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Analysis of munitions constituents in IMX formulations by HPLC and HPLC–MS

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ABSTRACT

The use of Insensitive Munitions eXplosives (IMX) is increasing as the Army seeks to replace certain conventional munitions constituents, such as 2,4,6-trinitrotolene (TNT), for improved safety. The IMX formulations are more stable and therefore less prone to accidental detonation while designed to match the performance of legacy materials. Two formulations, IMX 101 and 104 are being investigated as a replacement for TNT in artillery rounds and composition B Army mortars, respectively. The chemical formulations of IMX-101 and 104 are comprised of four constituents;2,4-dinitroanisole (DNAN), 3-nitro-1,2,4-triazol-5-one (NTO), 1-nitroguanidine (NQ), and Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) which are mixed in various ratios to achieve the desired performance. The current work details the analysis of the IMX constituents by single column HPLC–UV–ESI-MS. Detection limits determined are in agreement with similar HPLC analysis of compounds, ranging from 7 to 9 μg/L. Gradient mobile phases are used to allow separation of the 4 target compounds in more complex mixture of other concomitant compounds. Mass spectra are used to confirm analyte identity with chromatographic retention time.

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1. Introduction

The use of Insensitive Munitions eXplosives (IMX) is increasing as the Army seeks to replace certain conventional munitions constituents (MCs) for improved soldier safety. The IMX formulations are more stable and less prone to accidental detonation while designed to match the performance of legacy materials [1]. Time Magazine named, the BAE Systems developed IMX 101 as one of the top 50 inventions of 2010 [2]. Two formulations of IMX are currently being produced; IMX 101 is qualified as a replacement for trinitrotoluene (TNT) in artillery rounds while IMX 104 is a replacement for composition B (Comp B) [3,4].

The increase in potential IMX use results in the need for a simple detection method for the four constituents of IMX-101 and 104; 2,4-dinitroanisole (DNAN, $C_7H_6N_2O_5$), 3-nitro-1,2,4-triazol-5-one (NTO, $C_2H_2N_4O_3$), 1-nitroguanidine (NQ, $C_1H_4N_4O_2$), and Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX, $C_3H_6N_6O_6$). The standard environmental test method, U.S. EPA method 8330, for nitroaromatic, nitramine, and nitroester analysis uses high performance liquid chromatography (HPLC) separation and detection by ultra-violet light absorption [5]. The target analyte list for the U.S. EPA method 8330 contains 17 components: 2-amino-4,6-dinitrotoluene, 4-amino-2,6-dinitrotoluene, 3,5-dinitroaniline, 1,3-dinitrobenzene, 2,4-dinitrotoluene, 2,6-dinitrotoluene, Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), nitrobenzene, nitroglycerin, 2-nitrotoluene, 3-nitrotoluene, 4-nitrotoluene, [3-Nitrooxy-2,2-bis(nitrooxymethyl)propyl] nitrate (PETN), RDX, *N*-methyl-*N*,2,4,6-tetranitroaniline (tetryl), 1,3,5-trinitrobenzene, 2,4,6-trinitrotoluene. Variations of this method can use electrospray ionization mass spectrometry (ESI-MS) or tandem mass spectrometry (MS–MS) for detection and quantitation of these constituents. An alternative U.S. EPA method, 8095 [6], uses GC-ECD to quantify all of the target compounds in method 8330. However, three of the IMX constituents, NTO, NQ and DNAN, are not currently on the target analyte list of either U.S. EPA method 8330 or 8095. Of the three, DNAN has been shown previously to be separated from concomitant compounds under the conditions of the US EPA method 8330 by Chow et al. [7].

At present, there is not a simple method which efficiently separates and quantifies insensitive munitions constituents and legacy compounds on a single HPLC column [8]. Previous work has focused on either the separation of individual IMX munitions constituents or the separation of one component and its derivatives [7–11]. Consequently, the detection methods presently available in the literature utilize multiple columns for the analysis of IMX constituents, extending analysis time and cost.

Previous studies have utilized a two column approach in order to quantify the components of IMX formulations. The two column approach is documented in dissolution studies of NTO from IMX

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compositions [9]. The researchers used a Thermo Scientific Hypercarb column with an acidified eluent mixture for the analysis of the highly water soluble components, NQ and NTO, and a Dionex Acclaim® E1 column under the U.S. EPA method 8330 conditions for the analysis of RDX and DNAN. The separation of NQ and DNAN in the presence of RDX has been demonstrated by ultrafast liquid chromatography [10]. NTO and its derivatives have been analyzed by HPLC and capillary electrophoresis [11]. Recently Can and coworkers have studied NTO in complex nitro-explosive mixtures [12].

The objective of the present work was to develop a streamlined HPLC–UV–ESI-MS technique for detection and quantitation of IMX constituents in aqueous matrixes, such as ground and surface water. Modifications to the U.S. EPA method 8330 resulted in a single chromatographic separation and subsequent quantification of NQ, NTO, DNAN and RDX simultaneously, and in the presence of other explosive compounds. The results of water samples analyzed by HPLC–UV–ESI-MS are quantitatively compared to demonstrate the utility and evaluate any limitations of the single column method. The developed HPLC gradient was also used to analyze the compounds of interest on a second chromatographic column which can then provide for dual column analyte confirmation when MS analyte confirmation is not available.

The HPLC method presented allows for the separation of NQ, NTO, DNAN and RDX in a single analysis. The developed method uses an acidified mobile phase gradient, detailed below in Table 1. The gradient steps from an aqueous composition of 86% to 51% before returning to 86% over 45 mins. The mobile phase composition returns to 86% aqueous to allow the column to re-equilibrate prior to the injection of the following sample. The eluent composition consists of trifluoroacetic Acid (TFA), acetonitrile (ACN), methanol (MeOH), and water to separate the constituents on a Synergi 4 m Hydro-RP 80A column. The presented method significantly reduces analysis time, solvent use, and costs for simultaneous detection of the analytes of interest and traditional explosive compounds. This method advances the field of analytical chemistry for detection of insensitive munitions and has the potential to be useful in the analysis of IMX munitions constituents from complex matrixes, such as ground water, and ultimately, soil and tissue.

2. Materials and methods

2.1. Reagents and supplies

All commercially available chemicals were of analytical grade or higher purity and were used without further purification. MeOH and ACN were purchased from JT Baker (Phillipsburg NJ). DNAN was purchased from Alfa Aesar(Ward Hill, MA). RDX, NQ, EPA mix A, and EPA mix B were purchased from SigmaAldrich (St. Louis, MO). Military grade crystalline NTO, IMX 101 and IMX 104 were supplied by BAE systems (Holston Army Ammunition Plant, TN) and used without further purification. 18.3 MΩ cm resistivity deionized (DI) water was used for all experiments. Mixed analyte calibration standards containing U.S. EPA 8330 analytes at 1000 mg/L were purchased from Supelco (St. Louis, MO). Working calibration standards were prepared by volumetric dilutions of the stock explosive standard with 18.3 MΩ cm resistivity DI water.

2.2. Sample preparation

All samples were prepared in DI water unless otherwise stated and analyzed by the newly developed HPLC–UV–ESI-MS method. The developed method modifies US U.S. EPA Method 8330B [5] by acidifying the eluent and utilizing a gradient that ramps from 86% to 51% aqueous. Traditionally, samples analyzed by U.S. EPA 8330 are prepared in 50:50 water:ACN, however ACN adversely affected the chromatography of early eluting compounds (NQ and NTO) analyzed by the newly developed method. The effect of ACN

Table 1
Instrumentation and operating conditions for HPLC–UV and ESI-MS analysis.

HPLC				
Agilent 1200 system with quaternary pump				
RP column 1			Phenomenex Synergi 4-μm hydroRP; 80A 250 × 4.6 mm	
RP column 2			Restek Pinnacle II biphenyl; 5 μm, 150 × 4.6 mm2	
Autosampler and column temperatures			10 °C and 25 °C, respectively	
Mobile phase flow rate			1 mL/min	
UV absorbance wavelengths			254 nm & 315 nm	
Injection volume			50 μL	
Total chromatogram time			45 min	
Elution program and mobile phase				
Time (min)	DI water (%)	ACN (%)	0.1% TFA (%)	MeOH (%)
0	76	4	10	10
5	76	4	10	10
10	41	4	10	45
35	41	4	10	45
40	76	4	10	10
45	76	4	10	10
ESI-MS				
Bruker Esquire 6000				
Capillary potential			−850 V, 7 nA	
Nebulizer gas			50 psi	
Dry gas			10 psi	
Dry gas temperature			150 °C	
Skimmer			40 V	
Nitroguanidine (NQ) quantitation mass monitored, retention time			105 *m/z*, $[M+H]^+$, 3 min	
Nitrotriazalone (NTO) quantitation mass monitored, retention time			131 *m/z*, $[M+H]^+$, 4 min	
2,4-dinitroanisole (DNAN) quantitation mass monitored, retention time			199 *m/z*, $[M+H]^+$, 24.3 min	
Hexahydro-1,3,5-trinitro-1,3,5 triazine (RDX) quantitation mass monitored, retention time			245 *m/z*, $[M+Na]^+$, 16.2 min	
ESI-MS CID				
Isolation width			4 mass units	
CID amplitude			0.5 V	

concentration on the chromatography of NTO is discussed in further detail below. There was no notable consequence of ACN concentration in the sample on the traditional U.S. EPA 8330 analytes.

Replicate laboratory control sample (LCS) and matrix spike sample (MS) were prepared from DI water and a water sample created by bulk leaching 2.3 g of Memphis Silt soil with 20 mL of 0.1 M $CaCl_2$ for 24 h. The geochemical parameters of the Memphis Silt soil have been described elsewhere [14–15]. This leachate was used to determine the effects of concomitant matrix constituents that would be present in a natural water. The leachate was centrifuged and filtered though a 0.45 µm Millipore (Billerica, MA) Millex-LCR filter prior to fortification with the analytes of interest (NQ, NTO, RDX and DNAN) at 2 mg/L and analysis.

Percent recovery (% REC) and percent relative standard deviation (% RSD) were determined from eight replicate analyses at 2 mg/L using the single column HPLC–UV–ESI-MS analysis method.

Finally, a natural riverwater matrix was tested by spiking water collected from the Yazoo River (Vicksburg, MS) and filtered through glass wool to remove any large debris. 600 mL of the Yazoo river water was then further filtered to 0.45 µm using Whatman (Little Chalfont, United Kingdom) GD/XP filters. 500 mL aliquots of the glass wool and 0.45 µm filtered water were then fortified with the analytes of interest (NQ, NTO, RDX and DNAN) at a concentration of roughly twice the detection limit (0.020 mg/L). 1 mL aqueous aliquots were then analyzed using the newly developed method. Additionally, an aliquot of the 0.45 µm filtered 0.02 mg/L sample diluted 50:50 with methanol was also prepared, to further demonstrate any effect of added solvent on analysis of natural matrices.

2.3. Instrumentation

HPLC analysis was conducted using an Agilent (Palo Alto, CA) 1200 HPLC equipped with either a Phenomenex (Synergi 4-µm hydroRP) or a Restek (Pinacle II Biphenyl) reversed-phase column. The latter reverse-phase column was used as the second column for analyte confirmation when MS confirmation is not used. Mass spectrometric analysis was carried out using a Bruker Daltonics Inc. (Billerica, MA) Esquire 6000 ion trap mass spectrometer equipped with an electrospray ion (ESI) source. The operating conditions for the HPLC and the MS are described in Table 1 as is the HPLC gradient program.

2.4. Calibration

The calibration curve for the HPLC-UV-ESI-MS used mixed analyte standards with concentrations of 0.005, 0.01, 0.05, 0.1, 0.5, 1, 5, 10, 25, 50 and 100 mg/L. The UV linear correlation coefficients (Pearson's r) of the linear regression lines drawn between the peak area and the concentration were at 0.98 or greater when all 11 calibration standards are included. Analytes were quantitated via UV absorbance and confirmed by ESI-MS spectra.

The instrument calibrations were verified using second analytical preparations of 25 and 1 mg/L standards, recoveries were required to be within ±20% of the nominal concentrations. Continuing calibration verification (CCV) standards were analyzed at a frequency of 5% and bracketed the samples for each analytical batch. The analyte recoveries for the CCVs were required to be within ±10% of the nominal concentrations.

3. Results and discussion

3.1. Standard chromatograms and detection limits

HPLC–UV–ESI-MS analysis showed excellent separation between DNAN, RDX, NTO, and NQ on the single column method described. The retention times for the IMX munitions constituents are given in Tables 1 and 2 for the Phenomenex Synergi column. Fig. 1 shows the separation of IMX components NQ, NTO, RDX and DNAN from the analysis of a 10 mg/L standard. Two wavelengths are used for optimal detection of all analytes. The insensitive munitions components are easily separated from the solvent void volume and each other. The reconstructed positive ion chromatograms for the ions of interest (m/z 105 (NQ+H), 131 (NTO+H), 199 (DNAN+H) and 245 (RDX+Na)) are also shown in Fig. 1. The reconstructed ion chromatograms were offset for clarity. Collision induced dissociation (CID) mass spectra (Fig. 2) of the four chromatographic peaks, shown in Fig. 1, give characteristic ions for the four constituents of IMX to use as absolute compound identification. The ion of m/z 105 ($[NQ+H]^+$) shows a CID loss of 46 ($-NO_2$) resulting in a fragment ion of m/z 59. The CID of the ion of m/z 199 ($[DNAN+H]^+$) yields two fragment ions of m/z 111 (loss of 88) and 88 (loss of 111). CID of the ion of m/z 131 ($[NTO+H]^+$) yields an ion of m/z 74 (loss of 57). CID of the sodiated molecular ion of RDX (m/z 245) shows a loss of 60 resulting in an ion of m/z 185. RDX is also obsevered as a sodium bound dimer (m/z 467, not shown), which undergoes the loss of 222 (RDX) upon CID. The IMX constituents were easily identified using

Table 2
Retention times and compound identification for 5 mg/L 17 component mixed explosive standard (shown in Fig. 3) analyzed with a Phenomenex Synergi 4-µm hydroRP column. The IMX constituents are shown in bold.

Chromatographic Peak	RT	Compound
1	**3.0**	**NQ; 1-nitroguanidine**
2	**4.0**	**NTO; 3-nitro-1,2,4-triazol-5-one**
3	14.3	HMX; Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
4	**16.2**	**RDX; Hexahydro-1,3,5-trinitro-1,3,5-triazine**
5	18.1	1,3,5-TNB; 1,3,5-trinitrobenzene
6	21.2	Tetryl; *N*-methyl-*N*,2,4,6-tetranitroaniline
7	22.5	1,3-DNB; 1,3-dinitrobenzene
8	22.9	NB; nitrobenzene
9	23.5	2,4,6-TNT; 2,4,6-trinitrotoluene
10	**24.3**	**DNAN; 2,4-dinitroanisole**
11	25.8	4-Am-DNT; 4-amino-2,6-dinitrotoluene
12	26.4	2-Am-DNT; 2-amino-4,6-dinitrotoluene
13	28.4	2,6-DNT; 2,6-dinitrotoluene
14	28.9	2,4-DNT; 2,4-dinitrotoluene
15	33.5	2-NT; 2-nitrotoluene
16	35.2	4-NT; 4-nitrotoluene
17	37.2	3-NT; 3-nitrotoluene

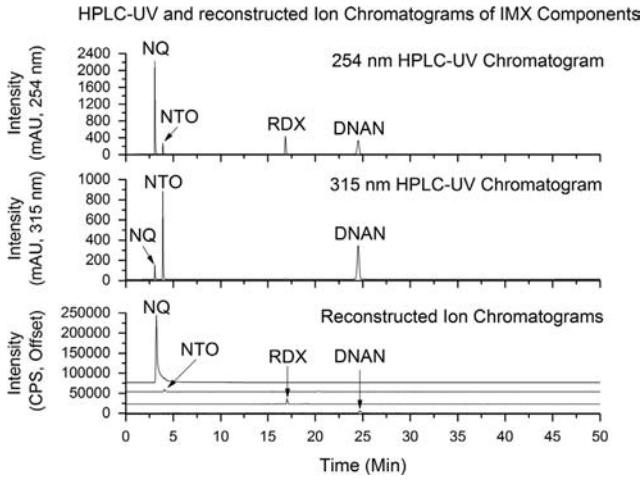

Fig. 1. HPLC–UV and reconstructed ion chromatogram of IMX components. The 254 nm (top) and 315 nm (middle) UV traces and reconstructed ion chromatograms (bottom) of NQ (m/z 105, $[M+H]^+$), NTO (m/z 131, $[M+H]^+$), RDX (m/z 245, $[M+Na]^+$) and DNAN (m/z 199, $[M+H]^+$)at 10 mg/L analyzed by HPLC–UV–ESI-MS.

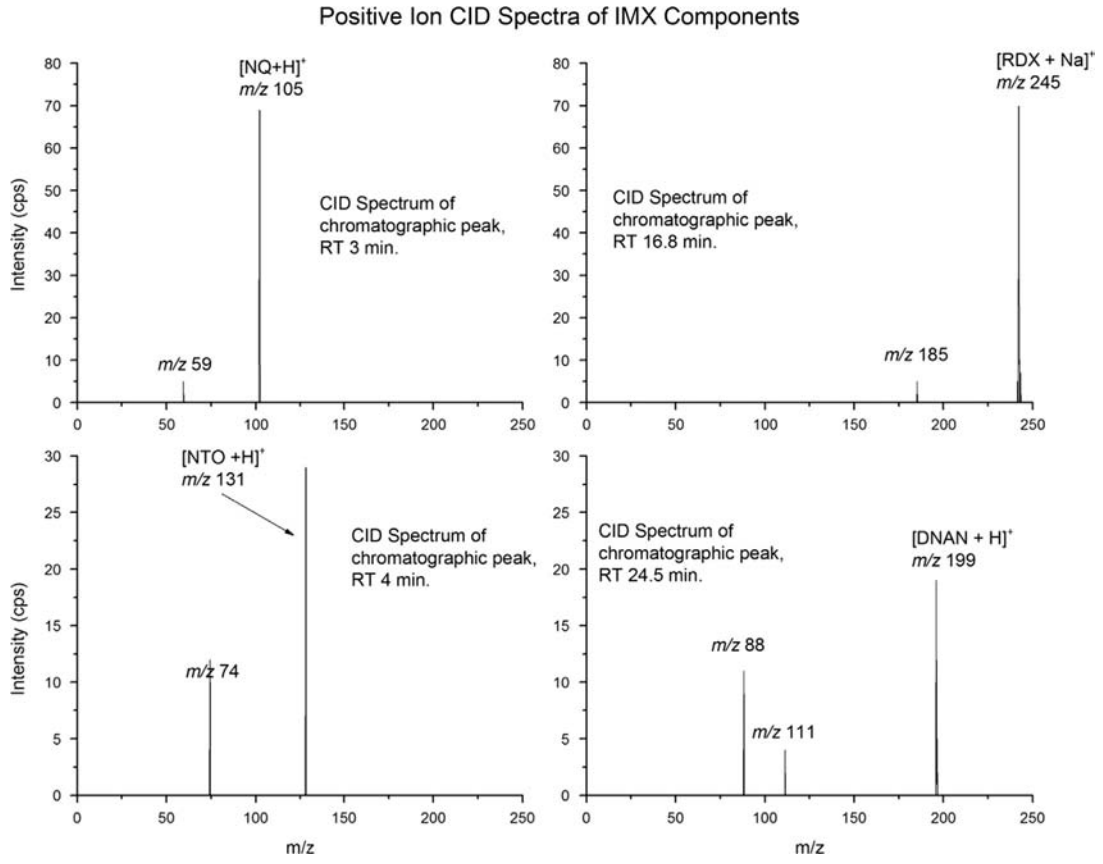

Fig. 2. Positive ion CID mass spectra of IMX components. CID mass spectra of the four UV chromatographic peaks identified in the analysis of a 10 mg/L IMX mixed standard, (shown in Fig. 1). The compounds of interest, NQ, RDX, DNAN, and NTO (clockwise from top left), are identified.

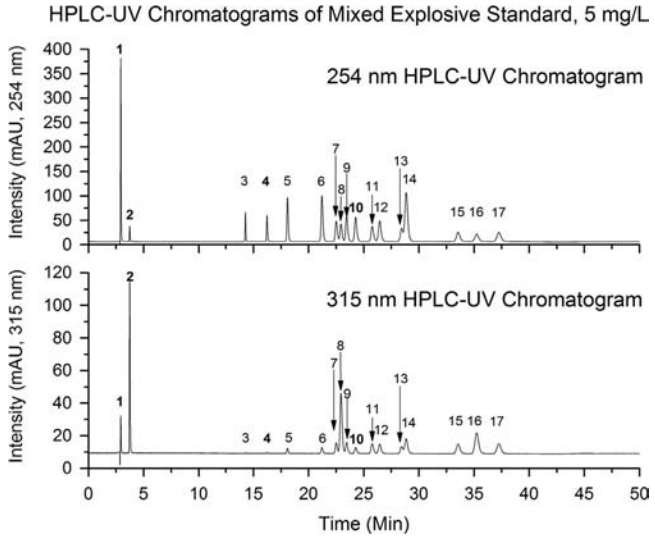

Fig. 3. HPLC–UV Chromatograms of Mixed Explosive Standard, 5 mg/L. 254 nm and 315 nm absorbance trace chromatograms of NQ, NTO, RDX, DNAN and 13 other common explosive compounds at 5 mg/L analyzed by HPLC–UV. NQ, NTO, RDX and DNAN are shown in bold.

these spectra which can be used to confirm the identity of components in unknown mixed samples.

Analysis of NQ, NTO and DNAN in the presence of 14 common explosive analytes (HMX, RDX, 1,3,5-TNB, 1,3-DNB, Tetyl, NB, 2,4,6-TNT, 4-Am-DNT, 2-Am-DNT, 2,4-DNT, 2,6-DNT, 2-NT, 3-NT, and 4-NT) resulted in separation of all 17 components (Table 2 and Fig. 3). Commercially available standards, EPA 8330 mix A and B (Sigma-Aldrich, PN 47283 and 47284), were used to prepare the mixture of 14 common explosives. A typical HPLC–UV chromatogram for a mixed calibration standard containing 5 mg/L of the 4 IMX constituents investigated and the 13 additional common explosive compounds is shown in Fig. 3. RDX is a member of both the IMX constituents and the mixture of the 14 common analytes. The identities and retention time of the 17 chromatographic peaks, observed in Fig. 3, is given in Table 2 with corresponding retention times.

UV chromatograms of 30 mg/L IMX 101 and IMX 104 solutions are shown in Fig. 4. Solid samples of IMX 101 and IMX 104 were dissolved by stirring in DI water for 24 h. The resultant solutions were filtered and analyzed by HPLC–UV–ESI-MS under the method conditions (Table 1).

3.2. Method detection limits

Method detection limits (MDLs) for the IMX compounds were determined for the HPLC method as described in 40 CFR Part 136 [13], and are listed in Table 3. Briefly, eight 1 mL volumes of DI water were fortified with the analytes of interest at a concentration of 0.050 mg/L and analyzed using the HPLC method described. The MDL was calculated by multiplying the standard deviation for each set of replicates by a factor of 3. A ninth sample was fortified at 0.010 mg/L, roughly the calculated MDL for the four IMX analytes, and used as the verification sample.

DI water was used as a method blank; no analytes were detected in any of the blank analyses above the MDL. The MDL's ranged from 7 μg/L (NTO) to 9 μg/L (NQ) and are on the order of MDL's observed for other common explosives analyzed by similar methods [5]. A laboratory control sample (LCS) was analyzed with a method blank with each batch of samples. The LCS was prepared by fortifying reagent water with all the analytes of interest at concentrations approximately one half highest calibration standard.

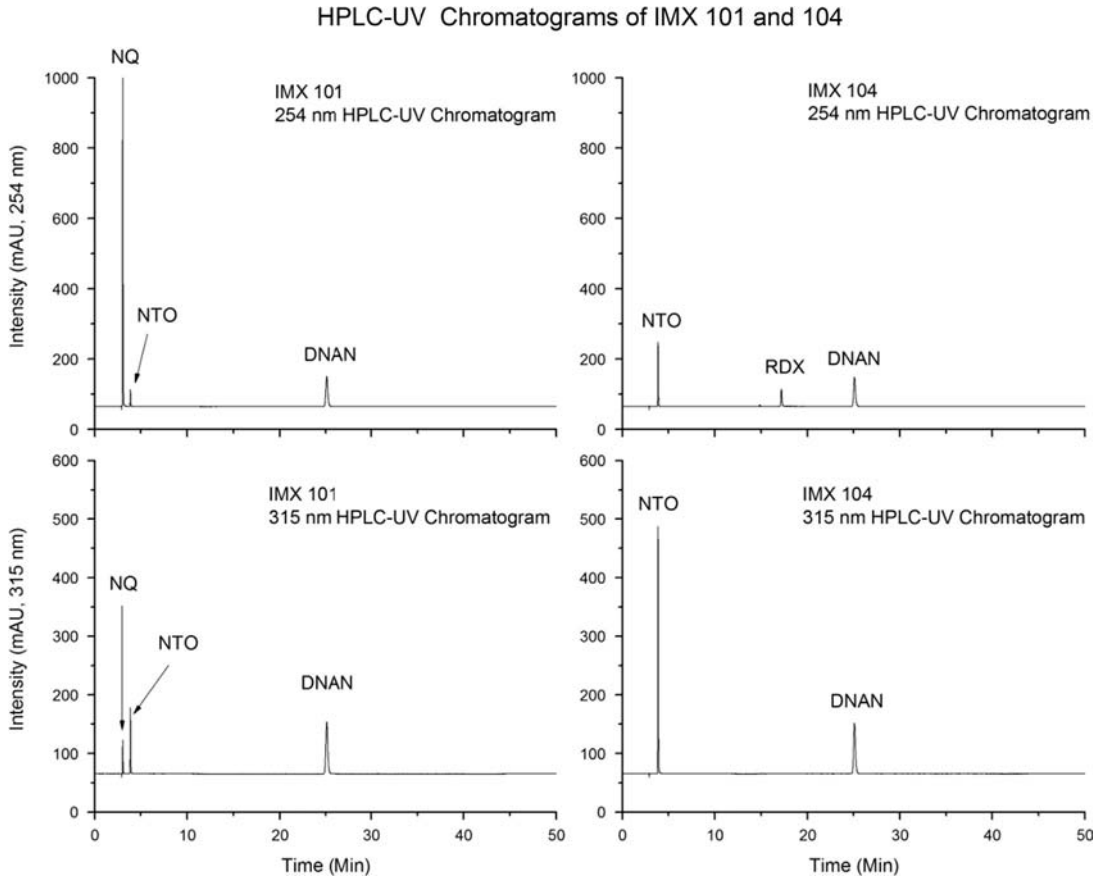

Fig. 4. HPLC–UV Chromatograms of IMX 101 and 104 analyzed with a Phenomenex Synergi 4-μm hydroRP column. HPLC–UV chromatograms of 30 mg/L IMX 101 (left) and 104 (right) samples. UV absorbance at 254 (top) and 315 nm (bottom) was monitored for detection. IMX 101 and 104 were dissolved in 100% DI water.

Table 3
Method Detection limits (MDLs) determined from eight replicate analyses at 0.050 mg/L, and analyte recoveries of a 0.010 mg/L verification sample using the single column HPLC analysis method Percent recovery (% REC) and percent relative standard deviation (% RSD) determined from eight laboratory control sample (LCS) and matrix spike sample (MS) replicate analyses at 2 mg/L using the single column HPLC analysis method.

Analyte	Calculated MDL (μg/L) $n=8$	Measured concentration of 10 μg/L verification sample	Verification Sample % REC	LCS % REC $n=8$	LCS % RSD $n=8$	MS % REC $n=8$	MS % RSD $n=8$	QSM Limits (% Rec)
NQ	9	10	104.9	93.7	13.4	100.9	7.2	
NTO	7	11	106.4	104.2	16.5	100.5	17.0	
RDX	8	11	109.4	89.0	17.3	86.1	30.3	50–160
DNAN	8	9	93.3	102.0	15.3	98.9	17.9	

The Department of Defense (DoD) Quality Systems Manual (QSM) [16] only lists recoveries for one of the IMX constituents, RDX. However, the recoveries of the mid-level LCSs in Table 3 were consistent with the acceptance ranges for other MC's in the DoD QSM [16], which range from 45 to 160% recovery.

Matrix spike (MS) and MS duplicate (MSD) analyses were performed on water samples that had been exposed to Memphis silt soil [14–15] and then filtered (0.45 μm Whatman GD/XP filter) prior to 2 mg/L fortification with the analytes of interest (NQ, NTO, RDX and DNAN) and analysis.. The average of 8 MS recoveries (Table 3) generally fell within the acceptance ranges, 80–120%, for the mid-level LCSs. The QSM [16] limits for RDX are also given in Table 3. The relative percent differences (RPDs) between replicates were generally less than 20% with the exception of RDX which had a RPD of 30.3 for the matrix spike samples.

River water samples were also collected from the Yazoo River (Vicksburg, MS) and filtered prior to fortification with the analytes of interest and analysis. Aliquots filtered with glass wool and 0.45 μm GD/XP were fortified at a concentration of roughly twice the detection limit (0.020 mg/L) prior to analysis. Recoveries for the glass wool filtered NQ, NTO, RDX, and DNAN were 95.9, 117.9, 99.8 and 84.1 respectively. The recoveries for the 0.45 μm filtered river water sample were 94.8, 123.1, 118.0, and 106.9 for NQ, NTO, RDX, and DNAN respectively.

An aliquot of the 0.45 μm filtered 0.02 mg/L fortified sample diluted 50:50 with MeOH was also prepared, to further demonstrate effect of added solvent on natural matrices. Recoveries for NQ, NTO, RDX, and DNAN were 101.1, 90.7, 107.7 and 114.9 respectively from the sample split with MeOH.

3.3. *Effect of ACN and MeOH in sample preparation*

Higher percentages of water in the initial eluent result in greater separation of NQ and NTO from the void volume and each other.

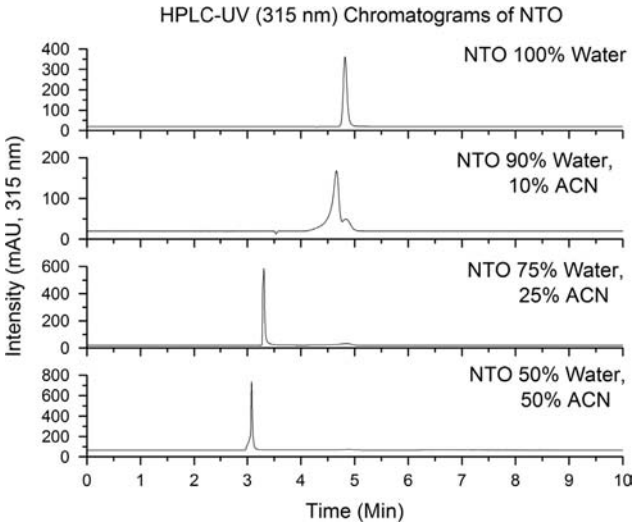

Fig. 5. HPLC-UV (315 nm) Chromatograms of NTO. UV chromatograms (315 nm) of 5 mg/L NTO samples at various ACN concentrations analyzed by HPLC–UV. The NTO chromatographic peak shifts significantly with increasing ACN.

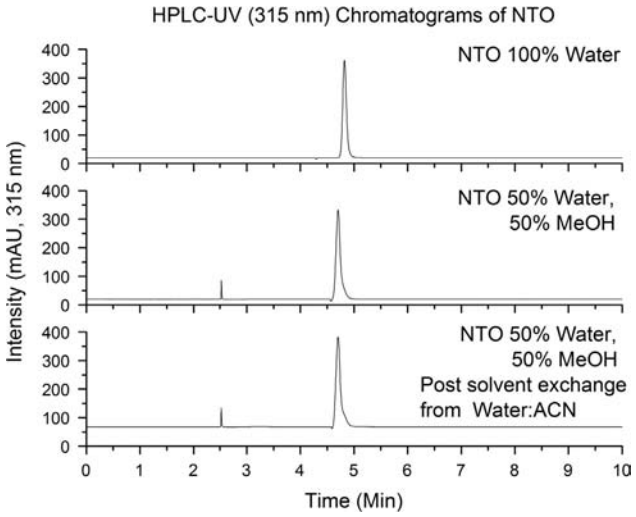

Fig. 6. HPLC–UV (315 nm) Chromatograms of NTO. UV chromatograms (315 nm) of 5 mg/L NTO samples analyzed by HPLC–UV. The top chromatogram is a 5 mg/L NTO sample in 100% DI water. The middle chromatogram is a 5 mg/L NTO in 50:50 MeOH and DI water. The bottom chromatogram is a 1mL 5 mg/L NTO sample that was prepared in 50:50 ACN:DI water, evaporated under nitrogen to 0.5 mL and then brought to a final volume of 1 mL with methanol.

Starting eluent conditions of 86% DI water, 4% ACN, and 10% TFA (0.1% TFA in water) result in the following analyte retention times; NQ, 4.5 min, NTO, 7 min, RDX, 21 min, DNAN, 24.5 min. However, solvents such as methanol and acetonitrile are often used to extract munitions constituents from ground water, soil, sediment and tissue. Solid phase extraction (SPE) of munitions from water, for example, results in munitions constituents dissolved in ACN, which are then diluted with DI water for analysis by the U.S. EPA method 8330. The tolerance of the newly developed method to ACN and or MeOH is then of great importance.

Analysis of the compounds of interest dissolved in 50:50 water:ACN showed no change for DNAN and RDX compared to the dissolved standards in 100% water, however the chromatography of the more hydrophilic NTO, deteriorated significantly. The effects of acetonitrile concentration on the chromatographic peak shape and retention time of NTO are shown in Fig. 5. The peak shape deteriorates rapidly and results in a nearly two minute chromatographic retention time shift. Increasing the solvent concentration of the starting eluent composition did not mitigate these effects for samples containing ACN. However, the addition of 10% methanol to the starting HPLC gradient conditions decreased these shifts and changes to peak. The addition of solvent (MeOH or ACN) to the initial eluent composition increases the elution strength and results in shorter retention times. The ACN shifts the equilibrium distribution of the NTO analyte between mobile and stationary phases such that retention time is reduced and the peak shape is deteriorated. MeOH does not appear to change the equilibrium distribution as significantly; possibly do to methanol's lower elution strength compared to that of ACN. The result is that methanol does not have as strong an effect on the peak shape and virtually no retention time shift for NTO, as shown in the top and middle chromatograms of Fig. 6.

The bottom chromatogram, of Fig. 6, shows the result of evaporating 1 mL of a 5 mg/L sample of NTO, prepared in 50:50 ACN: water, under nitrogen to 0.5 mL and adjusting to a final volume of 1 mL with methanol prior to HPLC–UV–ESI-MS analysis. The solvent exchange resulted in 95% recovery of NTO, and may represent a viable amelioration strategy of the retention time shift for application of this method to organic solvent used to extract IMX constituents from solid matrices (e.g. soils or tissues).

4. Conclusions

An HPLC method is described for the single column analysis of IMX munitions constituents. The developed method utilizes an acidified mobile phase gradient to separate the more hydrophilic compounds from the void volume, while maintaining the separation of the more hydrophobic compounds. The method provides quantitative results with acceptable quality control sample results for all four of the IMX munitions constituents. With no preparation changes, the method also allows for simultaneous detection of the traditional explosives analyzed by the U.S. EPA method 8330.

The method is UV and MS compatible allowing for compound confirmation by either dual column HPLC or HPLC–UV–ESI-MS analysis. The mass spectrometric detector reduces the likelihood of erroneous results owing to analyte ambiguity and unknown interfering compounds in complex matrixes, as well as quantitation and reliable confirmation from a single instrumental analysis. The use of the mass spectrometric detector enables the possible identification of unknown compounds present in the sample that non selective detectors, such as UV absorbance detectors, does not.

Further refinements may improve upon the detection of insensitive munitions in complex environmental media such as soils, natural water, and organism tissues where extraction and preconcentration protocols are needed for all analytes of interest prior to analysis.

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