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Optimized thermal desorption for improved sensitivity in trace explosives detection by ion mobility spectrometry†

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In this work we evaluate the influence of thermal desorber temperature on the analytical response of a swipe-based thermal desorption ion mobility spectrometer (IMS) for detection of trace explosives. IMS response for several common high explosives ranging from 0.1 ng to 100 ng was measured over a thermal desorber temperature range from 60 °C to 280 °C. Most of the explosives examined demonstrated a well-defined maximum IMS signal response at a temperature slightly below the melting point. Optimal temperatures, giving the highest IMS peak intensity, were 80 °C for trinitrotoluene (TNT), 100 °C for pentaerythritol tetranitrate (PETN), 160 °C for cyclotrimethylenetrinitramine (RDX) and 200 °C for cyclotetramethylenetetranitramine (HMX). By modifying the desorber temperature, we were able to increase cumulative IMS signal by a factor of 5 for TNT and HMX, and by a factor of 10 for RDX and PETN. Similar signal enhancements were observed for the same compounds formulated as plastic-bonded explosives (Composition 4 (C-4), Detasheet, and Semtex). In addition, mixtures of the explosives exhibited similar enhancements in analyte peak intensities. The increases in sensitivity were obtained at the expense of increased analysis times of up to 20 seconds. A slow sample heating rate as well as slower vapor-phase analyte introduction rate caused by low-temperature desorption enhanced the analytical sensitivity of individual explosives, plastic-bonded explosives, and explosives mixtures by IMS. Several possible mechanisms that can affect IMS signal response were investigated such as thermal degradation of the analytes, ionization efficiency, competitive ionization from background, and aerosol emission.

Introduction

Ion mobility spectrometry (IMS) is widely used for the rapid screening of trace explosives and narcotics residues collected by physical swiping of a suspect surface. In this technique, residues collected on a sampling swipe are thermally desorbed by rapid heating (typically 230 °C to 280 °C) to produce neutral vapor molecules that are subsequently ionized with a [63]Ni source at atmospheric pressure. These ions are then introduced as a discrete packet into the drift region of the IMS instrument where they are characterized by their gas phase mobilities in a weak electric field.[1–6] IMS sensitivity and specificity is further enhanced by the addition of a reagent chemical such as a chlorinated hydrocarbon to provide chloride reactant ions in the ionization region. Reactant ion formations usually take place by charge transfer, proton abstraction, adduct formation, or nucleophilic displacement. In typical screening applications, IMS operational parameters are selected to provide a rapid analysis

time (6 s to 7 s) for a wide range of analyte compounds which requires rapid heating at relatively high desorber temperatures.[1,7] However, if the typical requirements for fast analysis and high desorption temperatures are relaxed, commercially available IMS instruments could potentially be optimized to result in significant improvements in analytical figures of merit (*i.e.*, sensitivity, measurement repeatability, selectivity, *etc.*).

Explosives are thermally labile compounds with high propensity for instability, decomposition, and reactivity. In a conventional IMS screening analysis, the desorber temperature must be set high enough to effectively vaporize the analyte without inducing significant chemical degradation. The instrument operational parameters mentioned above are selected based on the premise that explosive particles sublime or evaporate and are introduced as a vapor into the IMS. However, recent results have shed new light regarding the physical transformations that trace explosives undergo during rapid high-temperature desorption.[8] This recent data reported by our laboratory raised the question as to whether explosives such as PETN, known for its thermal instability and rapid breakdown, could benefit from slower heating rates at lower desorber temperatures. Additionally, from a research standpoint, the use of optimized analytical conditions in a laboratory setting could provide significant

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improvements in the quantitative analysis of explosives by IMS. Therefore we decided to explore the influence of thermal desorption conditions on IMS sensitivity with the goal of improving overall performance. Past studies have focused on improving the sensitivity of IMS instruments by increasing the intensity of the ionization source, modifying the detector, and optimizing the detector temperature.[9–11] Karpas et al. were able to improve the limit of detection and increase sensitivity by either increasing the gate width or by enhancing the activity of the ionization source.[9] Denson et al. reported utilizing micro-Faraday finger array detector technology to achieve a significant increase in sensitivity for explosive detection.[10] McGann et al. demonstrated that by optimizing the detector temperature the detection of triacetone triperoxide (TATP) and ammonium nitrate was made possible without compromising the detection performance of other explosives.[11] In this paper we focus on optimizing the front-end of IMS instruments by determining desorber temperatures that provide optimal IMS response (defined in this paper as integrated peak counts for each explosive over total analysis time). Experiments were designed to first establish characteristic performance for the IMS instrument under typical operating conditions as recommended by the manufacturer. Measured sensitivity improvements are based on the comparison of response measurements established under standard desorption conditions to IMS response under optimized desorption conditions. This paper will also provide IMS measurement repeatability data under varying analytical conditions, which will expand upon the existing IMS literature.[12–14] The observed sensitivity improvements are discussed in the context of the explosives particles physical transformations occurring during the desorption process that lead to the most efficient production of neutral vapor-phase analyte molecules. Proposed mechanisms such as thermal degradation, ionization efficiency, and aerosol emission are investigated to determine if they play a significant role in IMS signal response.

Experimental

Materials

The high explosives cyclotrimethylenetrinitramine (RDX), trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN), and cyclotetramethylenetetranitramine (HMX) were purchased as standard solutions consisting of ampoules (approximately 1 mL) containing the explosive dissolved in either acetonitrile or methanol at nominal concentrations of 1 mg mL^{-1} (Restek, Bellefonte, PA, or Supelco, Bellefonte, PA). The purity of the solutions is reported by the manufacturer under the certificate of analysis as $99 \pm 0.05\%$. Solutions at nominal concentrations of 1 mg mL^{-1} of C-4 (RDX + polyisobutylene + di(2-ethylhexyl) sebacate + fuel oil), Detasheet (PETN + nitrocellulose + poly-isobutylene), and Semtex (RDX + PETN + poly (butadiene-styrene) + fuel oil) were prepared by the Transportation Security Laboratory (TSL, Atlantic City, NJ). Serial dilutions of the stock solutions were prepared gravimetrically at concentrations between 0.1 μg mL^{-1} to 100 μg mL^{-1}. Solutions were diluted in the solvent in which they were received from the manufacturer or laboratory. RDX and TNT solutions were diluted in acetonitrile and PETN in methanol. Plastic-bonded explosives were diluted

in tetrahydrofuran. All dilutions were made with high-performance liquid chromatography (HPLC) reagent grade solvent (Sigma Aldrich, St. Louis, MO). Each calibration solution was stored in amber glass vials equipped with Teflon caps and stored at 3 °C until use.

Instrumentation

IMS analyses were performed using a commercially available explosive trace detector (ETD) under the standard manufacturers operational conditions as shown in Table 1.[15] The explosives were deposited directly onto commercial Teflon-coated fiberglass swabs (Smiths Detection Inc., part number 15518)‡ using a pipette and the solution was allowed to dry in air for approximately 10 min before IMS analysis. We assumed there was no mass loss of the explosives during drying. Analysis time was increased from 7 s to 20 s (maximum analysis time permitted by the software) to maximize the amount of material desorbed from the swab. Mixture samples were prepared and analyzed under the same conditions. IMS response (peak intensity) was based on the numerical value of the cumulative amplitude (Cum A) for each analysis as calculated by instrument software.[15] Cumulative amplitude is the sum of the peak heights in a particular channel across all analysis time segments. The Cum A values for [RDX + Cl]$^-$, [PETN + Cl]$^-$, [HMX + Cl]$^-$, and [TNT − H]$^-$ were used for quantitation purposes (chloride adducts are a product of the IMS reactant ion, hexachloro-ethane, and each respective explosive molecule). The reduced mobility values (K_0) for the ions studied were as follows: 1.39 cm^2 V^{-1} s^{-1} for [RDX + Cl]$^-$, 1.15 cm^2 V^{-1} s^{-1} for [PETN + Cl]$^-$, 1.25 cm^2 V^{-1} s^{-1} for [HMX + Cl]$^-$, and 1.45 cm^2 V^{-1} s^{-1} for [TNT − H]$^-$. The desorber temperature range studied for each explosive was between 60 °C to 280 °C.

Results and discussion

Standard response curves

Standard instrument response curves were measured for each explosive using instrument manufacturer's operational conditions as previously defined in Table 1.

Table 1 Standard IMS operational conditions

Desorber temperature	230 °C
Drift tube temperature	111 °C
Inlet temperature	240 °C
Flow rate	350 cm^3 min^{-1}
High voltage	−2000 V
Absolute pressure	1000 kPa
Ionization source	^{63}Ni
Drift gas	Air (dried)
Analysis time	20 seconds

‡ Certain commercial equipment, instruments, or materials are identified in this document. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products identified are necessarily the best available for the purpose.

Fig. 1a–d shows the characterization of IMS response for each explosive as a function of mass. Each data point represents the mean (x_i) of five (5) replicate measurements over the mass range of 0.1 ng to 100 ng, which is well within the nominal operational range suggested by the IMS manufacturer.[15]

The uncertainty for each point represents the standard deviation of the IMS response measurements (referred to as measurement repeatability in this paper) to the deposited explosive mass as shown in the equation below. The percent relative standard uncertainty was calculated by determining (% RSU) *via* the formula below:[16]

$$\% \; RSU = \frac{Standard \; deviation}{Mean \; of \; results} \times 100 \qquad (1)$$

The measured response curves demonstrate typical IMS behavior for the analysis of trace explosives, where there is a linear response at low concentrations and a saturated or near saturated response at the higher concentrations.[1] Fig. 1a shows the IMS response curve for RDX measurements under standard operating conditions. The repeatability of the RDX measurements ranged from 4% to 47% (median repeatability = 9%). The R^2 value of 0.9373 is based on a 2nd order polynomial linear regression. Fig. 1b shows the IMS response curve to TNT measurements under standard operating conditions. The repeatability of the TNT measurements ranged from 4% to 16% (median repeatability = 10%). The R^2 value of 0.9948 is based on a 4th order polynomial linear regression. Fig. 1c shows the IMS response curve to PETN measurements under standard operating conditions. The repeatability of the PETN measurements ranged from 2% to 35% (median repeatability = 13%). The R^2 value of 0.9477 is based on a logarithmic linear regression. Fig. 1d shows the IMS response curve to HMX measurements

under standard operating conditions. The repeatability of the HMX measurements ranged from 15% to 28% (median repeatability = 23%). The R^2 value of 0.9976 is based on a 2nd order polynomial linear regression. We observed that the IMS has the greatest sensitivity (overall cumulative counts) for RDX > TNT > PETN > HMX. The repeatability of the measurements (% RSU) was similar for all explosives analyzed.

Temperature profile

In the second phase of the study, the desorber temperature for each explosive was varied and we determined the temperature that produced the highest instrument response (Cum A integrated over 20 s). A mass of 50 ng (of each deposited explosive) was selected because it corresponds to the approximate midpoint of the analytical range chosen for this study. The temperature range studied for each explosive was between 60 °C to 280 °C (increments of 20 °C). Table 2 shows literature values of melting points (mp) and decomposition temperatures for the explosives studied.[17–19]

Fig. 2a–d shows the characterization of IMS response for each explosive as a function of desorber temperature.

Table 2 Explosives melting point and decomposition temperature

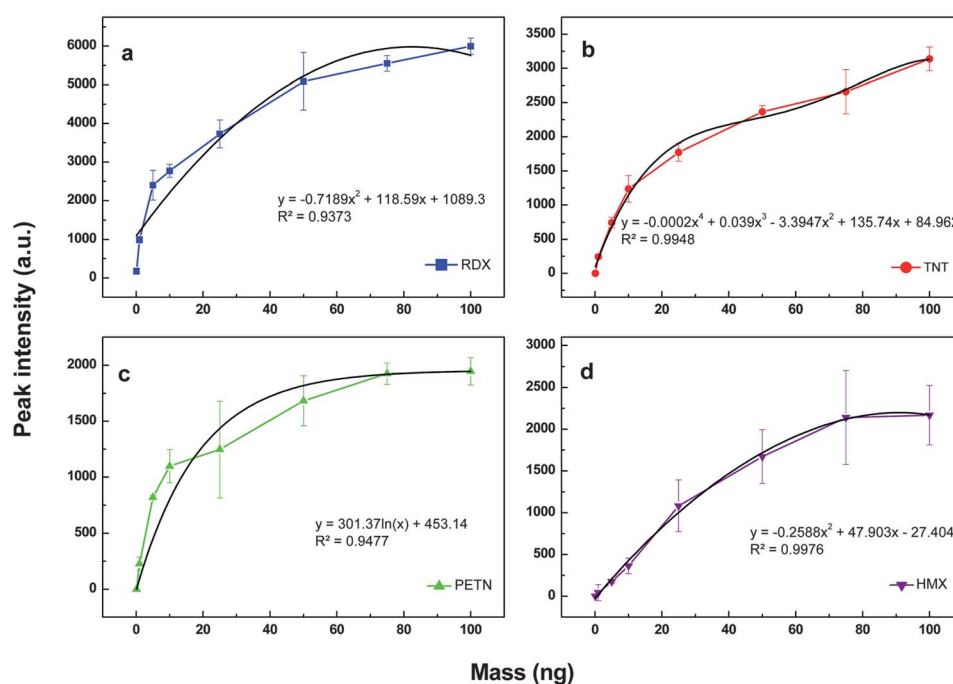| Explosive	Melting point (°C)	Decomposition (°C)
PETN	141.3	163
RDX	204	170
TNT	80.6	300
HMX	276–286	287

Fig. 1 IMS response curve to explosives measurements under standard operating conditions; (a) RDX, (b) TNT, (c) PETN and (d) HMX during 20 seconds analysis time.
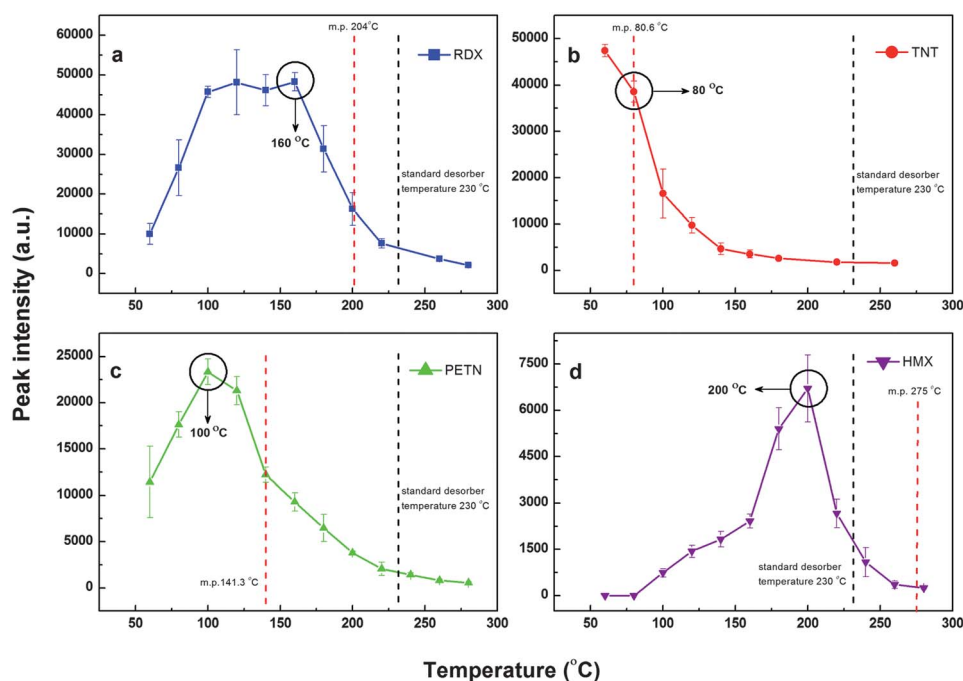
Fig. 2 Temperature profile of the IMS response to 50 ng of each explosive; (a) RDX, (b) TNT, (c) PETN and (d) HMX during 20 seconds analysis time. The dotted lines represent the explosive's melting point and the default desorber temperature the IMS.

Each data point represents the mean (x_i) of five (5) replicate measurements over the temperature range 60 °C to 280 °C. Fig. 2a shows the temperature profile of 50 ng of RDX. RDX exhibited a plateau in maximum response between 140 °C to 160 °C, however 160 °C was selected as the optimal desorber temperature due to better measurement repeatability and also to ensure a clear distinction from PETN's optimal temperature (100 °C). The repeatability of the RDX measurements ranged from 3% to 26% (median repeatability = 16%). Fig. 2b shows the temperature profile of 50 ng of TNT. Establishing an optimal desorber for TNT was challenging since the highest response was measured at the lowest possible temperature set-point (60 °C). However, at a desorber temperature of 60 °C we were concerned with compromising detection at the low concentrations (0.1 ng to 1.0 ng). Therefore, 80 °C was determined to be the optimal desorber temperature for TNT. The repeatability of the TNT measurements ranged from 3% to 32% (median repeatability = 23%). Fig. 2c shows the temperature profile of 50 ng of PETN, which exhibits the highest IMS signal response at a desorber temperature of 100 °C. The repeatability of the PETN measurements ranged from 5% to 35% (median repeatability = 11%). Fig. 2d shows the temperature profile of 50 ng of HMX. The highest IMS signal response for HMX was found to be at a desorber temperature of 200 °C which is the closest to the default desorber temperature of 230 °C. This is likely due to HMX having the lowest vapor pressure of the explosives studied.[20] Explosives with low vapor pressure require higher activation energy/temperatures to be sublimed/vaporized from a substrate. The repeatability of the HMX measurements ranged from 9% to 44% (median repeatability = 16%). RDX and PETN benefited the most from desorption at lower temperatures, possibly from increased thermal stability of the compounds.

The optimal desorber temperature determined for each explosive also correlates in most cases with better repeatability. By optimizing the temperature at which each explosive is desorbed, we were able to increase instrument response by a factor of 5 for TNT and HMX, and by a factor of 10 for RDX and PETN. If the swab is re-introduced and desorbed until the amount of analyte is completely depleted and the responses are summed, we observed an increase in response by a factor of 20 for RDX and PETN, and 30 for TNT (data not shown). HMX swabs were depleted after the first desorption cycle and did not benefit from the re-analysis. Similarly all swabs desorbed at 230 °C were flash vaporized during the first desorption cycle and did not give an additional response after repeated desorption of the substrate. The significant increase in sensitivity achieved by repeated desorption cycles at optimal desorber temperatures underlines the benefit of increasing analysis time to obtain the maximum integrated signal response.

After determining the optimal desorber temperature for each explosive at 50 ng, we tested whether the increase in response was observed across the mass range of 0.1 ng to 100 ng (Fig. S1†). The enhanced sensitivity obtained by low-temperature desorption was observed throughout the mass loading range studied for all explosives. Fig. S2† represents typical signal-to-noise differences as a function of desorber temperatures. The repeatability of the RDX measurements at 160 °C ranged from 2% to 43% (median repeatability = 8%). The repeatability of the TNT measurements at 80 °C ranged from 13% to 67% (median repeatability = 24%). The repeatability of the PETN measurements at 100 °C ranged from 3% to 18% (median repeatability = 4%). The repeatability of the HMX measurements at 200 °C ranged from 17% to 38% (median repeatability = 21%). PETN was the only explosive for which measurement repeatability was

significantly improved by the lower temperature desorption (median repeatability = 4% at 100 °C compared to median repeatability = 13% at 230 °C) suggesting decreased thermal breakdown. Results from the temperature profile of explosives suggest that low-temperature desorption leads to slower heating rates of the sample and the consequent slow introduction of material into the ionization region of the IMS enhancing the sensitivity to the analysis of trace explosives.

Plastic-bonded explosives

After successfully optimizing the detection of each pure explosive by lowering desorber temperatures, we tested whether more complex samples such as plastic-bonded explosives gave similar results. Data was not corrected for the composition of plasticizers/binders. Literature values indicate that there is typically 91% RDX in C-4 and 70% PETN in Detasheet. Semtex is composed of equal parts of RDX and PETN, which make up approximately 80% of the energetic by weight.[1] The samples were prepared and analyzed in the same manner as described above for the pure explosives. Fig. 3a and b shows the characterization of IMS response for plastic-bonded explosives compared to the individual explosive as a function of desorber temperature.

Each data point represents the mean (x_i) of five (5) replicate measurements over the temperature range 60 °C to 280 °C. Semtex is a plastic explosive that contains both RDX and PETN. Fig. 3a shows the temperature profile of the IMS response to 50 ng of RDX, 50 ng of RDX in C-4, and 50 ng of RDX in Semtex. The
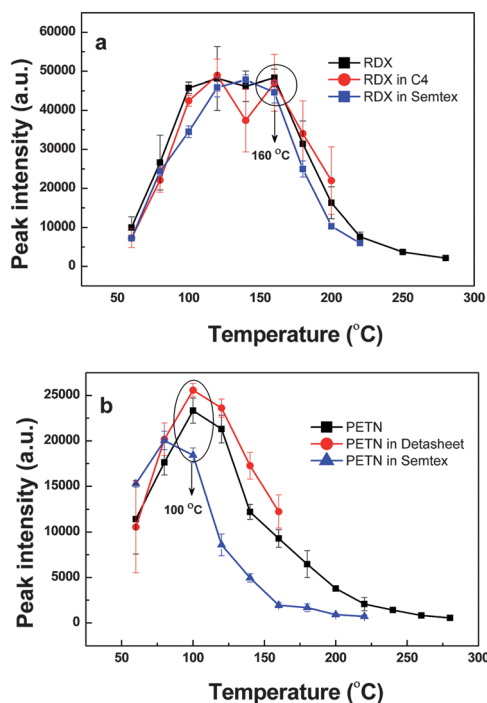
highest IMS response for RDX in C-4 and Semtex was obtained at the same optimal desorber temperature for pure RDX (160 °C). The repeatability of the RDX, RDX in C-4 and RDX in Semtex measurements ranged from 3% to 26% (median repeatability = 16%), 3% to 39% (median repeatability = 19%), and 3% to 10% (median repeatability = 6%), respectively. Fig. 3b shows the temperature profile of the IMS response to 50 ng of PETN, 50 ng of PETN in Detasheet and 50 ng of PETN in Semtex. The highest IMS response for PETN in Detasheet and Semtex was obtained at the same optimal desorber temperature for pure PETN (100 °C). The repeatability of the PETN, PETN in Detasheet, and PETN in Semtex measurements ranged from 5% to 35% (median repeatability = 11%), 3% to 48% (median repeatability = 9%), and 2% to 25% (median repeatability = 10%), respectively. Results show that the previously established optimal desorber temperatures for the individual explosives are comparable to those for the explosives in complex form. Plasticizers and binders added to explosives had no significant effect in the enhanced sensitivity seen for the explosives at a lower desorber temperature. For Semtex, even though both RDX and PETN were present in the sample at 50 ng each, enhanced sensitivity was achieved for both explosives under the previously determined optimal temperatures (RDX 160 °C and PETN 100 °C) as shown in Fig. 2a and c. The slower heating and analyte vapor introduction rates to the instrument caused by low-temperature desorption *versus* flash heating at 230 °C showed to also be advantageous in the analysis of plastic-bonded explosives by IMS.

Explosives mixture

Buxton previously observed enhanced selectivity and improved sensitivity by separating explosives mixtures and interferents by coupling temperature ramped desorption with IMS.[21] Following the study of plastic-bonded explosives, we investigated the temperature profile behavior of an explosives mixture of RDX, TNT, and PETN (50 ng each). Since HMX requires higher temperatures (>200 °C) for optimal desorption it was excluded from the mixtures study. Fig. 4 shows the results of the analysis for the three explosives in a mixture as a function of increasing desorber temperatures.

Similar sensitivity improvements were observed for both RDX and TNT at the same optimal temperatures previously
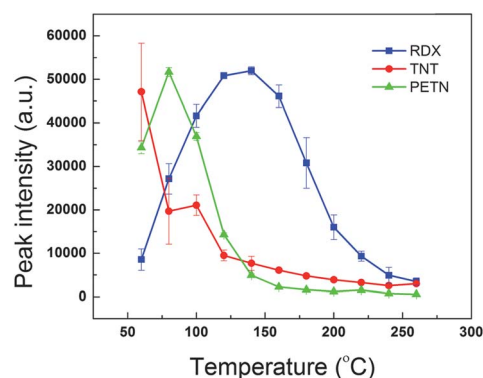

Fig. 3 IMS response to plastic-bonded explosives compared to the explosives in their pure form as a function of desorber temperature. (a) Temperature profile of the IMS response to 50 ng of pure RDX *versus* 50 ng of RDX in C-4 and 50 ng of RDX in Semtex. (b) Temperature profile of the IMS response to 50 ng of pure PETN *versus* 50 ng of PETN in Detasheet and 50 ng of PETN in Semtex.

Fig. 4 Temperature profile of the IMS response to 50 ng each of RDX, TNT, and PETN in a mixture. PETN results were multiplied by four for visualization purposes.

determined for the individual explosives. However, a decrease in response was observed for PETN (compared to the analysis of PETN alone) which is thought to be due to a competitive ionization effect that will be discussed in a later publication.[22] The repeatability of RDX, TNT, and PETN in a mixture ranged from 1% to 37% (median repeatability = 13%), 5% to 39% (median repeatability = 11%), and 2% to 9% (median repeatability = 4%), respectively. Even though there were multiple target analytes present in the sample, each explosive had its highest response at the previously determined optimal temperature when analyzed individually. The repeatability of the measurements appear relatively unaffected when explosives are found in a mixture. All explosives present within the sample were resolved and identified by IMS. For screening applications of IMS where samples are likely to contain two or more target analytes, this work would suggest that next-generation explosive trace detectors would benefit significantly from a front-end modification that includes temperature-programmed desorption. By ramping the desorber temperature throughout the analysis time, each explosive found in a mixture is expected to be "metered" into the IMS at its optimal temperature.

Similar studies have been attempted using other IMS-based detectors containing membranes and although a similar trend can be observed, improvements in sensitivity are not as significant as those reported here. Thus results appear dependent on the particular design of the instrument used in this study (no membrane in the inlet). In addition, the reader should note that the optimal temperatures identified for each explosive are dependent on the following experimental variables specific to this study: substrate composition, sample preparation, and sample purity/age.

Potential mechanisms affecting sensitivity

We have shown that optimized low-temperature desorption significantly improves the sensitivity for the high explosives studied here by IMS. The response of the explosives studied as a function of increased desorption temperature may best be described as an initial rapid increase in signal (resulting from increased sublimation as a function of increasing temperature), followed by a maximum in response, and a subsequent decrease in signal as the temperature further increases. We offer several possible mechanisms that may be responsible for the increase and subsequent decline in signal response as a function of increasing desorber temperature observed as listed below.

Thermal degradation

High desorber temperatures may cause significant thermal degradation of explosive compounds during desorption resulting in fewer intact analyte molecules for analysis. To test this, explosives at varying mass depositions (0.1 ng to 100 ng) were pipetted onto Teflon-coated fiberglass swabs and placed on a conventional hot plate to replicate the desorber in an IMS. Blank swabs (up to four) separated by aluminium spacers were placed above to collect the generated vapor. For example, RDX swabs were desorbed at 230 °C (standard) and 160 °C (optimal) for approximately 20 s (same as IMS). We analyzed both the original and the collector swabs and compared their IMS

response to a control (swab with the same mass deposited analyzed directly by the IMS). For the explosives studied, we found that the IMS response for control samples was not significantly different than the response for collected samples (total explosive recovered), suggesting thermal degradation does not account for the sharp drop in signal response observed at high desorption temperatures. Rabinowitz et al. reported similar results when they measured the thermal degradation of drugs after flash heating by verifying both the concentration and purity recovered on filter extracts with high-performance liquid chromatography mass spectrometry and gas chromatography mass spectrometry methods.[23] The overall high transport efficiency of explosives suggests that thermal degradation does not play a significant role in the decreased sensitivity observed at the high desorption temperature.

Competitive ionization from background contamination

We also investigated whether the decrease in sensitivity at high desorption temperatures is due to the introduction of background chemical contamination from manufacturer-supplied sample swabs which could lead to competitive ionization. If background contamination is being volatalized off the swipe and introduced into the ionization region of the IMS it can potentially participate in charge competition with the target molecules. Our results show that the higher desorber temperature analysis (>200 °C) were characterized by a raised IMS baseline, numerous small unidentified peaks, and a depleted reactant ion peak, all of which are not present in low-temperature desorption analysis (Fig. S3†). To evaluate the significance of this contamination, sample swabs were treated by extraction with 20 mL of acetone solvent for two hours followed by a 300 °C bake-out cycle (eight hours) in an oven to remove any impurities from the swabs. Following the treatment, swabs were spiked with known amounts of explosive and compared to controls (untreated swabs with the same mass deposited) and analyzed by IMS across the temperature range of 60 °C to 280 °C. Results show that even though treated swabs produce reduced background signals, the analyte response was not significantly different from untreated swabs. In addition, the temperature profile of the three explosives (Fig. 2) shows a significant drop in analyte response at temperatures well below those required for observation of contamination peaks. This would suggest any influence of volatile contamination on the swipe does not play a significant role in decreasing the analyte response.

Ionization efficiency

The ionization efficiency of analyte molecules is determined by the production rate of reactant ions limited by the strength of the ^{63}Ni β^- emission and the residence time of the analyte in the source region.[1] IMS literature describes analyte ionization behavior as typically characterized by an inverse relationship between the reactant ion peak and the analyte peak.[24] During a thermal desorption cycle, the analyte concentration in the ionization region initially increases resulting in a decrease in RIP with a commensurate increase in analyte peak intensity. This results from the consumption of chloride ions via adduct formation, charge transfer, or proton abstraction with neutral

explosive molecules. Once the available target molecules have been ionized, the RIP is expected to recover to its original relative intensity. However, if the analyte concentration exceeds a critical level, the available population of reactant ions is insufficient to provide further ionization of analyte molecules, resulting in the saturation in analyte response.[24]

The rapid introduction of the analyte through flash vaporization can potentially "flood" the ionization region and exceed the available pool of reactant ions leading to the partial ionization of the sample. For example, a typical ^{63}Ni β^- emission source produces 1×10^8 electrons per cubic centimetre per second. Typically 50 ng of RDX corresponds to 1.35×10^{14} neutral molecules where all molecules are introduced in 1 s to 2 s. Alternatively, low-temperature desorption introduces 1×10^{12} neutral molecules pulsed into the ionization region over 20 s. Thus, both desorption conditions can saturate instrument response by exceeding the critical level of analyte concentration.

The temporal profile of RDX, TNT, and PETN was studied under standard *versus* optimal desorption temperatures. We characterized the behavior of the reactive ion population (RIP) during the 20 s analysis time under varying analyte concentrations and desorber temperatures. We were particularly interested in studying the effect of desorber temperature on the availability of reactant ion for sample ionization. Such data can allow for evaluation of literature ion–molecule mechanisms as feasible explanations for differences in instrument response.

Fig. 5a–d shows the temporal profile for characteristic RDX and reactant ion peaks at varying analyte concentrations and desorption temperatures.

Fig. 5a and c show RDX concentrations of 10 ng and 100 ng respectively, at a 230 °C desorber temperature. These figures show that regardless of analyte concentration, high-temperature desorption results in the burst introduction of all molecules in

short time periods (<2 s for 10 ng, and <4 s for 100 ng), and excessive reactant ion depletion during the 20 s. On the other hand, at 160 °C desorber temperature, the temporal profile of RDX at 10 ng (Fig. 5b) shows a more typical inverse relationship response for both the reactant ion and the analyte, as mentioned in the literature.[24] Yet, the temporal profile of RDX at 100 ng and 160 °C desorber temperature (Fig. 5d) is not simply explained by the literature mechanisms. Fig. 5d data suggests that even if the reactant ion appears depleted, the "metered-in" analyte introduction maintains an adequate ion–molecule balance, whereby sufficient RIP is available for analyte ionization as demonstrated by the continuous and sustained response of RDX throughout the analysis time. Fig. 5 data shows that both desorption conditions can result in the depletion of the charge reservoir in the reactant region; however, it is the "metered-in" sample introduction achieved by low-temperature desorption that is conceivably responsible for the enhanced sensitivity observed. Results similar to those observed for RDX were found for TNT and PETN. The temporal profile of TNT and the reactant ion peak, as a function of concentration and desorber temperature, was included since TNT undergoes a different ionization mechanism (proton abstraction) than RDX and PETN (Fig. S4†).

Desorber effect on aerosol emission

Another plausible chemical and physical process responsible for the enhanced sensitivity observed is the thermochemical behavior of explosive particles as recently reported by our laboratory.[8] High-speed video microscopy showed that explosive particles melt and rapidly boil as a function of increased desorption temperatures. As the boiling begins, fine aerosols of approximately 100 nm to 200 nm were observed. In the final stages of
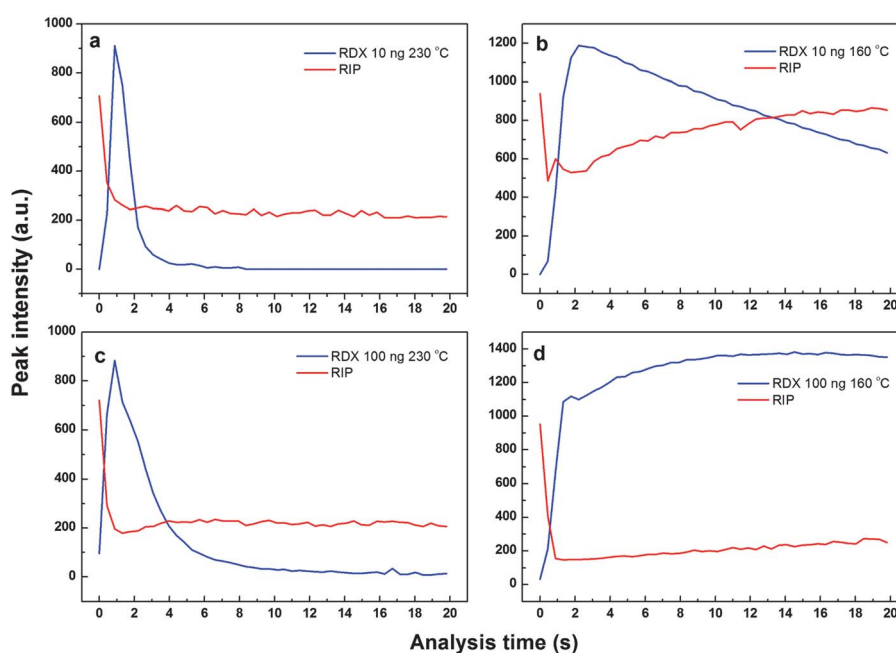

Fig. 5 Temporal profile for RDX and reactant ion peaks as a function of analyte concentration and desorption temperature; (a) 10 ng of RDX and 230 °C desorber temperature, (b) 10 ng of RDX and 160 °C desorber temperature, (c) 100 ng of RDX and 230 °C desorber temperature and (d) 100 ng of RDX and 160 °C desorber temperature.
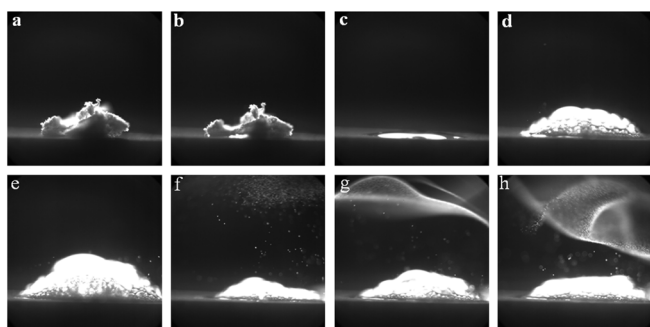
Fig. 6 High-speed video images of 100 µg of RDX as a function of temperature; (a) 60 °C, (b) 100 °C, (c) 120 °C, (d) 140 °C, (e) 160 °C, (f) 180 °C, (g) 205 °C and (h) 230 °C.

desorption (>2 s), the ejection of larger droplets of several micrometres in diameter were observed. Details of the experimental setup can be found in ref. 8. Here we repeated the experiment using liquid deposition of RDX, TNT, and PETN onto Teflon-coated fiberglass swabs and similar results were observed. However, high-speed video was not able to capture the crystalline deposit on the weaved fiberglass texture of the substrate (low contrast) as in the previous example where solid material was directly deposited on the heater interface. Therefore we chose to use images of the solid explosive crystal on a heater interface to illustrate the thermal desorption process. Fig. 6a–h shows images from a high-speed video of a 100 µg RDX explosive particle undergoing physical transformations as a function of increasing temperature.

Fig. 6a and b show that as the temperature increases from 60 °C to 100 °C, RDX solid particles begin to decrease in size and exhibit morphological changes indicative of the first stage of sublimation. Fig. 6c–e show that between 100 °C and 160 °C, RDX particles begin to undergo complete sublimation and small-sized particles begin to melt at the particle/heater interface. Fig. 6f shows RDX at 160 °C where we begin to see fine nano-aerosol production and as the temperature reaches 205 °C (Fig. 6g), the deposit completely melts and vapor "bubbles" begin to appear, indicating that the liquid explosive deposit is approaching a boiling phase. At temperatures above 205 °C (Fig. 6h), the deposit undergoes rapid and violent boiling and the ejection of liquid aerosols is observed. It is important to note that the RDX solid residue deposited (0.1 ng to 100 ng) for the IMS temperature profile study (Fig. 2a) is significantly smaller than that studied under high-speed thermal microscopy (100 µg). Previous studies demonstrate that the physical properties of small particles can be significantly different than bulk, in particular affecting the melting point of a wide range of compounds such as metals. As the size of a particle decreases, the ratio of surface to volume considerably increases and the melting temperature decreases.[25–27] Efforts to characterize the thermal behavior of energetic materials dispersed in the form of nanogram particles were recently reported and describe the use nanocalorimetry to evaluate thermodynamic melting and decomposition kinetic processes.[28] Also, the RDX sample was found to contain significant amounts of HMX which has previously been demonstrated to result in a lower melting RDX–HMX eutectic.[29] While all the mentioned effects are possible, at

this time we do not have a definitive answer for the origin of the temperature discrepancy. Future studies will focus on detailed experiments to characterize the thermodynamic processes of explosives during the desorption process of an IMS. Such studies will consider that explosives particles are also influenced by the hot air from the high temperature (240 °C) inlet transfer line above the sample during desorption.

Thermal desorption of explosives is a complex interaction of multiple-step processes that occur in solid, liquid, gas, and condensed phases. The emission of liquid aerosols further complicates the ion–molecule chemistry by the interplay of liquid and gas phase thermal decomposition of the analyte. This data shows that as the desorber temperature increases, aerosol emission increases, potentially decreasing IMS response. At 230 °C desorption temperature, explosive residue is flash vaporized and introduced into an IMS mostly as liquid droplets rather than vapor-phase molecules. At this point we are unable to definitively conclude whether the aerosols formed during thermal desorption at 230 °C survive throughout the subsequent processes (ionization and drift region) inside an IMS. There are at least two other temperature gradients (inlet and drift tube) that desorbed material must experience prior to ionization and subsequent detection. If the liquid aerosol generated by desorption is not vaporized as it travels through the inlet tube, then the neutral analyte would not be expected to be efficiently ionized and the explosive would pass through the chemical analyzer undetected. On the other hand if the inlet tube temperature is capable of vaporizing the liquid aerosols, the analyte is presented into the ionization region in the proper format (vapor-phase molecules). However, these ions must then overcome a drastic temperature gradient change from 240 °C to 111 °C as they enter the drift tube region. The cooler temperatures in the drift region could lead to the condensation of the analyte forming aerosol particles (leading to homogeneous nucleation and/or ion cluster formation) consequently affecting detection. Future studies will include particle size characterization of the aerosol emitted as a function of desorber temperature.

Conclusions

We completed a series of experiments to optimize IMS desorber temperatures for several common high explosives with 0.1 ng to 100 ng of deposited solid residues. By modifying the desorber temperature, we were able to increase cumulative IMS signal by a factor of 5 for TNT and HMX, to a factor of 10 for RDX and PETN. Optimal temperatures (giving the highest IMS sensitivity) were 80 °C for TNT, 100 °C for PETN, 160 °C for RDX, and 200 °C for HMX. Similar sensitivity improvements were demonstrated for plastic-bonded explosives containing the analyte compounds (C-4, Semtex, and Detasheet) as well as for mixtures of the pure high explosives. These increases in sensitivity are obtained at the expense of increased analysis times of up to 20 seconds. A slower sample heating rate as well as slower vapor-phase analyte introduction rate caused by low-temperature desorption enhanced the analytical sensitivity of individual explosives, plastic-bonded explosives, and explosives mixtures by IMS. High-speed microscopy showed that the signal response as a function of increasing desorber temperature could potentially be explained by an initial increase in signal resulting from

increased sublimation of the analyte (at optimal desorber temperature) followed by melting, boiling and aerosol droplet emission. Further studies include determining the fate of aerosols that are generated during high-temperature desorption of trace explosives and their effect on IMS sensitivity. Other factors, such as competitive ionization, thermal degradation, and ionization efficiency may contribute to the observed behavior but do not appear to explain the magnitude of the IMS signal enhancements.

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