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The predictive power of SIMION/SDS simulation software for modeling ion mobility spectrometry instruments

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ABSTRACT

The combined use of SIMION 7.0 and the statistical diffusion simulation (SDS) user program in conjunction with SolidWorks® with COSMSOSFloWorks® fluid dynamics software to model a complete, commercial ion mobility spectrometer (IMS) was demonstrated for the first time and compared to experimental results for tests using compounds of immediate interest in the security industry (e.g., 2,4,6-trinitrotoluene, 2,7-dinitrofluorene, and cocaine). The effort of this research was to evaluate the predictive power of SIMION/SDS for application to IMS instruments. The simulation was evaluated against experimental results in three studies: (1) a drift:carrier gas flow rates study assesses the ability of SIMION/SDS to correctly predict the ion drift times; (2) a drift gas composition study evaluates the accuracy in predicting the resolution; (3) a gate width study compares the simulated peak shape and peak intensity with the experimental values. SIMION/SDS successfully predicted the correct drift time, intensity, and resolution trends for the operating parameters studied. Despite the need for estimations and assumptions in the construction of the simulated instrument, SIMION/SDS was able to predict the resolution between two ion species in air within 3% accuracy. The preliminary success of IMS simulations using SIMION/SDS software holds great promise for the design of future instruments with enhanced performance.

1. Introduction

Before the advent of computer simulation software, scientific instruments were designed and optimized using a trial-and-error approach [1]. SIMION [2–4] revolutionized the ability to model instruments analyzing gas-phase ions in vacuum, especially mass spectrometers [5,6]. Simulations using computer models has become increasingly important in the design of scientific instruments because it permits an instrument to be designed and optimized prior to expending effort and resources on physical fabrication. Previously, the only computer modeling of ion mobility spectrometry (IMS) instruments has been either to evaluate the electrostatic fields of different drift tube designs [7–9] or to simulate the drift gas and carrier gas flow characteristics within the drift tube [10]. As stated by Baumbach and coworkers, an evolutional simulation approach is needed in order to model ions in electrostatic fields within the IMS taking into account the flow conditions of the neutral gaseous molecules [10]. In 2005, Sandia National Laboratory reported the use SIMION to simulate transportation of ions through an IMS/MS interface [11]. This study incorporated an external programming code that compiled within SIMION to take into account the collision effect of neutrals on ions; however, this programming did not account for the effect of diffusion, which is very important in IMS as well as IMS/MS interfaces [11,12]. The recent introduction of the statistical diffusion simulation (SDS) user program for SIMION [13] for modeling ion trajectories in viscous (i.e., atmospheric pressure) regimes in electrostatic and magnetic fields [3] has opened the door to model IMS instruments.

Unlike mass spectrometry, IMS operates at elevated and atmospheric pressures, and separates ions based on size and/or shape as opposed to mass. IMS was originally referred to as plasma chromatography [14–18] because ions of the chemical analytes are characterized using gas-phase ion mobility determined by the arrival times of the ion clouds [1,17,19]. The separation between ions of different sizes and/or shapes occurs while traveling along an electrostatic gradient in a drift tube at atmospheric pressure [1,16,17]. Without the electrostatic gradient, ions would merely diffuse within the buffer or collision gas. Therefore, the electrostatic gradient is critical for causing the ions to migrate through the gas

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molecules [1], [12,17]. Each ion has a specific mobility (K) at a given pressure and temperature for a specified collision gas [1,17]. As shown in Eq. (1), multiplying (K) by the local voltage gradient (E) gives the expected drift velocity (v_d) of an ion:

$$v_d = K \times E \quad (1)$$

The electrostatic field is much like a force dragging a sphere through a viscous medium where doubling the force on the sphere doubles its velocity. If the mobility coefficient is normalized to 273 K and 760 torr, then it is referred to as the reduced mobility (K_o) [1,17]. The thermal velocity of an ion in an IMS instrument is well over 100 m s^{-1} because it is a being bombarded by millions of collisions per second with the neutral gas molecules due to the gas kinetics at standard atmospheric conditions. These collisions create a sort of drunkard's walk (i.e., Brownian motion) that results in diffusion. The effect of the buffer gas reduced mass (μ) and collision cross-section (Ω_D) is easily seen in the following equation:

$$K = \frac{3e(2\pi)^{1/2}(1+\alpha)}{16N(\mu kT_{eff})^{1/2}\Omega_D(T_{eff})} \quad (2)$$

where e is the charge of an electron; N is the number density of buffer gas molecules; α is the correction factor; T_{eff} is the effective temperature [1,17].

In order to correctly model the ion trajectories inside an IMS instrument, the SDS user program must be incorporated into the SIMION ion optics modeling program to account for both the mobility and the longitudinal diffusion [18] terms which exist at atmospheric pressure [11,12]. A detailed description of the SDS algorithms and how they are integrated into the ion trajectory calculation in SIMION has been published previously [13]. Briefly, SDS treats viscous drift motion and diffusion as separate phenomena, even though they are not independent in reality. Viscous effects are treated with a relatively straightforward Stoke's Law model, while diffusion is emulated using a collection of tabulated collision statistics and randomized ion jumping to provide an unbiased approximation of diffusion over a wide range of ion mass to collision gas mass ratios [12,13]. Diffusion estimates will be unbiased as long as the number of collisions between time steps is sufficient to decorrelate successive velocity vectors of ion trajectories.

SIMION/SDS has been used to model ion behavior in viscous environments for comparison with ion motion in vacuum related to electrostatic refraction, influence of wire grids and electric fields, as well as magnetic fields and charge repulsion [12]. However, no attempt has been made to evaluate the predictive power of SIMION/SDS in simulating ion trajectories inside a complete IMS instrument nor has there been a comparison against experimental data for molecular ions of interest, such as 2,4,6-trinitrotoluene and cocaine. This paper presents insights into simulation of an actual commercial IMS, the challenges of using SIMION/SDS, and the comparison of the model with experimental data under various IMS instrumental conditions. It should also be noted that incorporating the effect of chemical reactions and their effect on IMS spectra, however, is beyond the capabilities of the SIMION/SDS program.

Ion formation, separation, and detection are dictated by instrument operating parameters such as the type of ionization source, temperatures in various zones (e.g., drift tube), dopant gas type, carrier and drift gas compositions and flow rates, imposed electrical field, gate mechanism and timing, as well as the physical geometry of the drift tube [1,9,18,20,21]. These parameters affect the overall selectivity, sensitivity, and peak resolving power of the instrument and can be optimized for a given analyte or class of compounds of interest [22]. Of the above listed parameters, drift tube temperature, gas flow rates, gas compositions, and gate width (i.e., duration the gate is open for ion passage) are readily changeable in commercial IMS instruments, while others are usually fixed by the manufacturers. To evaluate the predictive power of SIMION/SDS, the product ion peaks were monitored as some of the operating parameters were varied one-by-one both within the computer model and the physical instrument. The predicted changes were then compared to the experimental changes obtained from the real instrument to determine how well SIMION/SDS simulations mimicked the observed trends. The operating parameters studied were drift:carrier gas flow rates, drift gas composition, and ion gate width.

2. Experimental

2.1. Chemicals

The test compounds used in this study were standard explosives and drugs, selected to serve the purpose of collecting data for both positive and negative modes. Explosive standard 2,4,6-trinitrotoluene (TNT) was obtained from Accu Standard Inc. (New Haven, CT). Cocaine standard was obtained from Cerilliant (Round Wrap, TX). 2,7-Dinitrofluorene (DNF) was obtained from Aldrich Chem. Co. (Mil, WI). Dynacal permeation devices containing ammonia, and methylene chloride used as dopants were obtained from VICI Metronics Inc. (Poulsbo, WA) with a permeation rate of 3,100 ng min^{-1} ±10% at 30 °C and 460 ng min^{-1} ±15% at 30 °C, respectively. The solvents used to prepare test solutions were HPLC grade acetone from Fisher Scientific (New Jersey, NJ) and biotech grade acetonitrile from Sigma–Aldrich (St. Louis, MO).

Table 1
Operating conditions for various studies

	Drift gas flow rate (ml min^{-1})	Carrier gas[a] flow rate (ml min^{-1})	Drift gas composition	Gate width (μs)
Gas flow rate study				
Test 1	500	150	Air	250
Test 2	100	100	Air	250
Test 3	0	150	Air	250
Test 4	500	56	Air	250
Drift gas composition study				
Test 5	500	150	Air	250
Test 6	500	150	Helium	250
Test 7	500	150	Argon	250
Gate width study				
Test 8	500	150	Air	50
Test 9	500	150	Air	100
Test 10	500	150	Air	250
Test 11	500	150	Air	500

[a] Air was used as the carrier gas for all experiments.

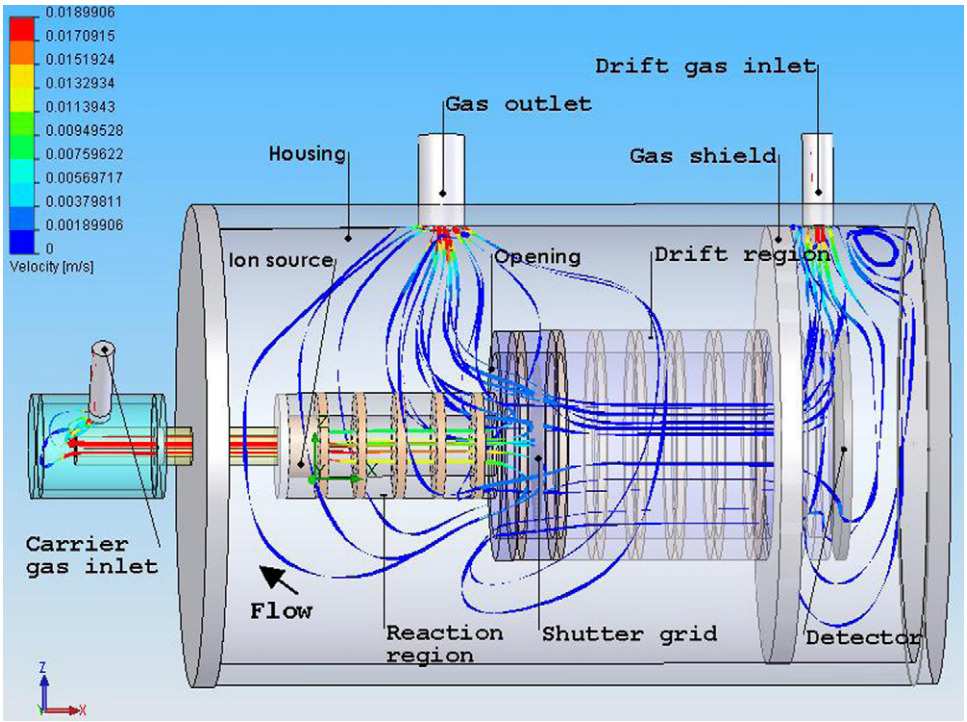

Fig. 1. Three-dimensional SolidWorks model of the PCP Phemto Chem 110 IMS instrument with COSMOSFloWorks gas flow trajectories.

2.2. Sample introduction

Standard compound 2,4,6-trinitrotoluene was diluted in acetone solvent to 5 ppm. Cocaine and 2,7-dinitrofluorene standards were diluted in acetonitrile to 50 ppm. Each sample was introduced by direct liquid injection at the inlet by depositing a 1 μL aliquot of the sample solution into the quartz sample tube inside the Teflon® cap, which was then inserted into the hot quartz showerhead tube of the PCP IMS 110. The sample solution in the tube was heated, desorbed, and carried into the IMS reaction region.

2.3. Instrumentation and parameters

The PCP Phemto-Chem Ion Mobility Spectrometer Model 110 (West Palm Beach, FL) was used in this study to obtain empirical (experimental) data for the compounds of interest. The PCP IMS can operate in both positive and negative mode by varying instrumental conditions. The standard or default operating conditions of the PCP IMS 110 were an operating drift tube temperature set at 200 °C, an inlet temperature at 250 °C, and gas-flow rates of 150 and 500 ml min^{-1} for carrier gas and drift gas, respectively. All experiments were conducted at the INL in Idaho Falls, ID (elevation 4700 ft) at atmospheric pressure, which varied from 635 to 650 mmHg for the PCP IMS 110 [23]. Typically, air was used for both carrier and drift gas flows with methylene chloride added to the carrier gas in negative mode, while ammonia dopant was added to the carrier gas in positive mode. The gate width was set at 250 μs with a cycling rate of 40 cycles per second. Standard parameters were used except as noted in Table 1 for Tests 1–11 for both experiments and simulations (unless stated otherwise) to study (1) drift gas flow rate, (2) drift gas composition, and (3) gate width. The first study of the drift gas flow rate used the test compounds TNT and cocaine. The second study of the drift gas composition used TNT in the single component test, followed by a mixture test using both TNT and DNF. The third study of the ion gate width used TNT as the test compound. For Tests 1–11, experiments were run in triplicate.

2.4. Simulation methods

The strategy for simulating ion trajectories within the PCP IMS 110 instrument utilized SIMION 7.0 (SIS, Ringoes, NJ) to model the electrostatic fields with the SDS user program [14] to account for the viscous pressure affects. The SDS user program can account for gas flow if the *x*, *y*, and *z* velocity vectors are provided in separate '.dat' files; therefore, the fluid dynamics program COSMOSFloWorks® in association with SolidWorks 2007 (Concord, MA) was used to determine the gas flow velocity vectors for importing into SDS. Because of the need to superimpose the carrier and/or drift gas flow vectors generated by COSMOSFloWorks onto the grid used by SIMION, the dimensions of the SolidWorks model must be set to be identical to those of the SIMION. In addition, care was taken to locate the origin at a common position in both models to avoid having to make corrections

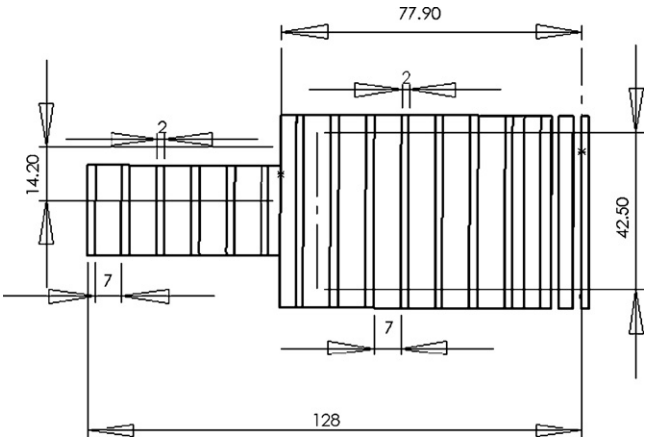

Fig. 2. Two-dimensional schematic and measurements (given in millimeters) of the PCP Phemto Chem 110 IMS reaction chamber and drift tube based on information provided in the vendor manual.

to register the coordinates between the SIMION and SolidWorks models.

The SIMION and SolidWorks (as shown in Fig. 1) computer models of the PCP IMS instrument were constructed to the best possible exactness based on the information available in the vendor manual. Estimations made during the construction of the PCP IMS computer model includes some minor details in the drift tube dimensions as shown on the 2D schematic Fig. 2. Assumptions made in the computer model include the estimates for the geometry of the inlet area, surrounding gas chamber, and gate. Of these, the gate geometry and the estimated voltage applied on the gate wires are the features that would have the greatest impact on the accuracies of the simulations. In the real PCP IMS instrument, the gate used to release ions from the ionization region into the drift tube consists of coplanar alternating parallel wires, essentially a Bradbury–Nielson shutter-grid gate [24]. Bradbury–Nielson gates have been described as difficult to fabricate [1]. The difficulty associated with modeling this gate type is that it would require 400 M grid units within SIMION to form a complete 3D model of the instrument because the symmetry of the gate (planar) is not the same as the cylindrical symmetry of the ionization and drift tubes of the PCP IMS instrument and the thin wires require 2–4 grid units to model so that they appear as real wires and not an ideal grid [12]. The symmetry options available in SIMION were exploited in order to reduce the computation time by decreasing the number of grid points by modifying the gate geometry. Instead of using alternating gate wires placed next to one another in a planar, rod-like configuration, the gate was created as a circular configuration of alternating wires, which is even more difficult to construct in reality compared to a coplanar Bradbury–Nielson gate. Simple SIMION tests of the two gate configurations revealed that the blocking and releasing of ions should be very similar. This variation of the gate geometry simplified the SIMION model of the complete PCP IMS by allowing the use of symmetry about the central axis and made the computational time manageable at ~2 h per simulation using a 3.06 GHz personal computer with 640 MB of RAM.

2.5. Fluid dynamics simulations

SolidWorks and the fluid dynamics COSMOSFloWorks software were used to obtain the flow velocities required by SIMION/SDS to simulate the flow of carrier and drift gases for the PCP simulations. Within COSMOSFloWorks, the gas composition and flow rates for the carrier and drift gases at their respective inlets (Fig. 1) were set according to the conditions for each simulation as given in Table 1. The two gases exit at the same outlet, which was set at atmospheric pressure. After completion of each simulation, the *x*, *y*, and *z* flow vectors that corresponded to the SIMION grid positions were extracted from the COSMOSFloWorks results and transposed into individual *x*, *y*, and *z* velocity '.dat' files for use by SDS.

2.6. Ion trajectory simulations

SIMION 7.0 software was used to model PCP IMS ionization reaction region and drift tube containing the alternating solid electrodes and insulator rings, the gate, and the detector (Fig. 3(A)). Fig. 3(B) shows an isometric view of the potential energy field for an overall electrical field gradient of 200 V/cm within the PCP IMS. Ion properties (e.g., charge, mass, number of ions) were defined within SIMION. The K_o values for specific masses are incorporated in the M_DEFS.dat file associated with SDS. While SDS will calculate K_o values for a mass if not provided by the user, these estimated K_o values may be quite different than the actual values because SDS assumes a spherical geometry; hence, the calculated drift times calculated with an SDS estimated K_o can be off by more than 40%

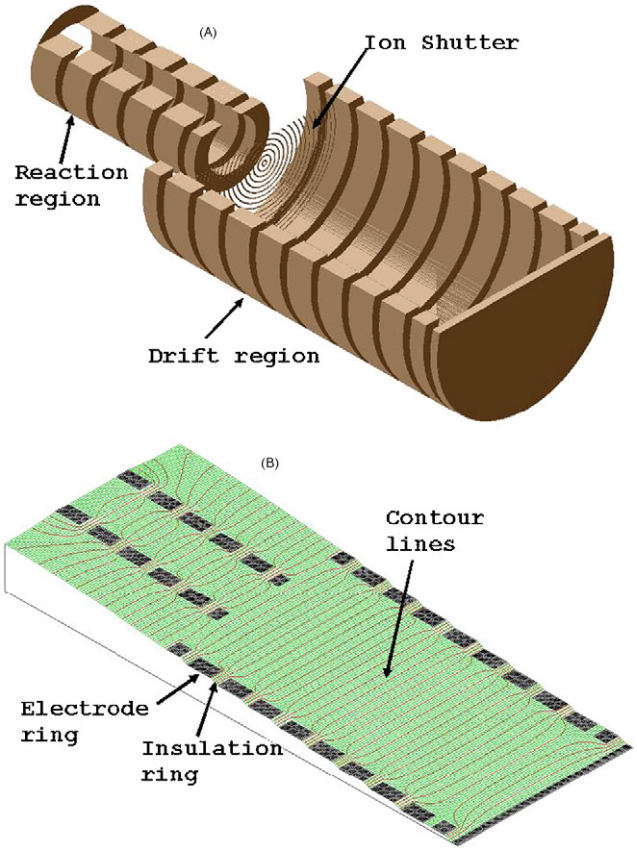

Fig. 3. (A) SIMION model of the commercial PCP IMS 110 instrument showing the electrodes of the ionization region, circular gate of alternating wires, and electrodes of the drift tube. (B) SIMION potential energy view of electrostatic field within the PCP IMS 110 instrument with a voltage gradient of 200 V cm^{-1}.

compared to experimental values. While SIMION allows the initial kinetic energy of the ions to be defined, it should be noted that this is not very important in atmospheric calculations because ions quickly lose any memory of their initial kinetic energy to collisions [12]. Space-charge effects, which are available in SIMION, were not included because they are computationally intensive and would be revealed as an increase in effective diffusion [12]. The source code of the SDS user program file was modified to include the change in voltage on the alternating gate wires to control the gate opening/closing mechanism, as well as the birth of ions at random locations within the reaction chamber to simulate the continuous ionization source, Ni^{63}, used in the PCP IMS. The drift tube temperature and pressure, collision gas mass and diameter, and gating parameters were all defined in the SDS user program. The ions were then prompted to fly down the model under the influence of the electrical field and the carrier gas flow, pass through the gate, and be subjected to the drift gas. The ions' trajectories and flight times (from birth to the detector) were recorded as output files. A recorded output file was saved in text format and later translated into a histogram (spectrum) by plotting only the ions that struck the detector electrode. The histogram was plotted with the *x*-axis representing the drift time and the *y*-axis representing the relative intensity (number of ions that hit the detector within each histogram bin) using a bin size of 50 μs.

With a 30 ms cycle for a typical IMS, the gate opened for 250 μs and closed for the remaining time, allowing only 0.8% of the total ions generated to enter the drift region. Four thousands ions were introduced in the ionization chamber during each cycle. If 0.8% of the ions passed through the gate, only 40 ions would reach the

detector. This number of ions was deemed insufficient to generate a smooth histogram. To allow more ions to reach the detector, instead of modeling the exact cycle time of the experimental PCP IMS, the gate closing time for the SIMION PCP model was reduced from 30 to 1.0 ms, while the gate open time remained the same at 250 μs. This allows approximately 1000 ions to pass through the gate. In general, the rest of the parameters for the simulations were the same as the respective experiments as noted in Table 1, except as noted for the drift gas composition study.

2.7. Gas flow rate study

Simulations 1–4 were designed to study the flow rate ratio between the drift and carrier gas at 500:150, 100:100, 0:150, and 500:56 ml min^{-1}, respectively. In the various tests of the gas flow rate study, all parameters in SIMION/SDS were kept the same. Only the gas flow vector '.dat' files from COSMOSFloWorks were replaced in SDS for the respective flow rate ratios. The test compound used in the negative mode was TNT, while cocaine was used for the positive mode.

2.8. Drift gas composition study

In Simulations 5–7, the drift gases used were air, helium, and argon, respectively. In the actual experiments, the carrier gas was air. While COSMOSFloWorks can accommodate multiple gases introduced at various inlets, SDS cannot. In SDS, only one type of collision gas can be defined; therefore, this was set as the drift gas. Because a change in the drift gas also changed the carrier gas, the gate timing had to be adjusted for each gas. In air, the time taken for the ions to reach the gate was approximately 8700 μs, thus the gate was prompted to open with this timing. For helium and argon the gate timing was changed to 2700 and 7000 μs, respectively, Two groups of different ions were created, $(TNT\text{-}H)^-$ and $(DNF\text{-}H)^-$, with 400 ions and 4000 ions, respectively, to mimic the 5:50 ppm aliquot used in the experimental analysis. The two groups of ions were spawned simultaneously. As expected, the two ion groups separated as they migrated down the drift tube and the resolution between these two adjacent peaks was calculated for each drift gas type using Eq. (3), where (t_d) is the ion drift time and (w_b) is the peak full width at the base (in microseconds) [25–27]. Measurements of the peak full width at the base and the peak full width at half maximum were conducted using standard analytical procedure.

$$R = \frac{2(t_{d2} - t_{d1})}{w_{b1} + w_{b2}} \quad (3)$$

2.9. Gate width study

Simulations 8–11 were set at gate widths of 50, 100, 250, and 500 μs, respectively. All SDS parameters except for the gate width were kept at the default conditions. The simulations were performed in negative mode with TNT as test compound to mimic the experiments.

3. Results and discussion

To test the predictive power of the SIMION/SDS modeling software, several parameters of the PCP IMS were varied to compare the effects they have on the spectrum drift time and peak shape. The drift and carrier gas flow rates were chosen to demonstrate how drift time, peak shape (i.e., full width at half maximum (FWHM)), and signal intensity change as flow rates were varied. The drift gas composition was varied to illustrate the effect on the resolution between two adjacent peaks. Finally, the ion gate width was varied to illustrate changes in ion intensity and peak broadening. The simulated spectra were compared to the experimental spectra to identify trends in the data due to each of the changes caused by varying the operating parameters. In general, it was expected that SIMION/SDS would correctly predict the trends related to the changes rather than the exact values of the experimental outcomes. How well the simulation data coincide with the observed data from the real instrument is dependent on how closely the computational models and methodology mimic the characteristics of the PCP IMS instrument.

3.1. Drift gas flow rate effects

Commercial IMS instruments incorporate two sources of gas flow: (1) the carrier gas, which is often air and directs the sample molecules into the ionization region, and (2) the drift gas, which produces a flow counter to the direction of the ion movement [1]. In the case of the PCP Phemto-Chem IMS Model 110, the carrier gas also helps to carry the ions to the proximity of the ion gate before exiting at the outlet opening (Fig. 1). The drift gas enters from the detector end and flows toward the gate before exiting at the same opening as the carrier gas. An increase or decrease in the drift gas counter flow rate is expected to alter the time ions take to reach the detector because ion mobility (K) is pressure and temperature dependent. The change in drift gas flow rate ultimately changes the pressure within the drift tube, which changes the ions' arrival time. The temperature of the drift tube was maintained at 200 °C throughout the study. However, the ion reduced mobility (K_o) should remain constant given there is no change in ion identity [21].

In the drift flow experimental and simulation studies, the drift:carrier gas flow rates varied from the manufacturer suggested settings of 500:150 ml min^{-1}, which were the conditions for Simulation 1. In Simulation 2, the two flow rates at the inlets were set to equal each other (100:100 ml min^{-1}); however, because the diameter of the ionization region is less than the diameter of the drift tube, the carrier and drift gas velocities are not equivalent. When the carrier gas velocity was higher than the drift gas velocity as in Simulation 2, the carrier gas penetrated through the gate before turning around and exiting the outlet with the drift gas as shown by the flow trajectories in Fig. 1. The inlet flow rates in Simulation 3 were set at (0:150 ml min^{-1}), where the drift flow was completely shut off. Lastly, in Simulation 4, the flow rates were set at 500:56 ml min^{-1} to achieve equal gas velocities at the point where the two gases met. Three output values; drift time, peak intensity, and FWHM were recorded to assess ability of SIMION/SDS to simulate and detect changes due to variation in the flow conditions.

Fig. 4(A) shows the effects of flow rates on the drift time of TNT in negative operating mode. Detection algorithms for commercial IMS instruments usually allow a variability window of ~50 μs for positive peak detection. Thus, the change reported for TNT drift times from 9.702 ms in Experiment 1 and 9.625 ms for Experiment 3 is significant and reflects the ions travel faster when the drift gas was completely shut off. Simulation 1 and 3 reported 10.69 and 10.67 ms, respectively. While trends for the experimental and simulated drift times were similar, the simulated drift times predicted were within 10% of the experimental values.

Additionally, both the experimental and the simulated results showed no significant effect of flow rates on the FWHM for TNT, which is in agreement with experimental data reported by Eiceman for benzene, toluene, naphthalene, and anthracene [21]. The peak intensity was highest at 771 mV for Experiment 3 without drift flow as compared to 418 mV when the flow rates were at the default settings in Experiment 1. There are examples in the literature that report the change in product ion intensity when the drift gas [21] or

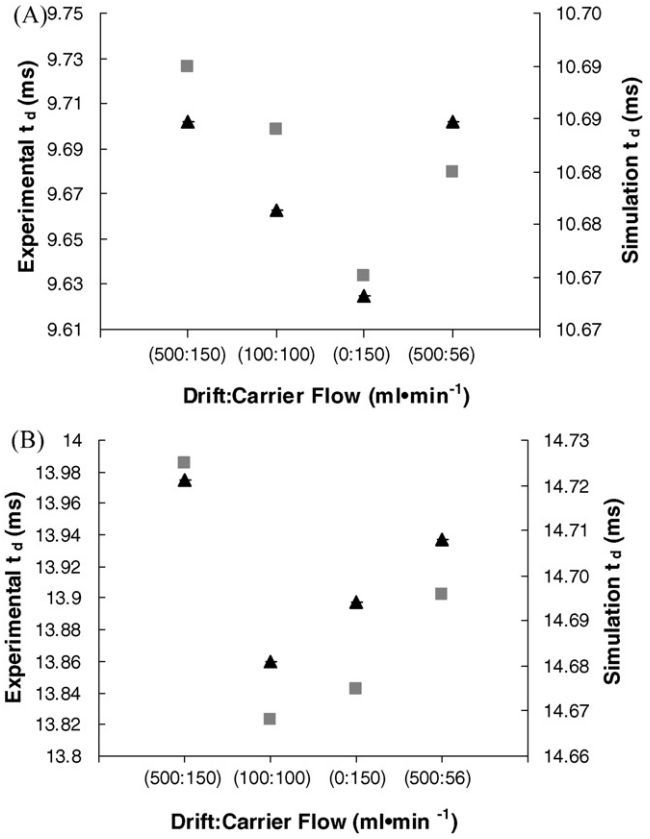

Fig. 4. Comparison of experimental and simulated drift times for (A) TNT and (B) cocaine at various flow-rate conditions. Experimental (▲) and simulated (■) data.

carrier gas [20] flow rates are varied. The simulated data, however, did not project such significant differences in peak intensity among the four simulations. This lack of peak intensity change in the simulations was because the flow conditions in the model allowed ions to pass through the gate at a constant flux. As a consequence of the gate width being held constant for all the four simulation conditions, each simulation allowed approximately the same number of ions to pass into the drift region.

Cocaine was used as the test compound for flow rate experiments and simulations in the positive operating mode. The simulated drift times predicted by the model were within 6% of the empirical experiments. The trends of ion drift time predicted by the simulations tracked the experimentally determined trends (Fig. 4(B)). The effect of different flow conditions on cocaine drift time was most noticeable between Experiment 1 (13.975 ms) and Experiment 2 (13.86 ms). Simulation 1 and 2 reported 14.725 and 14.668 ms, respectively. Lastly, the FWHM of cocaine peak was also not particularly affected by the flow rate conditions as observed in the experimental as well as the simulation results. The peak intensity in Experiment 1 was 856 mV and decreased to 771 mV in Experiment 3. Similar to TNT, the simulations did not predict significant change in peak intensity.

3.2. Drift gas composition effects

Both commercial and in-house built IMS instruments usually utilize ambient air as a drift gas. The use of SIMION/SDS in this study to predict the resolution between two adjacent compounds, TNT and DNF, in air produced excellent correlation between the simulation model and the experimental results (Fig. 5). The shoulder peaks seen in Fig. 5(B) are artifacts of the 'spline fit' function used to plot the simulated spectrum, which could be minimized if more ions are available for the simulation. The experimental and simulated resolutions obtained in air were 1.392 and 1.436, respectively (a difference of 3%). This result was achieved despite the simulation and experimental drift times of the individual peaks not matching exactly because of assumptions made related to the instrument dimensions. However, these assumptions should affect all ion species in the same manner. Therefore, it is not surprising that the SIMION/SDS simulation software correctly predicted the resolution within the PCP IMS instrument when air is used as the drift gas. The capability to predict the resolution of an IMS instrument design is a powerful tool for designing future instruments because it would reduce the costs of the trial-and-error approach.

Since K and the drift time reflect the collision cross-section and mass of the buffer gas as noted in Eq. (2), it is possible to resolve two peaks by changing the drift gas because the effect of the collision gas on drift time of the two ions may be different [28]. Citations in the literature report that, in general, ions travel faster in drift gases that are less massive and less polarizable [1,28]. The polarizability of helium gas is very low (0.205×10^{-24} cm^3) when compared to argon (1.641×10^{-24} cm^3), and He is also less massive [1,28]. It was expected and observed experimentally that the resolution between two peaks would be lower when using helium and higher when using argon as the drift gas. When the drift gas was changed from air to helium, the experimental resolution for TNT and DNF decreased to 1.296 from 1.392, and increased to 1.501 in argon. In a study by Asbury and Hill, improvement in resolution between chloroaniline and iodoaniline was experimentally observed when argon was used as drift gas [28]. However, another study by Hill's research group reported the opposite trend for two other compounds, lorazepam and diazepam, where helium drift gas provided better resolution [29]. Thus, the drift gas can be considered a dominant parameter to change when one wants to improve the resolution between

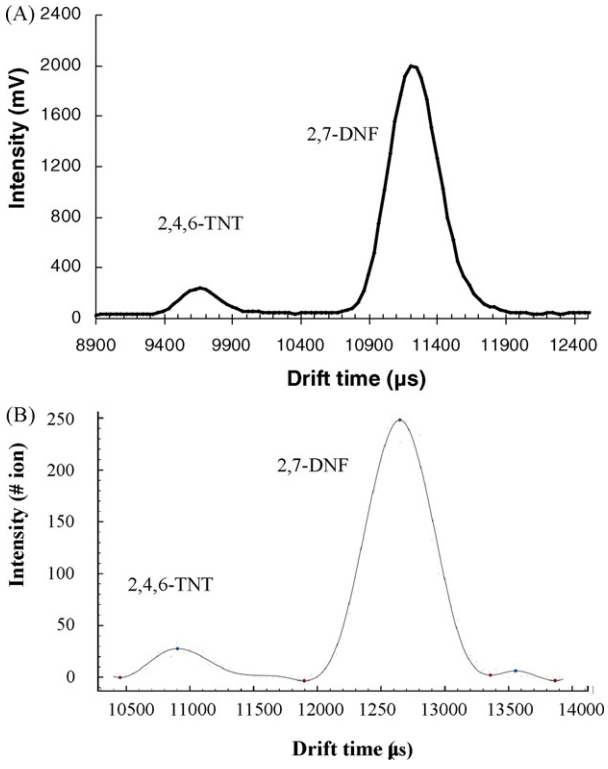

Fig. 5. (A) Experimental and (B) simulated spectra of 2,4,6-TNT and 2,7-DNF with air as both carrier and drift gas.

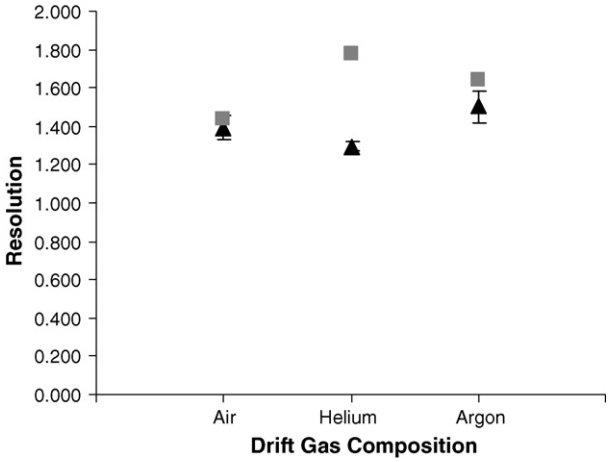

Fig. 6. Comparison of experimental vs. simulated resolution between 2,4,6-TNT and 2,7-DNF in different drift gases. Experimental (▲) and simulated (■) data.

two peaks without making physical changes to the IMS instrument. While the resolution in air was predicted within 3% accuracy, the resolution trends and values predicted in the simulations for helium and argon mediums were not as accurate. As shown in Fig. 6, the simulation predicted the increasing trend from air to helium, instead of decreasing trend as observed in the experimental data. For argon, the simulation predicted a much higher resolution than was observed experimentally. The lack of agreement between the simulation and experimental values in helium and argon drift gas is primarily due to a limitation of SDS, as it currently cannot accommodate two different gases introduced at different locations. Therefore, the helium and argon simulations had to use the same gas (He or Ar) for both the carrier and drift gas, which is not a perfect match for the experimental conditions. Attempts to experimentally change the carrier gas from air to He or Ar were made, but as expected, no ions were produced because the PCP IMS uses a Ni^{63} source that requires air or nitrogen to assist the ionization process. In addition, the current SDS user program calculates the ion gas molecule interactions based on a hard sphere model, which has been shown in a previous study by Jarrold and co-workers to be less accurate, especially for gases other than air [30]. Methods to use more advanced features of SIMION to work around this SDS limitation will be addressed in future work.

3.3. Gate width effects

The ion shutter or gate employed in most commercial IMS instruments is made of coplanar arrays of closely spaced, parallel thin wires [1,24,31]. The voltages on alternating wires are changed to open the gate and allow a pulse of ions to enter the drift region. Typically, ions from the reaction region are pulsed into the drift region for only 300 μs every 20–30 ms; thus, only ~1% of all ions are available for measurement [1]. The ion gate width is an important variable in establishing peak shape and intensity in the mobility spectrum [18,19,31]. The minimum pulse that is practical is between 10 and 100 μs, which is determined by the minimum time required for the ions to move through the wire structure from the reaction region side of the gate into the drift region side [1].

Almost all commercial IMS instruments have a duty cycle not exceeding 1% [1]. Other ion shutter designs such as the sinusoidal waveform were developed to improve the duty cycle of the gate for better sensitivity [32]. The capability of SIMION/SDS to simulate the ion behavior passing through the gate would give important insights to the development of new gating mechanisms. This study performed a simple evaluation of the SIMION/SDS simulation software by observing the peak intensity and peak broadening as the gate width varied from 50, 100, 250, and 500 μs. Peak broadening effect is the result of several mechanisms that occur within IMS instruments: gate width, diffusion, charge repulsion, ion–molecule reaction, and inhomogeneity in the electric field [9,18,26]. The two first mechanisms, gate width and diffusion are the major factors determining the shape and the width of the IMS peaks [26,28]. There are also previous reports in the literature that confirm that an increase in the gate width should result in increased peak intensities and peak widths [9,18].

The results shown in Fig. 7(A) for peak intensity and Fig. 7(B) for FWHM illustrate these expectations. Previously shown in Fig. 5, the difference between the experimental and simulated peak width was ~25%, however Fig. 5 is only a representation of one replicate. Fig. 7(B) shows average of three replicates, and the difference between the experimental and simulated full width at half maximum was ~6%. The FWHM predicted were within 6–7% of the experimental FWHM values, except for Experiment 8. The experimental FWHMs did not vary significantly when the gate width decreased from 100 to 50 μs, while the simulation predicted a decrease in FWHM. This difference may be due to the inability to accurately control the gate width down to 50 μs (which may be true for an instrument that was built in the 1980s), whereas virtual instruments will predict the ideal case. The high error bars in the experimental intensities at gate widths of 250 and 500 μs may be the result of inconsistencies in sample introduction within

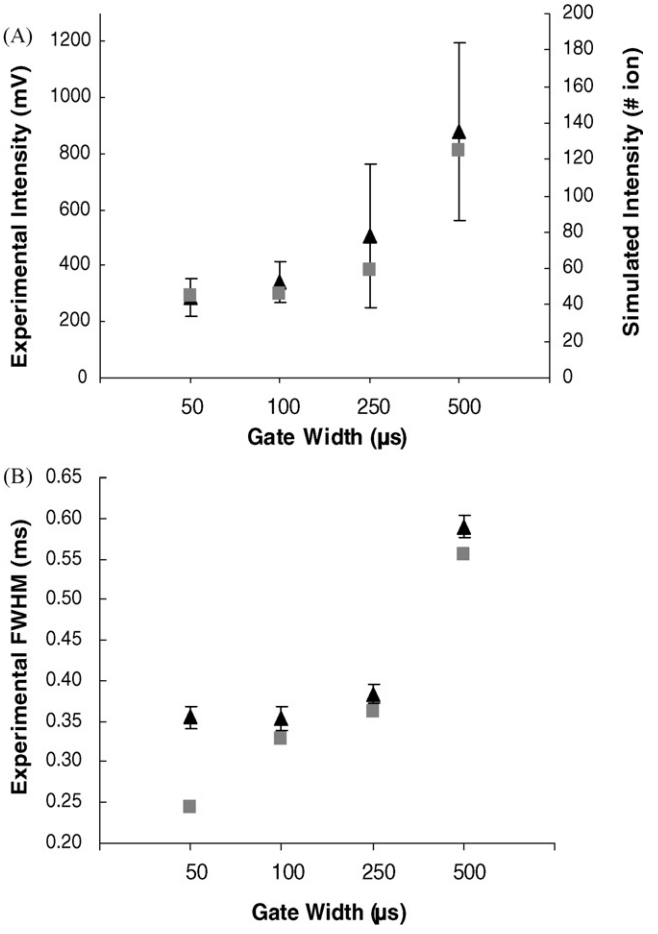

Fig. 7. Comparison of experimental vs. simulated (A) peak intensity and (B) FWHM at various gate width timings. Experimental (▲) and simulated (■) data.

the PCP instrument. In Experiment 8, when the gate was opened for 50 μs, not many ions pass through the gate resulting in a peak intensity of only 284 mV and a FWHM of 355 μs. At a gate width of 500 μs, the peak intensity increased to 878 mV and the peak shape was much broader (FWHM = 590 μs) as compared to the other three gate settings. As shown in Fig. 7(A) and (B), SIMION/SDS generally predicted the trends for both the peak intensity and peak broadening (FWHM). The trends observed are also in agreement with the experimental trends reported by Spangler and Collins [18] and Eiceman et al. [9].

In addition, a visual observation was made when the simulated ions were flying through the gate. The changes in voltage on the alternating wires caused some ions that just recently passed through the gate to slow down before they regained kinetic energy and continued down the drift tube. This effect occurs because the electrical field near these wires was altered as the voltage on the wires switched from 'open' to 'closed'. Because ions in viscous environments follow the electric field gradients, changes of electric field gradients can easily alter ion trajectories, especially around wires or grids where electric fields associated with electrostatic refraction can be complicated [12]. However, under the conditions of these experiments, this effect was minor and did not cause significant peak-tailing effects in either the experimental or simulated data.

4. Conclusions

Although the computer models incorporated several estimations and assumptions, SIMION/SDS simulations accurately predicted the resolution between two ion species when air was used for both the carrier and drift gas. The high quality of this result is because the parameters used for this simulation most closely matched the experimental conditions. As always for modeling scientific instruments with SIMION, the more accurately a simulation model matches the fabricated instrument and experimental conditions, the more exact the predicted ion behavior will reflect reality. While SDS does have the limitation of only being able to accommodate one collision gas, the SIMION/SDS simulations did track the trends observed in the experiments for gas flow rates, drift gas composition, and gate width variations. The results of this first utilization of SIMION/SDS to simulate a complete IMS instrument are encouraging and future efforts should be able to take advantage of more advanced features in SIMION to overcome some of the identified modeling issues to produce more robust and flexible virtual IMS instruments. These results show that SIMION/SDS is a valuable tool for the development of higher resolution IMS instruments and IMS–MS interfaces.

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