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-

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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 ester 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 (NICI) 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 isoamyl 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 $3\,\mu g\,kg^{-1}$ for RDX and $25\,\mu g\,kg^{-1}$ for HMX [8]. While it was possible to determine HMX accu-

rately 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 ^{63}Ni source (Agilent, Wilmington, DE, USA). The transfer line consisted of a 15 cm length of Silicosteel tubing (Restek, Bellafonte, 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

Table 1
Explosive compounds present in EPA Method 8095 Calibration Mix A standard

Analyte	Abbreviation[a]
2,6-Dinitrotoluene	2,6-DNT
1,3-Dinitrobenzene	1,3-DNB
2,4-Dinitrotoluene	2,4-DNT
2,4,6-Trinitrotoluene	TNT
1,3,5-Trinitrobenzene	1,3,5-TNB
4-Amino-2,6-dinitrotoluene	4-A-2,6-DNT
Hexahydro-l,3,5-trinitro-l,3,5-triazine	RDX
2-Amino-4,6-dinitrotoluene	2-A-4,6-DNT
Methyl-2,4,6-trinitrophenylnitramine	Tetryl
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	HMX

[a] Abbreviations used throughout remainder of text.

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

2.2. Standards and reagents

A series of standard solutions of concentrations 1, 2.5, 3, 5, 10, 20, 25, 30, 50, and 100 $\mu g\,mL^{-1}$, 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 $\mu g\,mL^{-1}$. All standards were prepared by serial dilution of the stock solution in acetonitrile (Optima-grade, Fisher Scientific, Pittsburgh, PA, USA). A 10 $\mu g\,mL^{-1}$ standard of 3,4-dinitrotoluene (3,4-DNT) was prepared by serial dilution of the stock solution (1000 $\mu g\,mL^{-1}$, 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 (Silcote[TM] CL7 Deactivation, Restek) at 4 °C.

2.3. General procedure

Filter membranes of 25 mm diameter were used as wipe materials. Two PTFE wipe materials (GE Osmonics, Minnetonka, MN, USA and Millipore, Bedford, MA, USA) and a glass fiber (GF) wipe (also Millipore) were considered initially. Both the PTFE and GF wipes were thermally stable within the temperature range used during desorption. In addition, PTFE is shred-resistant, which was considered an essential property for sampling real devices and post-explosion debris. The PTFE wipes (Osmonics and Millipore) had no backing material and a pore size of 10 μm. The Osmonics PTFE wipe was 260 μm thick while the Millipore PTFE wipe was only 125 μm thick. The GF wipe was also investigated since early experiments indicated that desorption of the standard mixture from glass (i.e. surface of the desorption tube) was efficient. The GF wipes were borosilicate microfiber glass, with no organic binders, and the thickness ranged from 0.32 to 0.36 mm.

Since the sample is essentially destroyed during thermal desorption, it is envisioned that, for the analysis of real samples, the wipe will be cut in half such that duplicate analysis is possible if required. Thus, during method development, wipes were cut in half prior to injecting the explosive standard onto the wipe. In this way, the analysis of real samples was reproduced, in terms of the surface area of the wipe analyzed. A 2 μL aliquot of the appropriate standard and a 1 μL aliquot of the 10 $\mu g\,mL^{-1}$ internal standard solution were injected onto the wipe. Once the solvent had evaporated, the wipe was rolled up, positioned in the glass desorption tube (Gerstel), and placed into the TDS.

The TDS was operated in splitless mode, the CIS in split mode, and the GC in pulsed splitless mode. This allowed a high total flow rate of carrier gas to pass through the TDS during the desorption stage (285 mL min^{-1}), which was subsequently split at the CIS. The flow rate of carrier gas through the column was constant at 16.8 mL min^{-1}. In addition, the pulsed splitless mode sweeps the sample out of the inlet and onto the column quickly, minimizing sample decomposition in the inlet.

To desorb explosives from the wipe, the TDS was heated from 45 to 280 °C at a rate of 40 °C min^{-1}, and held at this temperature for 3 min, then cooled to 80 °C, at which point the CIS was heated from 40 to 260 °C at a rate of 12 °C s^{-1} and held for 4 min. The transfer line was maintained at 280 °C throughout analysis to minimize loss of analytes by condensation. The GC was held at the initial temperature of 40 °C for a further 3 min after the CIS began heating. The GC was temperature programmed as follows: 40–120 °C at 15 °C min^{-1}, to optimize resolution of the early eluting analytes, then 30 °C min^{-1} to a final temperature of 280 °C and held for 3 min. The ECD temperature was 275 °C and the make-up gas flow was maintained at 60 mL min^{-1} throughout the analysis.

3. 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-

Table 2
Precision and desorption efficiency of an explosive mixture from three different wipe materials

	Precision[a] (%)			Relative mean desorption efficiency[b] (%)		
	Osmonics[c]	Millipore[c]	GF[d]	Osmonics[c]	Millipore[c]	GF[d]
2,6-DNT	10.3	20.1	3.24	82.5	74.5	101
1,3-DNB	7.98	17.8	2.83	85.7	78.2	99.7
2,4-DNT	6.26	10.7	3.23	87.6	82.5	97.1
TNT	4.59	6.56	4.05	108	104	111
1,3,5-TNB	3.72	7.07	5.24	106	108	110
4-A-2,6-DNT	5.51	8.74	3.77	87.0	77.8	89.4
RDX	7.49	9.38	3.58	106	108	55.9
2-A-4,6-DNT	3.52	6.61	2.67	83.5	81.4	91.6
Tetryl	4.06	5.56	2.81	108	104	67.5
HMX	ND[e]	ND	ND	ND	ND	ND

[a] Precision based on six replicate desorptions of 50 ng from a PTFE wipe.
[b] Relative mean desorption efficiency calculated as ratio of mean peak area for desorption ($n = 6$) from each wipe to the mean of all direct injections ($n = 8$) at a loading of 50 ng.
[c] Pure PTFE wipes.
[d] GF: glass fiber wipe.
[e] ND: not detected.

sorption tube. A comparison of the three wipe materials is 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. The DNTs and 1,3-DNB were the most volatile explosives considered and precision ranged from 12.2 to 20.2% for the same loading. 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%.

Table 3
Precision, desorption efficiency, and reproducibility of desorption of an explosive mixture from a PTFE wipe

	Precision (%)		Mean desorption efficiency (%)		Reproducibility (%)
	10 ng	50 ng	10 ng	50 ng	
2,6-DNT	20.2	10.3	66.4	85.7	10.1–37.3
1,3-DNB	19.5	7.98	69.6	88.1	10.1–34.3
2,4-DNT	12.2	6.26	80.2	89.1	6.00–29.6
2,4,6-TNT	7.7	4.59	98.5	110	5.22–14.9
1,3,5-TNB	14.2	3.72	91.8	107	6.72–25.1
4-A-2,6-DNT	7.28	5.51	74.7	89.3	7.84–25.6
RDX	18.4	7.49	169	105	7.23–41.5
2-A-4,6-DNT	4.56	3.52	91.8	81.5	5.44–16.5
Tetryl	8.47	4.06	116	110	4.40–20.6
HMX	ND[a]	ND	ND	ND	ND

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.

[a] ND: not detected.

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% for the desorption of 2 ng of RDX being the highest R.S.D. observed. On increasing concentration, the R.S.D.s reduced significantly, the lowest being 4.40%, which was observed for the desorption of 50 ng of Tetryl.

Although the CIS was held at 40 °C during desorption in order to trap and subsequently focus analytes onto the column, there is potential loss of the more volatile analytes during desorption and transfer into the CIS, which would explain the poorer precision observed for these analytes in all cases. While decomposition of explosives during analysis is also a possible contribution to the observed variation, no unidentifiable peaks were detected by the ECD. However, possible decomposition requires further investigation, using single explosive standards and a mass spectrometer as the detector to identify possible degradation products.

3.3. Dual column, dual ECD configuration

A second column, (Rtx-TNT column, 6 m, 0.53 mm i.d., 1.5 μm film thickness, Restek) and a second micro-ECD with a [63]Ni source were installed to enable simultaneous and confirmatory identification of the explosives desorbed, based on differences in retention time between the two columns. A 15 cm length of fused silica fed from the CIS into a "Y" Vu-Union connector (Restek), into which the two inlet ends of the columns were also connected. Each column was then connected to a separate detector. The total flow of carrier gas through the TDS and the flow through each column were unchanged from the single column configuration (285 and 16.8 mL min^{-1}, respectively). While MS also offers definitive identification of analytes, the dual column, dual detector

configuration was chosen since no additional vacuum systems are required, making the instrument more amenable to field-deployability. In addition, the ECD is considerably more sensitive than MS for the detection of explosives. Sigman and Ma reported detection limits that were generally an order of magnitude greater by GC-NICI (low nanogram range) compared to GC-ECD (low picogram range) [10].

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 determined. Since both columns were of the same length, internal diameter, and film thickness, it was assumed that the analytes desorbed were split equally onto the two columns. Thus, with a 100 ng of the standard mixture spiked onto a wipe, 50 ng was loaded onto each column, enabling direct comparison with the precision studies based on the single column configuration. Additionally, the mean desorption efficiency 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.

Calibration curves were plotted over the concentration range 2.5–50 ng for each explosive on both columns, with each standard being analyzed in triplicate. HMX was not de-

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

	r^{2a}		LOD[b] (ng)		LOQ[c] (ng)	
	Rtx-TNT column	Rtx-TNT2 column	Rtx-TNT column	Rtx-TNT2 column	Rtx-TNT column	Rtx-TNT2 column
2,6-DNT	0.987	0.989	2.47	2.22	7.48	6.74
1,3-DNB	0.990	0.988	2.14	2.33	6.49	7.07
2,4-DNT	0.988	0.989	2.30	2.23	6.97	6.75
TNT	0.987	0.986	2.45	2.48	7.42	7.51
1,3,5-TNB	0.988	0.986	2.35	2.49	7.13	7.55
4-A-2,6-DNT	0.986	0.982	2.50	2.86	7.56	8.66
RDX	0.985	0.979	2.63	3.12	7.97	9.46
2-A-4,6-DNT	0.991	0.989	2.06	2.19	6.23	6.64
Tetryl	0.991	0.988	2.02	2.35	6.13	7.13
HMX	ND[d]	ND	ND	ND	ND	ND

[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).
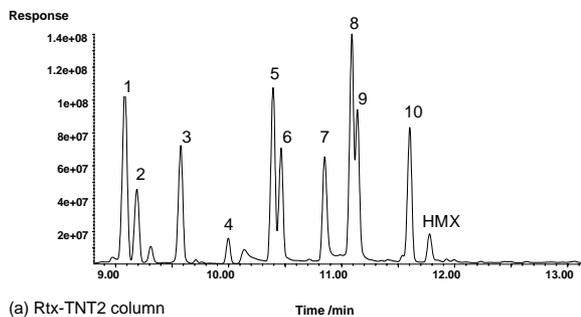[d] ND: not detected.

tected from the wipe within this range of loadings. A linear model was fitted to the data and r^2 values ranged from 0.979 to 0.991 for both columns (Table 4). The limits of detection (LOD) and limits of quantitation (LOQ) were calculated using the regression-based method, which measures uncertainties in both the measurement and the calibration [25]. There was little difference in the LODs between the two columns for each explosive, with a maximum difference of 0.49 ng, which was observed for RDX. All LODs were less than 4 ng, ranging from 2.02 ng for Tetryl on the Rtx-TNT column to 3.12 ng for RDX on the Rtx-TNT2 column.

Sigman and Ma reported limits of detection in the range 0.03–0.34 ng for 2,6-DNT, 2,4-DNT, TNT, and RDX, when desorbed from an abraded PTFE tube [10], which was subsequently placed directly into the injection port of the GC. In our study, sensitivity was at least an order of magnitude higher, ranging from 2.22 to 3.12 ng for the same explosives analyzed by Sigman and Ma. However, in the current study, the desorbed explosives were carried through a transfer line in the flow of carrier gas and trapped in the CIS. While the transfer line was maintained at 280 °C to minimize loss of analytes, this more indirect method of analysis is likely to make a significant contribution to the difference in sensitivity observed compared to Sigman and Ma's work.
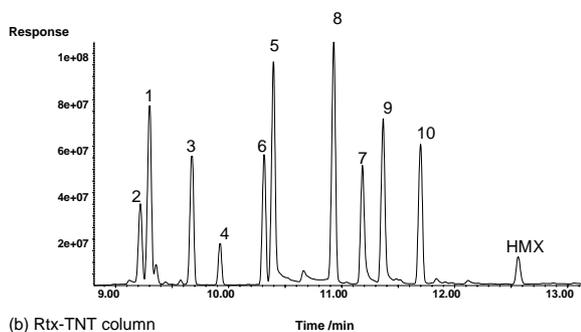
3.4. Desorption of HMX

Numerous researchers outline problems associated with the detection of HMX by GC [2,4,8,23] and, to our knowledge, no authors have published the thermal desorption of HMX from a PTFE wipe material with subsequent GC analysis. For successful GC analysis of HMX, columns less than 10 m in length (to minimize the surface area available for interaction), deactivated glass liners, high injection port temperatures (270 °C) for volatilization, and minimal contact between HMX and hot metal surfaces within the system have been recommended [2].

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.

1 = 2,6-DNT; 2 = 1,3-DNB; 3 = 2,4-DNT; 4 = 3,4-DNT (used as internal standard); 5 = TNT; 6 = 1,3,5-TNB; 7 = 4-A-2,6-DNT; 8 = RDX; 9 = 2-A-4,6-DNT; 10 = Tetryl

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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