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ANALYSIS OF CL-20 AND TNAZ IN THE PRESENCE OF OTHER NITROAROMATIC AND NITRAMINE EXPLOSIVES USING HPLC WITH PHOTODIODE ARRAY (PDA) DETECTION

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ABSTRACT

Several new explosives (CL-20 and TNAZ) have recently attracted attention as possible replacements for various explosive compounds. If these compounds become heavily used they may eventually come under regulation. A method for the analysis of CL-20 and TNAZ in the presence of 14 nitroaromatic and nitramine explosives and their degradation products currently included in EPA SW-846, Method 8330 has been developed using high performance liquid chromatography (HPLC). Photodiode array (PDA) detection was employed for peak identification and confirmation. Analysis times of less than 30 minutes was achieved using an isocratic HPLC mobile phase of water and isopropanol.

INTRODUCTION

Several new nitramine compounds have recently attracted attention as possible replacements for, or inclusion in, military and space propellants and explosives.(1) CL-20, hexanitrohexaazaisowurtzitane, is one of these

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compounds. Potential applications for CL-20 include boost propulsion for military or space vehicles and as minimum signature propellants. TNAZ, 1,3,3-trinitroazetidine, is another compound under evaluation as well. It is more powerful than HMX, tetranitrotetraazacyclooctane, and RDX, trinitrohexahydrotriazine, both of which are currently used.(1) The structures of both CL-20 and TNAZ are shown in figure 1. Currently most nitramine and nitroaromatic explosive ingredients and some degradation products are included in EPA SW-846, Method 8330. Figure 2 shows the structures and names for all compounds currently included in Method 8330. If CL-20 and/or TNAZ become used, a method of analysis in both propellant formulations and groundwater would be needed.

EXPERIMENTAL

Materials

Analytical standards were obtained from AccuStandard (New Haven, CT) with the exception of CL-20, which was provided by Dr. Jimmie Oxley of the New Mexico Institute of Mining and Technology and TNAZ which was provided by Dr. Tom Archibald of Aerojet. All solvents used were of HPLC grade or better. High purity water was obtained from a Milli-Q™ system (Millipore, Bedford, MA).

Procedures

Explosive standard mixtures, in acetonitrile, were diluted into mixtures containing 40% acetonitrile and 60 % water. The chromatographic system consisted of a Waters™ 600E solvent delivery system, 717+ autosampler,

and a Waters™ 996 photodiode array (PDA) detector collecting from 200-350 nm at a spectral resolution of 1.2 nm (Waters Chromatography, Milford, MA). The mobile phase for HPLC analysis was a mix of 82% water and 18% isopropanol at a flow rate of 1.0 mL/min. The column used was a Nova-Pak™ C_8 column (3.9 mm X 150 mm) obtained from Waters.

RESULTS

An HPLC method for the analysis of both CL-20 and TNAZ in the presence of all 14 currently regulated compounds has been developed. Figure 3 shows a chromatogram from the photodiode array (PDA) detector at 254 nm of the 16 compounds separated. Total analysis time was less than 30 minutes. Since most nitramines and nitroaromatic explosives have differing UV spectra, photodiode array (PDA) detection was used because it has the capability to monitor over the required range of wavelengths. Increased sensitivity and quantitation can be achieved by monitoring at several different wavelengths. A maxplot can be generated as well which provides a chromatogram of the maximum absorbance, extracted from the wavelengths collected, at each point throughout the run. Figure 4 demonstrates this by showing the same sample collected on the PDA and extracted at 254 nm (figure 4a) and a maxplot (figure 4b). This capability allows for the selection of several different wavelengths for monitoring, thus allowing for the maximum sensitivity for the compounds. Further, UV spectra for each compound can be obtained enabling the use of library searching of the spectra for peak identification and peak homogeneity.

Figure 5 is a spectrum index plot of the first 7 peaks from figure 3 with

the apex spectra of each peak displayed at the top. Using these spectra, peak homogeneity and library searching can be done by using various algorithms in the software.(2,3,4) The spectra obtained can be used to evaluate whether a peak is homogeneous or not by comparing the spectrum from the peak apex to all spectra across the peak. Any differences between the spectra is reported as the purity angle (a purity angle of 0 degrees is no difference and 90 degrees is maximum difference). This value is compared to a threshold (or noise) angle calculated from the system. The threshold (noise) angle is measurement based on the baseline spectrum obtained from the system during the run. This angle is considered a confidence level for the matching routine. If the purity angle is less than the threshold (noise) angle than you have a high degree of confidence that the peak is homogeneous. Figure 6 is a purity and library match report for CL-20 which demonstrates this. The purity angle calculated is 0.23 degrees while the threshold (noise) angle is 1.05 degrees, therefore the peak is considered spectrally pure.

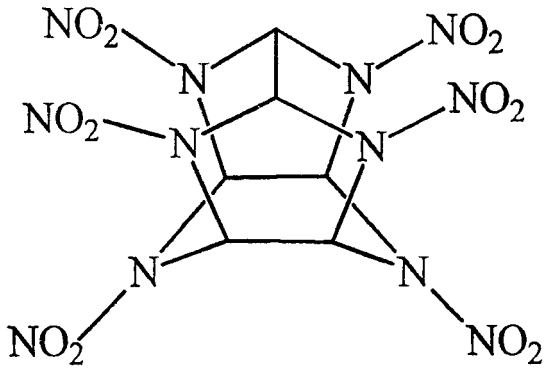
Further, the spectra obtained can be compared to a user created library and a match angle calculated as well. Just as with peak purity, the lower the match angle the higher the degree of match (a match angle of 0 degrees is considered a perfect match). Figure 6 demonstrates this by reporting the top 3 library matches in decreasing order of match for CL-20. The top match, #1, is considered the best match of the spectra in the libraries searched. In this case the best match is CL-20 and the match angle (0.495 degrees) is less than the threshold (1.043 degrees) which is considered a good match.

CONCLUSIONS

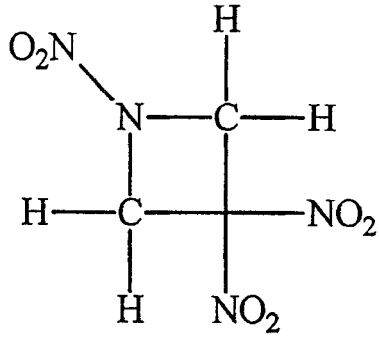
An HPLC method employing photodiode array (PDA) detection for the analysis of CL-20 and TNAZ in the presence of 14 other nitramine and nitroaromatic compounds has been developed. The photodiode array (PDA) detector provides the user with library searchable spectra as well as peak purity information for each compound. Using this HPLC method and PDA detection allows for both maximum sensitivity as well as compound identification. Run time of less than 30 minutes for all 16 compounds were accomplished.

ACKNOWLEDGEMENTS

The author would like to thank Dr. Jimmie Oxley of the New Mexico Institute of Mining and Technology and Dr. Tom Archibald of Aerojet for providing samples of CL-20 and TNAZ respectively.



CL-20



TNAZ

Figure 1. Structure of CL-20, hexanitrohexaazaisowurtzitane, and TNAZ, 1,3,3-trinitroazetidine.

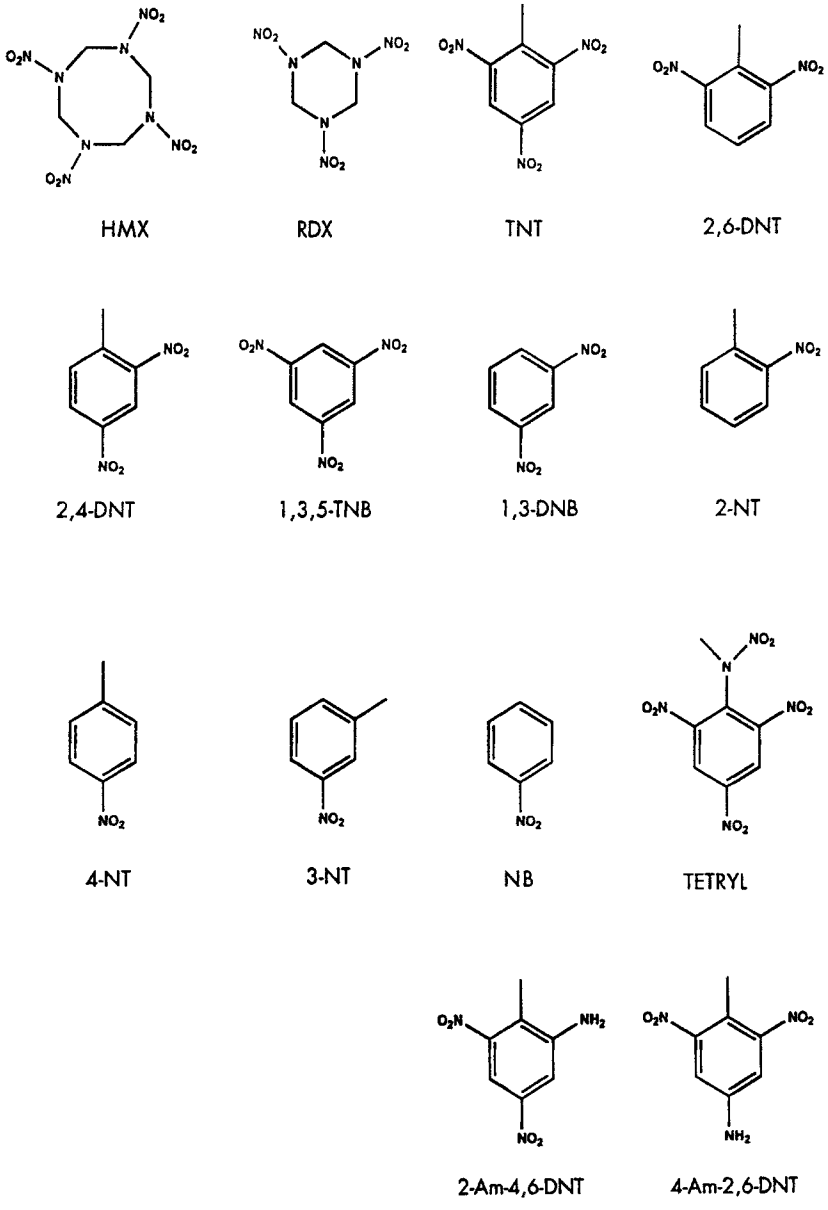


Figure 2. Structure of nitramine and nitroaromatic exlosives included in Method 8330.

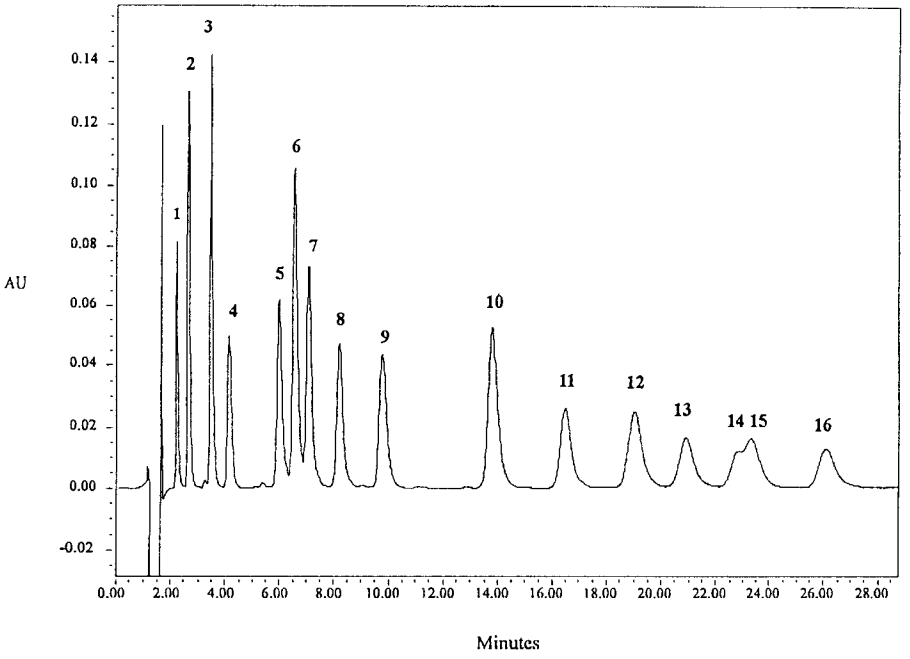


Figure 3. Chromatogram of explosive mix at 254 nm. Amounts are 3.0 mg/L for all compunds except CL-20 and TNAZ which are approximately 5.0 mg/L. Peaks: **1**: HMX, **2:** TNAZ, **3**: 1,3,5-TNB, **4**: RDX, **5:** Cl-20, **6**: 1,3-DNB, **7**: TNT, **8**: Tetryl, **9**: NB, **10**: 2,4-DNT, **11**: 2,6-DNT, **12**: 2-Am-4,6-DNT, **13**: 4-Am-2,6-DNT, **14**: 4-NT, **15**: 2-NT, **16**: 3-NT.

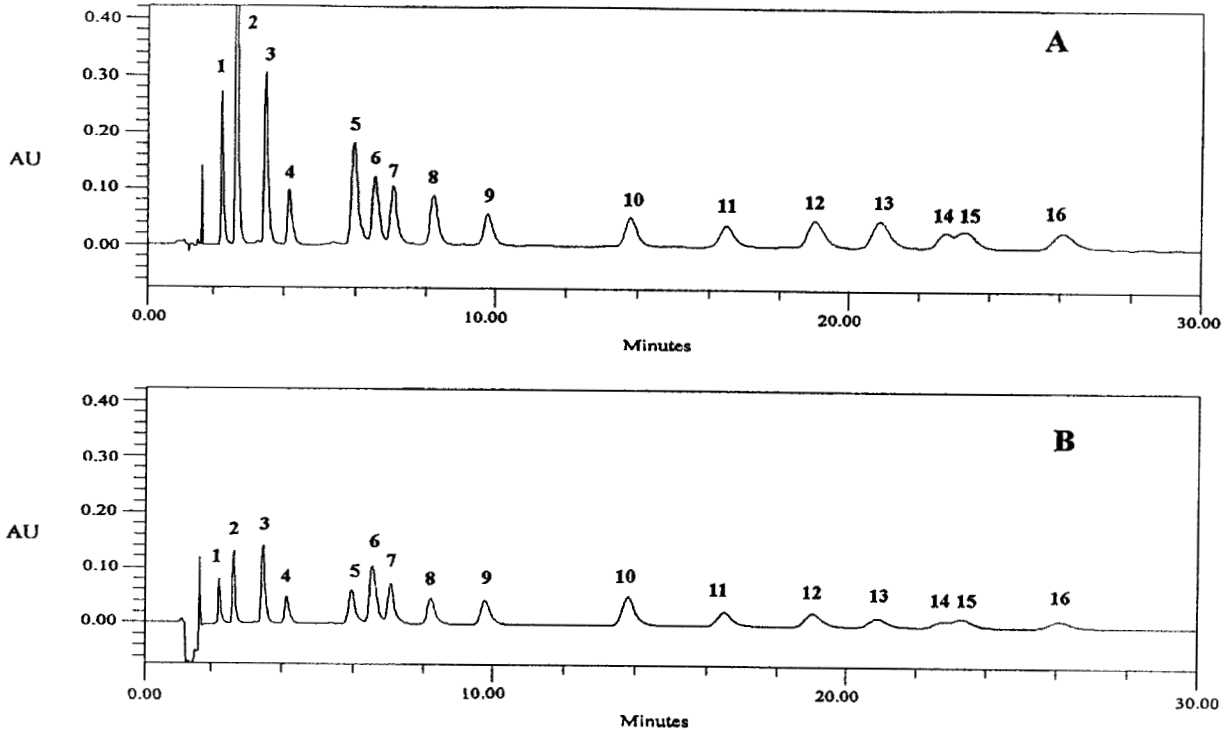


Figure 4. Chromatograms of explosive mix at, 254 nm (figure 4a), and a maxplot (figure 4b) from 210-350 nm. Peaks: **1**: HMX, **2:** TNAZ, **3**: 1,3,5-TNB, **4**: RDX, **5:** Cl-20, **6**: 1,3-DNB, 7: TNT, **8**: Tetryl, **9**: NB, **10**: 2,4-DNT, **11**: 2,6-DNT, **12**: 2-Am-4,6-DNT, **13**: 4-Am-2,6-DNT, **14**: 4-NT, **15**: 2-NT, **16**: 3-NT.

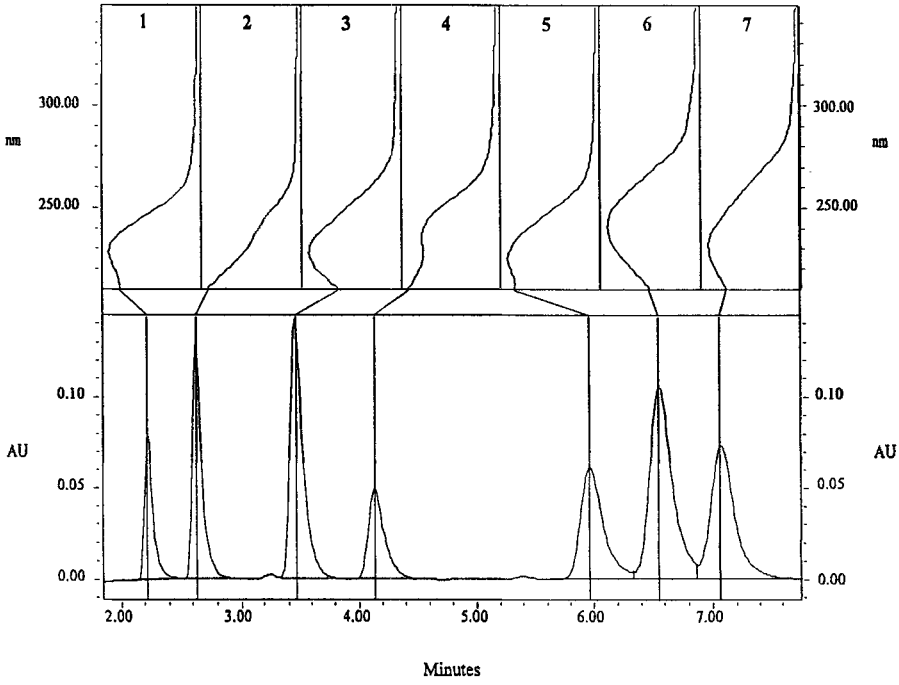


Figure 5. Spectrum index plot of the first 7 peaks from figure 3. UV spectra from the peak apex is displayed above the chromatogram Peaks: **1**: HMX, **2**: TNAZ, **3**: 1,3,5-TNB, **4**: RDX, **5**: Cl-20, **6**: 1,3-DNB, **7**: TNT

Purity Result for Peak 5: CL-20

Retention Time: 5.97 Purity Angle: 0.23 Threshold Angle: 1.05

Matching Spectra List

#	Match Angle	Match Threshold	Spectrum Name	Library Name	Ideal	Wvln RMS
1	0.495	1.043	CL-20	Explosives	Yes	0.0000
2	3.781	1.101	HMX	Explosives	Yes	0.0000
3	7.375	1.041	TNAZ	Explosives	Yes	0.0000

Figure 6. Peak purity and library match report of compound CL-20 (peak #5) from figure 3. Peak purity is calculated through spectral comparison of the spectra from the peak apex and all spectra across the integrated peak. Any spectral differences are calculated as a purity angle. If the purity angle is less than the threshold (noise) angle than the peak is considered pure. Library matching is done as well by comparing the spectra at the peak apex and the spectra in various libraries. If the match angle is less than the threshold than their is a high probability of a match. (a match angle of 0 is perfect).

REFERENCES

1. Borman, S., C&EN, 18, (January 17, 1994)

2. M.V. Gorenstein, J.B. Li, and D. Chapman, Presented at Pittsburgh Conference, (1993).

3. P.M. Young and M.V. Gorenstein, Genetic Engineering News, vol. 13, 19, (1994).

4. M.V. Gorenstein, J.B. Li, J. Van Antwerp, and D. Chapman, LC-GC, Vol. 12, 768, (1994)