Evaluation of suspected interferents for TNT detection by ion mobility spectrometry

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Abstract

The use of ion mobility spectrometry systems to detect explosives in high security situations creates a need to determine compounds that interfere and may compromise accurate detection. This is the first study to identify possible interfering air contaminants common in airport settings by IMS. Seventeen suspected contaminants from four major sources were investigated. Due to the ionization selectivity gained by employing chloride reactant ion chemistry, only 7 of the 17 compounds showed an IMS response. Of those seven compounds, only 4,6-dinitro-o-cresol (4,6DNOC) was found to have a similar mobility to 2,4,6-trinitrotoluene (TNT) with \( K_0 \) values of 1.55 and 1.50 cm² V⁻¹ s⁻¹, respectively. Although baseline resolution between TNT and 4,6DNOC was not achieved, the drift time for TNT was still easily identified. Alkyl-nitrated phenols, due to acidic fog, responded the strongest in the IMS. The effect of contamination on TNT sensitivity was investigated. Charge competition between TNT and 2,4-dinitrophenol (2,4DNP) was found to occur and to effect TNT sensitivity. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ion mobility spectrometry; Explosives; Interferents

1. Introduction

There is a growing interest in trace analysis of explosives due to illegal use of these compounds [1]. High security areas, such as airports and national buildings, have invested extensive research into the development of trace-level explosives detectors [2]. Ion mobility spectrometry (IMS) has been found to be a promising solution due to its portability, fast response times, and compatibility with ambient air sampling and particulate detection [3]. In addition, IMS is a sensitive detector for explosives due to their strong responses [4].

The possibility of IMS as an explosives detector was realized early after its inception by Karasek who employed an early plasmagraph to identify TNT at the ppb level [5]. Further experiments throughout the next 3 decades have proven IMS to be able to detect and separate a wide range of explosives [6] and to be amenable to field applications [7]. Additional selectivity for explosives in IMS has been achieved by altering reactant ion chemistry with chloride [8,9] and bromide [9]. In
addition to enhanced selectivity, the formation of chloride adducts with unstable explosive compounds were shown to enable ion stability, especially at higher IMS temperatures [10]. IMS instruments have been used in airport settings, for routine luggage checks and for post explosion settings [11].

A primary limitation of commercial IMS instruments has been the implication of false positive and negative responses for real-world systems [12]. Since IMS is selective for nitrated compounds (primary functional group of most explosives), discrimination of other nitrated compounds is difficult due to the similarity in structure. Investigations into false positive and negative responses on commercial IMS instruments have shown that several common household products show similar IMS responses to the explosives, although the identity of the interferent compounds was never clearly studied [12]. One report mistook musk ambrette for TNT at an Israel border crossing [13] and delayed the traveler. This example shows the importance of understanding the explosives and possible contaminants chemistry in IMS systems in order to minimize a misdiagnosis.

The objective of the study was to evaluate 17 common air contaminants for their effect on TNT detection (false positives) and TNT sensitivity (false negatives). A false positive response would occur due to the presence of a contaminant in the sample that had a similar mobility value with the analyte of interest. IMS responses for the seventeen compounds were obtained to determine the false positive probability for each compound. The absence of an analyte’s IMS response due to the coexistence of a second compound would be considered a false negative. Competitive ionization between the analyte and a contaminant could cause a false negative response and was investigated in the second part of this study.

2. Experimental

2.1. Reagents and chemicals

Standards of TNT (1000 µg ml⁻¹) in methanol were obtained from Supelco (Bellefonte, PA). 4-methyl-2-nitrophenol was purchased from Lancaster (Windham, NH). All other compounds were obtained from Sigma-Aldrich (Milwaukee, WI). All solvents were reagent grade (J.T. Baker, Phillipsburg, PA).

2.2. Instrumentation

The IMS instrument was constructed at Washington State University and has been described in detail elsewhere [14]. The IMS was operated in negative mode with a drift voltage of −5000 V. Air was employed as both the drift gas and carrier gas with flow rates of 1 l min⁻¹ and 100 ml min⁻¹, respectively. A constant temperature of 200°C was maintained for the drift tube, carrier line and gas chromatograph oven temperature in all experiments. Two ion gates were located at the entrance and exit of the drift region. The gates were constructed using parallel Alloy 46 wires (California Fine Wire, Grover Beach, CA) and were built based on the Bradbury-Nielsen design. Two 15 mCi ⁶³Ni foils were obtained from NEN Life Science Products (Boston, MA) and were employed as the ionization source. Methylene chloride was introduced via a heated transfer line into the IMS in order to obtained enhanced selectivity by manipulating the reactant ion chemistry.

The electronics of the IMS included a Bertran Associates (Hicksville, NY) high voltage power supply, Omega (Stamford, CT) temperature controllers, and a Keithley Model 427 amplifier (Keithley Instruments, Cleveland, OH). The signal processing and IMS gate control were performed with a home-built system that has been previously described [15].

Experiments were performed using one of two data collection methods; signal averaging or single ion monitoring (SIM). The signal averaging experiment took single IMS spectra and averaged them to obtain enhanced signal to noise ratios. All IMS spectra shown (Figs. 1–3) were obtained in averaging mode with 64 averages, 0.200 ms pulse width and 51.2 ms total drift time. In SIM mode, two IMS gates were employed; the first was opened for a 1 ms width at the beginning of each ion mobility experiment and the second gate was
opened for a 1 ms width that was started at 10 ms into the ion mobility experiment. The SIM data collection was employed for Fig. 4 in which quantitation of the TNT response was required. The experiments in Fig. 4 were performed in triplicate and the average values were designated by the points on the graph.

An HP 5890 (Palo Alto, CA) gas chromatograph (GC) instrument was utilized for sample introduction. The sample was injected into a typical packed-column injector and transported through a J&W Scientific DB-1 (Folsom, CA) column into the IMS. A 3-ft. piece of the column was employed as a transfer line. In order to use the packed column injector with the capillary

2.3. Calculations

In IMS, the ions travel based on their size, shape, and charge through a drift gas. The measured drift time \( t_d \) for ion migration through the drift region can be related to the ion’s mobility \( K \) by Equation 1:

\[
K = \frac{t_d}{E} = \frac{t_d}{t_dE}
\]
Where \( v_d \) is the ion’s drift velocity (cm s\(^{-1}\)), \( E \) is the electric field (V cm\(^{-1}\)) and \( l_d \) is the length of the drift region (cm). This mobility is then standardized for pressure and temperature and labeled the reduced mobility value (\( K_o \)) according to Equation 2:

\[
K_o = K \left( \frac{P}{760} \right) \left( \frac{273}{T} \right)
\]

Where \( P \) is atmospheric pressure (Torr) and \( T \) is temperature (K). The reduced mobility values are the values reported in the literature.

3. Results and discussion

3.1. IMS response for 17 suspected contaminants

Seventeen compounds were tested for their IMS response and a list of these is shown in Table 1. The compounds were chosen based on four suspected contamination sources; alkyl-nitrated phenols from air pollution [16], tobacco byproducts [17], musk compounds found in many perfumes, and pesticides [18]. All of the compounds were chosen due to their suspected strong IMS responses based on similar functionality to explosives. Although, from the four contaminant classes, there are a wide range of compounds included in each class, the seventeen studied compounds were chosen based on similarity in structure and functional groups. From Table 1, it can be seen that the suspected contaminants have at least one nitro functional group, with the exception of methyl parathion. The nitro functional group is the primary electron-withdrawing group present in most explosive compounds. Therefore, the contaminants were chosen based on their expected similarity in response to explosives. This is not to say that other air contaminants aren’t present, only that these seventeen are some of the most probable interfering compounds based on their structural similarity.

For all experiments, methylene chloride was added to the drift gas and introduced into the ionization region. The methylene chloride addition rate was increased until the chloride IMS signal intensity reached a maximum. Addition of methylene chloride to the ionization region produces chloride ions via a dissociative electron attachment reaction [19].

\[
e^- + \text{CH}_2\text{Cl}_2 \rightarrow \text{Cl}^- + \text{CH}_2\text{Cl}^-
\]
A proton abstraction reaction between the analyte and the chloride reactant ion occurs and forms the negative analyte ions that are then detected.

\[
\text{Cl}^- + M \rightarrow (M-H)^- + \text{HCl}
\]  \hspace{1cm} (4)

The gas phase acidities are a measure of how easily the analyte (M) will lose a proton and would provide a comparison of the relative selectivity of reaction 4. Thermodynamic free energies have been experimentally determined based on the following reaction [20–22]:

\[
M^- + \text{H}^+ \rightarrow MH
\]  \hspace{1cm} (5)

And some experimental \(\Delta G\) values are listed in Table 1. In evaluating the values, the lower the \(\Delta G\) value (kJ mol\(^{-1}\)) the more energetically favorable it will be for the analyte to lose a proton and form the anion.

Employing chloride as the reactant ion is common in explosives analysis due to the enhanced ion stability gained from chloride adduct formation and the selectivity for nitro-containing explosives over contaminants [8,23]. This selectivity advantage is exemplified in Table 2 in which ten of the seventeen compounds were not detected. Although nitrobenzene has been reported in the literature (using nitrogen as the drift gas) [24], the selectivity gained with the chloride reactant ion discriminated against the nitrobenzene and an IMS response was not observed. Besides 4-nitro-

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Source of contaminant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Musk ketone: 4-t-butyl-2,6-dimethyl-3,5-dinitroacetophenone</td>
<td>Synthetic fragrances</td>
</tr>
<tr>
<td>Musk tibetene: 2,6-dinitro-3,4,5-trimethyl-t-butyl benzene</td>
<td>Synthetic fragrances</td>
</tr>
<tr>
<td>Musk ambrette: 6-t-butyl-3-methyl-2,4-dinitroanisole</td>
<td>Synthetic fragrances</td>
</tr>
<tr>
<td>Musk xylene: 1-t-butyl-3,5-dimethyl-2,4,6-trinitrobenezene</td>
<td>Synthetic fragrances</td>
</tr>
<tr>
<td>4-nitrophenol</td>
<td>Acidic fog with nitrated phenols</td>
</tr>
<tr>
<td>2,4-dinitrophenol</td>
<td>Acidic fog with nitrated phenols</td>
</tr>
<tr>
<td>2-methyl-4-nitrophenol</td>
<td>Acidic fog with nitrated phenols</td>
</tr>
<tr>
<td>3-methyl-4-nitrophenol</td>
<td>Acidic fog with nitrated phenols</td>
</tr>
<tr>
<td>2-methyl-4,6-dinitrophenol</td>
<td>Acidic fog with nitrated phenols/</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>Tobacco nitrate byproducts</td>
</tr>
<tr>
<td>Nitroethane</td>
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</tr>
<tr>
<td>Nitromethane</td>
<td>Tobacco nitrate byproducts</td>
</tr>
<tr>
<td>2-nitropropane</td>
<td>Tobacco nitrate byproducts</td>
</tr>
<tr>
<td>1-nitropropane</td>
<td>Tobacco nitrate byproducts</td>
</tr>
<tr>
<td>Methyl parathion</td>
<td>Fertilizer/insecticide</td>
</tr>
<tr>
<td>Pentachloronitrobenzene</td>
<td>Fertilizer/insecticide</td>
</tr>
<tr>
<td>Nitrotetrachloromethane</td>
<td>Fertilizer/insecticide</td>
</tr>
</tbody>
</table>

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\text{Cl}^- + M \rightarrow (M-H)^- + \text{HCl}
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<tr>
<th>Compound</th>
<th>(K_o) value (cm(^2)V(^{-1}) s(^{-1})) (\Delta G) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Musk ambrette</td>
<td>1.23</td>
</tr>
<tr>
<td>Musk tibetene</td>
<td>Nd(^b)</td>
</tr>
<tr>
<td>Musk ketone</td>
<td>Nd</td>
</tr>
<tr>
<td>Musk xylene</td>
<td>Nd</td>
</tr>
<tr>
<td>4,6-dinitro-o-cresol</td>
<td>1.55</td>
</tr>
<tr>
<td>2,4-dinitrophenol</td>
<td>1.58 (1.86, N2, 1343 ± 8.4 [B])</td>
</tr>
<tr>
<td>4-nitrophenol</td>
<td>1.85 (1.86, N2, 1343 ± 8.4 [A])</td>
</tr>
<tr>
<td>3-methyl-4-nitrophenol</td>
<td>1.65</td>
</tr>
<tr>
<td>4-methyl-2-nitrophenol</td>
<td>1.68</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>Nd (1.87, N2, 1450 ± 13 [C])</td>
</tr>
<tr>
<td>1-nitropyrene</td>
<td>Nd</td>
</tr>
<tr>
<td>2-nitropropane</td>
<td>Nd</td>
</tr>
<tr>
<td>1-nitropropane</td>
<td>Nd</td>
</tr>
<tr>
<td>Nitromethane</td>
<td>Nd</td>
</tr>
<tr>
<td>Methyl parathion</td>
<td>1.78</td>
</tr>
<tr>
<td>Pentachloronitrobenzene</td>
<td>Nd</td>
</tr>
<tr>
<td>Nitrotetrachloromethane</td>
<td>Nd</td>
</tr>
<tr>
<td>Trichloro-methane</td>
<td>Nd</td>
</tr>
<tr>
<td>2,4,6-trinitrotoluene (TNT)</td>
<td>1.50 (1.49, Air, 1293 ± 8.4 [B])</td>
</tr>
</tbody>
</table>

\(^a\) \(K_o\) value in parentheses denotes literature value, drift gas, and associated reference.

\(^b\) nd, compound was not detected as an IMS peak.
phenol, the mono-nitro containing compounds were not seen even though there were six mono-nitro compounds tested. Based on the gas phase acidity values listed in Table 1, it can be observed that the nitrated phenols have values very similar to TNT and thus, would be expected to respond strongly in the IMS. Also, the $\Delta G$ value for nitrobenzene is much greater than for TNT and the nitrated phenols ($\sim 100$ kJ mol$^{-1}$). This would explain the difference in selectivity for nitrobenzene and the phenolic compounds.

Reduced mobility values were calculated for the seven detected compounds and are listed in Table 2. As observed in the table, only seven of the compounds were detected in the IMS. Of the seventeen compounds, only 4-nitrophenol and nitrobenzene have been evaluated previously by IMS [25,26]. From Table 2, it can be seen that the $K_0$ values for both TNT and 4-nitrophenol are in good agreement with the reported literature values (1.49 for TNT [27] and 1.86 for 4-nitrophenol [25]). Although, there are a wide range of reported literature values for both compounds [28], the literature values were chosen based on similarities in IMS conditions.

Since many of the compounds had not been studied previously, their IMS spectra are presented in Fig. 1. The peak at $\sim 5$ ms present in four of the five spectra was identified as the Cl$^-$ ion based on the $K_0$ reference value of 2.94 cm$^2$ V$^{-1}$ s$^{-1}$ (our experimental value was 2.91 cm$^2$ V$^{-1}$ s$^{-1}$) [29]. Each standard was injected three times for verification that the observed response was not due to carryover from previous samples and was reproducible within 2%. For each compound in Fig. 1, there was only one peak observed in the spectra and the corresponding peaks are denoted by the letters (a–e).

Some generalizations can be made based on the IMS spectra (Fig. 1) and reduced mobility values (Table 2). For three contaminant classes (tobacco byproducts, pesticides, and synthetic fragrances), only two of the compounds were observed in the IMS (musk ambrette and methyl parathion). Comparison of the $K_0$ values for TNT, musk ambrette, and methyl parathion in Table 2 showed that the values were significantly different (1.50, 1.23, and 1.78 cm$^2$ V$^{-1}$ s$^{-1}$, respectively) and could be separated by the IMS. The fourth class of compounds, the alkyl-nitrated phenols, were found to all show an IMS response (five compounds). $K_0$ values ranged from 1.85 to 1.55 cm$^2$ V$^{-1}$ s$^{-1}$ for the five compounds (see Table 2).

In IMS, separation efficiencies are typically reported as resolving power and are calculated based on the following equation:

$$R_p = \frac{t_d}{w_h}$$

where $R_p$ is resolving power, $t_d$ is the drift time, and $w_h$ is the ion pulse duration measured at half of the maximal intensity [30]. Typical $R_p$ values are around 30 for commercial instruments and up to 150 for high-resolution instruments [31]. Recently, our lab developed the equations to describe the separation efficiency in terms of theoretical plates and resolution similar to the equations predominantly used in chromatography [32]. Equation 7 shows the fundamental resolution equation derived for IMS:

$$R = \frac{\sqrt{N \pi - 1}}{4 - \pi}$$

where $R$ is resolution, $N$ is the number of theoretical plates, and $\pi$ is the selectivity factor defined as $K_{o1}/K_{o2}$. By evaluating the calculated mobility values for TNT and the contaminants, we can determine the possible coeluting compounds and the separation efficiency required to obtain baseline resolution between the two peaks. By inspection of Table 2, two nitrated phenols (2,4-dinitrophenol and 4,6-dinitro-o-cresol) were found to have the closest $K_0$ values (1.58 and 1.55, respectively) to the $K_0$ value of TNT (1.50). Employing Equations 6–7, the $R_p$ values for TNT:2,4DNP and TNT:4,6DNOC were found to be 0.68 and 1.07, respectively. Based on a standard resolution of 1.00 for confident resolution of two compounds, 2,4DNP could be separated from TNT while 4,6DNOC would not expected to be resolved from TNT. These calculations were performed based on a measured resolving power of 36 and N of 7200 theoretical plates.

Furthermore, the aforementioned equations allow the resolving power required for resolution of
the TNT/4,6DNOC pair to be estimated. Based on their $K_o$ values and a resolution of 1.00 for separation, $\sim 15\,000$ theoretical plates and a $R_p$ value of 52 is required for separation. The utility of the chromatographic equations and mobility values provide a way to approximate an instrument’s separation capabilities by knowing the attainable resolution and literature $K_o$ values.

3.2. IMS separation of TNT and interferent mixtures

In order to simulate the effect of each contaminant mixture on the TNT response, the four classes (musk compounds, alkyl-nitrated phenols, pesticides and tobacco nitrated byproducts) of contaminants were each added to a TNT solution in approximately equal concentrations. The IMS spectra for each mixture and TNT are shown in Fig. 2. The arrow in each spectra (from a to d) refers to the TNT peak. By referring to Table 1, the compounds included in each mixture can be seen. Similar to Fig. 1, the peak observed at 5 ms correlated with the chloride ion. In Fig. 2(a), the IMS spectra for TNT and the five compounds from tobacco byproducts were evaluated in the IMS. Of the six compounds injected, only the TNT peak (at $\sim 10$ ms) was observed. In Fig. 2(b) (TNT and the musk compounds), both the TNT peak and a second peak which corresponded to the mobility value for musk ambrette were observed. Similarly, Fig. 2(d) shows the IMS spectra for TNT and the three pesticides in which the only additional peak observed was at $\sim 8$ ms and correlated with the mobility for methyl parathion. Therefore, in three of the four mixes, TNT was easily detected and well resolved from the twelve compounds tested.

Based on the single standards analysis, it was expected that the alkyl-nitrated phenols would be the most probable interfering mixture. In Fig. 2(c), an IMS spectra of the five alkyl-nitrated phenols and TNT is shown. Several interesting features can be elucidated from the spectra. First, the chloride ion peak was significantly reduced and can barely be seen in the background noise. This suggests that the combined ionization of the 6 compounds resulted in a significant reduction in the available charge. The first peak correlated with the mobility value of 4-nitrophenol ($\sim 8$ ms). The other four peaks have longer drift times that are similar enough for their observed peaks to overlap as seen in Fig. 2(c). Although, baseline resolution between the phenols and TNT could not be obtained with our IMS, the drift time for TNT was still easily identified.

3.3. Effect of charge competition on TNT sensitivity

In order to understand the role that a compound with a similar gas phase acidity has on TNT sensitivity, TNT and 2,4-dinitrophenol were analyzed at different concentration ratios both qualitatively (Fig. 3) and quantitatively (Fig. 4). 2,4-dinitrophenol (2,4-DNP) was chosen because of its comparable gas phase acidity to TNT (gas phase acidities; 1293 and 1291 kJ mol$^{-1}$, respectively) and different mobility from TNT so that the response of each ion could be easily observed.

Fig. 3 shows the IMS spectra of a TNT standard (a) and a mixture of different concentration ratios of TNT and 2,4-DNP (b–d). Concentrations of the two compounds were chosen such that there was still charge available that was verified by the presence of the chloride reactant ion in each spectra. When TNT was present at ten times higher concentration (ratio 1:10, part b), 2,4-DNP was not observed as a peak. Increasing 2,4-DNP’s concentration by 10-fold (ratio 1:1, part c) showed that both compounds were detected and were present in similar intensities. Once the ratio was 10:1 (part d), the TNT response visibly decreased.

Fig. 3 suggested that charge competition between TNT and 2,4-dinitrophenol within the ionization region caused a loss of TNT signal. A more quantitative evaluation is shown in Fig. 4. The same concentration ratios were employed as in Fig. 3 and the TNT peak heights were normalized to the peak height of a TNT standard at the same concentration. Thus, a normalized TNT value of 1.0 indicates that a decrease in the TNT signal intensity was not observed. By evaluating Fig. 4, it is seen that TNT intensity decreased to $\sim 50\%$ of the original intensity when the concen-
tration ratio was 10:1 (2,4DNP:TNT) and a slight decrease was noticed when both compounds were present at the same ratio.

Although the chloride ion intensity decreased in Fig. 3(d), there was still a peak observed and thus, charge was still available for ionization of the TNT. However, this same concentration ratio (10:1 2,4DNP:TNT) was found to decrease the TNT intensity. Therefore, the combination of Figs. 3 and 4 point out that the presence of contaminants in the drift tube can affect TNT sensitivity (and other explosives) even though the TNT is easily separated from the contaminant.

3.4. Implications of study for explosives detection

This study addressed two issues of explosives detection by IMS; the probability and characterization of false positive responses and false negative responses. It was speculated that there were 17 possible compounds that may be interfering with TNT detection. If these compounds have similar mobility values, then the contaminant could provide a false positive response for TNT and cause misdiagnosis of a potential security issue. The evaluation of the seventeen suspected contaminants showed that only seven compounds even showed an IMS response. Of those seven compounds, only one ion (4,6DNOC) had a similar mobility to TNT and caused the two compounds responses to overlap. Although, the peaks overlapped, the drift time for TNT could be differentiated from 4,6DNOC upon careful speculation. Therefore, the possibility of a false positive caused by the presence of these 17 compounds is improbable.

The second issue was whether a contaminant can decrease the IMS sensitivity for TNT enough that the explosive residue would go undetected (false negative). By monitoring the peak intensity of TNT, it was found that the presence of a contaminant did in fact decrease the TNT sensitivity and could affect the IMS detection of a trace explosive. Although contamination can reduce explosive sensitivity, this was only found for compounds with similar or greater gas phase acidities. Therefore, the reduction in sensitivity may be limited to a minimal number of contaminants.

Acknowledgements

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References