Determination of nitroaromatic and nitramine explosives from a PTFE wipe using thermal desorption-gas chromatography with electron-capture detection

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Abstract

A method for the detection of nitroaromatic and nitramine explosives from a PTFE wipe has been developed using thermal desorption and gas chromatography with electron-capture detection (TD-GC-ECD). For method development a standard mixture containing eight nitroaromatic and two nitramine (HMX and RDX) explosive compounds was spiked onto a PTFE wipe. Explosives were desorbed from the wipe in a commercial thermal desorption system and trapped onto a cooled injection system, which was incorporated into the injection port of the GC. A dual column, dual ECD configuration was adopted to enable simultaneous confirmation analysis of the explosives desorbed. For the desorption of 50 ng of each explosive, desorption efficiencies ranged between 80.0 and 117%, for both columns. Linearity over the range 2.5–50 ng was demonstrated for each explosive on both columns with $r^2$ values ranging from 0.979 to 0.991 and limits of detection less than 4 ng. Desorption of HMX from a PTFE wipe has also been demonstrated for the first time, albeit at relatively high loadings (100 ng).

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1. Introduction

Chromatography techniques, principally HPLC and GC, are routinely used for the determination of explosives in a range of sample matrices including drinking and ground waters [1–6], sea water [7], soils [5,6,8,9], and post-blast debris [10,11]. HPLC is ideal for the analysis of thermally labile analytes that do not vaporize easily. However, sample preparation is generally time-consuming, solvents are required, and the technique suffers from poorer resolution and sensitivity than GC [12]. The utility of GC lies in the selective and sensitive detection methods available, for example the thermal energy analyzer (TEA), mass spectrometer (MS), and electron-capture detection (ECD). Of these detectors, ECD is the most sensitive for the detection of nitroaromatic explosive compounds. More recently, ion mobility spectrometry (IMS) has emerged as a viable technique for the detection of explosives [13–16]. Nowadays, over 10,000 ion mobility spectrometers are currently employed in airports across the world to screen hand-held items for residues of explosives and narcotics [16,17]. Advantages of the technique include ionization at atmospheric pressure, low detection limits, good sensitivity, portability, and rapid analysis [14,17,18]. Yinon and Zitrin have published an extensive and comprehensive review of all aspects of explosives analysis that includes a discussion of chromatographic and IMS techniques [19].

In the current climate, on-site analysis of explosives is highly desirable to enable rapid identification such that swift action may be taken. Additionally, for the analysis of pre-detonated devices or large pieces of post-blast debris for which transport to an off-site laboratory is neither possi-
ble nor practical, a dry sampling method offers further advantages. Thermal desorption (TD) analysis is an ideal dry sampling method since a wipe taken from a contaminated surface can be analyzed directly, eliminating sample preparation steps and thus increasing sample throughput. Commercial, hand-held IMS systems utilize thermal desorption as the sample introduction method and may seem particularly suited to such applications. However, IMS suffers from non-linear response, poor selectivity, and difficulties in the quantification of complex mixtures due to interactions between the reagent gas and contaminating species in the sample [18]. Interfacing a thermal desorption system with GC-ECD (TD-GC-ECD) affords selectivity and sensitivity in the subsequent analysis of the sample wipe. Although the analysis time is not as rapid as in IMS and the GC is not fully portable, a TD-GC-ECD system could easily be deployed in a mobile laboratory.

Despite advantages in minimizing sample preparation time, the wipe sampling method used in the field is a source of considerable variation, dependent upon factors such as the pressure applied during sampling, the sampling time, and the surface area covered. Furthermore, the adhesive properties of the wipe with respect to the analyte and the micro- and macro-structure of the wipe will contribute to the variability of the method. Although wipe samples are routinely taken in industrial hygiene applications, numerous authors have reported no correlation between wipe sampling and the more rigorous method of air-sampling [20–22]. Sigman and Ma were the first authors to report the desorption of a mixture of nitroaromatic, nitramine, and nitrate esters explosives from a PTFE surface, although in this case, an abraded tube rather than a wipe material was used [10]. The tube was placed directly into the injection port of the GC, with subsequent electron-capture detection and negative ion chemical ionization (NCl) detection. Desorption efficiencies were in the range 85–97% and an enhancement in the desorption of RDX was reported (113%).

However, the study did not consider the determination of the nitramine explosive HMX, which, along with RDX, is often considered unfeasible by GC, primarily due to low vapor pressures, high melting points, and thermal lability [4]. Despite this, both RDX and HMX have been determined successfully by GC-ECD [2,4,8,23], using short capillary columns [2], deactivated glass inlet liners [2], relatively high flow rates of carrier gas (in the order of 30 mL min⁻¹) [23], and by minimizing contact between the analyte and metal components in the injection port [2]. In these cases, HMX was extracted from the sample matrix using acetonitrile [8] or isooctyl acetate [2] and injected directly into the GC. A solid-phase extraction (SPE) method with acetonitrile elution has also been reported for the quantification of the nitramine explosives in water [4]. RDX and HMX have been determined in acetonitrile extracts of soil samples by GC-ECD with detection limits of 3 μg kg⁻¹ for RDX and 25 μg kg⁻¹ for HMX [8]. While it was possible to determine HMX accurately using this technique, the peak shape of HMX was the first to degrade following multiple injections of water or soil extracts. Furthermore, the concentration of HMX was underestimated by electron-capture detection, which was attributed to thermal decomposition during GC analysis. No literature is currently available that describes the determination of HMX via a dry sampling method.

The aim of this study was to develop a method for the bulk detection of explosive compounds from a dry wipe material, using thermal desorption-gas chromatography with electron-capture detection. Eventually, the method will be deployed in a field laboratory, enabling on-site identification of explosives on the surface of pre-detonated devices or on post-explosion debris. As a result of variation associated with dry sampling using a wipe material, the method developed in this study is essentially intended to be a qualitative method for the bulk detection of explosives and is not intended for use in security applications such as airports.

To our knowledge, this is the first report that investigates thermal desorption of HMX directly from a PTFE wipe. Previous studies have been limited to solvent extracts, which is undesirable for field applications due to more time-consuming sample preparation. In our method, HMX has been desorbed reproducibly from a PTFE wipe and analyzed using a dual column, dual detector configuration. While this has been achieved at relatively high loadings (100 ng), the detection of HMX meets our original criteria for a bulk detection method.

2. Experimental

2.1. Instrumentation

A Thermo Desorption System 2 (TDS) and Cooled Injection System 4 (CIS) (both Gerstel, Baltimore, MD, USA) were incorporated into an Agilent 6890 Series GC system, equipped with electronic pneumatics control and a micro-ECD with a 63Ni source (Agilent, Wilmington, DE, USA). The transfer line consisted of a 15 cm length of Silcosteel tubing (Restek, Belladone, PA, USA), which fed directly into the CIS. A glass liner filled with Tenax (Gerstel) was used as the inlet liner. The TDS and the CIS were controlled using MaSter software (revision 1.82, Gerstel) and the GC was operated using ChemStation software (G1701 CA version C.00.01, Agilent). Chromatograms were viewed and peak areas were integrated using Environmental Data Analysis software (G1701 CA version C.00.00, Agilent).

In initial experiments, a single column, single detector configuration was adopted. The GC was fitted with an Rtx-TNT2 column (6 m, 0.53 mm i.d., 1.5 μm film thickness, Restek). The carrier gas was ultra high purity helium (99.9995%, US Airweld, Phoenix) and a mass spectrometer gas purifier (Agilent Technologies) was positioned inline to remove oxygen, moisture, and hydrocarbon impurities. An argon–methane (90:10) mixture (Valley Gas & Specialty
DNT) was prepared by serial dilution of the stock solution 5, 10, 20, 25, 30, 50, and 100 μg L\(^{-1}\) /H9262.

### Standards and reagents

Equipment, Albuquerque, NM, USA) was used as the make-up gas for the ECD.

Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine HMX

Methyl-2,4,6-trinitrophenyl nitramine Tetryl

2-Amino-4,6-dinitrotoluene 2-A-4,6-DNT

Hexahydro-1,3,5-trinitro-1,3,5-triazine RDX

1,3,5-Trinitrobenzene 1,3,5-TNB

2,4,6-Trinitrotoluene TNT

2,4-Dinitrotoluene 2,4-DNT

1,3-Dinitrobenzene 1,3-DNB

2,6-Dinitrotoluene 2,6-DNT

A series of standard solutions of concentrations 1, 2.5, 3, 5, 10, 20, 25, 30, 50, and 100 μg L\(^{-1}\), were prepared from the stock solution (EPA Method 8095 Calibration Mix A, Restek), which contained the explosive compounds listed in Table 1, each at a concentration of 1000 μg L\(^{-1}\). All standards were prepared by serial dilution of the stock solution in acetonitrile (Optima-grade, Fisher Scientific, Pittsburgh, PA, USA). A 10 μg L\(^{-1}\) standard of 3,4-dinitrotoluene (3,4-DNT) was prepared by serial dilution of the stock solution (1000 μg L\(^{-1}\), Restek), also in acetonitrile, and was used as an internal standard to verify retention times of the explosives in each analysis. Standards were stored in amber vials (Silicote™ CL7 Deactivation, Restek) at 4 °C.

### Results and discussion

#### 3.1. Assessment of different wipe materials

The three wipe materials (two PTFE wipes and one GF wipe, as described in Section 2.3) were evaluated, in terms of the precision and mean desorption efficiency of a standard solution of explosives.

Six replicate desorptions of 50 ng of each explosive from each of the three wipe materials were analyzed, as described previously. The R.S.D. for each explosive was calculated and used as a measure of the precision of desorption from each wipe material. Using the Environmental Protection Agency (EPA) Method 8000B as guidance [24], a mean R.S.D. of less than 20% for all analytes in the standard mixture was considered acceptable, particularly due to the variation associated with the dry sampling method in the field. Six replicate injections of 50 ng of the standard solution were also spiked directly into the desorption tube and analyzed. The relative mean desorption efficiency of each explosive was determined as the ratio of the mean analyte peak area desorbed from the wipe to the mean peak area desorbed directly from the de-
The precision and desorption efficiency of an explosive mixture from three different wipe materials are summarized in Table 2.

HMX was not detected from any of the wipe materials at the loading of 50 ng. For the early-eluting DNTs and 1,3-DNB, the precision was significantly poorer for the Millipore PTFE wipe compared to both the Osmonics PTFE and GF wipes, with the GF wipe offering optimum precision for all explosives, with the exception of 1,3,5-TNB. Mean desorption efficiencies of each explosive from the two PTFE wipes varied by less than 10%, with more efficient desorption from the Osmonics wipe. Comparing the Osmonics PTFE wipe and the GF wipe, relative desorption efficiencies differed by up to 18.5% (2,6-DNT), with generally more efficient desorption from the GF wipe. However, the desorption of both RDX and Tetryl from the GF wipe was highly inefficient, with desorption efficiencies of only 55.9 and 67.5%, respectively, compared to 106 and 108%, respectively, from the Osmonics PTFE wipe.

Due to the range of volatility in the explosives considered, a compromise between precision and desorption efficiency had to be reached. The Millipore PTFE wipe was eliminated due to the poorer precision and lower desorption efficiencies observed for all explosives compared to the Osmonics PTFE wipe and the GF wipe. Despite improved precision observed using the GF wipe compared to the Osmonics PTFE wipe, the GF wipes were of limited use as a result of the poor desorption efficiency of both RDX and Tetryl. In addition, the GF wipe material was difficult to work with, ripping easily on being rolled up and positioned in the desorption tube. The precision observed for desorption from the Osmonics PTFE wipe was considered acceptable for a field-deployable method, with a mean R.S.D. less than 6% for the nine explosives detected. The desorption efficiencies of all explosives, and particularly RDX and Tetryl, were also acceptable when compared to the GF wipe. Consequently, the Osmonics PTFE wipe was used in all subsequent analyses.

While preferential loading-desorption of the explosives from the wipe material was not specifically tested, a random selection of wipes was re-analyzed directly after the first desorption to determine whether residual analytes continued to be present. In all cases, no significant peaks were detected by the ECD and the assumption was made that all explosives were desorbed as efficiently as possible in the initial desorption.

3.2. Precision, accuracy, and reproducibility of desorption

Six replicates of 10 and 50 ng of the standard solution were desorbed from a PTFE wipe to determine the precision of the method (Table 3). As observed previously, HMX was not detected from the wipe at either loading. Precision was less than 15% at a loading of 10 ng, with the exception of the DNTs, 1,3-DNB, and RDX. At the higher loading of 50 ng, R.S.D.s were less than 11% for all explosives, with a mean R.S.D. less than 6%, which was considered acceptable for a field-deployable method.

The analysis was repeated, spiking 10 and 50 ng of the standard solution directly into the desorption tube in replicate (n=6) and the mean desorption efficiency of each explosive at each loading was determined. At 10 ng, the mean desorption efficiencies were in the range 66.4–169% (Table 3), with lower efficiencies generally observed for the more volatile analytes. A significant increase in desorption efficiency was observed for RDX (169%), which was in accordance with previous results reported by Sigman and Ma where the desorption efficiency was 113% for a loading of 20 ng [10].

There was a significant improvement in the mean desorption efficiency for each analyte at the higher loading, with efficiencies ranging from 81.5 to 110%.
In order to assess the reproducibility of the method, 2 μL aliquots of standard solutions were spiked onto PTFE wipes, corresponding to analyte loadings of 2, 6, 10, 20, and 50 ng. Each solution was analyzed in triplicate on four consecutive days and the R.S.D. at each loading for each analyte was determined. As expected, higher R.S.D.s were observed at the lower loadings for all analytes (Table 3), with 41.5% was determined. As expected, higher R.S.D.s were observed for the desorption of 2 ng of RDX being the highest R.S.D.

Precision based on six replicate desorptions of 10 and 50 ng of each analyte from a PTFE wipe. Mean desorption efficiency based on six replicate direct injections/desorptions of 10 and 50 ng of each analyte. Reproducibility based on triplicate desorptions of 2, 6, 10, 20, and 50 ng of each analyte from a PTFE wipe, over four consecutive days.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Precision (%)</th>
<th>Mean desorption efficiency (%)</th>
<th>Reproducibility (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4-DNT</td>
<td>20.2</td>
<td>10.3</td>
<td>66.4</td>
</tr>
<tr>
<td>1,3-DNB</td>
<td>19.5</td>
<td>7.98</td>
<td>69.6</td>
</tr>
<tr>
<td>2,4-DNT</td>
<td>12.2</td>
<td>6.26</td>
<td>80.2</td>
</tr>
<tr>
<td>2,4,6-TNT</td>
<td>7.7</td>
<td>4.59</td>
<td>98.5</td>
</tr>
<tr>
<td>1,3,5-TNB</td>
<td>14.2</td>
<td>3.72</td>
<td>91.8</td>
</tr>
<tr>
<td>4,4-A-2,6-DNT</td>
<td>7.28</td>
<td>5.51</td>
<td>74.7</td>
</tr>
<tr>
<td>RDX</td>
<td>18.4</td>
<td>7.49</td>
<td>169</td>
</tr>
<tr>
<td>1,3-DNB</td>
<td>4.56</td>
<td>3.32</td>
<td>91.8</td>
</tr>
<tr>
<td>2,4-DNT</td>
<td>8.47</td>
<td>5.32</td>
<td>116</td>
</tr>
<tr>
<td>Tetryl</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>HMX</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>2,6-DNT</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>1,3,5-TNB</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

Precision was in the range 5.85–10.9% for both columns, with mean R.S.D.s of 7.64 and 7.89% for the Rtx-TNT and Rtx-TNT2 columns, respectively. The precision was comparable to that observed with the single column configuration, for which the R.S.D.s ranged from 3.52 to 10.3%. Mean desorption efficiencies ranged from 82.4 to 117% for both columns and differences in desorption efficiencies between the two columns for each explosive were 8% or less, with the exception of RDX. In this case, an increase in desorption efficiency (117%) was observed on the Rtx-TNT2 column, which confirmed earlier results for a single column and was in agreement with results observed in [10]. For the Rtx-TNT column, the desorption efficiency of RDX was 102%.

Six replicates of 100 ng of the standard solution were desorbed from a PTFE wipe and the precision of each explosive on both columns was calculated, compared to an injection of 100 ng of the standard solution directly into the glass desorption tube. For all explosives detected, desorption from the wipe resulted in peak areas that were lower on the Rtx-TNT column. Precision was in the range 5.85–10.9% for both columns, with mean R.S.D.s of 7.64 and 7.89% for the Rtx-TNT and Rtx-TNT2 columns, respectively. The precision was comparable to that observed with the single column configuration, for which the R.S.D.s ranged from 3.52 to 10.3%. Mean desorption efficiencies ranged from 82.4 to 117% for both columns and differences in desorption efficiencies between the two columns for each explosive were 8% or less, with the exception of RDX. In this case, an increase in desorption efficiency (117%) was observed on the Rtx-TNT2 column, which confirmed earlier results for a single column and was in agreement with results observed in [10]. For the Rtx-TNT column, the desorption efficiency of RDX was 102%. HMX was not detected on either column at a loading of 50 ng.
Table 4
Correlation coefficient, limit of detection, and limit of quantitation for a dual column, dual ECD configuration

<table>
<thead>
<tr>
<th></th>
<th>Rtx-TNT column</th>
<th>Rtx-TNT2 column</th>
<th>Rtx-TNT column</th>
<th>Rtx-TNT2 column</th>
<th>Rtx-TNT column</th>
<th>Rtx-TNT2 column</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,6-DNT</td>
<td>0.987</td>
<td>0.989</td>
<td>2.47</td>
<td>2.22</td>
<td>7.48</td>
<td>6.74</td>
</tr>
<tr>
<td>1,3-DNB</td>
<td>0.990</td>
<td>0.988</td>
<td>2.14</td>
<td>2.33</td>
<td>6.49</td>
<td>7.07</td>
</tr>
<tr>
<td>2,4-DNT</td>
<td>0.988</td>
<td>0.989</td>
<td>2.30</td>
<td>2.23</td>
<td>6.97</td>
<td>6.75</td>
</tr>
<tr>
<td>TNT</td>
<td>0.987</td>
<td>0.986</td>
<td>2.45</td>
<td>2.48</td>
<td>7.42</td>
<td>7.51</td>
</tr>
<tr>
<td>1,3,5-TNB</td>
<td>0.988</td>
<td>0.986</td>
<td>2.35</td>
<td>2.49</td>
<td>7.13</td>
<td>7.35</td>
</tr>
<tr>
<td>4-A-A-A-DNT</td>
<td>0.986</td>
<td>0.982</td>
<td>2.50</td>
<td>2.86</td>
<td>7.36</td>
<td>8.66</td>
</tr>
<tr>
<td>RDX</td>
<td>0.985</td>
<td>0.979</td>
<td>2.63</td>
<td>3.12</td>
<td>7.97</td>
<td>9.46</td>
</tr>
<tr>
<td>2-A-4,6-DNT</td>
<td>0.991</td>
<td>0.989</td>
<td>2.06</td>
<td>2.19</td>
<td>6.23</td>
<td>6.64</td>
</tr>
<tr>
<td>Tetryl</td>
<td>0.991</td>
<td>0.986</td>
<td>2.02</td>
<td>2.35</td>
<td>6.13</td>
<td>7.13</td>
</tr>
<tr>
<td>HMX</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

*a Correlation coefficient determined for calibration range 2.5–50 ng of each explosive on each column.
*b LOD: limit of detection, calculated using on regression-based method (see text for details).
*c LOQ: limit of quantitation, calculated using on regression-based method (see text for details).
*d ND: not detected.

Table 4: Correlation coefficient, limit of detection, and limit of quantitation for a dual column, dual ECD configuration

In this study, 6 m wide-bore capillary columns were used, glass liners and glass desorption tubes were deactivated, and the CIS was heated to a final temperature of 260 °C. HMX was desorbed successfully from a PTFE wipe at a loading of 100 ng on each column, as illustrated in Fig. 1. The precision of five replicate desorptions of HMX from the wipe was 23.6% on the Rtx-TNT column and 28.4% on the Rtx-TNT2 column. The mean desorption efficiency of HMX, based on five replicate desorptions, was 50.4% for the Rtx-TNT column and 53.7% for the Rtx-TNT2 column.

Fig. 1. Typical GC-ECD chromatograms of a standard mixture of explosives desorbed from a PTFE wipe using a dual (a) Rtx-TNT2 and (b) Rtx-TNT column configuration.
The response of HMX has also been reported to increase with increasing linear velocity of the carrier gas [4]. In the current study, HMX was injected directly into the column and detected, indicating that the column flow rate of 16.8 mL min\(^{-1}\) was sufficient to separate HMX in the standard mixture of explosives and that the ECD was sufficiently sensitive for the detection of HMX. Thus, the effect of the total flow rate of carrier gas through the TDS during desorption was investigated at 285, 470, and 700 mL min\(^{-1}\), which corresponded to inlet head pressures of 25, 35, and 45 psi. Triplicate desorptions of 100 ng of the standard solution from a PTFE wipe were investigated at each flow rate, using the dual column, dual detector configuration. However, there was no significant improvement in the response of HMX, or indeed the other explosives in the standard, as the total flow rate was increased above 285 mL min\(^{-1}\).

### 4. Conclusions

A method for the desorption of a mixture of nitroaromatic and nitramine explosives from a PTFE wipe has been demonstrated, with subsequent separation and identification by GC-ECD. Thermal desorption of explosives from the wipe eliminates sample preparation and associated clean up steps, thus increasing sample throughput. Additionally, the incorporation of a cooled injection system concentrates explosives at the head of the column and minimizes decomposition of thermally labile explosives. Explosives were desorbed from a PTFE wipe with precision and desorption efficiencies that were considered acceptable for a field-deployable method. With a dual column, dual detector configuration, simultaneous confirmation analysis was possible. This configuration not only offers improved sensitivity compared to MS, but also eliminates the vacuum system requirements associated with MS. Calibration curves were obtained for the dual column, dual detector configuration although the variability associated with the sampling method in the field may limit the method to semi-quantitative at best. The desorption of HMX from a PTFE wipe has been demonstrated, albeit at relatively high loadings (100 ng) and with a mean desorption efficiency of only 50.4 and 53.7% from each column. Increasing the total flow rate of carrier gas during the desorption stage did not have a significant effect in improving the HMX response.

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