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Reactant Ion Chemistry for Detection of TNT, RDX, and PETN Using an Ion Mobility Spectrometer

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Reactant Ion Chemistry for Detection of TNT, RDX, and PETN Using an Ion Mobility Spectrometer

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Abstract

This report describes the responses of three energetic materials (TNT, RDX, and PETN) to varying reactant ion chemistries and IMS cell temperatures. The following reactant ion chemistries were evaluated: air-dry; air-wet; methylene chloride-dry; methylene chloride-wet; methylene bromide-dry; nitrogen dioxide-wet; sulfur dioxide-wet. The temperature was varied between 160 - 220°C.

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Reactant Ion Chemistry for Detection of TNT, RDX, and PETN Using Ion Mobility Spectroscopy

Introduction

Ion mobility spectrometry is a technique that is being used and further developed for the detection and identification of explosives, among other applications. An ion mobility spectrometer (IMS) consists mainly of two parts: an ionization region where molecules in the gas phase are ionized, generally with a ^{63}Ni source, and a drift region where ionic species are separated according to their ionic mobilities. The IMS is operated at ambient pressure; thus the ionization region contains many molecules in addition to the molecules being analyzed. The molecules of the ambient atmosphere form a supply of reactant ions which in turn react with the analyte to form ionic species. The atmosphere of the ionization region can be controlled and is often doped with chemicals to produce specific reactant ions. For example halogenated compounds such as methylene chloride are widely used to produce chloride reactant ions.¹⁻³ Communication with PCP, Inc., a manufacturer of IMS systems, indicated good response for PETN with nitrogen dioxide providing the reactant ions.⁴

This study was done to determine the responses of three explosives (TNT, RDX and PETN) when varying reactant ion chemistry and temperature. The following reactant ion chemistries were evaluated: air-dry; air-wet; methylene chloride-dry; methylene chloride-wet; methylene bromide-dry; nitrogen dioxide-wet; sulfur dioxide-wet. IMS cell temperatures ranged from 160—220°C. Responses to known amounts of TNT, RDX and PETN were integrated, but the evaluation is also necessarily qualitative because peak shape is important in being able to detect an explosive as well as being able to do the analysis in a reasonable amount of time. Calibration curves were constructed for varying conditions with limited success. This study does not establish minimum detection limits. Also, the IMS was not interfaced with a mass spectrometer; thus exact species identification could not be done although it would have been of interest on several occasions during the study.

Experimental

Samples were run on a Phemto-Chem® Model 110 ion mobility spectrometer. Responses to explosive materials were integrated using a Spectra Physics 4270 integrator. Glassware for standards was passivated using a method developed by Rodacy.⁵ Concentrated solutions (1200—1300 ppm) were made by dissolving known weights of explosives in acetone and diluting to a known volume. Standards were made for TNT and RDX (0.13 ppm each) by injecting 1 μL of concentrate into 10 mL of methanol. The PETN standard (1.3 ppm) was prepared similarly except 10 μL of concentrate was used. Data were collected over a period of four weeks using the same set of standards which were sealed and refrigerated when not in use. The TNT standard was wrapped in foil to protect it from light.

Standard solutions were injected into a quartz sampling tube using the following procedure: 1) the Teflon sample holder and quartz tube were removed from the IMS and allowed to cool for 30 sec; 2) a specified amount of standard solution was injected into the sample tube with a microsyringe; 3) solvent was allowed to evaporate for 30 sec; 4) the integrator was started; and 5) the sample tube was inserted into the IMS. The integrator was stopped when the response had returned to baseline level. Methanol blanks were run to confirm that this procedure didn't allow carryover, and all injections were done by the same person to minimize variability based on injection technique.

The carrier gas was ultra high purity (UHP) air at 100 cc/min, and the drift gas was UHP nitrogen at 500 cc/min. To introduce water into the carrier gas, the flow was bubbled through deionized water. Dopants were added to the carrier by placing permeation tubes containing the desired dopant in the carrier line flow path. When both dopant and water were in line, the water was placed upstream from the dopant. The dopants used and their permeation rates are shown in Table 1.

Table 1. Dopants and Permeation Rates Used in IMS Response Study

Dopant	Permeation Rate	Source of Permeation Tubes
Methylene Chloride	1.91 $\mu\text{g}/\text{min}$ at 22°C	Made in our lab. Rate determined gravimetrically*
Methylene Bromide	52 ng/min at 22°C	Made in our lab. Rate determined gravimetrically
Nitrogen Dioxide	540 ng/min at 30°C	VICI Metronics, Inc.
Sulfur Dioxide	336 ng/min at 30°C	Kin-Tek Laboratories, Inc.

*The tubes were weighed before and after a known amount of time had elapsed. Permeation was assumed to occur at a constant rate.

Spectra were collected using a system composed of a Phemto-Chem® Model ASPB-1 Interface Board and a Waveform Analysis Software Package (WASP) Version 1.35 by

Graseby Ionics. Software parameters and instrument parameters are shown in Table 2. The delay was changed occasionally to allow detection of ions with longer drift times, but all other parameters were held at the values shown.

Table 2. Software and Instrument Parameters Used in IMS Response Study

Acquisition:	Averages 64 Samples 512	Frequency, kHz 32 Waveforms 1
Gating Pulse:	Frequency, Hz 42 Delay, μ s 4000	Width, 180 Source Internal
Instrument Gain, 2 Negative Ion Mode		

Reduced mobilities were calculated using the following equation:⁶ For the Phemto-Chem ® Model 110 IMS, $d = 8\text{cm}$ and $E = 193\text{ V/cm}$.

$$K_0 = (d / Et)(P / 760)(273 / T)$$

where

K_0	=	reduced mobility in cm^2/Vsec	
d	=	distance of the drift region, cm	
P	=	atmospheric pressure, torr	
E	=	electric field strength, V/cm	
t	=	drift time, seconds	
T	=	drift tube temperature, °K	(1)

Results and Discussion

The IMS response to explosives is plotted in three dimensions: x being the time it takes to traverse the drift tube; y being the intensity of the response, and z being the time from

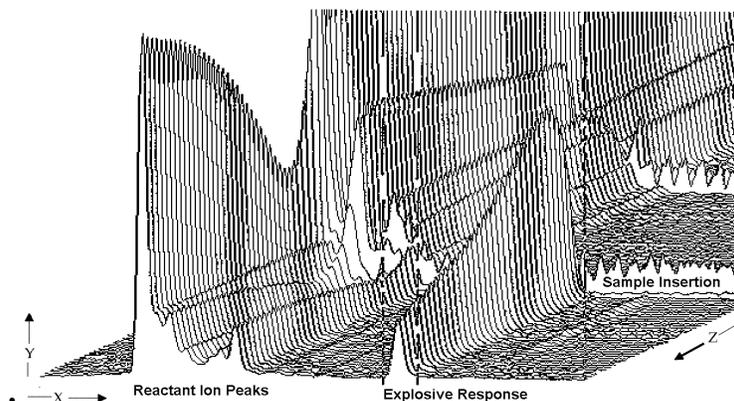


Figure 1. An example of an IMS response plot

insertion of the quartz sampling tube. An example is shown in Figure 1. An IMS is sensitive to vibration, and insertion of the tube into the IMS causes a momentary shift in intensity as also seen in Figure 1. Reactant ion peaks are seen at shorter drift times and explosive responses at longer drift times. Tables 3 —5 give a qualitative assessment of the

results for TNT, RDX, and PETN, respectively. The injections were 2 μl of standard at each condition so that comparisons could readily be made by looking at the plots. A good response shape is shown in Figure 2a. It rises and then falls off again rapidly, in less than a minute or so, giving a response with good intensity (and, therefore, good detectability) and a short analysis time. A poor response shape is shown in Figure 2b. The explosive desorbs from the quartz tube so slowly that intensity is low and analysis time is long—sometimes as much as ten minutes. IMS cell temperature has a large affect on response shape for a given explosive material—the lower the temperature, the poorer the response shape.

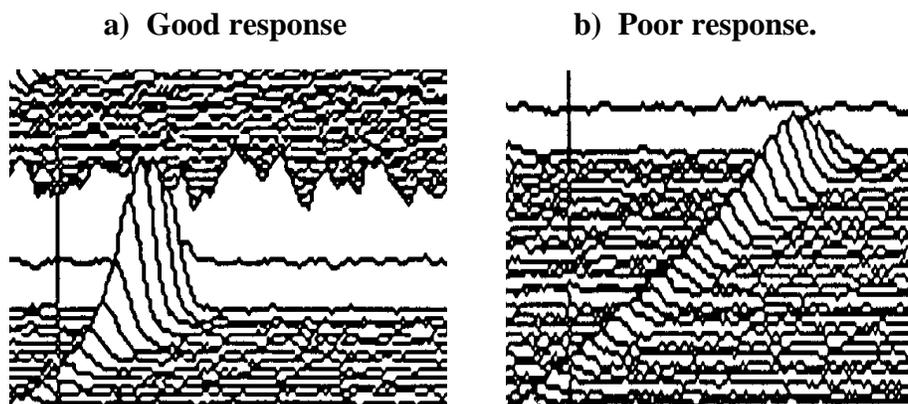


Figure 2. IMS Response Shapes.

TNT Results

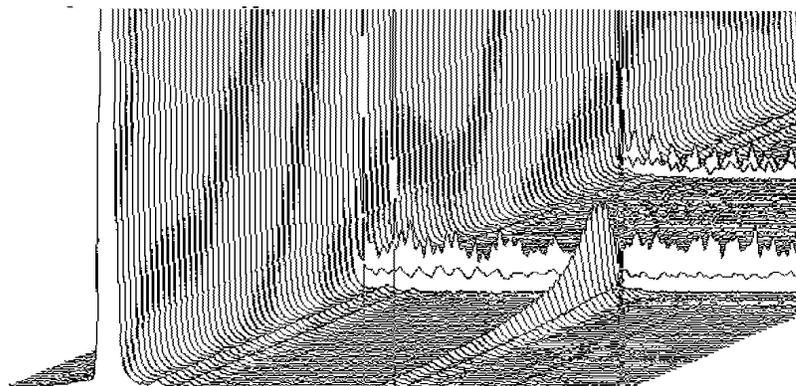


Figure 3. IMS response for TNT with CH₂Cl₂ dopant at 200°C.

A qualitative assessment of TNT response is given in Table 3. The best response at 200°C was obtained by using CH₂Cl₂ in a dry air carrier gas and is shown in Figure 3. When TNT was tested with CH₂Cl₂ in a moist air carrier gas, a variation in

intensity of response was seen, and the water adds reactant ion peaks in the region of interest for explosives. The reactant ion peaks due to water do not interfere with TNT, however.

Raising the temperature to 220°C gave less tailing and a somewhat more intense response. Higher temperatures generally give less tailing probably because the explosive material desorbs from the quartz tube more readily as temperature increases. Thus this same observation would probably be true for CH₂Cl₂ in a dry carrier gas. A good response was also obtained with NO₂ in a moist carrier gas and is shown in Figure 4. Raising the temperature to 220°C gave less tailing, but also a less intense peak. Lowering the

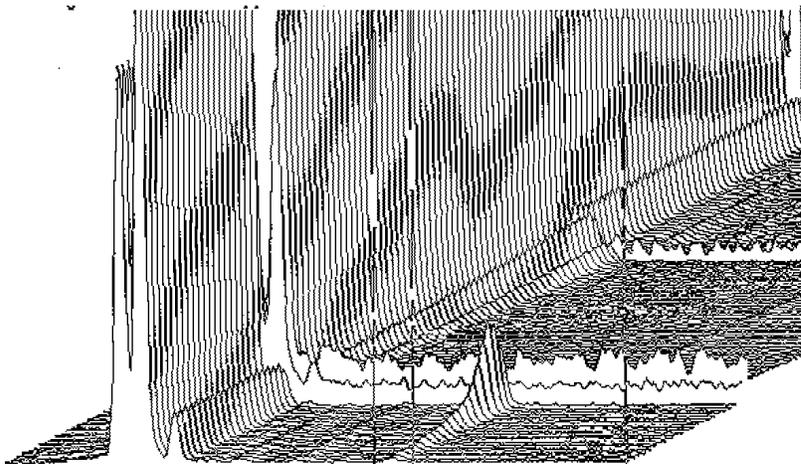


Figure 4. IMS response for TNT with NO₂ dopant at 200°C.

temperature resulted in lower intensities and broader responses for both NO₂ and CH₂Cl₂ especially for CH₂Cl₂. These responses were so broad it took 10—15 minutes before they returned to baseline levels. Figure 3 also shows a second, less intense response at a slightly longer drift time which is absent when temperatures lower than 200°C were used with

CH₂Cl₂. A halide ion may be involved since a second response is also seen with CH₂Br₂ but at better resolution. TNT does not show good sensitivity with CH₂Br₂, however, since about five times the TNT needed to be injected before a response equivalent to that obtained with CH₂Cl₂ in dry air was seen. The TNT responses with other reactant ion chemistries were weak and broad, and no second response such as that shown in Figure 3 was seen at any temperature; except when using SO₂ in a moist air carrier at 160°C.

Table 3. Qualitative Assessment of TNT response (200 picograms) to Various Reactant Ion Chemistries at Various Temperatures

	Air-dry	Air-wet	CH₂Cl₂ -dry	CH₂Cl₂ -wet	CH₂Br₂-dry	NO₂-wet	SO₂-wet
160°C	Poor response shape No Second response	Can be seen but broad response shape No Second response.	Poor response shape No Second response	Can be seen but broad response shape No Second response.	--	Best response shape at 160°C but still poor.	Can be seen but broad response shape. Relatively strong second response.
180°C	--	--	--	Better response intensity and shape than NO ₂ . No Second response	--	Not as good as CH ₂ Cl ₂ .	--
200°C	Better than air-wet but still broad. No Second response.	Less intense than air dry. Broad response. No Second response	Stronger intensity response than wet but tails. Second response visible	Good response shape. Second response somewhat visible	Not Detected at 200 picograms. Second response is visible with 1000 picograms and better resolved than with CH ₂ Cl ₂ .	Best response shape. Good intensity. No Second response	Comparable to air-dry. No Second response
220°C		--	--	A little better than NO ₂ . Less tailing than at 200°C. No Second response	--	Comparable to CH ₂ Cl ₂ . Very good response shape. No Second response	--

RDX Results

A qualitative assessment of RDX response is given in Table 4. The best response at 200°C was using CH₂Cl₂ in dry air as shown in Figure 5. A comparison of Figures 3 and 5 also show how much more sensitive the IMS is to RDX than TNT under these conditions. RDX is not always more sensitive than TNT, however. The relative sensitivity depends on the reactant ion chemistry. For example, in dry air TNT and RDX show about the same sensitivity, which is low. Raising the temperature to 220°C with CH₂Cl₂ dopant gave much less tailing for the RDX response with about the same intensity. Comparable

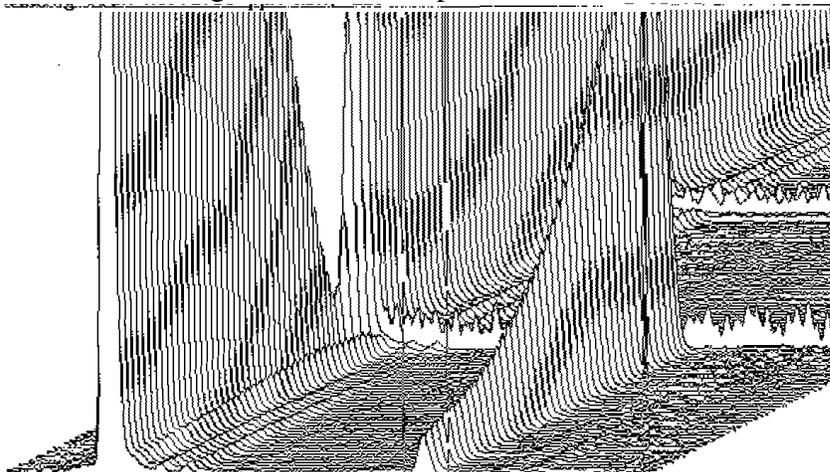


Figure 5. IMS response for RDX with CH₂Cl₂ dopant at 200°C.

responses, but not quite as intense as CH₂Cl₂ in dry air, were seen with moist air, moist CH₂Cl₂ and moist SO₂. If one didn't wish to use CH₂Cl₂, moist air would be a good substitute. The air must be moist, however, as the IMS is not sensitive to RDX in dry air. Moist

air with NO₂ shows a second less intense response at longer time; which could be consistent with an NO₃⁻ adduct of RDX, as reported in the literature.⁷ This second response is not seen with other reactant ion chemistries nor with NO₂ at 220°C.

PETN Results

Since PETN is not detected in the IMS at as low of levels as TNT and RDX, a standard was used which contained ten times the amount of PETN as either TNT or RDX. A qualitative assessment of PETN response is given in Table 5. Communication with a

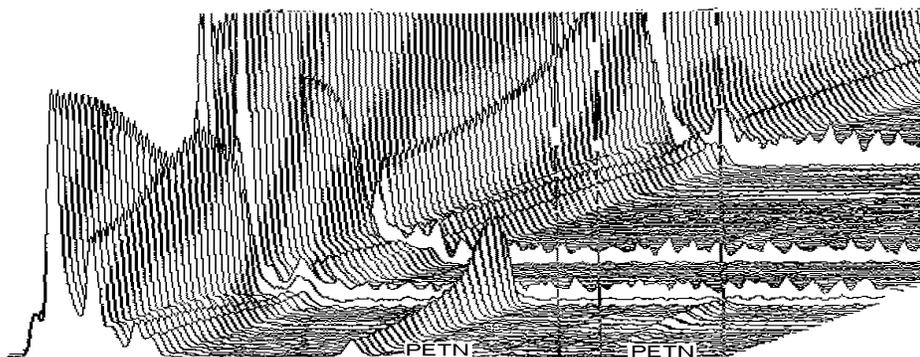


Figure 6. IMS responses for PETN with NO₂ dopant at 160°C.

chemist at PCP, Inc.,⁴ showed that moist air doped with NO_2 at 160°C was an effective way to detect PETN. Two responses to PETN were seen as shown in Figure 6. The weaker response has a drift time longer than RDX, but the stronger response has a drift time similar to TNT. HPLC analysis of the PETN used in this study showed no TNT present, however. Analysis of unknowns using these conditions may be confusing since one could not be sure if TNT were present or not. PETN was also tested in moist air doped with SO_2 as shown in Figure 7. One response was seen which had a different drift time than either TNT or RDX. The response shape, however, is broad. Two weak, broad responses with a drift time greater than RDX were seen with CH_2Cl_2 in a dry carrier at 200°C , as shown in Figure 8. Figure 8 also shows an example of the response that was seen in the area of the reactant ion peaks for 180°C and above for many of the reactant ion chemistries. This response may be due to a decomposition product of PETN, and might be seen with any nitrate ester, thus it wouldn't be specific to PETN. Mass spectral data and studies with other nitrate esters would be helpful in determining this.

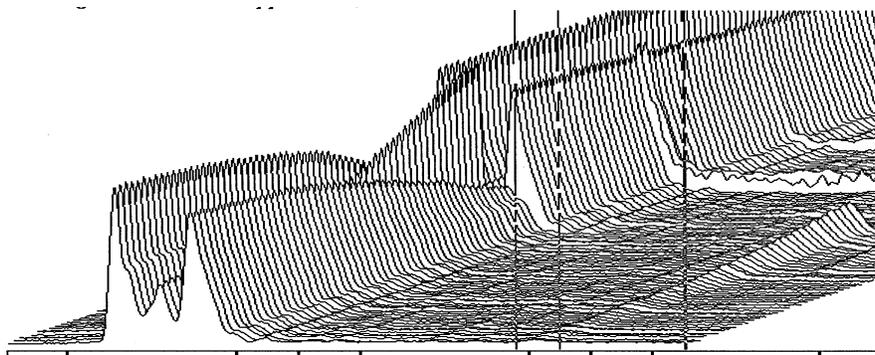


Figure 7. IMS response for PETN with SO_2 dopant at 160°C .

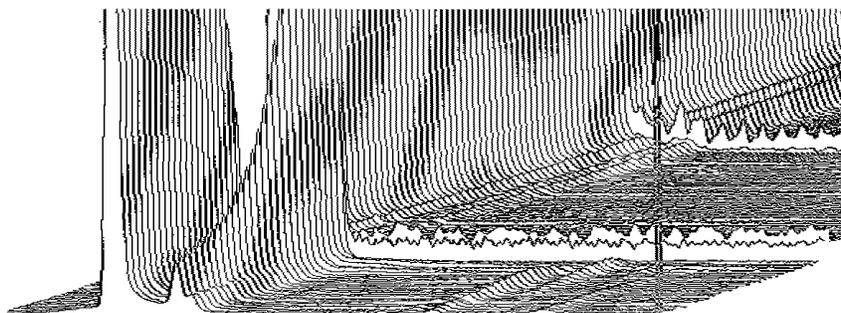


Figure 8. IMS response for PETN with CH_2Cl_2 dopant at 200°C .

Table 4. Qualitative Assessment of RDX Response (200 Picograms) to Various Reactant Ion Chemistries and Various Temperatures.

	Air-dry	Air-wet	CH₂Cl₂ -dry	CH₂Cl₂ -wet	CH₂Br₂-dry	NO₂-wet	SO₂-wet
160°C	Almost no response.	Moderate intensity but broad response shape.	Comparable to air wet.	Comparable to air wet.	--	Best response at 160 but still broad. A second response is visible.	Comparable to NO ₂ .
180°C	--	--	--	Strong response, better shape, but still broad.	--	Good response about half of CH ₂ Cl ₂ -wet. A second response is visible.	--
200°C	Stronger response shape than 160°C but still poor and broad.	Strong response, comparable to CH ₂ Cl ₂ -wet.	Strongest response	Comparable to air-wet.	Poor response compared to CH ₂ Cl ₂ but better than dry air	Moderate intensity, good shape. A second response is visible.	Response better than NO ₂ . Comparable to wet air.
220°C				Comparable intensity to 200°C better shape.		Comparable intensity to 200°C, better shape. About half of CH ₂ Cl ₂ -wet in intensity.	

Table 5. Qualitative Assessment of PETN Response (2,000 Picograms) to Various Reactant Ion Chemistries at Various Temperatures.

	Air-dry	Air-wet	CH₂Cl₂ -dry	CH₂Cl₂ -wet	CH₂Br₂-dry	NO₂-wet	SO₂-wet
160°C	No Response.	Broad response, same place as RDX. Also see response located among reactant ion peaks.	Response near reactant ion peaks.	Faint broad response.	--	Two peaks-one near TNT-large response other longer drift time than HMX-small. Also response located among reactant ion peaks.	See one broad response for 10,000 picograms. No response for 2000 picograms. Also response located among reactant ion peaks.
180°C	--	--	--	Response located among reactant ion peaks.	--	Same as 160 but diminished response	--
200°C	Response located among reactant ion peaks	Response located among reactant ion peaks.	Two broad low responses at longer drift time than HMX. Also see large response among reactant ion peaks.	--	Minor change in reactant ion peaks	--	Several small broad peaks plus large response among reactant ion peaks.
220°C	--	--	--	--	--	--	--

Reactant Ion Peaks and Explosive Reduced Mobilities

The pattern of reactant ion peaks varied with the dopant used as was expected. The patterns obtained at 200°C are shown in Figures 9-15 for each reactant ion chemistry in this study. Selected peaks are labeled with their reduced mobility values. CH₂Cl₂ in dry air gives the simplest, cleanest reactant ion spectrum; and while addition of moisture to the flow path may sharpen the response shape, it can also clutter the spectrum with many additional reactant ion peaks. The main reactant ion for moist air is different from the main reactant ion for dry air but is similar in reduced mobility to the reactant ion for moist CH₂Cl₂; which may explain why RDX was more sensitive in moist air than dry air. From previous work,³ RDX is known to be more sensitive in CH₂Cl₂ than in dry air.

The reactant ion patterns usually changed with temperature. For example, see Figure 16 for moist NO₂ at 160°C compared to Figure 14 for moist NO₂ at 200°C. Only CH₂Cl₂ in dry air retained basically the same reactant ion pattern over the range 160—220°C. Presumably CH₂Br₂ would have also had it been observed at other temperatures besides 200°C. Reduced mobilities for TNT, RDX, and PETN are shown in Table 6. TNT reduced mobilities only vary by 0.01 no matter what the reactant ions are, which is consistent with literature reports of a TNT anion (TNT minus H⁺) being formed.^{7,8} RDX reduced mobilities show more variability indicating different products may be formed. Literature reports a number of adducts with negative ions for RDX.⁷ Therefore, the difference in reduced mobilities for CH₂Cl₂ and CH₂Br₂ is not surprising, since, presumably, chloride ion and bromide ion adducts are formed with the bromide ion adduct being heavier, leading to a longer drift time and lower reduced mobility. The reasons for the similarities of the air, NO₂, and SO₂ RDX reduced mobilities to CH₂Cl₂, however, is not clear. Many observations could be made about the chemistry if data from a mass spectrometer were available .

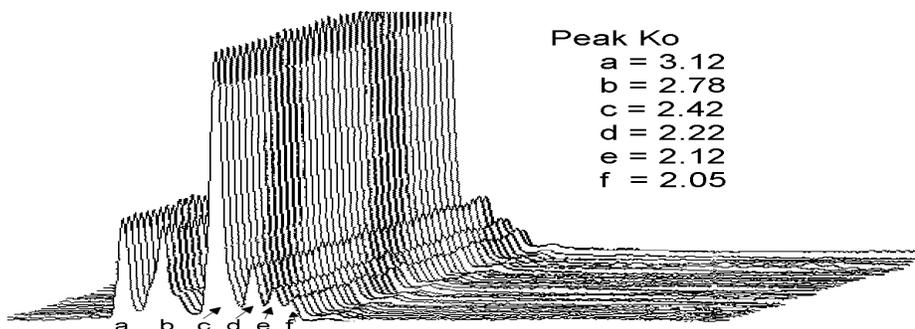


Figure 9. IMS response for reactant ion peaks for dry air carrier gas at 200°C.

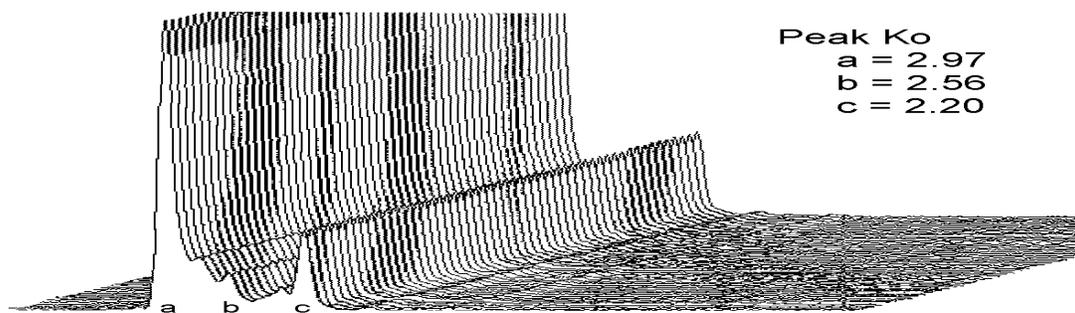


Figure 10. IMS response for reactant ion peaks for moist air carrier gas at 200°C.

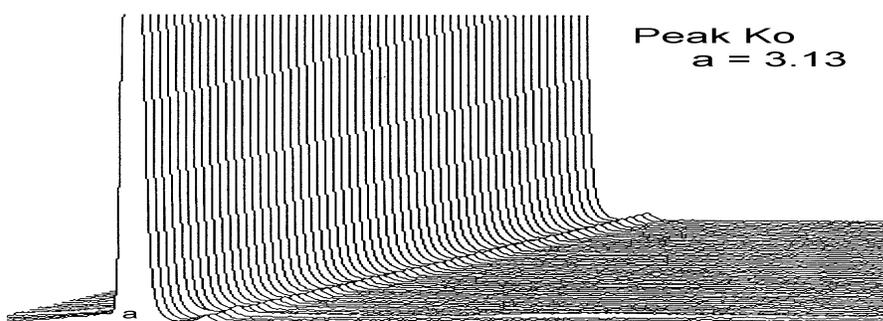


Figure 11. IMS response for reactant ion peaks for dry air carrier gas and methylene chloride dopant at 200°C.

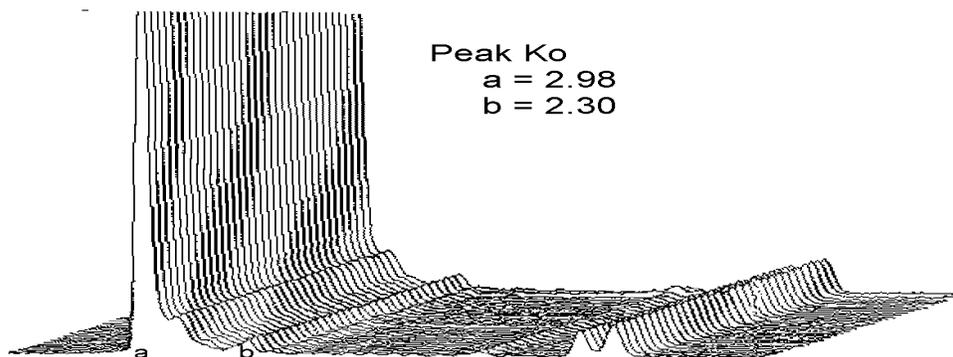


Figure 12. IMS response for reactant ion peaks for moist air carrier gas and methylene chloride dopant at 200°C.

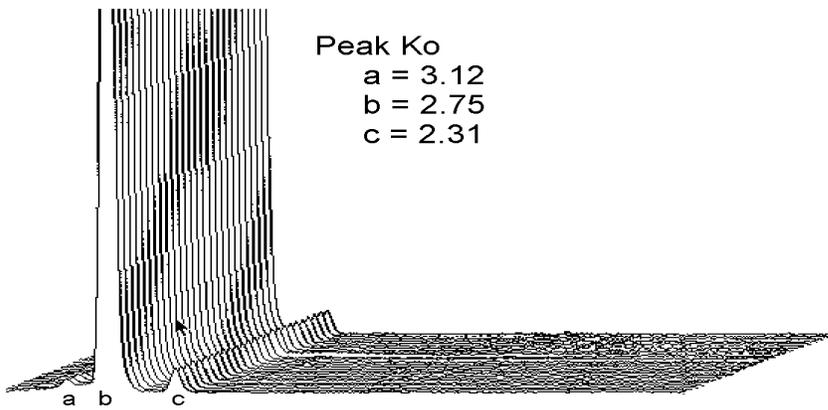


Figure 13. IMS response for reactant ion peaks for dry air carrier gas and methylene bromide dopant at 200°C.

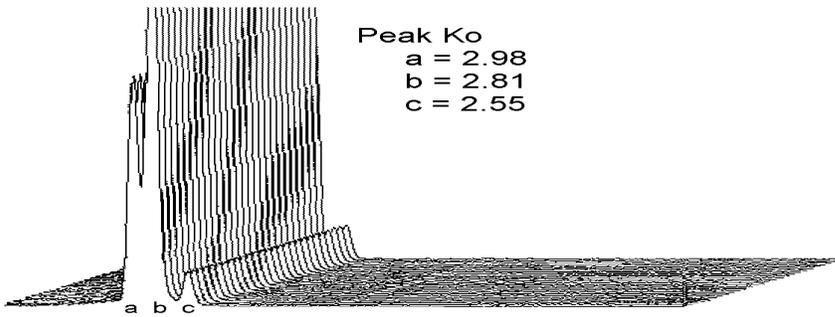


Figure 14. IMS response for reactant ion peaks for moist air carrier gas and NO₂ dopant at 200°C.

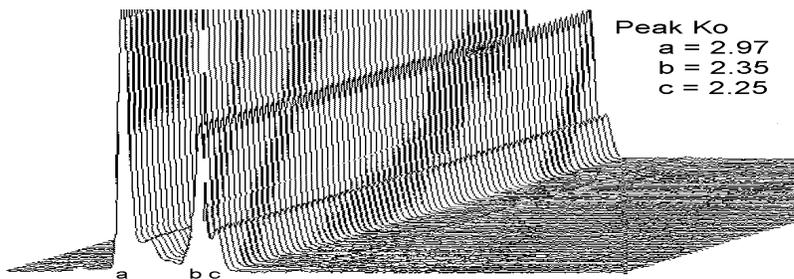


Figure 15. IMS response for reactant ion peaks for moist air carrier gas and SO₂ dopant at 200°C.

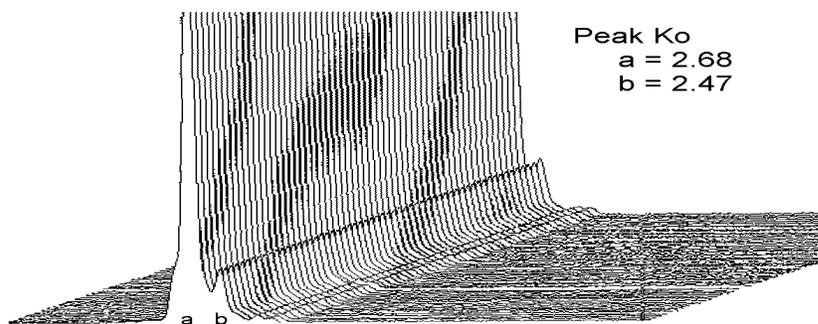


Figure 16. IMS response for reactant ion peaks for moist air carrier gas and NO₂ dopant at 160°C.

Quantitation

Most injections were done in triplicate to evaluate reproducibility. Data were also obtained with three different injection sizes of standard to allow construction of calibration curves. Average integration counts, standard deviations, and coefficients of variation are shown in Tables 7—9 for TNT, RDX, and PETN, respectively. In general RDX gives lower coefficients of variation than TNT. This is also reflected in the correlation coefficients for the calibration plots; i.e., r^2 values are generally higher for RDX calibration curves than TNT curves. Most of the plots showed curvature, and a quadratic fit was used. The range of sample amounts used in this study was as follows: for TNT 200 — 1000 picograms; for RDX 50—200 picograms; and for PETN 2000—10,000 picograms. The problem with reproducibility is compounded by variability in injection technique. An automated system would probably improve reproducibility.

Summary and Conclusions

Reactant ion chemistries for TNT, RDX, and PETN were evaluated at different temperatures. The best responses for TNT were obtained using either CH₂Cl₂ in a dry air carrier gas or NO₂ in a moist air carrier gas at 200°C. The IMS is more sensitive to RDX than TNT, and the best response was obtained with CH₂Cl₂ in a dry air carrier gas at 200°C. Acceptable responses were also obtained with moist air, CH₂Cl₂ in moist air, and SO₂ in moist air at 200°C. The IMS is not as sensitive to PETN as either TNT or RDX. PETN can be detected with NO₂ in moist air at 160°C. If TNT is present, the sample should also be run with SO₂ in moist air at 160°C. The IMS is an excellent tool for detection of small amounts of explosive, but the results of manual injection would be semiquantitative at best. If semiquantitative results are desired, the best results would be obtained with RDX.

Table 6. Reduced Mobilities for TNT, RDX, and PETN with Various Reactant Ion Chemistries and Temperatures.

	Air-dry	Air-wet	CH₂Cl₂ -dry	CH₂Cl₂ -wet	CH₂Br₂-dry	NO₂-wet	SO₂-wet
160°C	TNT 1.57 RDX 1.47	TNT 1.57 RDX 1.47	TNT 1.58 RDX 1.51	No reduced mobilities obtained	--	TNT 1.58 RDX 1.48 PETN 1.19*	TNT 1.57 RDX 1.50 PETN 1.31
180°C	--	--	--	TNT 1.58 RDX 1.51	--	TNT 1.57 RDX 1.48	--
200°C	TNT 1.57 RDX 1.50	TNT 1.57 RDX 1.50	TNT 1.58 RDX 1.51	TNT 1.58 RDX 1.50	TNT 1.57 RDX 1.46	TNT 1.57 RDX 1.50	TNT 1.58 RDX 1.50 PETN 1.31
220°C	--	--	--	TNT 1.57 RDX 1.50	--	TNT 1.57 RDX 1.50	--

*plus another more intense response near TNT

Table 7. Average Integration Counts, Standard Deviation in parentheses, and Coefficient of Variation for different size injections of TNT standard. Integration Counts and Standard Deviation Values are shown times 10^{-3} .

	Air-dry	Air-wet	CH₂Cl₂ -dry	CH₂Cl₂ -wet	CH₂Br₂-dry	NO₂-wet	SO₂-wet
160°C						2μL r ² = 0.639 638 (141) 22% 5μL 1655 (542) 33% 10μL 7191 (4134) 57%	2μL r ² = 0.956 1221 5μL 3652 (2168) 59% 10μL 14480
180°C				2μL r ² = 0.925 1366 (451) 33% 5μL 4925 (918) 19% 10μL 19,656 (4679) 24%		2μL r ² = 0.986 597 (182) 31% 5μL 1666 (447) 27% 10μL 11155 (1159) 10%	
200°C	2μL r ² = 0.955 2070 5μL 3607 10μL 14376	2μL r ² = 0.996 1418 (1016) 72% 5μL 3668 10μL 9520	2μL 5032	2μL r ² = 0.848 1186 (545) 46% 5μL 3626 (894) 25% 10μL 9666 (3019) 31%	7μL 358 (114) 32% 8μL 537 (152) 28% 10 μL 4133 (2140) 52%	2μL r ² = 0.654 1904 (575) 30% 5μL 2104 (783) 37% 10μL 8155 (4372) 54%	2μL r ² = 0.901 1248 (433) 35% 5μL 2934 (502) 17% 10μL 14844 (4209) 28%
220°C				2μL r ² = 0.850 1651 (635) 38% 5μL 5178 (814) 16% 10μL 6945 (1250) 18%		2μL r ² = 0.921 482 (15) 3% 5μL 2209 (663) 30% 10μL 5122 (999) 20%	

Table 8. Average Integration Counts, Standard Deviation in parentheses, and Coefficient of Variation for different size injections of RDX standard. Integration Counts and Standard Deviation Values are shown times 10^{-3} .

	Air-dry	Air-wet	CH₂Cl₂ -dry	CH₂Cl₂ -wet	CH₂Br₂-dry	NO₂-wet	SO₂-wet
160°C						0.5μL r ² = 0.995 10831 1μL 25007 (1327) 5% 2μL 47506 (3364) 7%	0.5μL r ² = 0.979 5919 (880) 15% 1μL 13061 2μL 40414
180°C				0.5μL r ² = 0.956 10234 (606) 6% 1μL 16882 (1084) 6% 2μL 37967 (5259)14%		1μL r ² = 0.884 11347 (5628) 50% 2μL 17907 (1737) 10% 4μL 33077	
200°C	1μL r ² = 0.862 2129 2μL 3367 (732) 22% 3μL 4756	0.2μL r ² = 0.989 5796 0.5μL 15563 2μL 41988	2μL 48578	0.5μL r ² = 0.956 9227 (1594) 17% 1μL 19583 (2244)11% 2μL 35220 (4041)11%	2μL 9961 (1273)13% 3μL 23005 (7264)32% 4μL 30005 (562) 2%	1μL r ² = 0.922 4395 (547) 12% 2μL 11483 (2327)20% 4μL 15741 (1119) 7%	0.5μL r ² = 0.974 8448 (1307)15% 1μL 19274 (2094) 11% 2μL 31126 (2057) 7%
220°C				0.5μL r ² = 0.966 7020 (378) 5% 1μL 14923 (1868) 12% 2μL 19684 (808) 4%		0.5μL r ² = 0.946 2201 (1690)77% 1μL 4821 (784) 16% 2μL 8105 (509) 6%	

Table 9. Average Integration Counts, Standard Deviation in parentheses, and Coefficient of Variation for different size injections of PETN standard. Integration Counts and Standard Deviation Values are shown times 10^{-3} .

	Air-dry	Air-wet	CH₂Cl₂ -dry	CH₂Cl₂ -wet	CH₂Br₂-dry	NO₂-wet	SO₂-wet
160°C						2μL $r^2 = 0.930$ 645 (222) 34% 4μL 2085 (617) 30% 8μL 4373 (509) 12%	3μL $r^2 = 0.914$ 2702 (454) 17% 5μL 4377 (782) 18% 10μL 11128 (2188) 20%
180°C							
200°C							3μL $r^2 = 0.928$ 172 (26) 15% 5μL 248 (86) 35% 10μL 745 (120) 16%
220°C							

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