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RESEARCH ARTICLE

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Integration of paper spray ionization high-field asymmetric waveform ion mobility spectrometry for forensic applications

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Rationale: Paper spray ionization (PSI) is an attractive ambient ionization source for mass spectrometry (MS) since it allows the combination of surface sampling and ionization. The minimal sample preparation inherent in this approach greatly reduces the time needed for analysis. However, the ions generated from interfering compounds in the sample and the paper substrate may interfere with the analyte ions. Therefore, the integration of PSI with high-field asymmetric ion mobility spectrometry (FAIMS) is of significant interest since it should reduce the background ions entering the mass analyzer without complicating the analysis or increasing analysis time. Here we demonstrate the integration of PSI with FAIMS/MS and its potential for analysis of samples of forensic interest.

Methods: In this work, the parameters that can influence the integration, including sampling and ionization by paper spray, the FAIMS separation of analytes from each other and background interferences, and the length of time that a usable signal can be observed for explosives on paper, were evaluated with the integrated system.

Results: In the negative ion analysis of 2,4,6-trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), amounts as low as 1 ng on paper were readily observed. The successful positive ion separation of a set of illicit drugs including heroin, methamphetamine, and cocaine was also achieved. In addition, the positive ion analysis of the chemical warfare agent simulants dimethyl methylphosphonate (DMMP) and diisopropyl methylphosphonate (DIMP) was evaluated.

Conclusions: The integration of PSI-FAIMS/MS was demonstrated for the analyses of explosives in negative ion mode and for illicit drugs and CW simulants in positive mode. Paper background ions that could interfere with these analyses were separated by FAIMS. The compensation voltage of an ion obtained by FAIMS provided an additional identification parameter to be combined with the mass spectrum for each analyte.

1 | INTRODUCTION

Wipes or swabs are commonly employed media for surface sampling methods used in forensic sample collection protocols. The preparation of wipes or swabs prior to sampling and the extraction steps needed prior to instrumental analysis can be time-consuming. In addition, these samples are often quite complex, requiring extensive chromatographic methods for their analysis, which takes more time to complete. A recent focus in mass spectrometric research involves the development of ambient ionization sources in which samples are ionized under ambient conditions with minimal sample preparation that can reduce analysis time.[1-6] One such technique, paper spray ionization (PSI), developed by Wang et al,[7] is of particular interest. The setup of PSI is simple. In addition, the ionization mechanism is theorized to be the same as electrospray ionization (ESI). Therefore, analyses that are typically performed using ESI could potentially be performed using PSI. Applications of PSI to the analysis of pharmaceuticals in dry blood spots, urine samples, and other samples have been demonstrated.[8-10] Using such an approach, forensically relevant samples can be analyzed in a quicker fashion. This not only helps to reduce any potential backlogs, but also reduces solvent waste and the overall cost of the analysis.

Despite the advantages of PSI, there are practical challenges. One such challenge that could limit its application is the presence of background interferences resulting from the paper substrate. In a previous

work, we investigated the performance of PSI in negative mode for the ionization of explosives.[11-13] The experiments focused on reducing discharge by applying solvents with lower surface tension to the paper triangle. In these previous experiments, ions from substances on the paper were observed that could dominate the mass spectrum when the signal intensities of analytes of interest were low (e.g. due to low concentration or suppression). An ion mobility device could serve as a filter and only allow the transmission of the ions of interest. While there are other reports on the combination of PSI with ion separation methods,[14-17] here we evaluate the use of high-field asymmetric waveform ion mobility spectrometry (FAIMS) to reduce background ion interference, while attempting to maximize information about the analytes in the samples.

FAIMS is a relatively new technology in comparison with other separation techniques; in contrast to chromatographic separation methods, FAIMS is capable of separating sample ions in the gas phase at atmospheric pressure. The fundamental principles of FAIMS have been described elsewhere,[18,19] but a brief description is provided here. The instrumental setup and ion separation process may be easier to explain when considering the simplest design of FAIMS that utilizes planar electrodes (also named differential mobility spectrometry, DMS, when in a planar geometry). The electrodes are kept a uniform distance apart: one electrode is grounded and an asymmetric waveform is applied to the other. The base to peak amplitude of the waveform is the dispersion voltage (DV). Ions collide with drift gas while passing through the electrodes. Due to the difference in the mobilities of the ions at high versus low field, ions travel toward one or the other electrode and are annihilated. Applying a direct current potential, the compensation voltage (CV) across the electrodes corrects the net displacement of a specific ion, permitting it to be transmitted through the electrodes and on to the mass spectrometer. The CV needed for ions with the same differential mobility to be transmitted is different. Hence, FAIMS could be employed to give one of the identification markers for an analyte, which allows an additional level of confidence especially when a unique value is not observed by MS, e.g. for isomer analysis.[20,21] A CV-gram, analogous to a mass chromatogram or an extracted ion chromatogram (EIC), can be obtained by scanning the CV across a voltage range. The separation of ions can be improved by changing the drift gas. This is accomplished due to interactions between the ions and the drift gas, which have been shown to be different for different drift gases.[22,23] Nitrogen, helium, and carbon dioxide are common choices of drift gas. The addition of solvent vapor to the drift gas can also improve the separation drastically.[24-26] Again, this process is similar to the one described above for the drift gases. However, in this case, the ions interact with neutral solvent vapor molecules to form clusters. As these clusters form and break apart, the movement of the ion down the drift tube is changed. As each type of ion is likely to form a different cluster with the same solvent vapor, additional separation is achieved.

Here we report the first integration of paper spray ionization to planar FAIMS, coupled to a mass spectrometer, as well as the first application of the integrated system for the analysis of analytes with forensic relevance. We report the optimization of PSI and FAIMS parameters to provide reproducible FAIMS separation and signal. However, realizing that commercial FAIMS cells are available, only the general approach used in this study to find the optimized parameters is described. This is because the actual optimized values found herein are unlikely to hold true for other FAIMS cell geometries, making the overall process of finding them the more important aspect of this work. Furthermore, the reproducibility of paper spray ionization and ion transmission was investigated from paper triangle to paper triangle. Once these parameters had been optimized, mixtures of explosives, drugs, and chemical warfare agent simulants were analyzed to demonstrate the analytical capabilities of the integrated PSI-FAIMS-MS system.

2 | EXPERIMENTAL

Data were collected on a ThermoFinnigan LTQ linear quadrupole ion trap mass analyzer (Thermo Fisher Scientific, San Jose, CA, USA). The LTQ was operated over a *m/z* range of 50 to 500. Paper triangles with dimensions of 10 mm base and 20 mm height, which gives a 28° angle, were created from Whatman grade 1 chromatography paper (Fisher Scientific, Pittsburgh, PA, USA). Paper triangles were clamped on a custom fabricated holder made from polyether ether ketone (PEEK) and mounted on an x-y-z stage and a rotational stage (Newport Corp., Irvine, CA, USA).

The FAIMS electrodes are also custom fabricated; the design was adapted from previous work published by Rorrer et al[25,26] and modified to compensate for the differences between the mass spectrometers utilized. Planar electrodes with dimensions of 20 mm width (W) × 50 mm length (L) were kept at 2 mm apart for all experiments included in this work, although a smaller gap between the electrodes was possible by adding layers of spacers. The asymmetric waveform was supplied by a FAIMS waveform generator from Thermo Fisher Scientific. FAIMS was performed under atmospheric pressure and at a temperature of ~100°C, set by the temperature of the heated capillary inlet of the mass spectrometer. The curtain plate voltage was provided by an external dc power supply. Drift gas was introduced between the curtain plate and FAIMS electrode. A portion of the gas was drawn into the FAIMS electrode by the mass spectrometer vacuum, while the balance of the gas flowed through the curtain orifice toward the ionization source and serves as a curtain gas that can assist in the desolvation of ions. The FAIMS DV, CV, bias voltage, and gas flow were controlled through Selectra software (version 1.1.B8; Ionalytics Corp., Ottawa, ON, Canada).

For experiments with the addition of solvent vapor to the drift gas, the solvent vapor was created as described in Rorrer et al.[25,26] A stream of filtered nitrogen gas controlled by a mass flow controller and the Selectra software was split two ways. One portion remains as filtered dry nitrogen and the other portion passes through a 1-L high-performance liquid chromatography (HPLC) solvent bottle filled with ~200 mL of the selected solvent (in the studies reported here, isopropanol (IPA)). Approximately 1 h of equilibration time was given prior to experiments to generate a stable vapor concentration in the headspace of the HPLC solvent bottle and thus the FAIMS cell. To change the solvent vapor concentration, the solvated nitrogen stream could be mixed with the stream of dry nitrogen. In all experiments reported here, fully solvated nitrogen was used.

Experiments were performed using a continuous infusion of solutions, as described in the appropriate subsection in Results and Discussion. The analytes studied were 2,4,6-trinitrotoluene (TNT),

pentaerythritol tetranitrate (PETN), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), dimethyl methylphosphonate (DMMP), diisopropyl methylphosphonate (DIMP), heroin (H), cocaine (C), and methamphetamine (Meth). The explosives standards and DIMP were obtained from Cerilliant (Round Rock, TX, USA). The DMMP standard was obtained from Chem Service (West Chester, PA, USA) and the drug standards were obtained from Sigma (St Louis, MO, USA). Ammonium nitrate (AN) (Fisher Scientific) was the additive to the PSI spray solvent when analyzing explosives, while acetic acid (AA) (Fisher Scientific) was added when analyzing drugs and chemical warfare (CW) agent simulants. Isopropanol (IPA) obtained from Fisher Scientific was utilized as the solvent for all analytes.

3 | RESULTS AND DISCUSSION

Optimization of PSI, FAIMS, and MS parameters was performed first in negative ion mode using explosives standards; the results of PSI of explosives in negative mode are described elsewhere.[13] Parallel experiments were then performed in positive ion mode using drugs and CW standards. As such, the primary discussions will focus on explosives, with results and observations unique to drugs or CWs being mentioned.

Instability in ion intensity arising from variations in the paper triangles used limits the quantitative performance of PSI-MS and PSI-FAMS-MS unless internal standards are employed. Nevertheless, as demonstrated in our previous work,[13] the signal intensities of the characteristic ions from the analytes (see Table 1) provide reference data for evaluation of the performance of PSI-FAIMS/MS. Therefore, all the comparisons were based on absolute signal intensities.

3.1 | PSI-FAIMS/MS Integration

Although the ionization of analytes in PSI is thought to be the same as in ESI,[7,9] the optimization of experimental parameters for ESI may not be directly applicable to PSI. For example, ESI is typically operated with a sheath gas and sometimes with the addition of heat to aid in ion desolvation; neither option is typically employed in PSI. The sheath gas in ESI can help the transmission of ions into the FAIMS cell in ESI-FAIMS/MS. In contrast, when integrating PSI with FAIMS/MS, ion transmission into the FAIMS cell relies solely on the electric field, and therefore on the potential difference and distance between the PSI tip and the FAIMS curtain plate.

TABLE 1 Analytes of interest and corresponding ions

Analyte	Abbreviation	Species	*m/z*
2,4,6-Trinitrotoluene	TNT	$[M+NO_3]^-$	226
Pentaerythritol tetranitrate	PETN	$[M+NO_3]^-$	378
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	HMX	$[M+NO_3]^-$	358
1,3,5-Trinitro-1,3,5-triazacyclohexane	RDX	$[M+NO_3]^-$	284
Dimethyl methylphosphonate	DMMP	$[M+H]^+$	125
		$[M+Na]^+$	147
		$[2\ M+H]^+$	249
		$[2\ M+Na]^+$	271
Diisopropyl methylphosphonate	DIMP	$[M+H]^+$	181
		$[M+Na]^+$	203
		$[2\ M+H]^+$	361
		$[2\ M+Na]^+$	383
Heroin	H	$[M+H]^+$	370
Cocaine	C	$[M+H]^+$	304
Methamphetamine	Meth	$[M+H]^+$	150

Here we describe the configuration and settings that influenced the transmission of analyte ions generated by PSI using our specific instrumental design. A few variables and observations may also be applicable to integrating FAIMS-MS with other ionization sources. In the following discussion, it will be noted if the considerations are unique to the integration of PSI to FAIMS-MS. For the following integration experiments in this subsection, a mixture of the following four explosives was prepared at a concentration of 20 ppm in isopropanol (IPA) with 0.4 mM ammonium nitrate (AN): TNT, PETN, HMX, and RDX. The explosives sample solution was continuously infused onto the paper triangle through a fused-silica capillary at a flow rate of 40 μL/min.

The parameters pertaining to the PSI-FAIMS interface in our setup include the distance between the paper tip and the curtain plate, the distance between the curtain plate and the FAIMS electrode, the gas flow rate, and the curtain plate voltage. The distance from the paper tip to the curtain plate affects the signal intensity in the same manner as when the PSI source is coupled to a mass spectrometer. Adjusting the tip-to-inlet (either FAIMS or MS inlet) distance will change the onset voltage of ionization,[27] the kinetic energy of ions due to the field change, and the desolvation of ions. In the experiments reported here, the tip-to-inlet distance was kept at approximately 2 cm. A spray voltage in the range of 2.5 to 3.5 kV was applied throughout all experiments; adjustment of the spray voltage was needed to ensure a similar level of signal intensity. The curtain plate to FAIMS electrode distance was also kept at 2 cm. When placing the curtain plate at distances less than 1 cm from the FAIMS electrode, the counter current curtain gas flow led to unstable ion transmission. Conversely, placing the curtain plate further than 2.5 cm away reduced ion transmission due to the decreased electrical field. The FAIMS electrodes used in this work are shown in Figure S1 (supporting information).

Since the gas introduced into the FAIMS cell serves as both the drift gas and the curtain gas, the gas flow rate influences ionization, transmission, and separation. The counter current curtain gas flow assists in the desolvation process, as in an ESI-FAIMS interface. However, a consideration unique to PSI is that when the curtain gas flow is too high, the paper triangle may become too dry,[17] resulting in either a non-conductive medium or the onset of electrical discharge. In addition, ions would experience a higher counter gas flow and could be less efficiently transmitted to the FAIMS cell. The portion of the gas that serves as the drift gas inside the FAIMS electrode is determined by flow through the heated capillary into the mass spectrometer vacuum. Collision-induced dissociation (CID) of weakly bound nitrate adducts induced between the curtain plate and the heated capillary (or in the heated capillary or in the interface between it and the mass analyzer) can significantly reduce ion signal for the adducts (and increase the signal for the nitrate ion). For the experimental conditions employed here, a total gas flow rate of 0.75 L/min was found to provide a balance for adequate separation without compromising ionization and transmission.

An additional experimental parameter for the drift gas is its composition. As mentioned earlier, inert gases such as nitrogen and helium are often utilized in FAIMS, but it was recently demonstrated that the addition of solvent vapor into the drift gas can improve separation and increase signal intensity.[24-26] In the current experiments, addition of solvent vapor dramatically increased both signal and FAIMS separation of the explosives. Therefore, all data were collected with solvent vapor addition.

To transmit ions efficiently through the counter current gas flow into the curtain plate and then into the FAIMS cell, the electrical field is critical. In contrast to ESI-FAIMS-MS, where the sheath gas from the ESI source helps direct ions through the curtain gas, transmission of ions in PSI-FAIMS-MS relies solely on potential differences. In our setup, a dc voltage supplied by an external power supply was applied to the curtain plate; an additional dc bias voltage was applied to the FAIMS electrode from the FAIMS waveform generator giving a potential difference that allows the transmission of ions. The curtain plate voltage influences the potential difference at both the PSI–curtain plate interface and the curtain plate–FAIMS electrode interface. This potential difference at the interfaces also changes when the bias voltage changes. For the explosives studied in this work, ammonium nitrate was added in order to form nitrate adduct ions. It was observed that experimental parameters had to be carefully optimized to efficiently transmit these fragile adduct ions from atmosphere to the mass spectrometer. The optimum parameters included a curtain plate voltage of −500 V and a FAIMS bias voltage of −30 V, which yielded a reasonable signal intensity for ions from explosives including the nitrate adduct ions.

3.2 | CV/DV curve and separation of explosives

In FAIMS, both the dispersion voltage (DV) and the compensation voltage (CV) can be optimized; plots of CV vs DV can be generated to help determine the DV value that provides the best separation of the analytes. A mixture of four explosives at 20 ppm with 0.4 mM AN in IPA was continuously infused onto paper triangles through a fused-silica capillary at a flow rate of 40 μL/min. Deprotonated TNT ($[M-H]^-$) and nitrate adducts of PETN, HMX, and RDX ($[M+NO_3]^-$) were monitored. A range of DV values from 2500 to 3000 V, with increments of 100 V, was applied to determine the optimum DV, as shown in Figure 1. Data were acquired over a CV range of −40 to 0 V for the four explosives, with the CV scanned at 10 V/min over 4 min. The ions from the four explosives yielded similarly shaped CV/DV curves, with larger (more negative) CV required at higher DV. The best separation between analyte ions was observed at the maximum DV of 3000 V; higher DVs were not evaluated because of the potential for discharge.[9] For all the following experiments, the DV was set at 3000 V. Note that the CV and DV values are shown both in voltage (as specified in the instrument control software) and in Townsends (Td) for inter-laboratory data comparison.

Figure 2 displays the total ion CV-gram (TIC) and extracted ion CV-grams (EICs) of the *m/z* values of interest collected at DV = 3000 V, along with the mass spectra averaged across the CV peaks. Baseline FAIMS separation of explosives ions was achieved. FAIMS

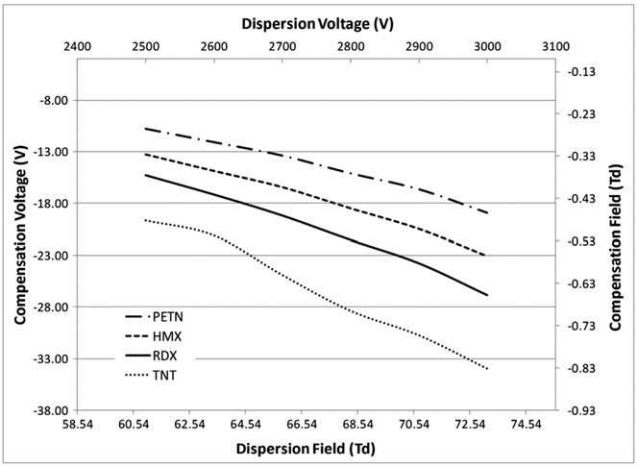


FIGURE 1 CV/DV curves for the TNT, PETN, HMX, and RDX ions listed in Table 1

provided much cleaner mass spectra for the explosives than without FAIMS separation,[7] clearly demonstrating the increased selectivity (reduced ion interferences) provided by FAIMS.

3.3 | Signal longevity at various concentrations

All the experiments described up to this point were performed with continuous infusion of an explosives mixture solution. The signal intensities of analytes were stable at approximately the same level throughout the 4 min needed for a 40 V CV scan, as shown in Figure S2 (supporting information). In contrast, when using PSI-FAIMS-MS to analyze samples collected by wiping a surface with a paper triangle, continuous infusion of analyte solution would not be practical. Nevertheless, the continuous infusion of spray solution on a deposited or wiped sample improved the analysis, providing longer lived and more intense signals than if the paper had been wetted only once. As the infused solvent dissolves and carries the analyte toward the tip of the paper where ionization occurs, the quantity of analyte left on the paper will decrease. Therefore, it is necessary to know how long a usable analyte signal will last at different quantities of analyte before experiments are conducted to estimate the limit of detection of PSI-FAIMS-MS. A series of such experiments was performed; the experiments and the resulting data are described in the supporting information. In summary, a usable signal was consistently maintained over the 4 min time range tested.

3.4 | PSI-FAIMS-MS analysis of explosives: Pre-loaded

To simulate the scenario of surface wipe analysis, an explosives mixture was pre-loaded onto a paper triangle to give 0.1 μg of each explosive analyte. As in the signal longevity study, 40 μL of spray solution (IPA + 0.4 mM AN) was placed onto paper triangles, followed by continuous infusion of spray solution at a flow rate of 40 μL/min. All other settings were the same as in the CV/DV curve collection. The resulting CV-gram, EICs of the *m/z* values of interest, and mass spectra are shown in Figure 3. Five CV peaks were observed on the CV-gram. Mass spectra were extracted over the five CV peaks. The first CV peak corresponds to *m/z* 62, the NO_3^- ion. The nitrate ion could arise from both ESI fragment ions of the explosives and the

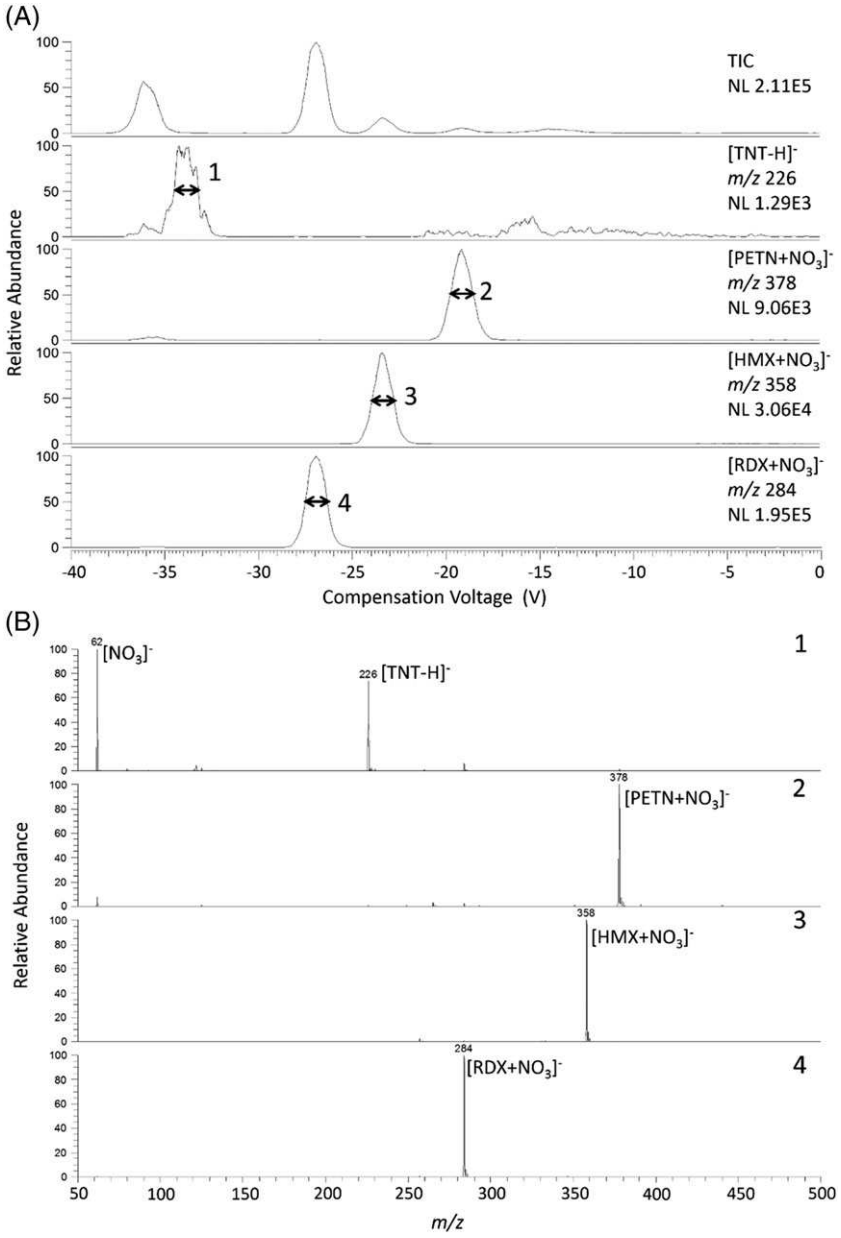


FIGURE 2 PSI-FAIMS-MS data for a 20 ppm explosives mixture continuously infused at 40 μL/min onto a paper triangle at DV = 3000 V: (A) CV-gram and (B) the corresponding mass spectra

ammonium nitrate added to the solution to form adducts. The nitrate ions could also arise from CID of nitrate adducts of the explosives as the $[M+NO_3]^+$ ions are accelerated through the curtain gas. Similar effects have been observed due to ion heating in the source, as well as the presence of neutral contaminants in the gas stream.[19] The three explosives that generate a usable signal, PETN, HMX, and RDX, were readily separated by FAIMS, and produced mass spectra across the CV peaks without interferences. However, characteristic TNT ions were not observed. As demonstrated in our previous work,[13] the signal intensity of the TNT ion was not as high as that of other explosives. The nitrate adduct of TNT could be lost in the transmission from the ionization source to mass spectrometer. Further experiments are necessary to develop a PSI-FAIMS-MS method for TNT analysis.

One of the CV peaks (peak 5), interestingly, was composed of four ions, separated by 14 *m/z* units, also observed from PSI of a blank paper triangle, as shown in Figure 3. Figure S3 (supporting information) shows that each ion was transmitted through the FAIMS cell at a slightly different CV. The identities of these background ions were not further investigated. However, they may correspond to four related compounds (differing by a CH_2 group) or related fragment ions corresponding to the paper itself (for instance, cellulose fragments) or from compounds used in treatment of the paper in the manufacturing process.

3.5 | PSI-FAIMS-MS analysis of illicit drugs: Pre-loaded

Experiments parallel to the explosives analysis described above were also performed on heroin (H), cocaine (C), and methamphetamine (Meth). The observations from the PSI-FAIMS-MS of explosives hold true for that of drugs. Therefore, all settings remained the same, except that the polarity is opposite and the spray solutions are different. The experimental details are as follows: spray voltage of +3500 V, curtain plate voltage of +500 V, FAIMS electrode bias voltage of +30 V, 0.75 L/min flow rate of curtain gas with IPA vapor, and 0.1 μg of each of the drug analytes preloaded onto a paper triangle, and acetonitrile with 0.1% v/v acetic acid continuously infused onto the paper triangle at a flow rate of

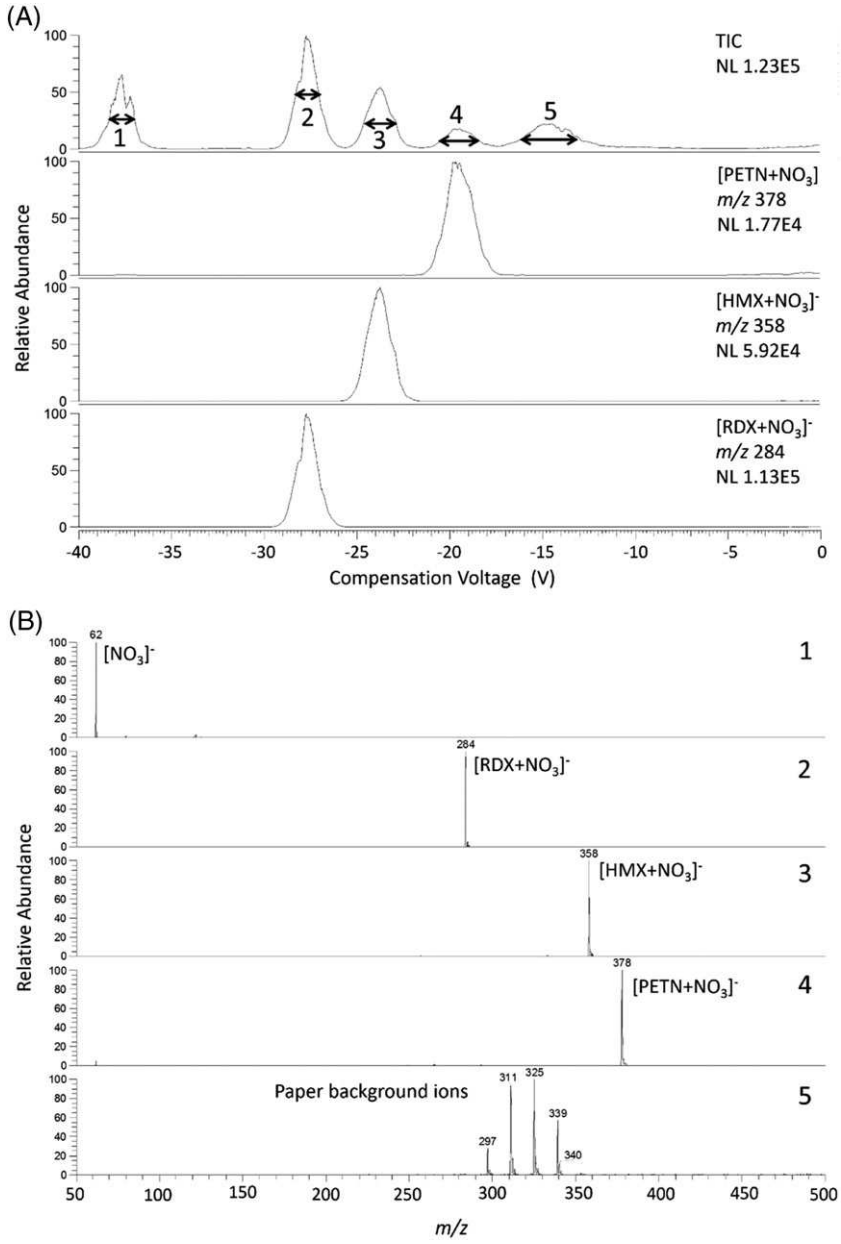
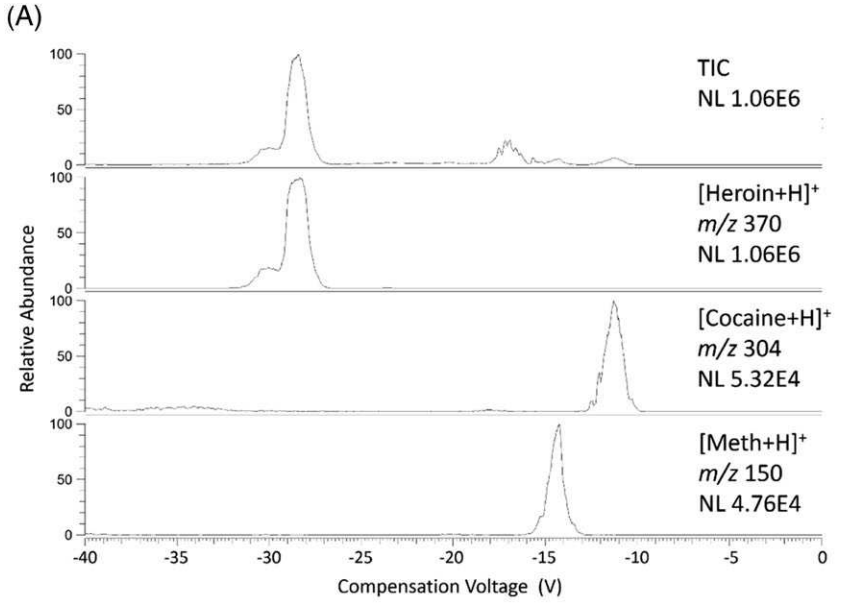


FIGURE 3 (A) CV-gram of 0.1 μg explosives mixture pre-loaded onto paper triangle with continuous infusion of isopropanol with 0.4 mM ammonium nitrate as spray solution (40 μL/min) and (B) the corresponding mass spectra

35 μL/min. A representative PSI-FAIMS-MS analysis result of the drug mixture collected with the DV at −2900 V and the CV scanned from 0 to 40 V is provided in Figure 4, along with the corresponding mass spectra. Each of the drug analytes exhibited a unique CV value, resulting in relatively clean mass spectra with good separation from the ions observed from the blank paper triangle. The background paper ions observed in positive ion mode are different from those in negative ion mode. Assuming that all the observed background ions are singly charged, the source of these ions is less likely to be from cellulose due to the lower *m/z* values, and they may be the result of ionization of impurities on the paper triangle and/or in the solvent.

3.6 | PSI-FAIMS-MS analysis of CWs

Experiments parallel to those performed for explosives and illicit drug mixtures were performed for DMMP and DIMP. Without the FAIMS cell in place, PSI-MS of the CW mixture generated $[M+H]^+$ and $[M+Na]^+$ ions in both monomer and dimer species. PSI-FAIMS-MS was attempted under the same experimental setup and conditions as for the drug mixtures. However, the characteristic CW ions observed in PSI-MS mode were greatly diminished, while the most abundant ions observed were from IPA. Proton transfer between the analyte and vapor was thought to be the reason for the reduced intensity of the characteristic CW ions. Some common solvents including IPA, MeOH, ACN, and water were added as vapors to the FAIMS drift/curtain gas and were tested to see if the characteristic CW ions could be increased to a usable level. Among the tested solvents, water yielded the same ions as observed in PSI-MS (Figure 5). Although no proton transfer between water vapor and the analyte ions was observed, the resulting CV-gram using water vapor yielded poor peak shapes. This is thought to be due to an inadequate level of vapor in the FAIMS cell, since water has a much lower vapor pressure than most common organic solvents. With the current instrumental setup, increasing the amount of water vapor entering the FAIMS cell beyond what was done here is not possible and these analytes cannot be reliably detected using this specific system.



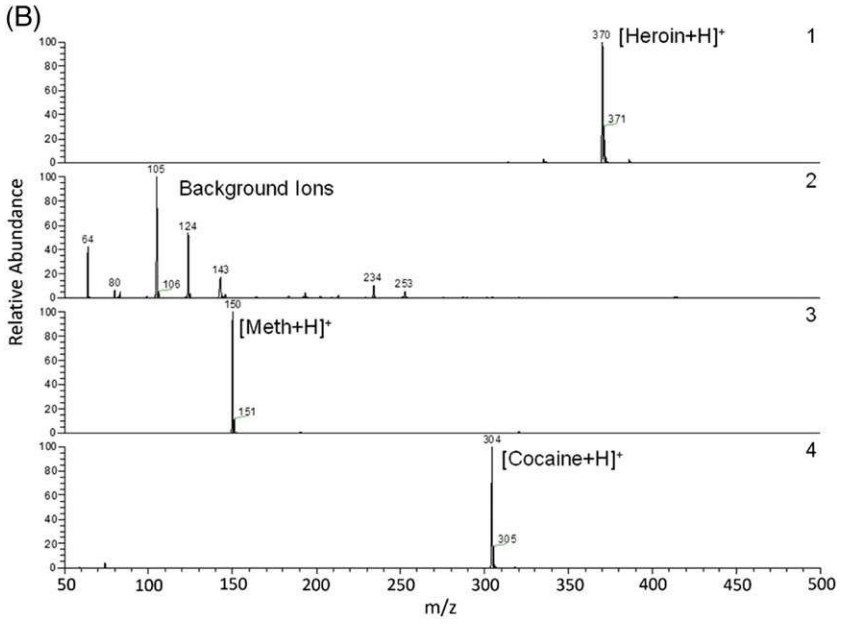


FIGURE 4 CV-gram of 0.1 μg illicit drugs mixture pre-loaded onto a paper triangle with continuous infusion of acetonitrile with 0.1% v/v acetic acid as spray solution, and the corresponding mass spectra [Color figure can be viewed at wileyonlinelibrary.com]

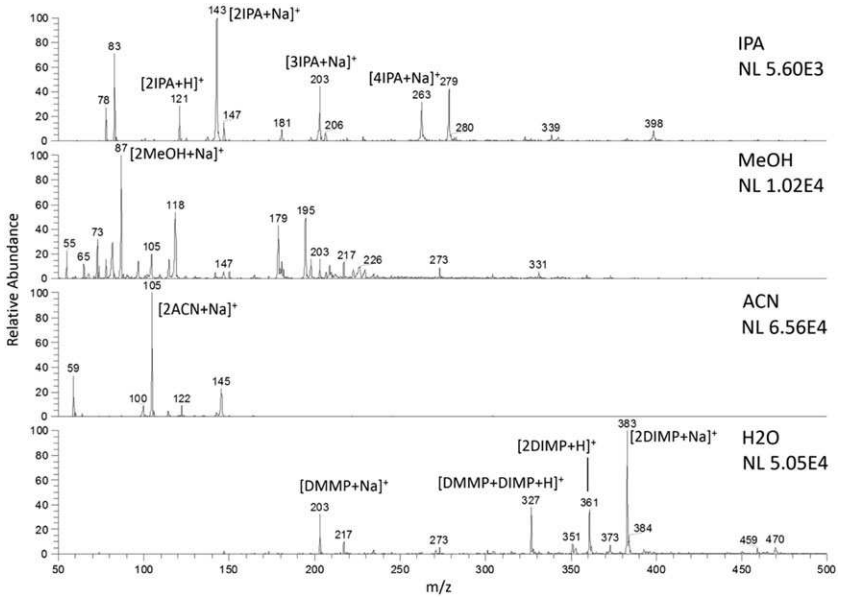


FIGURE 5 Analysis of CW mixture with various solvents as vapor introduced into the FAIMS cell [Color figure can be viewed at wileyonlinelibrary.com]

4 | CONCLUSIONS

We have demonstrated the integration of PSI-FAIMS-MS, along with the optimization of experimental parameters, for the detection of explosives. Optimizing the distances and potentials between the PSI source, curtain plate, and FAIMS electrodes maximized the sensitivity and selectivity. For weakly bound adduct ions such as the nitrate adduct of explosives studied in this work, optimization of experimental parameters is critical to maximize sensitivity. Similar optimization of distances and voltages at various interfaces will be important when applying PSI-FAIMS-MS to other analytes, but the studies here will be useful in those optimization studies. The FAIMS gas flow rate should also be adjusted, along with the spray solvent flow rate onto the paper, to prevent drying of the paper triangle and prevent discharges.

The PSI-FAIMS-MS parameters found in these studies generated adequate signal intensity and separation for the detection of explosives. The signal also lasted long enough for full FAIMS CV scans at levels as low as 1 ng on paper. Lower detection limits could be achieved by employing selected mobility monitoring (SMM) at selected CV values, analogous to selected ion monitoring (SIM) and selected reaction monitoring (SRM) for achieving the best detection limits. The goal of reducing interferences from other ions was realized.

Experiments parallel to that performed on explosives in negative ion mode were conducted on drug and CW mixtures in positive ion mode. The observations and optimum parameters found in the PSI-FAIMS-MS of explosives were beneficial for the analysis of the drug mixture. Adequate signal intensity and separation among drugs were achieved. When analyzing CW simulants, the choice of solvent for solvent vapor addition to the FAIMS drift gas was critical. In particular, attention must be paid to differences in proton affinity, since proton transfer can occur between CW ions and solvent vapor.

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SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

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