to be below of 0.1 eV. The low value of kinetic energy allows organizing an effective collection of fragment ions into a MR-TOF analyzer and getting narrow fragment ion peaks. Indeed, for a 20 cm secondary TOF stage a resolution of 300 was observed. Using MR-TOF with much larger flight path will further improve the resolution. To conclude, the observed characteristic of SID supports the possibility of high resolution tandem TOF-TOF mass spectrometer based on SID cell.

Novel Aspect

Multi-reflecting time of flight mass analyzer coupled with a surface induced dissociation cell. Directly measured kinetic energies of product ions.

Development of a Hybrid Ion Mobility Spectrometry/Time-of-Flight Mass Spectrometer with Printed Circuit Board Technology

Tue 714 - [Ian K. Webb](#); Tsung-Chi Chen; Xinyu Zhang; Sandilya V. B. Garimella; Randolph V. Norheim; Gordon A. Anderson; Yehia M. Ibrahim; Keqi Tang; Richard D. Smith; *Pacific Northwest National Laboratory, Richland, WA*

Introduction

Ion mobility spectrometry (IMS) entails gas phase separation of ions by shape during the field-driven drift motion of ions through a gas. IMS has been applied to various biomolecules, e.g. for protein and protein complex structural analysis. In addition, a hybrid IMS/Time-of-flight Mass Spectrometer (IMS/TOF) following reverse-phase liquid chromatography (RPLC) allows for increased confidence of LC-MS identifications in proteomics experiments as well as higher peak capacity and signal-to-noise ratio measurements. Recently, Structures for Lossless Ion Manipulation (SLIM) have been introduced. SLIM devices are constructed of printed circuit board (PCB) segments that can be assembled to form geometries for effectively lossless ion transmission and mobility separation followed by high resolution time-of-flight mass analysis.

Methods

SLIM devices were assembled with parallel PCB boards spaced ~5mm apart. Following an ion funnel trap, a path of 6 SLIM segments (each 7.62cm long) shuttles ions at 4 Torr into a rear ion funnel followed by a short quadrupole and a 1.5m flight tube Agilent 6224 TOFMS. Segments of SLIM devices contain RF electrodes with opposing phases of RF applied to consecutive electrodes to confine ions between parallel SLIM segments. Typical RF potentials were 730 kHz at $\approx 60 V_{p-p}$. Electric fields are established by applying a DC gradient across multiple SLIM segments. DC-only 'guard' electrodes, placed on either side of central electrodes, are biased ~5V above neighboring central electrodes for lateral ion confinement.

Preliminary Results/Abstract

Initially, a 6 straight segment path was evaluated to determine achievable IMS resolving power as a function of electric field. The electric field was varied from 8 V/cm (6 Td) to 21.5 V/cm (16 Td) by 0.5 V/cm. The applied RF was 730 kHz, 60 V_{p-p} . Ion release times from the ion funnel trap were 160 microseconds. At 10V/cm (7.5 Td), the IMS resolving power of the m/z 922 peak (from positive mode Agilent Tuning Mix) was 33. Increasing the electric field to 15 V/cm (11.2 Td) yielded a resolving power of 39, and at 20 V/cm (15.0 Td), a resolving power of 48. These data agree with both predictions from SIMION 8.1 and equipotential modelling. The effects of the guard biases and RF amplitude were also examined. While signal can be obtained from guard biases from 4 V to 9 V, signal is maximized when the guards are biased 5 V above neighboring RF electrodes. RF amplitudes lower than ~45 V_{p-p} prohibit efficient ion transfer through the device. Varying either the guard bias or RF amplitude did not have any observable effects on IMS resolving power.

In addition, ions have been transferred through a SLIM configuration including a 90 degree turn. For this arrangement, RF amplitude significantly affects both ion transmission and IMS resolving power. At 60 V_{p-p} and an electric field of 15 V/cm, ion transfer is poor through the 90 degree 'elbow' segment. Increasing the RF to 70 V_{p-p} significantly increases both transmission and IMS resolving power due to a decrease in the so called 'racetrack' effect due to improved ion confinement through the turn. At 80 V_{p-p} , the resolving power and signal intensity increase by a factor of ~2 over 70 V_{p-p} . At 18.5 V/cm (13.8 Td), the IMS resolving power was equivalent to the straight-only arrangement.

Novel Aspect

Several geometries of PCB ion mobility/TOF devices have been demonstrated, transmitting mobility separated ions in an effectively lossless fashion.

Effect of Electrode Geometry on FAIMS Gas Flow Focusing and Lateral Diffusion

Wed 762 - [Jean-Jacques Dunyach](#); Satendra Prasad; Michael Belford; *Thermo Fisher Scientific, San Jose, CA*

Introduction

Under standard conditions, the velocity of the carrier gas in a cylindrical FAIMS device is high enough to cause ions to impinge on the inner electrode before they can make the turn into the analytical gap to be separated. In order to reduce these losses, the entrance orifice of the outer electrode was modified with a progressively curved orifice to replace the standard square orifice. As a gas stream flows over the curved surface, a boundary layer is formed wherein the gas flow at the surface is slower than the gas flow in the analytical gap. This allows the incoming gas stream to bend away from its initial angle, following the curve, and flow into the gap.

Methods

COMSOL Multiphysics, version 4.2a, was used to simulate gas flow in FAIMS flow channels. The flow vectors were first de-coupled into its X, Y, Z components and exported in MATLAB, version R2011a, for post processing. Each velocity component was then converted and loaded into a SIMION, version 8.1, workbench as an array. This is similar to a potential array. The FAIMS electrode assemblies were constructed in SIMION using GEM scripts with alignment between the electrode assembly in SIMION space and the flow array. This was verified through contour plots. FAIMS spectra were acquired for bromochloroacetate anion [BCA⁻, $m/z = 173$] and [ubiquitin]¹²⁺ using the SIMION-FAIMS module.

Preliminary Results/Abstract

A FAIMS electrode was modeled where the ion inlet orifice of the outer electrode is elliptically shaped. The shape arises from having two different radii of curvature progressing from the entrance of the orifice into the analyzer gap where the shorter radius, labeled 'a', is defined to achieve a more gradual change in curvature than the longer radius, labeled 'b'. The FAIMS gas is introduced through a narrow gap between the outer electrode and the entrance plate. The gas flowing along the curvature defined by radius 'a' experiences less separation of gas flow from the walls owing to the gradual change in curvature. This focuses the gas away from the inner electrode and into the gap. However, the streamlines flowing over the surface defined by radius 'b' undergo rapid flow separation. The overall effect is that the bulk of the FAIMS analyzer gas gets squeezed in the lateral direction and flows around the inner electrode with little lateral spread. The resulting width of the gas flow through the new assembly is only 6mm versus a width of 14mm using the standard electrode model. With such lateral confinement of the FAIMS analyzer gas, the inner electrode can be significantly reduced in length without clipping ion signal. An electrode set assembled with a length of 1cm confirms this. Furthermore, by reducing the length of the electrode from 2.5cm to 1.0cm, the volume of the FAIMS cell is reduced by a factor of 2.5 times. This reduces the ion residence time and allows for faster FAIMS analysis.

Novel Aspect

An elliptical, progressively curved inlet focuses gas laterally as well as into the gap allowing for faster, more sensitive analysis.

Effect of Extraction Electric Field on Radial Ion Confinement in a Linear Quadrupole Ion Trap Equipped with Angled-Wire Extraction Electrodes

Mon 648 - Steve C. Beu¹; Yu Chen²; Christopher L. Hendrickson²; Nathan K. Kaiser²; Alan G. Marshall^{2, 3}; ¹S C Beu Consulting, Austin, TX; ²National High Magnetic Field Laboratory, Tallahassee, FL; ³Dept. of Chem. and Biochem., Florida State Univ., Tallahassee, FL

Introduction

The 21 T FT-ICR MS under development at the National High Magnetic Field Laboratory incorporates a linear quadrupole ion trap for accumulation of ions from an external source prior to injection into the trapped ion cell. Angled-wire electrodes are positioned between the poles to induce an axial electric field that improves ion extraction speed and efficiency when a DC potential is applied [1]. Prior simulation of the angled-wire extraction field was based on an axial approximation that did not account for the radial structure of the field. In this work we employ a complete 3D model of the angled-wire equipped quadrupole to determine the effect of the radial components of the extraction field on ion confinement during extraction.

Methods

Simulations were performed with SIMION (Version 8.1, Scientific Instrument Services) running on a homebuilt 3.00 GHz AMD Phenom II Quad-Core PC with 16 GB DDR3 ram. A linear quadrupole ion trap (6.35 mm pole diameter; 127 mm long; 5.54 mm inscribed diameter) equipped with angled-wire extraction electrodes (0.1 mm diameter; 2.56 mm radial offset at quadrupole entrance; 5.38 mm radial offset at quadrupole exit) [1] was modeled with an array resolution of 0.01 mm in the radial dimension and 0.1 mm in the axial dimension. Collisional damping in the accumulation region was simulated with a SIMION user program based on the HS1 hard-sphere collision model included with SIMION 8.1.

Preliminary Results/Abstract

The radial electric field created by the angled-wire electrodes has an octopolar structure and the radial force it exerts on an ion may be either toward or away from the axis according to the ion's position within the field. The structure of this field is most easily visualized in terms of the associated radial potential distribution. In a plane that contains the quadrupole axis and bisects any pair of angled-wires, there is a radial potential well centered on the axis. An ion displaced from the axis within this plane is subject to a force from the wire electric field that is directed toward the axis. In a plane that contains the quadrupole axis and bisects any pair of quadrupole electrodes, there is a radial potential hill centered on the axis. An ion displaced from the axis within this plane is subject to a force from the wire electric field that is directed away from the axis. Computer simulations demonstrate that this force has an effect similar to that of the DC pole bias used for mass selection in a quadrupole mass filter, and this force reduces the mass range than can be confined at a given axial position when the wires are 'on'. The force imposes significant constraints on the RF parameters that can confine a specified broad m/z range over the full length of the quadrupole.

This work was supported by NSF Division of Materials Research through DMR-0654118, CHE-1019193, and the State of Florida.

[1] Wilcox, B. E., Hendrickson, C. L., Marshall, A. G.: Improved ion extraction from a linear octopole ion trap: SIMION analysis and experimental demonstration, *J. Am. Soc. Mass Spectrom.* **13**, 1304-1312 (2002)

Novel Aspect

Computer simulations determine the effect of extraction field on ion confinement in a linear QIT equipped with angled-wire extraction electrodes.

Experimental Validation of an Analytical Model for Trapped Ion Mobility Spectrometry

Wed 686 - Melvin A. Park¹; Karsten Michelmann²; Joshua Silveira¹; Mark Ridgeway¹; ¹Bruker Daltonics, Inc., Billerica, MA; ²Bruker Daltonik GmbH, Bremen, GERMANY

Introduction

Ion mobility spectrometry (IMS) involves the electrophoretic transport of ionic gas-phase species through a neutral gas medium. Recently, interest in reduced pressure (~0.5 to 5 torr) IMS has been renewed as instruments coupling IMS to MS have become

more widely available. As the analytical figures-of-merit of such instruments continue to improve so will their applicability. In this respect, trapped ion mobility spectrometry (TIMS) offers several attractive features including rapid (ms) gas-phase separations, a compact design enabling efficient integration with time-of-flight mass spectrometry, the ability to tune the experimental parameters in accordance with the particular analytical challenge, and R exceeding 200. In the present work, experimental validation of a 1-dimensional analytical TIMS model is presented.

Methods

Low concentration tune mix (Agilent PN G1969-85000) was analyzed using a prototype ESI-QqTOF (Impact HD™ Bruker) equipped with a TIMS source. The details of the instrumentation have been previously described.[1] To validate our current analytical model, the time of elution and peak resolution were measured as a function of key user-defined experimental parameters including the electric field ramp rate (?) and range, and gas pressure. Additionally, the ion dynamics inside the TIMS tunnel were modeled in SIMION 8.0 using the collision_hs1.lua program. An RF potential (850 kHz, 50-300 Vpp) was applied to the quadrupolar segments to confine the ions radially, while the flow of nitrogen gas (~100 m/s) facilitates ion transport against an axial electric field barrier.

Preliminary Results/Abstract

SIMION simulations confirm that ions in TIMS are trapped along the rising edge of the electric field barrier against the flow of buffer gas. During the accumulation and trapping cycles, ions are dispersed according to their mobility along the rising edge of the barrier. That is, ions of lower mobility are able to climb further 'up' the repulsive barrier, coming to rest closer to the TIMS exit whereas ions of higher mobility come to rest closer to the TIMS entrance. At the time of elution, the forces acting upon the ions in the axial dimension are equivalent such that, $v_g = K \cdot E_{\text{plateau}}(t_{\text{elution}})$ where $E_{\text{plateau}}(t_{\text{elution}})$ is the electric field strength at the TIMS barrier when ions of mobility K elute. However, the total time ions spend inside the TIMS analyzer also includes the transient time across the plateau and falling edge.

With respect to elution time and elution potential, experimental results are in good agreement with our model. Fits with coefficients of determination (R^2) greater than 0.9 were observed. Similarly, experimental and theoretical results were in good agreement as a function of gas pressure and velocity. Though our results are in reasonable agreement with the predicted (?)^{-0.27} dependence, experimentally measured resolutions are consistently somewhat lower than values predicted by theory. Because post-TIMS peak broadening in the downstream transfer optics of the time-of-flight mass spectrometer prevent direct comparison of theory and experiment, current efforts are focused on inclusion of a secondary in-line detector to measure ion swarms directly as they elute from the TIMS analyzer.

[1] M.A. Park, Apparatus and Method for Parallel Flow Ion Mobility Spectrometry Combined with Mass Spectrometry, USPN 8,288,717; F. Fernandez-Lima, D.A. Kaplan, J. Suetering, and M.A. Park, *Int. J. Ion Mobil. Spec.* **14**, 93 (2011).

Novel Aspect

1-dimensional analytical model for trapped ion mobility spectrometry is validated by experiment

Fundamental ion-molecule reaction studies at elevated ion temperatures and analytical application of an ion activation stage ('ion tunnel')

Tue 733 - [Sonja Klee](#); Albrecht Brockhaus; Marco Thinius; Walter Wissdorf; Thorsten Benter; *University of Wuppertal, Wuppertal, GERMANY*

Introduction

Recently we have introduced an RF driven ion activation stage, which is seamlessly integrated in the intermediate (1 ... 10 mbar) pressure range of atmospheric pressure ionization mass spectrometers which utilize inlet capillaries as first flow restriction elements. The RF stage is designed to increase the kinetic energy of relatively small ion species well above thermal conditions by means of electrical RF fields. In contrast to conventional ion activation stages (e.g., collision cells) the tunnel is operating on reagent ion species rather than analyte ions. It is envisaged that thermally equilibrated reagent ion analyte mixtures with low overall reactivity are activated in a controlled fashion within the tunnel structure. Ultimately, an user selectable reagent ion reactivity scale is sought.

Methods

Efficient charge transport as well as controlled ion energy manipulation within the same device was achieved with an hexagonal electrode tunnel structure supplied with suitable RF and DC potentials. Coupled ion trajectory/ion-molecule kinetics simulations provide detailed information on the field/ion interaction. Collisional effects are taken into account either with fluid dynamics models or by more advanced particle-in-cell codes (SIMION/SDS/RS). The upstream part of the tunnel device is directly coupled to the exit port of a typical inlet glass capillary (e.g., length 200 mm, i.d. 0.5 mm). In the present experiments a Bruker amaZon ion trap, Bruker micrOTOF time-of-flight instrument as well as a Hiden Analytical HPR-60 plasma monitor were used for mass selective analysis of the tunnel effluent.

Preliminary Results/Abstract

The main purpose of the ion tunnel is a controlled activation of reagent ion populations generated within an atmospheric pressure

ion source region. Gas phase ionization methods such as APCI and dopant assisted APPI rely on chemical ionization pathways dominated by cluster chemistry. At atmospheric pressure, the present cluster population comprising the reagent ions is generally of low reactivity. It is demonstrated that a controlled activation of the cluster population, i.e., RF potential induced shifts towards smaller reagent ions leads to strongly enhanced formation of analyte ions.

The extent of ion activation within the tunnel structure was studied using two ion-molecule reaction systems: The proton bound water cluster system and the toluene radical cation water cluster system. The shift in the recorded ion distribution upon manipulating the RF field in the tunnel structure was used to estimate the ion mobility dependent temperature for the ion species present in the tunnel. Coupled ion trajectory/ion-molecule kinetics simulations with SIMION/SDS/RS were performed. By adjusting the individual equilibria temperatures in the simulations, good agreement with experimental data was frequently obtained. For low molecular mass species such as toluene, ion temperatures exceeding 800 K are readily achieved in the tunnel structure. The step-wise activation of the proton bound water cluster system was studied by monitoring the RF amplitude dependent formation of protonated molecules. The results strongly suggest that the ion tunnel is ideally suited for operation in combination with our recently introduced capillary-APCI set-up. This source is based on a corona discharge operated at a sharply curved water surface emerging from the exit of a stripped fused silica capillary. The surface is constantly replenished by pumping purified water at flow-rates around 100 $\mu\text{L/h}$ through the capillary and therefore completely maintenance free (e.g. due to degradation of the tip surface of conventional Corona needles)

Novel Aspect

Controlled activation of reagent ion clusters in the first differential pumping stage of API mass spectrometers

How far can ion trap miniaturization go? Space-charge limits and scaling parameters for very small cylindrical ion traps (CITs)

Mon 707 - Yuan Tian; Daniel Austin; Brigham Young University, Provo, UT

Introduction

The work explores the reduced trapping capacity of miniaturized ion traps. Space-charge reduces the number of ions that can be trapped and analyzed and poses a significant issue for the sensitivity and resolution of very small ion trap mass analyzers. The applied RF amplitude must also scale with trap size due to electrical constraints, and also plays a role in trapping capacity. Here we report on simulations using the optimized geometry of CIT and several possible ways of scaling RF voltage to study the relationship between the number of ions being trapped and the trap radius in CIT.

Methods

Simulations in CITs with radii ranging from 1 cm down to 1 micrometer were conducted using SIMION 8.0. For each simulation, a group of 150 ions with m/z 140 and 141 was run. Simulations with no charge repulsion provided a baseline resolution, and was compared with experimental results on full-size CITs. The space-charge effects were explored by changing the repulsion factor until the mass resolution becomes half the value when there was no repulsion in a given trap size, thereby providing the number of analyzable ions within that trap size. Simulations included RF voltage that scaled as the 1/3, 1/2 and 2/3 power of trap radius. Stability parameter qz is maintained the same at 0.697 for all simulations.

Preliminary Results/Abstract

The data shows that the number of analyzable ions as a function of r_0 , the trap radius, for CIT ranging from 10 mm down to 30 microns under the voltage scales as square root of r_0 is approximated by a function of the form $N = k \sqrt{r_0}$, which in this case $k=1.70$ and $A=1.3$. Similar analysis in voltage scaling as 1/3 and 2/3 power of r_0 yield values of k of 1.55 and 1.75, respectively. Log-log plots of these data are strongly correlated as a straight line ($R^2 > 0.99$). Simulated results compare well with published results where available.

Novel Aspect

First simulations of space-charge effects and trapping limits with voltage scaling in small ion traps

Improved Electrostatic Ion Trap for Charge Detection Mass Spectrometry

Mon 698 - Deven Shinholt; Martin Jarrold; IU Chemistry Dept., Bloomington, IN

Introduction

There is a growing interest to studying viruses and large protein complexes via mass spectrometry. Unfortunately, conventional techniques begin to lose charge state resolution for multiply-charged ions above hundreds of kilodaltons. Charge detection mass spectrometry (CDMS) avoids this by measuring the charge and m/z of each electrosprayed ion individually. This allows for the mass

of each ion to be calculated directly, avoiding charge state convolution. A new electrostatic ion trap has been developed for CDMS to significantly enhance the m/z resolution.

Methods

In our previous trap (which was based on the cone trap of Cederquist and coworkers) the ion oscillation frequency had a relatively strong dependence on the ion energy. Since the ions m/z is determined from the oscillation frequency, this led to a relatively large uncertainty in the m/z . To minimize the dependence on the energy we have used Simion simulations to redesign the trap. The new design incorporates several electrodes to shape the fields in order to simultaneously reduce the dependence on the ion energy while minimizing variations in the frequency due to the ions entering the trap with different entrance angles and axial positions. The new trap has been evaluated through both simulations and experiments.

Preliminary Results/Abstract

Simulations of the new trap show that over a wide range of ion energy, the average oscillation frequency does not change for an ion of a particular m/z . In comparison, an ion beam defined with $\pm 2\%$ energy bandwidth has a resulting frequency distribution of $\pm 1.8\%$ in the current trap. A trapped ion follows a curved path that is reminiscent of a Lissajous curve. As the ion cycles back and forth, its path gradually changes in time. This generates a frequency wobble, which results in a lower m/z resolution. The new trap has been designed to minimize this wobble, reducing it by a factor of 7, from $\sim 0.7\%$ to $\sim 0.1\%$ of the base frequency. Preliminary experimental data from electrosprayed pyruvate kinase show that the m/z resolution improves significantly faster with trapping time than the current trap.

Novel Aspect

An improved electrostatic trap will allow for significantly enhanced m/z (and mass) resolution for charge detection mass spectrometry measurements.

Improving Ion Mobility Measurement Sensitivity by Utilizing Helium in an Ion Funnel Trap

Wed 698 - [Yehia Ibrahim](#); Sandilya Garimella; Aleksey Tolmachev; Erin Baker; Richard D. Smith; *Pacific Northwest National Laboratory, Richland, WA*

Introduction

Ion mobility spectrometry (IMS) is a gas phase separation technique in which ions are distinguished according to their collision cross sections. Ion packets are pulsed into a drift cell that contains a buffer gas (usually He or N₂) and pulled by a uniform weak electric field. Traditionally, ion traps that precede drift cell utilize the same buffer gas composition as the drift cell. In this work we show that introducing helium into the trap while operating the drift cell with nitrogen further improves the sensitivity of the platform, in some cases by more than an order of magnitude. This improvement is attributed to the faster ejection of ions from the trap.

Methods

The instrumental platform consisted of a home-built drift-tube IMS coupled to an Agilent QTOF MS. The IMS consisted of an 81-cm long drift cell coupled to an exit ion funnel. The drift cell rings and ion funnel electrodes were fabricated from Printed Circuit Boards (PCB). The source incorporated a dual funnel interface that consists of a high pressure ion funnel and an ion funnel trap also made from PCB. A source curtain plate design allowed independent flow of different buffer gas compositions into the IFT as well as into the drift cell regions. The performance of the ion funnel trap was evaluated using Bovine Serum Albumin (BSA) tryptic digest.

Preliminary Results/Abstract

Our initial experiments involved determining the effect of He on the performance of the ion funnel by disabling the IMS mode (i.e. no ion trapping). The IFT region was filled with He rich gas while the drift cell was filled with pure nitrogen. We observed no effect of He on the transmission properties of the instrument as compared to pure nitrogen. However, a dramatic effect was observed when the IMS was enabled (using ions released from the IFT). We observed an order of magnitude increase in sensitivity for peptides of high m/z (>500) in He enriched buffer gas as compared to pure nitrogen. Investigation of rate of ions release from the trap indicated a faster rate of ion ejection in the case of He enriched buffer gas as compared to pure nitrogen. The experimental results were supported by ion simulations using SIMION which indicated that ions in He exit the trap much faster than in nitrogen. We also observed that utilizing buffer gas compositions that is rich in He in the drift tube did not degrade the IMS resolving power.

Novel Aspect

A method to improve IMS sensitivity utilizing different buffer gas compositions in the trap and in the drift cell.

Investigation of Gas- and Ion-Dynamics in Heated Glass and Metal Inlet Capillaries: Work in progress

Introduction

The most common first gas flow restriction stages in commercial API MS Instruments are heated, critically operated glass or metal capillaries. Despite the considerable progress in understanding the dynamics present in such capillaries over the last years, even some fundamental characteristics of the gas dynamics, e.g. the turbulence degree of the capillary flow, remain unclear. Systematic measurements of capillary gas flows in dependence of the capillary temperature revealed a significantly different behavior of glass and metal capillaries with comparable geometry, which possibly indicates the presence of different flow conditions. We present recent results of our ongoing experimental and numerical studies of the gas- and ion-dynamics in inlet capillaries, to get closer to a comprehensive picture of the flow characteristics.

Methods

We investigated the gas flow through different capillaries in dependence of the capillary temperature, the pressure gradient along the capillary, and the gas type. The experiments were conducted with an experimental setup presented in earlier contributions, consisting of two vacuum recipients. In addition, the setup allowed the measurement of gas phase ion currents, which were pumped through the capillaries. Spatially resolved ion packets were generated via laser ionization (APLI) and the ion current was detected with an electrometer. Ion velocity profiles in quartz capillaries were measured by generating ions within the capillary duct and recording the transfer times at different ionization positions. Numerical modeling of the dynamical processes were performed with Comsol-Multiphysics and Simion.

Preliminary Results/Abstract

Systematic flow measurements revealed a surprisingly different behavior of the temperature dependent flow through glass or metal capillaries, which differed from our initial assumptions about the gas dynamics in inlet capillaries. It appears as if parameters as for example the wall roughness has a much more pronounced effect on the gas dynamics and lead to rather different flow conditions in glass and metal capillaries. Furthermore, for selected capillary geometries and material combinations unexpected discontinuities in the profile of the gas flow through the capillary in dependence of the pressure difference were observed, which potentially indicate a sudden change in the flow characteristics.

With increasing capillary temperature and decreasing capillary diameter, the hitherto used empirical model for entirely turbulent flow, which nearly quantitatively predicts the experimentally found flow of standard capillaries at room temperature, more and more diverged from the experimental data. Systematic measurements with variation of capillary geometry, temperature, and gas types are used to estimate the applicability of the empirical model.

For standard glass inlet capillaries (inner diameter 0.5 mm, length 18 cm), the notion of a fully developed turbulent gas flow is supported by obviously overcritical Reynolds numbers, the experimentally observed velocity profile along the capillary, the measured gas flow rates through the capillary, and measured gas temperature at the capillary outlet. These findings are further supported by numerical modeling studies of the temperature distribution with the capillary flow. Systematic investigations are used to assess whether or not the flow becomes laminar for selected capillary geometries. Additional measurements of the ion transmission through inlet capillaries will be presented to further assess the dynamics of ions in the capillary flow.

Novel Aspect

Systematic investigation of the gas flow and electrodynamics in glass and metal inlet capillaries.

Investigation of the Influence of Laser Spot Size and Ion Trajectory to Mass Resolving Power of Dual-Polarity Time-of-Flight Mass Spectrometer

Introduction

The synchronized dual-polarity time-of-flight (DP-TOF) mass spectrometer is a unique device developed for comprehensive imaging mass spectrometry, but the mass resolving power was limited by the electric field of the ion source. We have conducted detailed ion trajectory simulations to analyze the impact of the spatial distribution of ions that initially generated and ejected from the MALDI sample surface. The result suggests that the laser spot size is one of the major parameters determining the spread of ion trajectory, so reducing the size improves the mass resolving power significantly. This prediction was verified experimentally using a laboratory-made DP-TOFMS and discussed in this work.

Methods

Electrodynamical simulations were conducted with a commercial finite-element method package (COMSOL) and SIMION. The ion used in the simulation has an m/z of 169 and an upward initial velocity of 500 m/s. One thousand ions started from circular areas with diameters of 25 and 120 micron were used to simulate the change of the laser spot size. The extraction voltages were applied

after an extraction delay, and the flight time from source plate to the entrance of the flight tube was roughly 12.5 microseconds. For the experimental test, two 130 cm TOF tubes were installed with 30 degrees in between them. The laser beam examined the MALDI sample perpendicularly with a diameter ranging from 25 and 120 micron.

Preliminary Results/Abstract

The prediction shows that the mass resolving power of DP-TOFMS increases with the decrease of laser spot size. Such change of the mass resolving power was mainly due to the asymmetric electric field with respect to the center of the ion source; for example, the potential geometry changes not only with the vertical distance above the center of the sample plate surface, but also with the lateral position to the surface center. Thus, the larger the laser spot size, the larger the potential energy difference among the ions in the ion clouds. As a consequence, the positive ions produced near the negatively biased extraction plate traveled a shorter distance than those produced near the positively biased extraction plate. Taking into account the difference in potential gradient direction, the time spent from different initial positions to a pre-defined end positions become a more pronounced optimization parameter than that in a conventional (single-polarity) MALDI-TOFMS. Specifically, reducing the laser spot size from 120 to 25 micron considerably improves the resolving power in time (t/t) from the sample surface to the entrance of TOF region by roughly a factor of 4; that is, the difference of arrival time significantly reduced. This prediction was examined in the V-shaped DP-TOFMS by reducing the laser beam size also from 120 to 25 micron. On average, it resulted in an improvement of mass resolving power by a factor of 3 in a wide mass range; the result agrees reasonably well with the prediction. Further improvement of the mass resolving power by the installation of apertures in the ion beam paths were also studied both theoretically and experimentally. The result of the detail analysis is discussed.

Novel Aspect

The mass resolving power of dual-polarity TOFMS was analyzed and considerably improved by tightly focused laser beam.

Miniaturized Planar Electrode Linear Ion Trap (LIT) Mass Analyzer

Mon 706 - [Ailin Li](#); Brett J. Hansen; Andrew T. Powell; Yuan Tian; Aaron R. Hawkins; Daniel E. Austin; *Brigham Young University, Provo, UT*

Introduction

We present experiments directed at miniaturization of a linear-type ion trap (LIT) made using two ceramic plates with lithographically patterned electrodes. One set of ceramic plates with spacing of 4.38 mm and 1.90 mm ($y_0 = 2.19$ mm and 0.95 mm, respectively), and a set of smaller ceramic plates with spacing of 724 micrometers ($y_0 = 362$ micrometers) were studied. Miniaturization using the larger plates included moving the plates closer together and adjusting the electric fields. The resolution was optimized by varying the RF voltage ramp, ionization time, cooling time, and AC frequency and voltage. The use of lithographically patterned plates for miniaturized ion traps overcomes obstacles resulting from machining precision and electrode alignment, and shows promise for portable MS.

Methods

Each ion trap consists of two ceramic plates, the facing surfaces of which are lithographically patterned with electrode lines. A thin germanium layer eliminates charge build-up and establishes uniform potentials between electrodes. For the larger LIT design, a capacitive voltage divider provides different RF amplitudes to each of 10 electrodes, and the capacitor values are adjusted to provide the correct electric field. For the smaller LIT design ($y_0=362$ micrometers), only 5 electrodes were patterned on each plate, and no capacitors are needed, reducing RF power requirements. Precision actuators adjust the alignment between the two plates. The electric field and higher-order nonlinear effects were simulated using SIMION 8.0 to provide a reference of electrode configuration for plate microfabrication.

Preliminary Results/Abstract

Mass analysis was performed using dipole resonant ejection, and shows better-than-unit mass resolution. For the $y_0=2.19$ mm plate spacing ion trap, the mass resolution has reached 190 ($m/?m$ FWHM). The thickness of the germanium layer deposited on top of the electrode pattern was also studied, and was found to be best at 400 nm. The higher-order nonlinear effects in the trapping field of the two ion traps were optimized to provide good resolution theoretically.

For the $y_0=0.95$ mm plate spacing ion trap, electron-ionization mass spectra of toluene were obtained using resonance ejection. The resolving power ($m/?m$ FWHM) of the 91/92 peaks of toluene was measured to be 120-130, comparable to the resolution using $y_0=2.19$ mm plate spacing.

Experiments with the smaller plates with $y_0=362$ micrometers are underway. The higher-order nonlinear electric trapping field of this LIT has been simulated by SIMION 8.0 and was found to be similar to the field of the rectilinear ion trap.

Novel Aspect

The linear ion trap with two lithographically patterned planar ceramic surfaces has been miniaturized to $y_0 = 362$ micrometers.

Optimization of the Cylindrical Ion Trap Geometry Using Mesh Endcaps

Introduction

One of the greatest challenges in developing a hand-portable mass spectrometer that has limited pumping capacity due to size, weight and power restrictions is maintaining mass analyzer performance at the consequently high background pressure. It's possible to compensate for reduced mass resolution of ion trap analyzers at elevated pressures by driving the ring electrode at higher frequencies. In order to keep the driving voltage manageable over a constant mass range, the trap dimensions can be scaled reciprocally with ring drive frequency according to the Mathieu stability parameters. For ease of fabrication at small dimensions, the cylindrical trap geometry is employed. This deviation from the ideal hyperbolic profile gives rise to higher order fields that are experimentally optimized for satisfactory performance.

Methods

Stainless steel ring electrodes were conventionally milled with radii (r_0) of 0.500 mm with various thicknesses between 0.55-0.80 mm. Ring-endcap electrode spacing was adjustable in 0.025 mm increments from 0.075-0.500 mm using lapped alumina washers. Mesh endcaps were made using copper TEM grids (200 wires per inch) soldered to beryllium copper support electrodes. All mechanical tolerances were maintained at 1% or better. The ion traps were experimentally evaluated at helium buffer gas pressures in the 10-1000 mTorr range using an electron impact ionization source and an electron multiplier for detection. The multipolar coefficients were determined by calculating the static trap potentials using SIMION and fitting to the expanded polynomial expression for the potential with MATLAB.

Preliminary Results/Abstract

The use of mesh screens in place of the typical macroscale aperture endcaps eliminates the need for precise axial alignment, while maintaining high ionization and ion transfer efficiency. A fine mesh (relative to r_0) approaches a uniform surface potential and reduces the geometric degrees of freedom to r_0 and z_0 (trap center-to-endcap distance). Electrode parallelism is sufficiently controlled by spacer and machining tolerances. The parameter space therefore consists of the spacing between electrodes, the thickness of the ring electrode and r_0 , which are experimentally investigated systematically to map out the spectral performance over a broad applicable range. The mass resolution was found to improve with thinner ring electrodes and with the spacing adjusted such that the sum of the octopole and dodecapole coefficients relative to the quadrupole approached -10%. The ultimate resolution achieved at 10 mTorr with mesh endcaps is equivalent to results previously obtained with aperture endcaps, with peak widths below 0.4 Th FWHM at scan rates of 30,000 Th/sec. Double-resonance ejection was utilized for optimal performance, with ion energy uptake from both a nonlinear resonance condition and corresponding supplementary axial RF. Most geometries performed best at z_2 values around 0.70, while thicker rings exhibited stronger resonances at several lower values. Under standard boundary ejection conditions, peak widths were typically greater than 1 Th FWHM. The space-charge-limited signal maximum is reported for the evaluated parameters, with a general decrease in signal observed with increasing z_0 . Although good resolution can be achieved over an extensive set of parameters, the choices are narrowed by the need to maximize mass range. Performance metrics are established at high background pressures as the baseline for further improvement through drive RF scaling.

Novel Aspect

The performance of a practical mesh-endcap configuration of the cylindrical ion trap geometry is optimized over a broad parameter range.

Optimizing Ion Optical Rail for Coupling a Drift Tube to a Mass Spectrometer

Introduction

Ion mobility drift tubes can provide an additional dimension in separation for MS, however, coupling of the two devices together is challenging. The ion mobility drift tube operates typically at around 5Torr, while MS has a background pressure limit below 0.1mTorr. The development of the ion optics in the transitional pressure region is complex, since both time resolution and broad mass transmission need to be taken into consideration.

Methods

A uniform-field ion mobility (IM) drift cell was interfaced to a quadrupole time of flight mass spectrometer (MS) with an experimental interchangeable ion optics module between IM and MS. The 80cm uniform-field drift mobility cell was operated at about 4Torr of nitrogen. Two experimental ion optics configurations were studied: the first was comprised of two differentially pumped funnels, while the second configuration had a differentially pumped funnel and a resistive ion guide. Standard QTOF fluorinated calibration mix compounds were used to study ion mobility (IM) resolution and transmission across the mass range. Also, extensive ion modelling was used with SIMION 8.1 package for these two configurations.

Preliminary Results/Abstract

While the simplest two funnel design offered a fairly uniform ion transmission, it was found that ions in the second funnel can be trapped, losing time resolution. The experimental second design, with an ion funnel coupled to a resistive ion guide, showed a little degradation in time resolution at DC gradient of about 1V/cm or higher. Overall IMS resolutions above 50 to 60 for singly charged ions and above 70 for triply charged ions were obtained. The relationship between the obtained IM resolution and DC gradient is measured experimentally over the range of DC gradient from 0 to 1.5 V/cm. In this configuration it was possible to transmit simultaneously ions over the broad mass range as verified with reference molecules with mass-to-charge ratios from 118 to 2722. Experimental results are in good agreement with SIMION simulations that also will be presented. For practical purposes, the resistance of the resistive ion guide also had to be optimized to minimize both DC and RF heating in the device.

Novel Aspect

Drift-mobility tube coupled to MS utilizing an ion funnel and resistive guide, providing low time dispersion and broad mass transmission

Rectangular Ion Funnel (RIF): Conceptualization and Analytical Performance of a New ESI-MS Interface for Structures for Lossless Ion Manipulations (SLIM)

Thu Room 307-308 - [Tsung-Chi Chen](#); Ian Webb; Marques Harrer; Spencer Prost; Sandilya Garimella; Xinyu Zhang; Jonathan Cox; Randy Norheim; Brian Lamarche; Erin Baker; Aleksey Tolmachev; Gordon Anderson; Keqi Tang; Yehia Ibrahim; Richard D. Smith; Pacific Northwest National Laboratory, Richland, WA

Introduction

SLIM devices make use of capabilities for near lossless ion focusing, transfer, and trapping in regions of elevated pressure, and are advantageous for fast ion mobility separation and gas phase reactions. As advanced methods and instrumentation related to SLIM develop, the ion introduction through the ring electrode ion funnel to SLIM with rectangular lens entrance constitute additional technological challenges. Ions can experience discontinuities in electric fields that results in losses during transmission. In this work, we are investigating a new funnel that can seamlessly couple to SLIM devices with a proper electric field at the funnel exit. The newly designed RIF for SLIM essentially aims to achieve lossless ion introduction at elevated pressure region.

Methods

Initially, an ion simulation model was used to simulate the RIF which has one pair of the electrodes (x) on each lens independently connected to a dc power supply and another electrodes pair (y) on the same lens having an rf waveform applied for ion confinement. Adjacent electrodes in the axial direction have an rf waveform of equal amplitude but opposite phase for optimal ion confinement. A dc gradient was applied to the pairs of electrodes (x and y) that was continuously decreasing toward the end of the funnel to drive ions in the axial direction (z). For performance evaluation, the ions over wide m/z range were simulated in the RIF coupled to a PCB-based SLIM design.

Preliminary Results/Abstract

The newly designed RIF prototype consists of a stack of PCB fabricated lenses. Each lens has two electrode pairs forming a rectangle shape. The first 40 lenses has a dimension of 25x25 mm and the last 35 lenses dimensions decrease linearly from 25x25 mm to 5x5 mm in x and y direction respectively (the same dimensions as the SLIM entrance). The RIF lenses are 0.75 mm thick and spaced 0.75 mm apart. The ion trajectory modeling was performed with SIMION 8.1 software with the Statistical Diffusion Simulation model for the ion mobility and diffusion at a pressure of 4 torr. In the simulation model, the RIF was synchronized with the first 4 trace electrodes of the SLIM board. The result shows a near-circular trapping potential in the region near the central of the RIF is similar to that from ion funnel with ring electrodes. The current approach to avoiding ion loss is to apply proper rf and dc bias on x and y pair of the electrodes for better ion confinement. With 1 MHz rf potential and 2 V dc bias, ion simulation results indicate 100% transmission efficiency for ions of m/z 50-1000 with an rf potential (100-200Vp-p,) and a dc gradient (4 to 30 V/cm) from the beginning of RIF lens to the fourth lens of the SLIM device.

Novel Aspect

A newly designed rectangular ion funnel that is capable of highly efficient ion transmission into PCB-based SLIM devices.

Simulation Driven Design and Development of Structures for Lossless Ion Manipulations

Tue 716 - [Sandilya V.B. Garimella](#); Ian K. Webb; Yehia M. Ibrahim ; Aleksey V. Tolmachev; Keqi Tang; Gordon A. Anderson; Richard D. Smith; Pacific Northwest National Laboratory, Richland, WA

Introduction

Complex manipulations of gas phase ions prior to mass analyzers, significantly benefit and expand mass spectrometry (MS) applications; for example in biological systems analysis using different 'omics' methodologies. Such gas phase ion manipulations are limited by ions losses, limited ion drift time and other geometry constraints. Systems for lossless ion manipulation (SLIM) aim to provide a set of building blocks based upon electrodes fabricated on planar surfaces, initially using printed-circuit board (PCB) technology, that attempt to address these challenges. In the present work, using computational methods and SIMION simulations, we explore the feasibility, performance and designs of SLIM for effective ion confinement, complex ion manipulations and high resolution IMS separations in conjunction with MS.

Methods

SLIM components with 0.75mm thick 'trace' electrodes, spaced 1.5mm apart were initially fabricated. Alternating RF phase (200 Vp-p, 720 kHz) is applied to each adjacent central (trace) electrode and the trace electrode chain is flanked by guard electrodes with a DC bias. Solutions of the Poisson equation for these configurations demonstrate effective pseudo-potential trapping wells. Using SIMION, various voltage and geometry configurations have been explored to examine extended confinement, drift separations, and more complex manipulations of gas phase ions. An SDS collision model is used to account for background gas collisions at a pressure of ~4 torr. Together, SIMION simulations and potential calculations were used to refine the design of SLIM devices for IMS/MS applications.

Preliminary Results/Abstract

The three basic SLIM building blocks/units - the straight, the elbow (90 degree bend) and the T sections (switch) have been studied. Pseudo-potential calculations showed the dependence of the potential well upon the geometries and RF and DC voltages applied upon the central and guard electrodes. Using appropriate variations, ions can be confined symmetrically either at the axis of the device or off-axis (possibly allowing controlled RF heating). SIMION simulations show effective ion confinement and drift. Separations can be effected based on ion mobility. The simulated IMS performance of SLIM devices is in close agreement with classical theory in an ideal drift field. The predicted resolving power from simulation also was in good agreement with data. Ion trajectory simulations indicate feasibility of turning ions around a corner. The initial SLIM 'elbow' design showed 100% transmission with marginal (~7.7%) loss of resolving power (due to the 'race track' effect) in the 90 degree turn. The resolving power was highest (and comparable to a straight section) at E/N of 10 Townsends. At higher E/N there is drop in resolving power possibly, due to an increased race track effect, consistent with experimental observations. Ion trajectory simulations have been used to refine the elbow design and also design 'T-section' to move ions into orthogonal channels. Initial simulations with the present design show ~10% loss of signal intensity at a T junction. At the junction, the sudden change of electrode orientation results in ions encountering two adjacent electrodes of same polarity; leading to loss of potential well depth. Simulations have been used to explore improved T switch designs for eliminating losses of either ions or resolving power. Other, more complex designs such as an 'ion elevator' between different SLIM layers, as well as designs for effective trapping, release and reactions of ions, will be presented.

Novel Aspect

Novel lossless ion manipulation sequences have been studied and characterized using ion trajectory simulations.

Simulations of Ion Motion in Toroidal Ion Traps

Mon 687 - [Jessica M. Higgs](#); Daniel E. Austin; *Brigham Young University, Provo, UT*

Introduction

Ion traps have been used in miniaturized mass spectrometers because of their small size and sensitivity. Using flat and cylindrical electrodes instead of hyperbolic electrodes simplifies manufacturing especially for miniaturization. The toroidal ion trap was developed to increase ion capacity and maintain sensitivity. These two developments have previously been combined for the simplified toroidal ion trap. To gain understanding of the effects of higher-order term contributions, this present study gives the potential maps, calculates the higher-order term contributions, and simulates ion motion of three toroidal ion trap designs (symmetric, asymmetric, simplified).

Methods

The electrode arrays were entered into SIMION 8.0. The potential was recorded across the radial and axial dimensions of the trapping region. Higher-order term contributions were calculated from a polynomial fit of the potential maps. The derivative of the potential maps visualized the field of the trapping region, and the linear field contributions were subtracted. Ion simulations were performed with user programs controlling the voltage, RF frequency, background gas pressure, and collision cross section. An ion of m/z 100 simulated with varying initial kinetic energy and direction of velocity with and without considering background collisions. MATLAB's Fourier transform function was used to identify the frequencies of motion.

Preliminary Results/Abstract

The values of the calculated higher-order fields in the axial and radial dimensions of the trap are different, untypical for ion traps. The fields of the simplified toroidal ion trap resemble that of the symmetric toroidal ion trap more than the asymmetric toroidal ion trap, but its reported performance is more comparable to that of the asymmetric toroidal ion trap. The frequencies of motion seen in the symmetric toroidal ion trap indicate the presence of odd-ordered field components. For the asymmetric toroidal ion trap, the

frequencies of motion indicate low levels of odd-ordered field components. The frequencies seen in the simplified toroidal ion trap indicate the amount of odd-ordered field components is between that of the symmetric and asymmetric toroidal ion traps. As the ion traveled around inside the toroidal ion traps without considering collisions, higher kinetic energies shifted the average radial position of the ion towards the outside of the trapping region. There is less of this effect in the simplified toroidal ion trap than the symmetric and asymmetric toroidal ion traps. When considering collisions, increasing temperature slightly shifts the average radial position outwards in the symmetric toroidal ion trap and more so in the asymmetric toroidal ion trap, but this was not evident in the simplified toroidal ion trap. The values of average kinetic energy, average velocity, collisional frequency, and mean free path are reported for the three toroidal ion traps at 273 K and 473 K.

Novel Aspect

First simulated ion motion reported for toroidal ion traps

Study of the Impact of Gas Flow in a Microscale Ion Trap Operated at High Pressure

Mon 693 - [Bruno Couplier](#); Dmitry Chernookiy; Sorin Mitran; J. Michael Ramsey; *UNC Chapel Hill, Chapel Hill, NC*

Introduction

Operating miniature cylindrical ion traps (CIT) at pressures of ≈ 1 Torr is the approach chosen by our group to realize handheld mass spectrometry. Significant reduction in size, weight, and, power (SWaP) results from the diminished pumping requirements of high-pressure operation. Standard electron multiplier detectors cannot be utilized at high pressures, and dual differentially pumped chambers are used to simultaneously achieve reduced pumping requirements and high detector sensitivity. In this configuration the ionizer/trap and detector are held at two different pressures. One result of differential pumping is gas flow through the CIT mounted on the partition between the chambers. In this work, we compare simulations and experimental studies of the impact of buffer gas flow on mass spectral performance.

Methods

Theoretical flow modeling included the use of three software programs. CITSIM (Collisional Ion Trap Simulator), a package of programs developed within our group, uses a GPU-implemented lattice Boltzmann method to determine non-equilibrated buffer gas velocity distributions. CITSIM results are compared to results from commercially available software SIMION and COMSOL. Experimental measurements were made utilizing a dual chamber with the trap mounted between the chamber walls. A Faraday cup and CoolFET amplifier were used to detect ions at various differential pressures. Micro-pirani gauges were placed at the trap and near the detector in each chamber to monitor relative pressures. Spectra of toluene in nitrogen and helium buffer gas were recorded at several differential pressures.

Preliminary Results/Abstract

Due to the occurrence of rarefaction effects in our miniature traps ($r_0=0.5$ mm) at pressures below a few Torr, gas dynamics are more realistically described by the Lattice Boltzmann equation. CITSIM implements a D3Q19 Lattice Boltzmann Method on a NVIDIA C2070 GPGPU for speed. Inelastic collisions are modeled to account for the transfer of energy into the internal degrees of freedom of the collision partners. Differential pressures differences of up to two orders of magnitude were investigated in a trap operated in the range 1-1000 mTorr. Comparison of spectra obtained with increasing gas flow demonstrates the enhancement of signal intensity due to the action of buffer gas flow facilitating the ejection of ions from the trap. Nitrogen and helium buffer gas flow are compared. Simulations with CITSIM reproduce the effect of flow seen experimentally and are compared to simulations made with SIMION 3D using flow calculation performed with the COMSOL molecular flow module.

Novel Aspect

Utilization of gas flow to improve the performance of miniature ion traps at high pressure.

Technical Advances and Theoretical Performance Assessment of a Spatially Multiplexed Ion Mobility-Mass Spectrometer

Wed 688 - [Katrina L. Leaptrot](#); Jody C. May; John A. Mclean; *Vanderbilt University, Nashville, TN*

Introduction

Ion mobility-mass spectrometry (IM-MS) is a two-dimensional separations technique which has demonstrated significant utility in the analysis of complex mixtures. Although a spatially multiplexed IM-MS has not yet been developed, such an instrument is expected to provide improved figures-of-merit in throughput, sensitivity, and versatility, among others. Here we discuss details from the ongoing development of an IM-MS with 8 discrete parallel ion channels. The instrument is being designed to perform with spectral

reproducibility across each channel and figures-of-merit comparable to existing single channel IM-MS instruments in terms of resolving power and sensitivity. We present the progress of constructing this instrument with emphasis on computer simulations for performance evaluation and modification of tandem ion funnels to facilitate pumping and low-powered electronics.

Methods

Development of the spatially multiplexed IM-MS has been organized into three phases. Phase one involves designing an 8-channel ion mobility spectrometer (IMS) with an electrospray ionization (ESI) source array. Phase two focuses on the development of a matrix assisted laser desorption/ionization (MALDI) source and adaptation of a commercial time-of-flight mass spectrometer (TOFMS) to simultaneously accept multiple ion beams. Phase three integrates the 8x IMS and the modified TOFMS and establishes data acquisition/visualization software. Though all phases have been initialized, the instrument is considered in the first development phase. AutoCAD, SIMION 8.1, and COMSOL Multiphysics software are used to design instrument components, evaluate ion trajectories, and investigate flow dynamics, respectively. Successful designs are commissioned for fabrication and assembled in-house.

Preliminary Results/Abstract

Theoretical performance assessment and construction has occurred for several instrument components including the ESI source, tandem ion funnels, IMS drift tube, and post-mobility converging array ion funnel to refocus ions and converge the 8 beams before introduction into the TOFMS. The 8x ESI source was developed with linear and angular adjustment for ion signal optimization at each channel. First principles pumping and electrical calculations, along with fluid dynamics computer simulations of the pressure drop from 760 Torr to 1 Torr for eight atmospheric apertures, led to the design of tandem ion funnels of stacked printed circuit boards for low circuit capacitance with differential pumping speeds of 14 L/s at 15 Torr and 4 L/s at 1 Torr. Developed interface components include a heated capillary block to assist in ESI droplet desolvation, an inner vacuum chamber to isolate the first ion funnel at higher pressure, a conductance limiting aperture array with gating electrodes to pulse ion packets into the drift tube, and a Faraday plate detector array to benchmark the performance of the 8-channel IMS of phase 1. Ion trajectory simulations indicate near 100% ion transmission through the tandem ion funnels and into the drift tube via 1000 μ m diameter apertures. The drift tube, which consists of a 30 cm stack of brass electrodes, is pressurized with helium and was designed based on desired resolution and limitations set by the breakdown voltage of helium. Despite the low Paschen limits of helium, the instrument was designed with these conservative parameters to facilitate IMS operation with various drift gases such as nitrogen, argon, and dry air.

Novel Aspect

Advances in development of a spatially multiplexed ion mobility-mass spectrometer with improved sample throughput, sensitivity, and experimental versatility.

The Aerolens: An Evaluation Study based on Computational Methods and Mass Spectrometric Tests

Mon 668 - Dimitris Papanastasiou¹; Diamantis Kounadis¹; Alexander Lekkas¹; Athanasios Zacharos²; Ioannis Nikolos²; Ioannis Orfanopoulos¹; Emmanuel Raptakis¹; ¹Fasmatech, Athens, GREECE; ²Technical University of Crete, Chania, Greece

Introduction

The increasing demand for enhanced sensitivity in mass spectrometry (MS) has brought significant attention to the aerodynamical properties of atmospheric pressure - vacuum interfaces. An evaluation study of the aerolens is accomplished using ion tracing in realistic flow fields produced by gas flow visualization techniques and gas dynamics computations. An orthogonal TOF MS platform is briefly outlined and preliminary data are presented for this novel ion optical element operated in the fore vacuum region of the instrument over a wide range of pressures. The advantages of the aerolens compared to existing intermediate pressure ion optical devices are highlighted.

Methods

The evaluation study involves the application of Particle Tracking Velocimetry (PTV) for visualization of the high speed transient gas flows established in the fore vacuum region and the use of Direct Monte-Carlo Calculations (DSMC) and Reynolds-Averaged Navier-Stokes (RANS) as complementary computational methods. Particle tracking is exercised using quantum dots and fluorescent molecules as tracers. The flow fields are subsequently introduced into SIMION and ion tracing is performed in the presence of RF and DC electric fields to illustrate the ion focusing mechanism involved. Experimental characterization of the aerolens is carried out on a prototype of a TOF MS platform. Preliminary data to demonstrate transmission efficiency are presented for ions produced by electrospray ionization.

Preliminary Results/Abstract

The reduced relaxation time of the fluorescent molecules compared to previous studies employing aluminum nanoparticles reveal the properties of the high speed transient flow throughout the length of the domain in great detail. The mechanism responsible for suppression of turbulence in the far field region of the free jet is discussed. The onset of a laminarized low-pressure fully-developed subsonic flow is demonstrated inside the aerolens. The flow fields obtained experimentally and computationally are contrasted and introduced into SIMION where ion tracing is performed to illustrate the focusing mechanism in the presence of RF and DC electric

fields. A model of the aerolens is considered comprising a series of ring electrodes with a predetermined spacing. Ion optical simulations are performed to optimize ion focusing by varying the thickness of the electrodes (0.5 mm to 4 mm) and their separation distance (0.5 - 1 mm). Preliminary data obtained on a prototype on a TOF MS platform incorporating a first model of aerolens with 3 mm thick rings and 0.6 mm spacing are also presented. Ion transmission for different ion species including papaverine and loperamide protonated molecular ions is investigated over a range of pressures extending from 1 mbar to 30 mbar and for RF fields with amplitudes and frequencies up to 300 Vp-p and 3 MHz respectively. In these first set of experimental tests the aerolens is positioned between a capillary inlet and a short ion funnel. The advantages of coupling the aerolens to a compressed version of the ion funnel compared to the standard elongated ion funnel design are discussed.

Novel Aspect

Ion focusing accomplished in a novel ion optical device also capable of simultaneously laminarizing the supersonic free jet gas flow.

The after-life for radially ejected ions in the linear ion trap.

Mon 673 - Viatcheslav V. Kovtoun; *Thermo Fisher Scientific, San Jose, CA*

Introduction

The tendency for the growing complexity in biological samples in mass spectrometry brings new challenges in all related areas: the separation of compounds prior to mass analysis, the speed and quality of the mass analysis, and post-analysis data processing. Among major benefits of ion trap mass spectrometry is the ability to provide high selectivity in structural analysis through consecutive MSn (n \geq 2) events. This normally requires selection of the target precursor ion using data-dependent filters, isolation and fragmentation of the precursor and mass analysis of fragments. Significant boost in speed could be achieved if isolation and fragmentation steps are removed from the traditional chain of events in the ion trap. Instead, fragmentation occurs in a post ejection event during normal scan.

Methods

The instrument geometry includes a first linear ion trap (LIT1) operated in non-balanced RF mode, an ion optics, an ion storage device, further interface ion optics, and a second mass analyzer (LIT2). Ions from the LIT1 were ejected radially and accelerated past the ejection slot. The ejected ions final deceleration occurs at the entrance to the gas-filled ion storage device, an assembly of parallel RF+DC rods, capable of capturing, trapping, fragmenting and transferring the ions. After fragmentation and collisional cooling surviving precursors and fragment ions were transferred to the LIT2 for mass analysis. A non-stretched, modified geometry of the LIT1 and ejection conditions (phase-locked resonant excitation, $\nu = 2/3$) were optimized to reduce the kinetic energy (KE) spread of ejected ions.

Preliminary Results/Abstract

Depth of fragmentation was controlled by using various collision gases such as pure N₂, pure He or mixture of He and N₂ and also by ion energy at the entrance to the ion-storage device. Fragmentation of several compounds: Ultramark (1+), Angiotensin I (2+) and ACTH 1-16 (3+, 4+ and 5+) have been investigated. Optimal RF levels and parameters of DC asymmetric potential well were identified for efficient ion trapping in the ion storage device. Trapping efficiency was estimated near 40% for Ultramark ions of 1122 amu, based on ion current direct measurements. He was a gas of choice for low to middle m/z, above 300 and below 700 m/z, with high charge states. Further investigation is required for higher m/z ions with lower charge states. SIMION simulations were used to optimize the LIT1 geometry for low KE spread, the transfer optics transmission, and the trapping efficiency in the ion storage device.

Novel Aspect

Precursor ions are scanned out radially at $\nu = 2/3$ in phase-locked mode, trapped, fragmented, and those fragments are mass analyzed.

Theory and application of instantaneous frequency in FTMS

Mon 700 - Oleg Yu. Tsybin¹; Anton N. Kozhinov²; Konstantin O. Nagornov²; Yury O. Tsybin²; ¹*Saint-Petersburg State Polytechnical University, Saint-Petersburg, Russia*; ²*Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland*

Introduction

Recent advances in FTMS fundamentals reveal presence of time-dependent frequency components in transients. These components manifest themselves as non-linear features in frequency (mass) spectra, e.g., magnetron sidebands. What is the true nature of generation of signals with time-dependent frequencies? How they can be accounted for in spectral analysis and instrument development to maximize FTMS analytical characteristics? Here, we first present a theory of ion motion in FTMS that considers ion motion frequencies dependent on time (instantaneous frequencies). In the following we apply the described theory to develop

algorithms for ion excitation and ion detection (transient generation). We then establish a relationship between the analytically constructed mass spectra and those obtained with SIMION and experimentally to validate the developed analytical approaches.

Methods

Theoretical analysis of charged particles' trajectories in an electromagnetic field was performed via translation of the Newtonian equations of motion into a certain complex variable phase space. We thus derived the differential equations that describe non-linear dependencies of phase and instantaneous frequency on time for ion motion in ion trapping mass analyzers, ICR and Orbitrap FTMS. We then developed methods for solving these differential equations and solved them in linear and non-linear fields for ion oscillations along radial, azimuthal, and axial directions. We compared the obtained results with those derived with SIMION modeling of ion motion in an open-ended cylindrical ICR cell installed in a 10 T magnet and experimental results obtained with 10 T LTQ FT-ICR MS, Orbitrap FTMS.

Preliminary Results/Abstract

Preliminary results of ion motion theory development and application include the following ones: (i) in the plane perpendicular to the ion trap axis in ICR or Orbitrap FTMS, the ion motion is shown to be represented by two coupled oscillators: radial and azimuthal. In the longitudinal plane the ion motion is described as radial and axial coupled oscillators; (ii) exact analytical solutions are found for ion motion in the plane perpendicular to magnetic field in FT-ICR MS in a quadratic potential distribution. Importantly, these analytical solutions describe explicit dependence of ion motion on time and initial values of ion radius and azimuth, as well as radial and azimuthal velocities; (iii) general solutions of the derived differential equations are found in non-harmonic electric fields, including excitation RF field and space-charge field; (iv) for the first time in FT-ICR MS field, ion RF excitation is taken into account while deriving the post-excitation solution of ion motion. The coordinate and velocity taken at the end of the excitation are the initial parameters for the subsequent ion detection; (v) algorithms for transient generation are derived for diverse detection electrode geometries, boundary conditions, initial parameters of ion motion, and the corresponding ion trajectories. Obtained transients correlate with those generated with SIMION and experimentally. (vi) Fourier spectra derived from the analytically generated transients revealed the relationship between ion trajectory parameters and non-linear features in frequency (mass) spectra. Overall, the obtained results improve the general understanding of FTMS and shall be useful for its further hardware and signal processing development. Particularly, we aim to optimize the calibration equations in FTMS and improve the achievable mass accuracy levels.

Novel Aspect

Theory of ion motion with phase non-linearly dependent with time and its application to ion excitation and detection in FTMS

Toroidal Multipole Expansion for the Design of Circular Ion Traps

Mon 696 - [Steve Lammert](#)¹; [Ed Lee](#)¹; [Joe Oliphant](#)¹; [Randy Waite](#)¹; [Daniel Austin](#)²; [Dennis Tolley](#)²; [Karl Warnick](#)²; ¹Torion Technologies, Inc, American Fork, UT; ²Brigham Young University, Provo, UT

Introduction

The toroidal ion trap has conceptual origins in traditional 2D (Bier & Syka) and 3D (Lammert & Wise) quadrupole devices. Early toroidal traps were designed using electric field profiles similar to traditional devices, but rotated into circular geometries. To correct for the distortions introduced by this transformation, Lammert and Wise empirically adjusted the endcap spacing and electrode shapes. This produced devices with good trapping and resolution performance, but without a systematic mathematical framework for further performance optimization. To address this limitation, we present an exact, analytic toroidal multipole expansion based on hypergeometric functions that provides a new design framework for toroidal and planar halo ion traps and opens up the possibility of new parametric families of device geometries.

Methods

Initial attempts at field optimization for toroidal ion traps used conventional quadrupole theory and the Laplace equation in Cartesian coordinates. Simulations using SIMION (SIS, Inc.) and experiment showed that while this approach provided a useful first approximation, further progress required a mathematical treatment specialized to the toroidal geometry.

The key observation in this work is that the Laplace equation has a separable solution in a toroidal coordinate system. In a rectangular geometry, the quadrupole field is a simple polynomial. The analogous toroidal quadrupole and higher order multipole field profiles are given by a combination of hyperbolic trigonometric functions and hypergeometric functions. Despite their complexity, these functions can be evaluated using a suitable numerical programming package such as MATLAB (Mathworks, Inc.).

Preliminary Results/Abstract

The optimized toroidal ion trap has many operational characteristics that are similar to what would be expected from a traditional quadrupolar trapping device. The stability diagram was determined using SIMION and its general characteristics are remarkably similar to those of a 2D quadrupole stability diagram. As is the case for a quadrupole device, the mass scan is linear with the amplitude of the RF voltage used to sequentially move ions of increasing m/z into a fixed resonance point. It is shown, however, that unlike the 2D and 3D quadrupole devices, where the calculated q -eject is a constant under resonance ejection conditions, the expected constant $q = k \cdot V/m$ relationship (where k is comprised of the fixed geometry dimensions, frequency, electron charge) does not hold for the toroid.

While the rectangular quadrupole field provides a useful starting point for toroidal ion trap design, a torus is topologically different from either a 2D or 3D quadrupole device, which are a cylinder or sphere, respectively. No combination of the Laplace coefficients for the standard rectangular quadrupole field will give rise to an equipotential surface that matches the symmetry and topology of a toroidal device. For these reasons, the toroidal multipole expansion is a fundamentally new way to understand, parameterize, and optimize families of toroidal ion trap designs.

By varying the coefficients of toroidal multipoles of different orders, families of parametric device designs can be obtained. MATLAB was used to generate a representation of the first through fourth harmonic degrees of a toroidal geometry, and each degree was weighted in a systematic fashion to match the trapping field of an existing empirically optimized toroidal ion trap geometry. The resulting candidate trapping fields were evaluated in SIMION to investigate ion trapping and ejection behavior.

Novel Aspect

Field analysis using toroidal mathematics allows predictive optimization and illustrates the fundamental uniqueness of the toroidal ion trap mass analyzer.

Understanding the Impact of Space Charge Upon the Sensitivity of Atmospheric Ion Sampling

Tue 374 - [Charles Jolliffe](#); Serguei Savtchenko; Reza Javahery; *IONICS Mass Spec Group, Inc., Bolton, CANADA*

Introduction

The present majority of mass spectrometric analyses utilize atmospheric ion sources, such as Electrospray ionization, chemical ionization, and photo-ionization. Typically, ions from such atmospheric sources are then electrically drawn through a counter-flow of gas into the first stage of a mass spectrometer.

In order to increase sensitivity, more ion flux is an obvious direction. This study uses computational methods to identify in detail the initial ion current losses in sampling atmospheric ions.

This study is intended to identify an initial limitation to increasing sensitivity of atmospheric sampling.

Methods

We assume a typical physical configuration for the modeling of sampling atmospheric ions, namely a 'curtain cap', counter-flow gas, and circular entrance aperture into the first (lower pressure) stage of a mass spectrometer. A needle at high voltage provides the ion current. The ion source is assumed to be located between the needle and 'curtain cap', namely a circular area located perpendicular to the axis of symmetry. Ions are released randomly with zero initial kinetic energy from different points of the source.

Computational fluid dynamics and Simion (with space charge consideration) use the physical configuration to produce a gas flow and electric field profile. This profile is then used to examine the motion of charged particles into the mass spectrometer.

Preliminary Results/Abstract

For a given flux of ions from the ion source, we examine the individual ion motion and determine relative to the initial ion current, the ratio of the ion current that is neutralized upon the 'curtain cap', the entrance aperture, or is transmitted through the aperture into the first stage of the mass spectrometer. These various ion current ratios are then examined as a function of total ion current. The influence of the flow of counter-flow gas upon the ion current ratios is also observed.

The ion current into the mass spectrometer first stage can be seen to drop exponentially as the total ion current is increased.

As an example, although high flow (approximately 500uL/m) Electrospray sources produce atmospheric ion currents from 250nA to more than 500nA, our modeling shows that for an ion source current of 500nA, less than 10% of the initial ion current enters the mass spectrometer, and the majority neutralizes on the 'curtain cap'.

Novel Aspect

Specific atmospheric ion current sampling losses are examined as function of total ion current.