

# Secondary Electrospray Ionization-Ion Mobility Spectrometry for Explosive Vapor Detection

Maggie Tam and Herbert H. Hill, Jr.\*

Department of Chemistry, and Center for Multiphase Environmental Research, Washington State University, Pullman, Washington 99164

**The unique capability of secondary electrospray ionization (SESI) as a nonradioactive ionization source to detect analytes in both liquid and gaseous samples was evaluated using aqueous solutions of three common military explosives: cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX), nitroglycerin (NG) and pentaerythritol tetranitrate (PETN). The adducts formed between the compounds and their respective dissociation product, RDX·NO<sub>2</sub><sup>-</sup>, NG·NO<sub>3</sub><sup>-</sup>, and PETN·NO<sub>3</sub><sup>-</sup>, gave the most intense signal for the individual compound but were more sensitive to temperature than other species. These autoadducts were identified as RDX·NO<sub>2</sub><sup>-</sup>, NG·NO<sub>3</sub><sup>-</sup>, and PETN·NO<sub>3</sub><sup>-</sup> and had maximum signal intensity at 137, 100, and 125 °C, respectively. The reduced mobility values of the three compounds were constant over the temperature range from 75 to 225 °C. The signal-to-noise ratios for RDX, NG, and PETN at 50 mg L<sup>-1</sup> in methanol–water were 340, 270, and 170, respectively, with a nominal noise of 8 ± 2 pA. In addition to the investigation of autoadduct formation, the concept of doping the ionization source with nonvolatile adduct-forming agents was investigated and described for the first time. The SESI-IMS detection limit for RDX was 116 μg L<sup>-1</sup> in the presence of a traditional volatile chloride dopant and 5.30 μg L<sup>-1</sup> in the presence of a nonvolatile nitrate dopant. In addition to a lower detection limit, the nitrate dopant also produced a greater response sensitivity and a higher limit of linearity than did the traditional volatile chloride dopant.**

Ion mobility spectrometry (IMS) is the established method of choice for the detection of explosives,<sup>1–7</sup> in which radioactive <sup>63</sup>Ni ionization source is used to ionize explosive vapors thermally desorbed from solid particles. A volatile dopant is frequently employed in <sup>63</sup>Ni IMS to provide a reactant ion.<sup>8</sup> The most common dopant is methylene chloride.<sup>3,5,8–16</sup> Other dopants have

also been experimented with, including *o*-dichlorobenzene,<sup>3</sup> carbon tetrachloride,<sup>4,15</sup> hexachloroethane,<sup>6</sup> methyl chloride,<sup>15</sup> trichloromethane,<sup>15</sup> chlorobenzene,<sup>15</sup> methylene bromide,<sup>9,11,16</sup> methyl bromide,<sup>15</sup> methyl iodide,<sup>9,15</sup> and nitrogen dioxide.<sup>10</sup> The use of dopants is also common in explosives detection by liquid chromatography–mass spectrometry (LC–MS) with electrospray ionization or atmospheric pressure chemical ionization. The dopant was either added to the LC mobile phase or added postcolumn. Salts of ammonium were often used, including ammonium acetate,<sup>17–19</sup> ammonium formate,<sup>20,21</sup> ammonium chloride,<sup>22,23</sup> and ammonium nitrate.<sup>23</sup>

The use of a radioactive ionization source such as the <sup>63</sup>Ni source in IMS explosive detection increases the bureaucracy associated with using these detectors in the field and limits the type of doping agents that can be employed to produce sensitive and selective reactant ions. Electrospray ionization<sup>24</sup> and corona discharge<sup>25,26</sup> have been examined as an alternative nonradioactive ionization source. In this study, a novel nonradioactive ionization source called secondary electrospray ionization (SESI)<sup>27,28</sup> was investigated for the detection of explosives.

Secondary electrospray ionization was first introduced by Chen and Hill<sup>27</sup> in 1994 when they demonstrated that electrospray

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\* Corresponding author. Tel: (509) 335-5648. E-mail: hhhill@wsu.edu.

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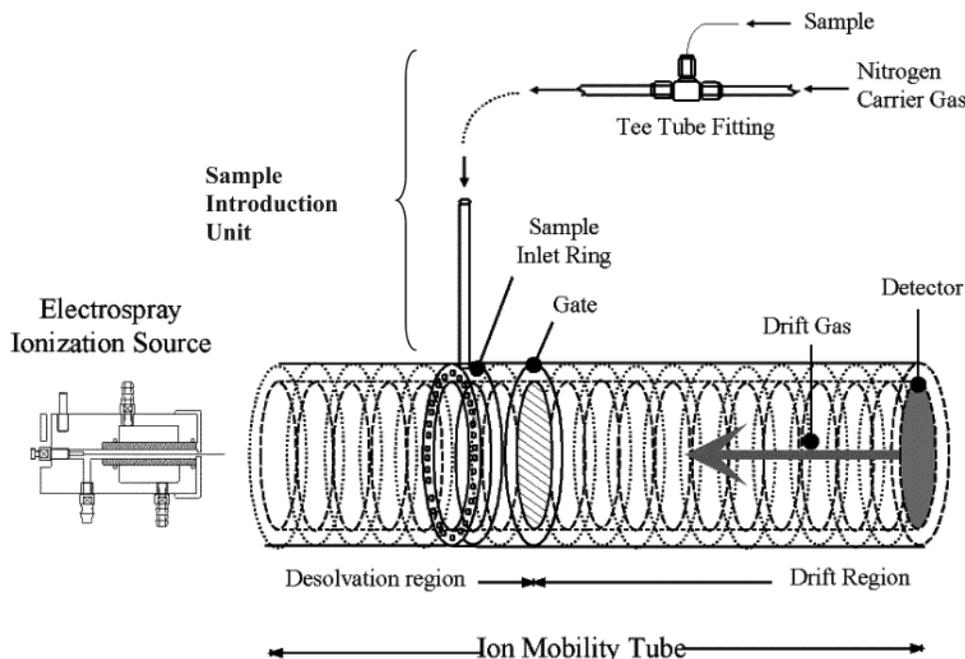


Figure 1. Schematic of secondary electro spray ionization-ion mobility spectrometer.

ionization (ESI) not only could ionize solvated analytes but also could be used to produce reactant ions, from electro spraying a solvent, to ionize neutral gaseous analytes. Later, Wu et al.<sup>28</sup> evaluated the analytical figures of merit of SESI, in comparison with ESI, in the analysis of illicit drugs, and concluded that SESI was a more sensitive ionization technique than ESI.

The ionization mechanism for SESI is similar to that of atmospheric pressure chemical ionization, where gas-phase reactant ions are produced in the ionization source and reacted with the sample analyte in the gas phase forming a charged analyte, which can then be separated and detected by IMS. In SESI, reactant ions are produced from the electro spray process. Wu et al.<sup>28</sup> reported that SESI had higher ionization efficiency than ESI in the IMS analysis of illicit drug samples.

The primary purposes of this study were to evaluate the unique capability of SESI to ionize both liquid and gaseous samples using three common military explosives and to demonstrate the use of nonvolatile doping agents for the production of unique reactant ions. Additionally, this paper investigated the temperature effect on the stability of the response ions of these explosives, reporting the effect of temperature on both  $K_0$  and sensitivity of the compounds studied.

## EXPERIMENTAL SECTION

**Instrumentation.** The SESI-IMS system was constructed at Washington State University (Figure 1). The SESI-IMS system consisted of a water-cooled ESI source, a sample introduction unit, and an ion mobility spectrometer.

The water-cooled ESI source used in this study has been described in detail by Clowers et al.<sup>29</sup> A voltage of  $-10$  kV was applied to the electro spray needle. The electro spray solvent was delivered by a Micro-Tech Ultra Plus II MicroLC system (Micro-Tech Scientific, Vista, CA) at  $10 \mu\text{L min}^{-1}$  via a fused-silica capillary. Nitrogen carrier gas flowed at  $50 \text{ mL min}^{-1}$  inside the

cooling cavity of the ESI source. In these studies, the sample was not introduced into the IMS through the electro spray process as in normal electro spray IMS.

The sample introduction unit was an assembly of a stainless steel Tee tube fitting ( $1/8$  in.) and a perforated stainless steel sample inlet ring connected via a Teflon tubing. The sample, which was pumped at  $10 \mu\text{L min}^{-1}$  by a Harvard syringe pump "11" (Harvard Apparatus, Holliston, MA), entered the Tee tube fitting through a fused-silica capillary ( $75\text{-}\mu\text{m}$  i.d.) and was carried to the sample inlet ring by nitrogen gas flowing at  $573 \text{ mL min}^{-1}$ . The sample introduction unit was heated to  $\sim 210^\circ\text{C}$  with heating tape. The elevated temperature of the sample introduction unit ensured that the sample was completely volatilized before entering the ion mobility tube. The sample inlet ring was located between the electro spray needle and the ion entrance gate. In the ESI-IMS experiments, the explosive compounds were introduced through the electro spray. In the SESI-IMS experiments, the explosive compounds were introduced through the sample introduction unit in Figure 1.

The ion mobility spectrometer was made of a stack of stainless steel guard rings ( $47\text{-mm}$  i.d.), which were connected in series by resistors and insulated from one another with alumina rings. The drift region was  $14.1$  cm in length, with a constant electric field of  $-379 \text{ V cm}^{-1}$ , unless stated otherwise. A Bradbury-Nielsen-type shutter gate was used.<sup>30</sup> A target screen and an aperture grid were located at the front and at the end of the ion mobility tube, respectively. Nitrogen drift gas flowed at  $800 \text{ mL min}^{-1}$  counter-current to the direction at which ions were traveling. The temperature of the IMS housing was varied between  $75$  and  $225^\circ\text{C}$ . The TNT experiments were operated at  $\sim 235^\circ\text{C}$ .

Signal was detected by a Faraday plate, collected and amplified ( $10^9$  gain) by a Keithley 427 current amplifier (Keithley Instru-

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ments, Cleveland, OH), and then processed by a Labview (National Instruments, Austin, TX)-based data acquisition system written in-house. Spectra were collected at either 25- or 30-ms intervals with a pulse width of 0.2 ms and were averaged 500 times.

The ITEMISER (Ion Track Instruments, Wilmington, MA), a commercial  $^{63}\text{Ni}$  IMS instrument, was operated in the explosive mode with purified air as drift gas and methylene chloride as dopant. A 10- $\mu\text{L}$  aliquot of a 10 mg  $\text{L}^{-1}$  sample solution was pipetted on a precleaned microscope slide (Becton Dickinson Labware, Franklin Lakes, NJ), which was then placed in the vapor desorption unit of the instrument after solvent had evaporated. This 10-ng sample was then introduced to the IMS by thermal desorption at 175  $^{\circ}\text{C}$ . The sampling time was 5 s. Spectra were collected at 15-ms intervals and were averaged 70 times.

**Chemicals and Solvents.** The explosives used in this study were trinitrotoluene (TNT), cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX), nitroglycerin (NG) and pentaerythritol tetranitrate (PETN) (Radian International, Austin, TX). Test solutions ranging in concentration from 0.1 to 50 mg  $\text{L}^{-1}$  were prepared by diluting a 1000 mg  $\text{L}^{-1}$  stock standard in acetonitrile with HPLC grade methanol–water (9:1, v/v) solution (J. T. Baker, Phillipsburg, NJ). Methylene chloride, sodium nitrite (Fisher Scientific, Fair Lawn, NJ), sodium chloride (J. T. Baker), and sodium nitrate (Sigma Chemical, St. Louis, MO) solutions were made by dissolving the respective compound in methanol–water (9:1, v/v) solution.

**Calculations.** Reduced mobilities were calculated from the following equation:

$$K_0 = \frac{L}{t_d} \frac{P}{E} \frac{273}{T} \quad (1)$$

where  $L$  is the length of ion mobility drift region (cm),  $t_d$  is the drift time of the species (s),  $E$  is the electric field strength of ion mobility drift region ( $\text{V cm}^{-1}$ ),  $P$  is the pressure (Torr), and  $T$  is the temperature of the ion mobility tube (K).

## RESULTS AND DISCUSSION

**Nonvolatile Dopants.** The IMS spectra of TNT ionized by ESI (Figure 2a), SESI (Figure 2b), and  $^{63}\text{Ni}$  in the presence of a methylene chloride dopant (Figure 2c) illustrated that TNT responded well in IMS with different ionization sources. All three spectra showed an intense TNT peak with a reduced mobility value,  $K_0$ , of 1.54  $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ .

The ESI-IMS and SESI-IMS of TNT both operated with an electric field of  $-270 \text{ V cm}^{-1}$ . The ESI-IMS spectrum was run at 233  $^{\circ}\text{C}$  and 705 Torr, while SESI-IMS was run at 236  $^{\circ}\text{C}$  and 702 Torr. This difference in operating temperatures and pressures of ESI-IMS and SESI-IMS accounted for the slight deviation in drift times between the two. The faster drift time of TNT in the  $^{63}\text{Ni}$  IMS spectrum was obtained on a different instrument (the ITEMISER) with a shorter drift region and operated under different conditions. All three ionization sources were well suited for detecting TNT. Thus, the preference in choosing one ionization source over another is determined by detector availability, sample medium, and convenience of use.

For explosive compounds that thermally decompose, it was necessary to introduce a dopant to reduce the extent of fragmentation and to form more stable product ions. RDX, for example,

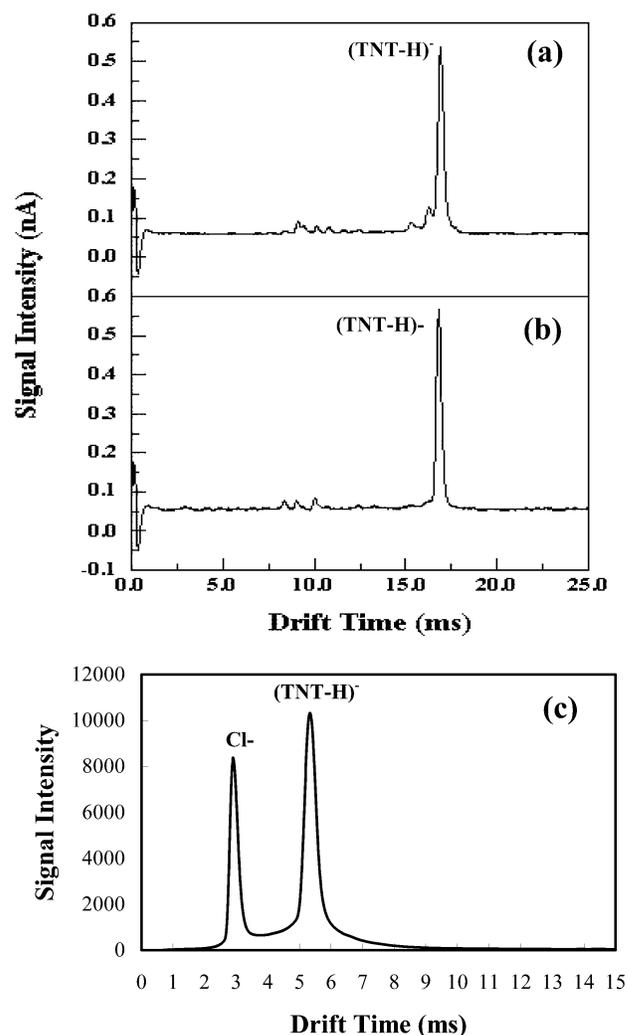


Figure 2. (a) ESI-IMS spectrum of 10 mg  $\text{L}^{-1}$  TNT; (b) SESI-IMS spectrum of 10 mg  $\text{L}^{-1}$  TNT; (c)  $^{63}\text{Ni}$  IMS spectrum of 100 ng of TNT with methylene chloride as dopant.

forms stable adduct ions with several anions, including chloride.<sup>24,31</sup> Methylene chloride is often employed as a dopant in IMS analysis of explosive compounds.<sup>5,8,16</sup> Figure 3 showed the  $^{63}\text{Ni}$  IMS spectra of 100 ng of RDX, NG, and PETN obtained with the ITEMISER at 200  $^{\circ}\text{C}$ , where the chloride adduct of RDX and dissociation product of NG and PETN were observed. The absence of chloride adducts of NG and PETN suggested the need to explore the use of other dopants in search of more sensitive and more thermally stable adducts that remain associated at higher temperatures. The hypothesis of this project is that both volatile and nonvolatile dopants could be introduced and ionized by the SESI process, whereas  $^{63}\text{Ni}$  IMS is limited to the use of volatile dopants.

Figure 4 shows the SESI-IMS spectra of RDX, NG, and PETN at 125  $^{\circ}\text{C}$  without a dopant. The major reactant ions produced from electrospraying methanol–water were chloride, nitrite, and nitrate.<sup>32</sup> Two peaks were observed for RDX and three for both

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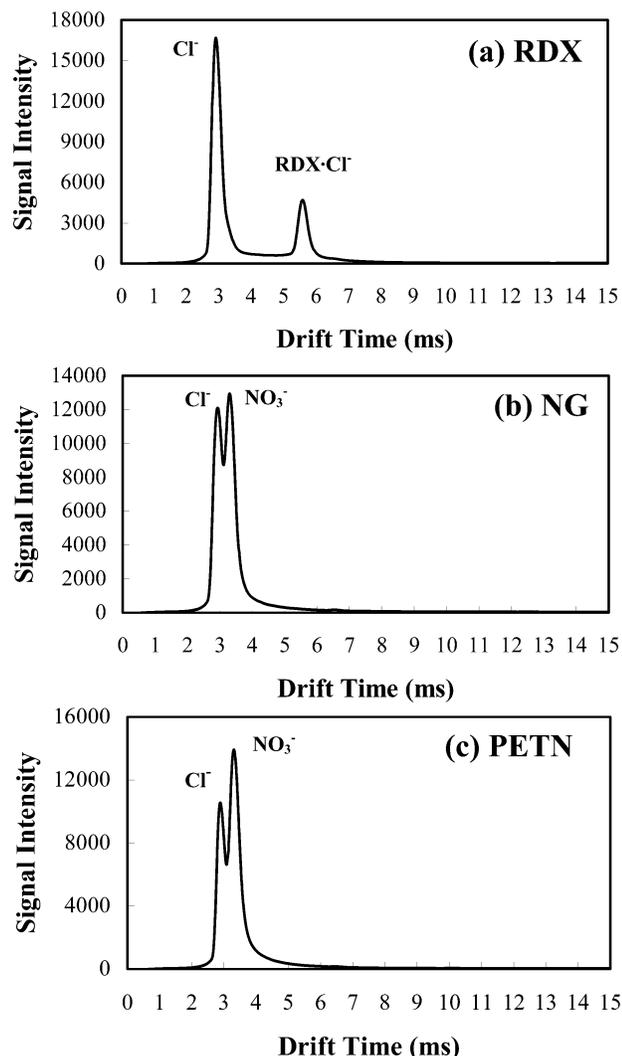


Figure 3.  $^{63}\text{Ni}$  IMS spectra of 100 ng of (a) RDX (b) NG, and (c) PETN. Spectra were obtained at 200 °C with methylene chloride as dopant.

NG and PETN. In the absence of mass identification, peak assignments for individual explosive species in this experiment were achieved as described below. The study was performed at a temperature at which all species of the explosive were thermally stable. The temperatures were 135 °C for RDX and 100 °C for both NG and PETN.

All three explosives studied in this experiment have been reported to form adducts of chloride, nitrite, and nitrate in ion mobility experiments.<sup>5,24,33–38</sup> Therefore, nonvolatile sodium salts of these anions were selected as dopants and were dissolved in the electrospray solvent of methanol–water.

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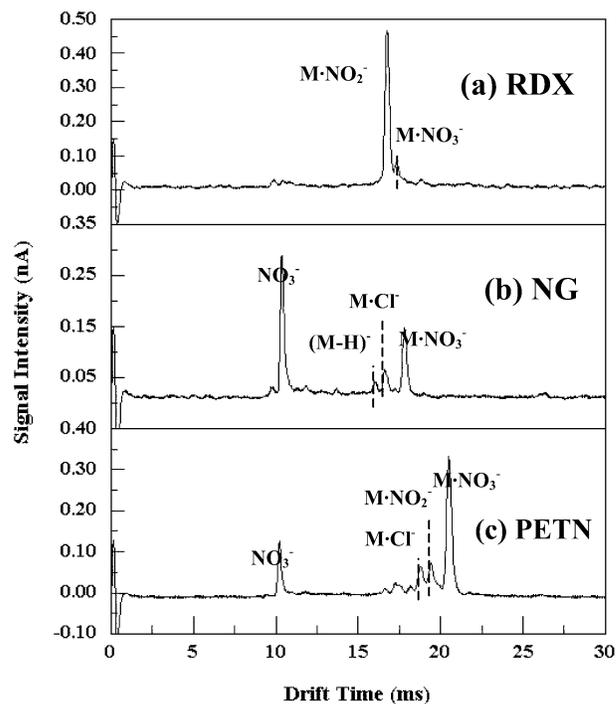


Figure 4. SESI-IMS spectra of 50 mg L<sup>-1</sup> (a) RDX (b) NG, and (c) PETN in methanol–water. All spectra were run at 125 °C.

Initially, two product ion peaks (peaks 5 and 6 in Figure 5a) were observed in the ESI-IMS spectrum when RDX was introduced in the absence of a dopant. Peak 5 had a  $K_0$  value of 1.40 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and peak 6 had a  $K_0$  value of 1.35 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. Peaks 2 and 3, in all of the spectra in Figure 5, corresponded to nitrite and nitrate ions, respectively. Figure 5b is the resulting spectrum when RDX was electrosprayed in the presence of nitrite dopant. Compared with Figure 5a, the signal intensity of peak 5 increased; Similarly, RDX was electrosprayed in the presence of nitrate dopant, and the signal intensity of peak 6 increased (Figure 5c). When RDX was electrosprayed in the presence of chloride dopant, a third peak—peak 4—with a  $K_0$  value of 1.44 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> appeared (Figure 5d). The increase in intensity of specific peaks in different dopant environments suggested that the three peaks of RDX were M·Cl<sup>-</sup> ( $K_0$  1.44), M·NO<sub>2</sub><sup>-</sup> ( $K_0$  1.40) and M·NO<sub>3</sub><sup>-</sup> ( $K_0$  1.35).

Peak assignments for NG and PETN were performed in the same manner, with the exception of (M – H)<sup>-</sup> of NG and of PETN, by observing the increased intensity in different analyte peaks in the presence of different dopant additives. The (M – H)<sup>-</sup> species of NG and PETN were assigned based on comparison with literature data. Peak assignments for species of the three explosive compounds are tabulated along with their respective literature values in Table 1.

The nonvolatile dopant studies were repeated with SESI-IMS. The SESI-IMS spectra of RDX in the absence of any dopant and in the presence of the added dopants (Figure 5e–h) showed that RDX peaks were more intense when ionized by SESI than by ESI. It was interesting to note that while reactant ions were present in the ESI-IMS spectra, no reactant ions of considerable intensity were observed in the SESI-IMS spectra of RDX. The only difference between the ESI-IMS and SESI-IMS experiments was the sample introduction method. In ESI-IMS, the analyte was

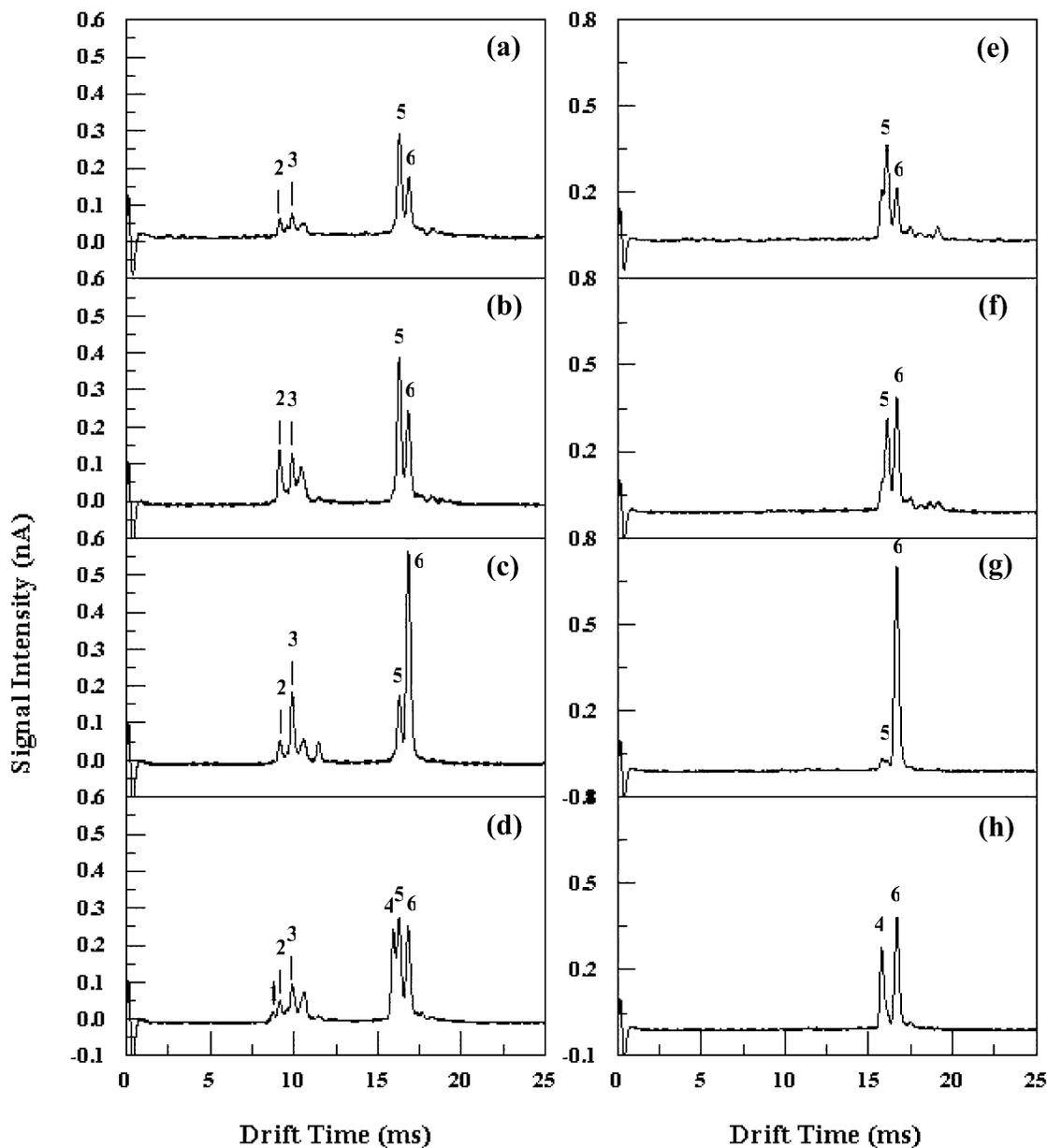


Figure 5. Effect of nonvolatile dopants: ESI-IMS spectra of  $50 \text{ mg L}^{-1}$  RDX in (a) methanol–water, (b)  $2 \text{ mM NaNO}_2$ , (c)  $2 \text{ mM NaNO}_3$ , and (d)  $2 \text{ mM NaCl}$ . SESI-IMS spectra of  $50 \text{ mg L}^{-1}$  RDX in methanol–water with electrospraying (e) methanol–water, (f)  $1.45 \text{ mM NaNO}_2$ , (g)  $2 \text{ mM NaNO}_3$ , and (h)  $2 \text{ mM NaCl}$ . All spectra were run at  $135^\circ\text{C}$ . Peak assignments: (1)  $\text{Cl}^-$ , (2)  $\text{NO}_2^-$ , (3)  $\text{NO}_3^-$ , (4)  $\text{RDX}\cdot\text{Cl}^-$ , (5)  $\text{RDX}\cdot\text{NO}_2^-$ , and (6)  $\text{RDX}\cdot\text{NO}_3^-$ .

introduced through electrospray and the analyte was ionized in ESI process. In SESI-IMS, the analyte was ionized by charge transfer from electrosprayed solvent ions. The reduction in reactant ions intensity, together with the enhanced intensity of RDX peaks in SESI-IMS, indicated that the charges from solvent ions had mostly transferred to RDX. This resulted in more RDX ions being formed in SESI than in ESI.

Nonvolatile nitrate dopant was selected to compare with a common volatile dopant in the SESI-IMS analysis of RDX at  $135^\circ\text{C}$ , because at the  $2 \text{ mM}$  concentration level of dopants introduced by electrospray, the nitrate dopant resulted in the most intense RDX peak (Figure 5e–h). Two methanol–water electrospray solvents were prepared, one containing  $4\%$  methylene chloride and the other containing  $2 \text{ mM}$  sodium nitrate. Calibration data

showed that the detection limit of RDX was  $116 \mu\text{g L}^{-1}$  in the presence of chloride dopant, with a sensitivity of  $60.2 \mu\text{A L mg}^{-1}$  and a limit of linearity at  $5 \text{ mg L}^{-1}$ . While the detection limit of RDX was  $5.30 \mu\text{g L}^{-1}$  in the presence of nitrate dopant, with a sensitivity of  $81.4 \mu\text{A L mg}^{-1}$  and a limit of linearity at  $10 \text{ mg L}^{-1}$ . In addition to a lower detection limit, the nitrate dopant also provided a better sensitivity and a higher limit of linearity than did the chloride dopant.

While nitrate may not be the most suitable dopant for explosive analysis, this study demonstrated the ability of SESI to introduce both volatile and nonvolatile dopants, thus widening the selection of possible dopants that can be employed to select ionization chemistry for increased response of analyte through the formation of more stable adduct ions.

Table 1. Experimental and Literature Reduced Mobility Values of Explosive Species

compd	species	expl $K_0$ / $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$	lit. $K_0$ / $\text{cm}^2 \text{V}^{-1} \text{cm}^{-1}$
RDX <sup>a</sup>	M·Cl <sup>-</sup>	1.44	1.39 <sup>33</sup> 1.40 <sup>24,34</sup>
	M·NO <sub>2</sub> <sup>-</sup>	1.40	1.43 <sup>35</sup> ; 1.45 <sup>36</sup>
	M·NO <sub>3</sub> <sup>-</sup>	1.35	
NG <sup>b</sup>	(M - H) <sup>-</sup>	1.45	1.45 <sup>33</sup>
	M·Cl <sup>-</sup>	1.40	1.47 <sup>5</sup>
PETN <sup>b</sup>	M·NO <sub>3</sub> <sup>-</sup>	1.31	1.32 <sup>37</sup> ; 1.37 <sup>36</sup> ; 1.40 <sup>5</sup>
	M - H <sup>-</sup>	1.25	1.22 <sup>c38</sup>
	M·Cl <sup>-</sup>	1.20	1.15 <sup>c38</sup>
	unidentified	1.17	
	M·NO <sub>3</sub> <sup>-</sup>	1.14	1.10 <sup>c38</sup>

<sup>a</sup> Reduced mobility values observed at ion mobility drift tube temperature of 135 °C. <sup>b</sup> Reduced mobility values observed at ion mobility drift tube temperature of 100 °C. <sup>c</sup> Reduced mobility values calculated on assumption of (TNT - H)<sup>-</sup> being 1.450 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>.

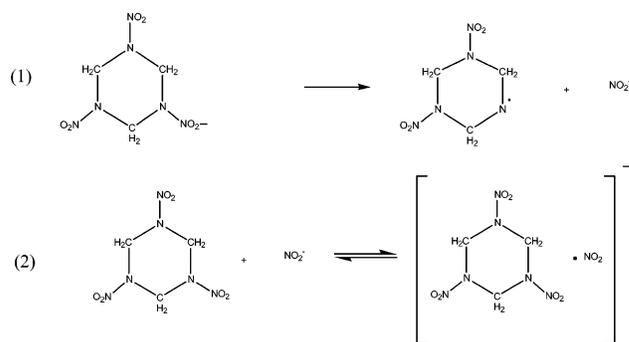
**Thermal Stability of RDX, NG, and PETN.** The thermal stability of the adduct ions of RDX, NG, and PETN created by SESI-IMS was investigated at drift tube temperatures ranging from 75 to 225 °C. A high concentration of 50 mg L<sup>-1</sup> was used to ensure that the absence of the explosive species at high temperatures was due to thermal instability rather than limitation of detection. The species RDX·NO<sub>2</sub><sup>-</sup>, NG·NO<sub>3</sub><sup>-</sup>, and PETN·NO<sub>3</sub><sup>-</sup> were chosen as the adduct ions to monitor because they gave the most intense signal for their parent compound at 125 °C (Figure 4).

At drift tube temperatures higher than 150 °C, (M - H)<sup>-</sup>, adduct ions of NG and PETN, were absent (Figure 6b and c), while NO<sub>3</sub><sup>-</sup>, their dissociation product, was prominent. However, at 225 °C, adduct ions of RDX were still detectable, although at a reduced signal intensity compared to that at a lower drift tube temperature (Figure 6a), together with an increased signal of NO<sub>2</sub><sup>-</sup>, the dissociation product of RDX. These data indicated that adduct ions of RDX were more thermally stable than those of NG and PETN and that the binding energies of the RDX adducts were relatively higher than those of NG and PETN.

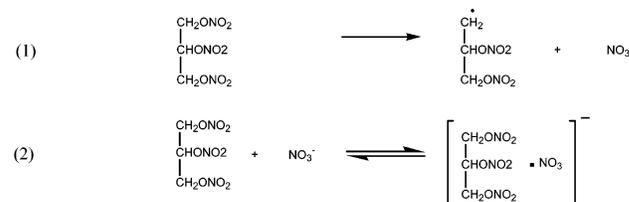
Figure 6 also revealed that some adducts, particularly RDX·NO<sub>2</sub><sup>-</sup>, NG·NO<sub>3</sub><sup>-</sup>, and PETN·NO<sub>3</sub><sup>-</sup>, were more sensitive to temperature changes than others. These three adducts were the same species that gave the most intense signal for their parent compound. RDX·NO<sub>2</sub><sup>-</sup>, NG·NO<sub>3</sub><sup>-</sup>, and PETN·NO<sub>3</sub><sup>-</sup> had maximum signal intensity at 137, 100, and 125 °C, respectively.

From 75 °C up to their optimum temperature, the signal intensity of RDX·NO<sub>2</sub><sup>-</sup>, NG·NO<sub>3</sub><sup>-</sup>, and PETN·NO<sub>3</sub><sup>-</sup> increased with increasing temperature. This effect of temperature on response indicated the mechanism of adduct formation. Apparently, RDX·NO<sub>2</sub><sup>-</sup>, NG·NO<sub>3</sub><sup>-</sup>, and PETN·NO<sub>3</sub><sup>-</sup> were adducts formed between the compound and its decomposition product ion. Since RDX dissociated to NO<sub>2</sub><sup>-</sup> and NG and PETN dissociated to NO<sub>3</sub><sup>-</sup>, the nitrite and nitrate adduct ions originated from the dissociation products of their respective compound. This involved two steps: (1) the molecular ion dissociated to form nitrite or nitrate and (2) the molecule reacted with the dissociated nitrite or nitrate thus forming an autoionization product.

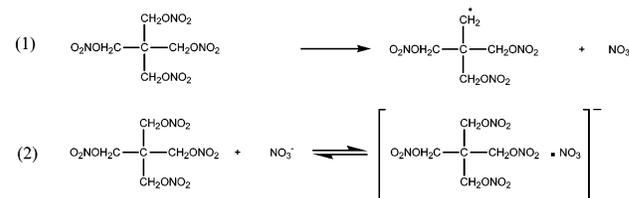
**RDX:**



**NG:**



**PETN:**



Above their optimum temperatures, the signal intensity of RDX·NO<sub>2</sub><sup>-</sup>, NG·NO<sub>3</sub><sup>-</sup>, and PETN·NO<sub>3</sub><sup>-</sup> decreased with increasing temperature. This decrease in signal intensity can be attributed to the thermal decomposition of the autoionization products or the advance decomposition of the compound itself into NO<sub>2</sub><sup>-</sup> or NO<sub>3</sub><sup>-</sup>, as evidenced by the presence of NO<sub>2</sub><sup>-</sup> for RDX and NO<sub>3</sub><sup>-</sup> for NG and PETN at high temperatures.

**Temperature Effect on  $K_0$ .** The reduced mobility values of the molecular ions and the various adduct ions of RDX, NG, and PETN were plotted versus the drift tube temperature used in this study, from 75 to 225 °C (Figure 7). Error bars were omitted from the plot because they were smaller in size than the  $K_0$  markers. The average standard deviation for the  $K_0$  values was 0.001 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, with a maximum standard deviation of 0.002 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. The  $K_0$  values of the various explosive species showed a slight negative dependence on temperature, with the  $K_0$  value decreasing by 2% at most over the temperature range. In conclusion, the  $K_0$  values of the explosive species appeared to be constant ( $< \pm 2\%$ ) over a 150 °C temperature range where SESI-IMS is used.

**Signal-to-Noise Ratio.** With 50 ng  $\mu\text{L}^{-1}$  of liquid sample entering the sample introduction unit at 10  $\mu\text{L} \text{min}^{-1}$ , being volatilized at a temperature of 210 °C, and carried by nitrogen gas flowing at 940 mL min<sup>-1</sup>, a 50 ng  $\mu\text{L}^{-1}$  liquid sample was, therefore, equivalent to 0.53 mg m<sup>-3</sup> or 102 ppbv, of RDX, 101 ppbv, of NG, and 72 ppbv, of PETN in nitrogen.

In the SESI-IMS experiments, in the absence of added dopant, the signal-to-noise ratios for 50 mg L<sup>-1</sup> or 0.53 mg m<sup>-3</sup> RDX (137 °C), NG (100 °C), and PETN (125 °C) were 340, 270, and 170, respectively with a nominal noise of  $8 \pm 2$  pA. At this level of

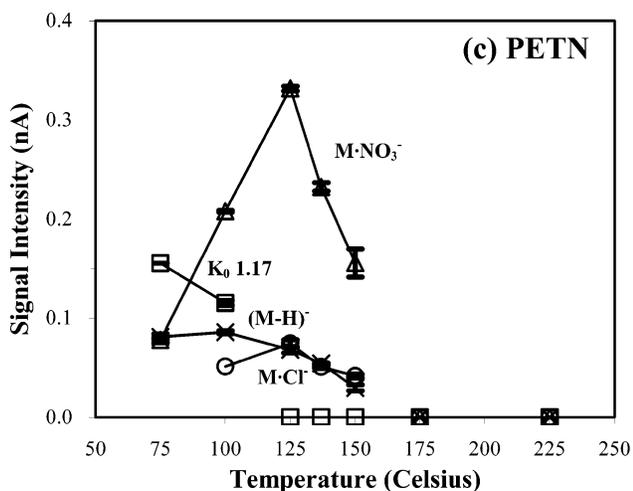
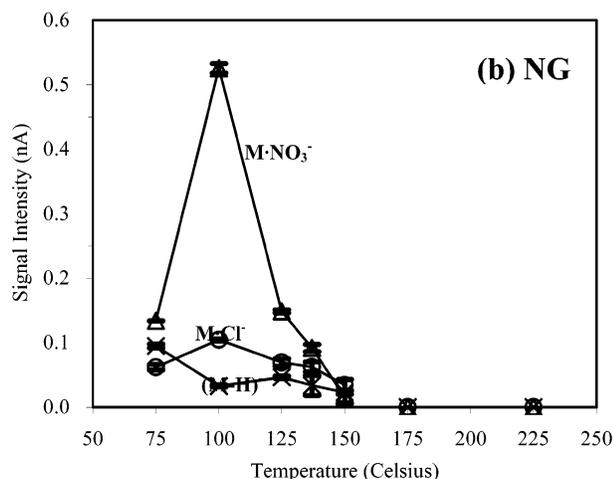
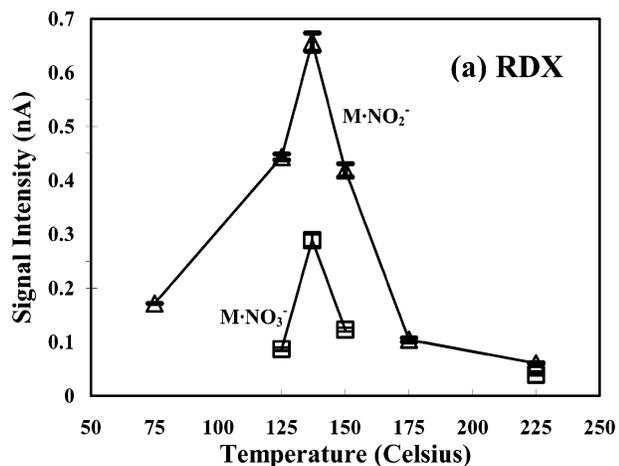


Figure 6. Thermal stability of RDX, NG, and PETN species: Plots of SESI-IMS signal intensity versus drift tube temperature of (a) RDX, (b) NG, and (c) PETN.

signal-to-noise ratio measured, the sensitivity of the SESI-IMS system was sufficient to detect explosives in workplace air

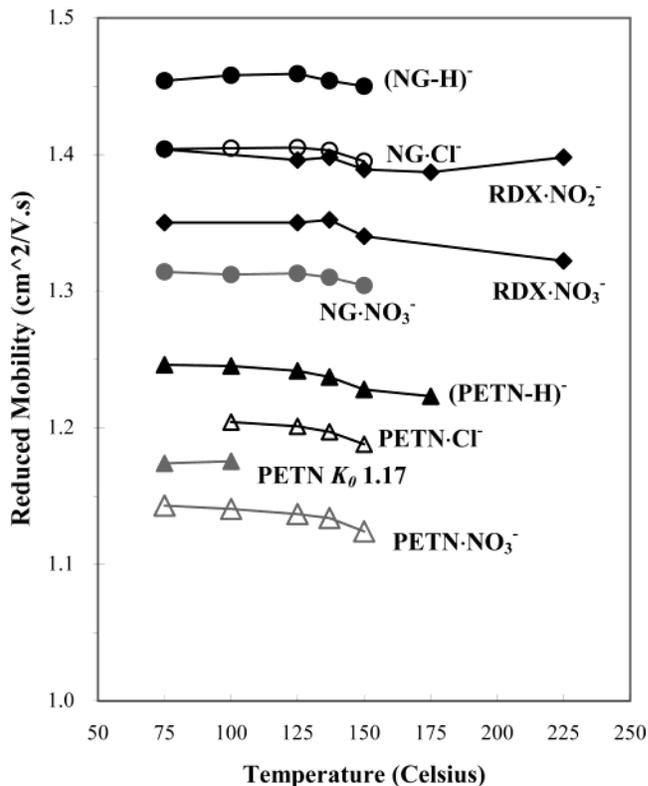


Figure 7. Plot of SESI-IMS reduced mobilities of RDX, NG, and PETN species versus drift tube temperature. Average standard deviation for the  $K_0$  values was  $0.001 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , with maximum standard deviation at  $0.002 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . Error bars were omitted from the plot because they were smaller in size than the data point markers.

samples, where the maximum airborne concentration of explosives recommended by the American Conference of Governmental Industrial Hygienists (1986) was  $0.5 \text{ mg m}^{-3}$  for NG and  $1.5 \text{ mg m}^{-3}$  for RDX.

## CONCLUSIONS

SESI is a nonradioactive ionization source, which can be used to detect both vapor-phase and aqueous-phase explosives. Non-volatile dopants can be used with SESI to enhance both sensitivity and selectivity. Data showed that SESI-IMS analysis of RDX, in the presence of a nonvolatile nitrate dopant, produced not only a lower detection limit but also a greater response sensitivity and a higher limit of linearity than in the presence of a common volatile chloride dopant.

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