Analysis of New Generation Explosives in the Presence of U.S. EPA Method 8330 Energetic Compounds by High-Performance Liquid Chromatography

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Abstract

U.S. EPA Method 8330 was evaluated and modified for the analysis of DNAN (2,4-dinitroanisole) and MNA (*n*-methyl-*p*-nitroaniline) by high-performance liquid chromatography in various aqueous media in the presence and absence of the 14 energetic compounds currently assigned to the method. DNAN and MNA are two of the four components in PAX-21, a new generation explosive formulation. An optimized method was developed to separate all 14 energetic compounds from DNAN and MNA using a tertiary mobile phase of water–methanol–acetonitrile (68:28:4) in an isocratic run of 35 min. The limit of detection (LOD, $3S_0$) was calculated to be 10 ppb for both MNA and DNAN. The limit of quantitation (LOQ, $10S_0$) was 40 ppb for both compounds. The dynamic ranges for the two compounds were very wide, a nearly 5 orders of magnitude range from 0.02 to 1,000 parts per million (ppm). The spike recoveries of MNA and DNAN in environmental matrix samples were excellent for DNAN, from 87% to 113%. For MNA, the recoveries were slightly high at the low level (60 ppb), probably due to some contamination in the ditch and pond matrices; but they were satisfactory at higher levels ranging from 85% to 121%.

Introduction

Through the years, Picatinny Arsenal has pioneered the development of new explosive formulations that achieved increased power and reduced sensitivity. From the 1920s to 1940s, high explosive materials such as TNT, RDX (1), and Haleite were used. The 1960s brought new explosives such as HMX that gave greater lethality capability. In this time frame, Arsenal researchers undertook a pioneering effort in insensitive munitions (IM) that lead to the development of Flex-X, which could be transported by automobile. This explosive was significantly more stable than dynamite. In the mid 1980s, Picatinny Arsenal and Thiokol Propulsion developed a new melt pour energetic, PAX-21 (2). This explosive is designed to be low cost and require little or no re-facilitization for production or projectile filling. It contains no TNT and is slightly less toxic than the Composition-B it replaces. It is easily loaded into various munition items, and also exhibits good IM, thermal stress characteristics, and low shock sensitivity.

PAX-21 is an explosive formulation composed of RDX, a highly sensitive and detonable energetic material; 2,4-dinitroanisole (DNAN), an energetic binder; ammonium perchlorate, an oxidizer; and, trace amounts of *n*-methyl-*p*-nitroaniline (MNA), a processing aid or stabilizer (2). The formulation poses safety and environmental concerns (3); for example, groundwater contamination by RDX (4) has been detected at many sites where manufacturing, storage, and testing activities of munitions have been practiced. Perchlorate is a new additive to conventional explosives, but has received wide application in solid rocket motors as well as commercial fireworks. Similar to RDX, perchlorate has been found where rocket motors have been manufactured, tested, or disassembled (5).

Research is planned on examining degradation of DNAN and MNA in waste streams emanating from production facilities and in wastes from other military operations. Reliable and robust analytical methods for these constituents are essential to the conduct of such work. U.S. EPA Method 8330 (6) was evaluated and modified for the reliable measurement of DNAN and MNA by high-performance liquid chromatography (HPLC) in the presence and absence of the 14 energetic compounds assigned to the method in various aqueous media. Areas of method optimization were explored and include limits of quantitation, precision, accuracy, method robustness, extraction efficiency, and overall reliability. This reports an analytical method to analyze DNAN, MNA, RDX, and ammonium perchlorate, separated from other energetic compounds in the new explosive formulation (PAX-21) and the resulting wastewater. This is not intended to be a fully validated EPA method.

Experimental

Chemicals and reagents

Analytical standards for DNAN and MNA were purchased from Sigma-Aldrich (St. Louis, MO) and were greater than 99% pure. The M-8330 standards mix was obtained from AccuStandard, Inc. (New Haven, CT). HPLC-grade acetonitrile and methanol

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were obtained from Fisher Scientific (Pittsburgh, PA). HPLC-grade water was obtained from a Millipore (Bedford, MA) Ultrapure Water System (Milli-Q) in the laboratory. Waters Porapak RDX SPE cartridges (6 mL, 500 mg) were purchased from Waters (Milford, MA).

Solid-phase extraction

Filtered pond water and filtered stream water samples were spiked with MNA and DNAN in concentrations of 0.6 ppb, 1.0 ppb and 2.0 ppb. Then 100 mL samples of each concentration were extracted in duplicate using Waters Sep-Pak Porapak RDX Cartridges (6 cc, 500 mg) (7), which were pre-conditioned by passing 15 mL of acetonitrile followed by 10 mL of methanol through at gravity flow rate, then rinsing with 30 mL of DI water at a flow rate of approximately 10 mL/min. The samples were passed through the cartridges at flow rates of approximately 4.5 mL/min using a Supelco Visiprep 12-port solid-phase extraction manifold (Bellefonte, PA) attached to house vacuum. After all the samples were extracted, the cartridges were rinsed with 15 mL of water, and air was drawn through for 2 min to dry the cartridges. The extracted analytes were then eluted off the cartridges using 5-mL portions of acetonitrile by gravity flow into glass vials. Silicone tubing attached to a cylinder of compressed nitrogen (UHP-grade) and fitted with glass pipets were used to concentrate the collected eluants to about 0.5 mL by evaporating off the solvents. They were then transferred to 1-mL volumetric flasks by glass pipets and brought up to volume using water before HPLC analysis.

Chromatography

HPLC analysis was performed on a Waters Alliance 2695 Separation Module with autosampler and a 996 photodiode array detector using a Supelco LC-8 analytical column (150 × 4.6 mm, 3 µm) with a guard column (Bellefonte, PA). The optimized conditions were: mobile phase, water–methanol–acetonitrile (68:28:4) to separate DNAN and MNA from the 14 analytes in M-8330 mix in an isocratic run of 35 min; injection volume, 30 µL; flow rate, 1 mL/min. Photodiode data were collected from 210–300 nm. The chromatograms were extracted at 220 nm for quantification of the compounds. Identification of the extracted DNAN and MNA was carried out by comparing retention times and spectra from 210–300 nm to those of authentic standards before extraction.

Results and Discussion

Optimization of DNAN and MNA separation

Initially, mobile phase using water–methanol (60:40) was employed for the explosive analysis. Once the suitability of the system was shown by the analysis of the 8330 standard mix (Table I), individual DNAN and MNA solutions were injected to observe retention times and absorbance spectra for characterization of the analytes. Then a mixed standard of the 8330 mix, DNAN and MNA, all at 1 ppm (1,000 ppb) concentration was used for the optimization of the separation of all the analytes. By varying organic solvents and mobile phase composition, the method was optimized to 68:28:4 (water–methanol–acetonitrile) to separate DNAN and MNA from the 14 analytes in an isocratic run of 35 min (Figure 1). The addition of acetonitrile solvent increased the resolution of MNA from DNAN in the presence of the other energetics. All the analytes were well separated except a pair of coeluted peaks (2-amino-4,6-dinitrotoluene and 2,6-dinitrotoluene). Coelution of the two peaks was not important in this application since the PAX-21 formulation did not contain TNT or DNT.

Detection limits, dynamic range, and precision

The detection limits of the 16 analytes including MNA and

Table I. 14 Energetic Compounds in Method 8330 Mix

Compound Name	Abbreviation
Octahydro-1,3,5,7-tetranitro-1,3,5-7-tetrazocine	HMX
Hexahydro-1,3,5-trinitro-1,3,5-triazine	RDX
1,3,5-Trinitrobenzene	TNB
1,3-Dinitrobenzene	1,3-DNB
Methyl-2,4,6-trinitrophenylnitramine	Tetryl
Nitrobenzene	NB
2,4,6-Trinitrotoluene	TNT
4-Amino-2,6-dinitrotoluene	4-A-2,6-DNT
2-Amino-4,6-dinitrotoluene	2-A-4,6-DNT
2,4-Dinitrotoluene	2,4-DNT
2,6-Dinitrotoluene	2,6-DNT
2-Nitrotoluene	2-NT
3-Nitrotoluene	3-NT
4-Nitrotoluene	4-NT

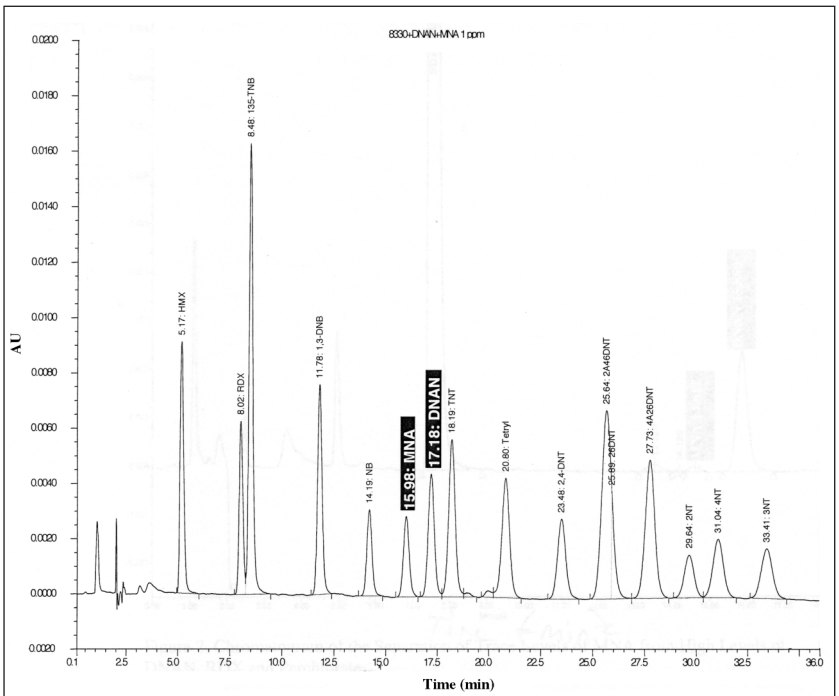

Figure 1. Chromatogram of the separation of the 16 energetic compounds by HPLC with UV detection.

DNAN were investigated. The studies were conducted in a deionized water matrix. Using the optimized method (water–methanol–acetonitrile, 68:28:4, isocratic), the mixture was analyzed at concentrations of 5, 10, 20, 50, 100, 200, 500, and 1000 ppb at injection volumes of 15, 30, 50, and 100 µL. The best peak shape and sensitivity was found at the 30-µL injection volume. The detection limits for the 14 analytes in the Method 8330 were found to be: 10 ppb for TNB, HMX, RDX, 1,3-DNB, TNT, 26-DNT, 2A46-DNT, 4A26-DNT, and 3-NT; 20 ppb for NB, Tetryl, 2,4-DNT, and 4-NT and 50 ppb for 2-NT. These were comparable to the detection limits measured by the unmodified Method 8330.

The robustness of the method was investigated by measuring the precision of the peak areas and retention times of MNA and DNAN. Four concentrations (20, 50, 100, and 200 ppb) of the 2 analytes were injected ten times each and the peak areas were integrated. The relative standard deviation (RSD) of each peak area and retention time was calculated (Table II). The data showed the method was robust with RSD less than 1% for retention times for both analytes. The RSD for peak area was less than 15% near the limit of quantitation (LOQ, around 50 ppb) and less than 6% at higher levels. From the experimental data of the robustness work, the standard deviations of the 20, 50, and 100 ppb were plotted against the concentrations to find S_0 (intercept of the curve). Limit of detection (LOD = $3S_0$) was calculated to be 10 ppb for both MNA and DNAN (8). Limit of quantitation (LOQ = $10S_0$) was 40 ppb for both compounds. For comparison, we also used a point method at 50 ppb, with the standard deviation from 10 injections taken as S_0. LOD was found to be 10 ppb also for both analytes (8).

The dynamic ranges of the 16 energetic analytes in the method were defined as follows. A mixture of MNA and DNAN in concentrations ranging from 0.01 to 1000 ppm (0.012, 0.025, 0.05, 0.1, 0.2, 0.4, 0.8, 1.6, 3.1, 6.3, 12.5, 25, 50, 100, 200, 400, 600, 800, and 1000 ppm) was prepared and analyzed by the method. With an injection volume of 30 µL, the two compounds showed a very wide dynamic range of 5 orders of magnitude from 0.02 to 1000 ppm. The linearity coefficients (R^2) of the calibration curves for MNA and DNAN for the range were excellent at 0.9996 and 0.9990, respectively.

Then concentrations of 0.02, 0.05, 0.1, 0.5, 1.0, 5.0, 10.0, 20.0, 50.0, 100, 200, 400, 600, 800, and 1000 ppm of the M-8330 mix were prepared and tested in similar fashion. All analytes have excellent linearity up to 100 ppm ($R^2 > 0.998$). The following compounds: 1,3-DNB, NB, TNT, Tetryl, 4A26-DNT, and 4-NT have linearity up to 1000 ppm ($R^2 > 0.998$).

Table II. Precision Data for Area and Retention Times (t_R) at Four Levels

Conc (ppm)	MNA		DNAN	
	Area RSD %	t_R RSD %	Area RSD %	t_R RSD %
0.02	13	0.2	15	0.2
0.05	12	0.1	8.0	0.1
0.1	4.3	0.1	2.9	0.1
0.2	3.7	0.1	5.8	0.1

Environmental matrix studies

For most applications of the method, analytes will likely be isolated from the matrix of interest via extraction. Usually this procedure also concentrates the compounds from the solution, thereby potentially increasing the sensitivity of the method. Ideally, matrix studies should be conducted in matrices relevant to potential applications of the method. Currently, our understanding is that PAX 21 is not in full-scale production in the US, so no "authentic" production wastewaters are available.

Initial experiments in real-world aqueous matrices will focus on filtered pond water and filtered stream water that is impacted by domestic sewage disposal. Samples were collected from residential lake water from SW Champaign and the Saline Ditch at Perkins Road below the outfall of the Urbana Wastewater Treatment Plant. They were used for the extraction efficiency studies for MNA and DNAN in real-world aqueous matrices. We spiked each matrix sample with MNA and DNAN in concentrations of 0.6, 1.0, and 2.0 ppb. Then 100 mL samples of each concentration were extracted in duplicate using Waters Sep-Pak Porapak RDX Cartridges and eluted with 5 mL of acetonitrile which was concentrated to 1 mL in acetonitrile–water. This gave a 100-fold concentration of the original sample and the final concentrations in the extracts were 60, 100, and 200 ppb (low, medium, and high levels). The SPE extracts including a Saline Ditch Blank and a Pond Blank were analyzed for both MNA and DNAN. For the Saline Ditch Blank, there was a peak eluted at the same retention time as MNA with an area similar to a 60 ppb standard. However, the spectrum index of the peak did not match the standard, therefore all the Ditch samples were corrected for this blank area, prior to calculating analyte recoveries. Table III shows the spike recoveries of the three levels of MNA and DNAN in the Pond and Saline Ditch samples. They were excellent for DNAN ranging from 87% to 113%. For MNA, the recoveries were slightly high at the low level (60 ppb) for the pond sample, probably due to the contaminants found in the ditch blank. The recoveries were satisfactory at higher levels, ranging from 85% to 121%.

Real sample scenario

The PAX-21 formulation is composed of RDX, DNAN, ammonium perchlorate, and trace amounts of MNA. Depending on the application of the developed method, the analyst might be faced with analyzing trace levels of MNA in the presence of much higher concentrations of RDX, DNAN, and perchlorate. Because we did not have access to the formulation, or to the exact proportions of each component in the formulation, we contrived a

Table III. Spike Recoveries of MNA and DNAN in Real-World Matices

Sample	MNA recovery (%)	DNAN recovery (%)
Pond 0.06 ppm	146	100
Pond 0.1 ppm	121	99
Pond 0.2 ppm	100	95
Ditch 0.06 ppm	146	100
Ditch 0.1 ppm	106	97
Ditch 0.2 ppm	85	90

mixture containing 40 ppb of MNA, 10 ppm of RDX, 500 ppb of DNAN, and 500 ppb of ammonium perchlorate for testing the method. Calibration standards were prepared with similar proportion of the 4 analytes. No problems were encountered in the analysis of trace levels of MNA in the presence of higher levels of RDX, DNAN, and ammonium perchlorate. The contrived sample was run four times giving 93%, 94% and 94% recoveries for RDX, MNA, and DNAN, respectively. Since the method provides complete baseline separation of MNA from RDX and DNAN, we anticipated this positive result. Perchlorate ion is anionic, elutes as a negative peak in the void, and does not have a UV chromophore, hence will not interfere with the other peaks. In the actual PAX-21 formulation, ammonium perchlorate concentration is much higher than 500 ppb, probably in high ppm level, but that will not pose any problem to the method because it is not detected by UV. Figure 2 shows the chromatogram of the separation of the trace level of MNA at 40 ppb from 10 ppm of RDX and 500 ppb of DNAN and 500 ppb ammonium perchlorate. Analysis of waste or environmental samples for MNA will depend on the actual concentrations of the four energetic compounds in the PAX-21 explosive formulation but the levels of detection and quantitation should compare well to levels of concern. If the RDX level is high and falls outside of the calibration curve, then the sample would need to be analyzed at different dilutions to accurately measure the quantities of all these formulation components.

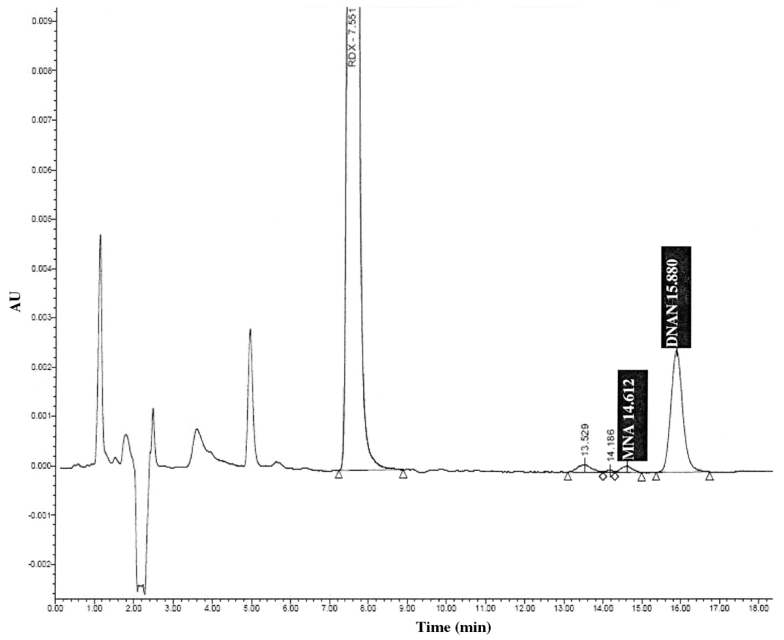

Figure 2. Chromatogram of the separation of trace levels of MNA from high levels of DNAN, RDX, and perchlorate.

Conclusion

An analytical method was developed for the new generation explosives, MNA and DNAN, components in PAX-21 formulation. The method was a modification of the U.S. EPA Method 8330 for analyzing 14 energetic compounds. The developed method was able to separate all 14 energetic compounds from DNAN and MNA using a tertiary mobile phase of water/methanol/acetonitrile (68:28:4), flow rate at 1 mL/min in an isocratic run of 35 minutes on a Supelcosil LC-8 (150 × 4.6 mm, 3 µm particle size) column with UV detection at 220 nm wavelength. The addition of acetonitrile solvent increased the resolution of MNA from DNAN in the presence of the 14 energetic compounds. There was a pair of coeluted peaks (2-A-4,6-DNT and 2,6-DNT). The method was robust with retention time RSDs less than 1% and peak area RSDs less than 15% near the LOQ at 50 ppb and less than 6% at higher levels. Using an injection volume of 30 µL, the LOD ($3S_0$) was calculated to be 10 ppb for both MNA and DNAN. LOQ ($10S_0$) was 40 ppb for both compounds. The dynamic ranges of the two compounds were very wide, a nearly 5 orders of magnitude range from 0.02 to 1000 ppm. The spike recoveries of MNA and DNAN in environmental matrix samples were excellent for DNAN from 87% to 113%. For MNA, the recoveries were slightly high in the low level (60 ppb), probably due to some contaminants in the matrix. They were satisfactory at higher levels, ranging from 84% to 122%. The method also encountered no problem in the analysis of trace levels of MNA in the presence of higher levels of RDX, DNAN and ammonium perchlorate as in the PAX-21 formulation.

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