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ANALYSIS OF STABILIZER DEGRADATION PRODUCTS IN PROPELLANTS USING HPLC AND PHOTODIODE ARRAY (PDA) DETECTION

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ABSTRACT

Analysis of stabilizer and stabilizer degradation products in nitrocellulose based propellants was done using high-performance liquid chromatography (HPLC) with photodiode array (PDA) detection. Analysis of these compounds was done in less than 12 minutes using an isocratic mobile phase. Using PDA detection provided the capability of monitoring at several different wavelengths as well as providing UV spectra which could be used to asses peak purity and match the spectra against known library spectra.

INTRODUCTION

To prevent autocatalytic decomposition of nitrocellulose based propellants diphenylamine (DPA) is typically added to act as a stabilizer. The amount of DPA added varies depending on the type and lot of propellant, but is typically less than 1%. This amine reacts with nitrogen oxides forming several different degradation products.[1,2] Some of these products also act as stabilizers while others contribute to stabilizer depletion.[1-3] Figure 1 shows the structure and names of various stabilizer and degradation products analyzed in this paper. N-nitrosodiphenylamine (NNO-DPA) is typically the first degradation product seen with others forming as an excessive amount of the first forms.

Monitoring of munitions for these stabilizers is important in determining shelf-life, and stability. High-performance liquid chromatography (HPLC)

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employing electrochemical[4,5] or UV detection[2,6,7] has been used in the past for monitoring of these stabilizer degradation products. The purpose of this paper is to demonstrate the usefulness of photodiode array (PDA) detection for the identification and spectral confirmation of the stabilizer and degradation products. Analysis of three different lots of IMR 8350 small arms propellant were investigated using HPLC and PDA detection.

PDA detection offers the user the ability to collect several wavelengths at once during an analysis as well as obtain spectral information on the compound which can be used for comparison to a library of compounds. The ability to collect data at several wavelengths simultaneously is beneficial since many of the compounds of interest have varying UV spectra as shown in figure 2. Also important is the spectral quality of the UV spectra obtained. The higher the spectral resolution the less spectral information obtained. For this analysis a spectral resolution of 1.2 nm was used which provides the highest resolution possible, thus allowing for high quality UV spectra to be obtained for library searching.

EXPERIMENTAL

Materials

Analytical standards of the stabilizers and IMR propellant samples were provided by Sandia National Labs as a gift. All solvents used were of HPLC grade or better. High purity water was obtained from a Milli-Q™ system (Millipore, Bedford, MA).

Procedures and Equipment

The IMR samples were cut into small cubes approximately 1 cm square and a 0.03 g sample weighed out and extracted in 10 mL of acetonitrile overnight. Samples were then filtered and injected onto the HPLC system for analysis. The chromatographic system consisted of a Waters™ 600E solvent delivery system with column heater, 717+ autosampler, and a Waters™ 996 photodiode array (PDA) detector collecting from 200-500 nm at a spectral resolution of 1.2 nm (Waters Corporation, Milford, MA). The mobile phase for HPLC analysis was a mix of 52% water and 48% acetonitrile at a flow rate of 1.5 mL/min. The column used was a Nova-Pak™ C_{18} column (4.6 mm X 250 mm) at a temperature of 50 degrees celcius..

RESULTS

Analysis of a standard containing all eight compounds of interest is shown in figure 3. As can be seen a total analysis time of less than 12 minutes is possible. A maxplot can be generated as well which provides a chromatogram of the maximum absorbance, extracted from all of the wavelengths collected, at each point throughout the run. Figure 3 demonstrates this by showing the same sample collected on the PDA and extracted at 254 nm (figure 3a), 360nm (figure 3b), 415nm (figure 3c), and a maxplot (figure 3d) all scaled at the same absorbance range. This capability allows for the selection of several different wavelengths for monitoring, therefore allowing for the maximum sensitivity for identification of the compounds as well as providing a quick means of seeing what peaks are present in a samples. 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 4 is a spectrum index plot of the standard shown in 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.[8-10] 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 5 is a purity and library match report for 4-NDPA which demonstrates this. The purity angle calculated is 1.22 degrees while the threshold (noise) angle is 2.90 degrees, therefore the peak is considered spectrally pure.

Analysis of an several aged IMR samples was done using this method. Using standards, a UV spectral library of stabilizers was created. Figure 6 shows a chromatogram of a sample extracted at 254nm. In addition to peak purity, 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 7 demonstrates this by reporting the top library matches in decreasing order of match for NNO-DPA as well as it's purity. The top match, #1, is considered the best match of the spectra in the libraries searched. In this case the best match is NNO-DPA and the match angle (0.37 degrees) is less than the threshold (1.24 degrees) which is considered a good match. Further, the peak was found to be spectrally pure. Even for small, partially separated peaks the spectral library searching can be of benefit. Using library searching the small peak at 6.70 minutes before NNO-DPA was matched to 2,4'-NDPA with a match angle of 4.37 degrees as compared to a threshold of 5.13 degrees. The point of maximum spectral impurity (in minutes) is also listed in the report.

Analysis of the other samples was done using this method with various degradation products found. Table I summarizes the compounds found in all three samples analyzed. Library searching was used to aid in peak identification. The three samples analyzed were of different lots and ages. As can be seen there was a wide variety of minor degradation products found in the samples.

CONCLUSIONS

An HPLC method employing photodiode array (PDA) detection for the analysis of stabilizer degradation products 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 12 minutes for all 8 compounds were accomplished.

ACKNOWLEDGEMENTS

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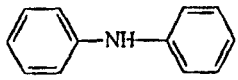
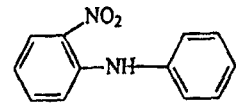
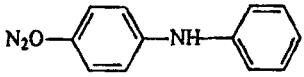


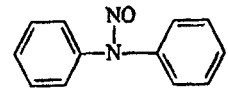
diphenylamine (DPA)



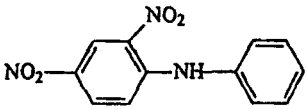
2-nitrodiphenylamine (2-NDPA)



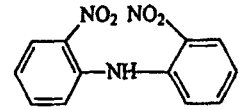
4-nitrodiphenylamine (4-NDPA)



N-nitrosodiphenylamine (NNO-DPA)



2,4-dinitrodiphenylamine (2,4-DNDPA)



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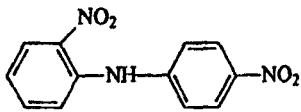
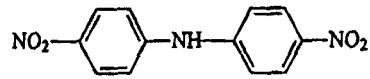


2,4'-dinitrodiphenylamine (2,4'-DNDPA)



4,4'-dinitrodiphenylamine (4,4'-DNDPA)

Figure 1. Structure and names of stabilizer and degradation products analyzed.

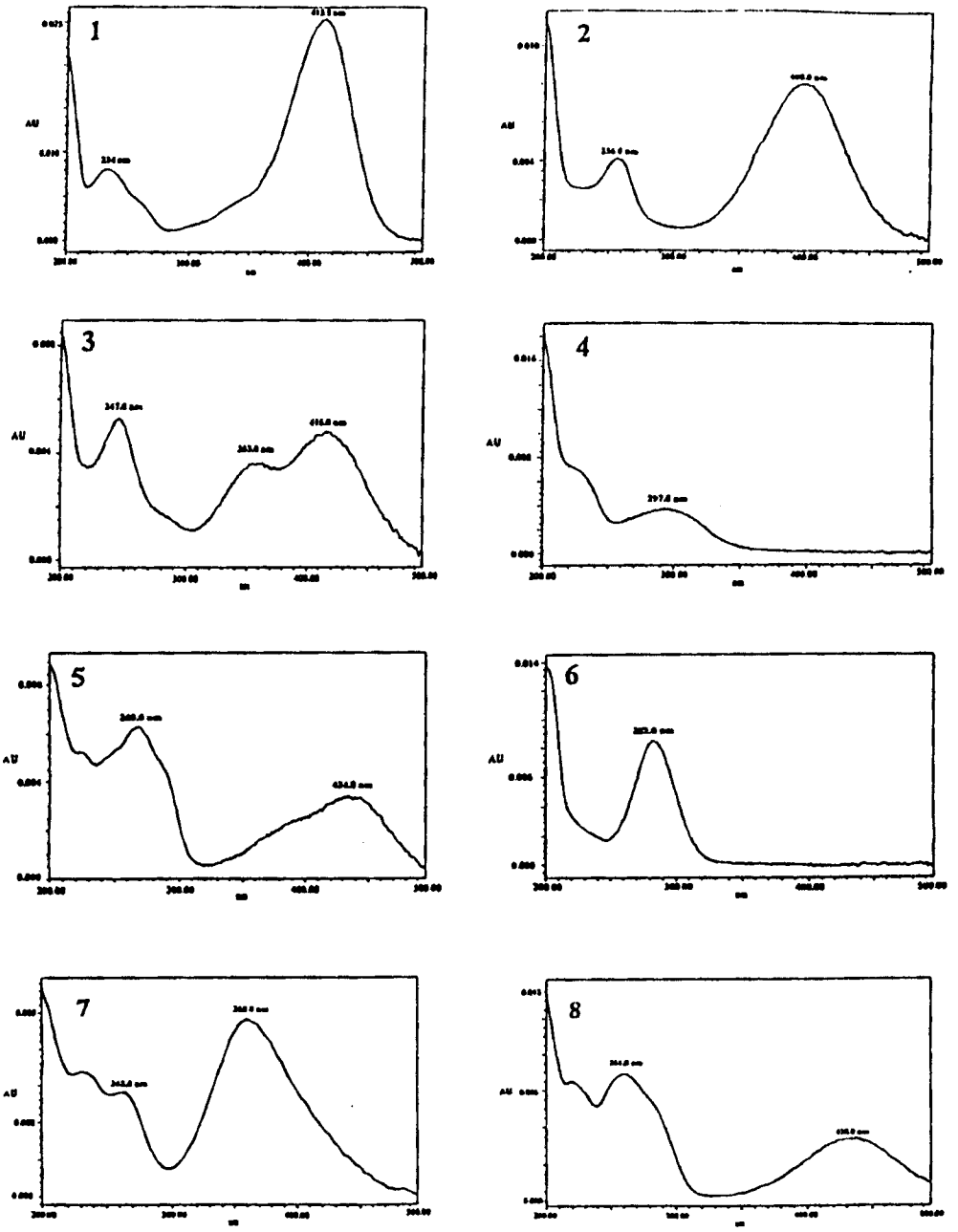


Figure 2. UV spectra of stabilizer and degradation products studied. Spectra: 1: 4,4'-DNDPA, 2: 4-NDPA, 3: 2,4'-DNDPA, 4: NNO-DPA, 5: 2,2'-DNDPA, 6: DPA, 7: 2,4-DNDPA, 8: 2-NDPA.

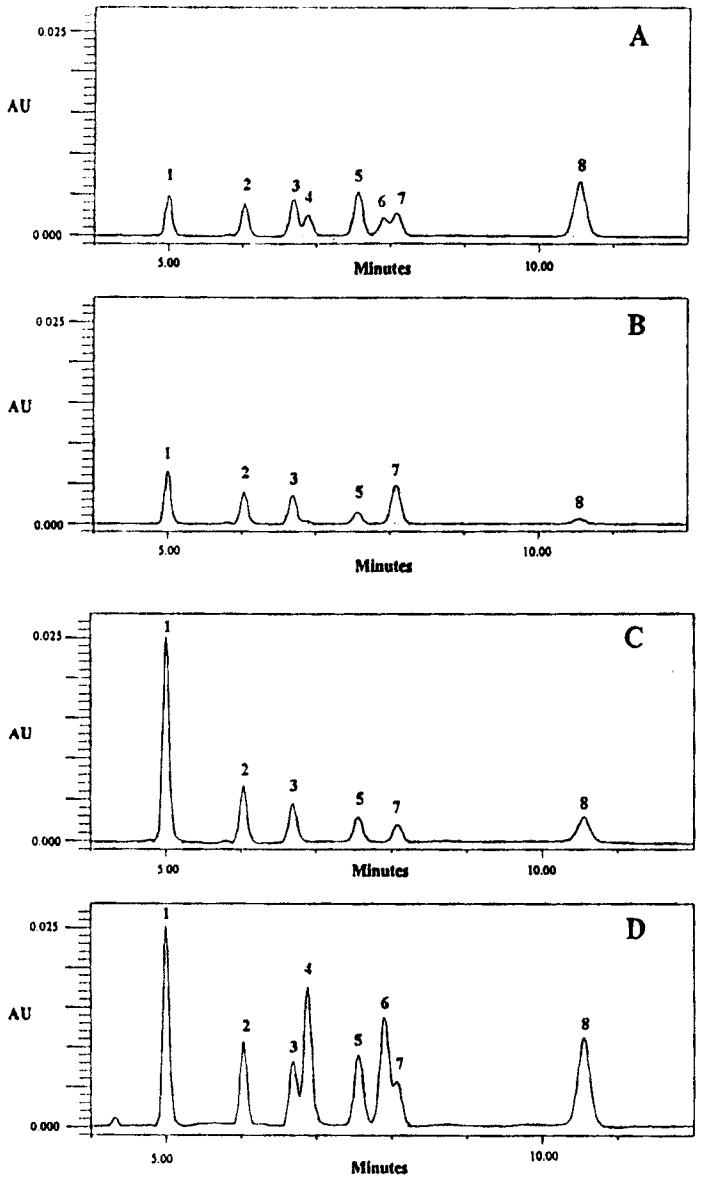


Figure 3. Chromatogram of stabilizer mix analyzed using the PDA detector and chromatograms extracted at 254 nm (figure 3a), 360nm (figure 3b), 415nm (figure 3c), and a maxplot (figure 3d) all scaled at the same absorbance range. Amounts are in parenthesis. Conditions as stated in experimental section of text. Peaks: 1: 4,4'-DNDPA (1.6 mg/mL), 2: 4-NDPA (1.1 mg/L), 3: 2,4'-DNDPA (1.0 mg/L), 4: NNO-DPA (2.0 mg/L), 5: 2,2'-DNDPA (1.3 mg/L), 6: DPA (1.4 mg/L), 7: 2,4-DNDPA (1.2 mg/L), 8: 2-NDPA (2.2 mg/L)

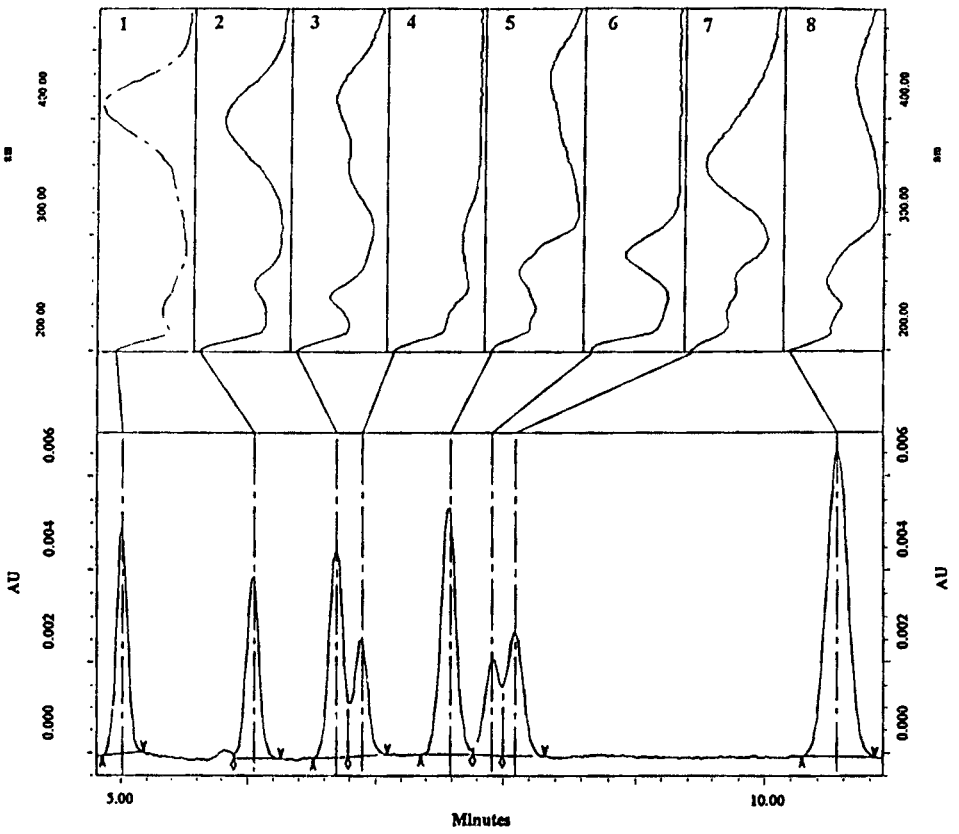


Figure 4. Spectrum index plot of the peaks from figure 3. UV spectra from the peak apex is displayed above the chromatogram. Peaks: **1**: 4,4'-DNDPA, **2**: 4-NDPA, **3**: 2,4'-DNDPA, **4**: NNO-DPA, **5**: 2,2'-DNDPA, **6**: DPA, **7**: 2,4-DNDPA, **8**: 2-NDPA.

Peak: 6.05 min. Purity Angle: 1.02 degrees Threshold Angle: 2.72 degrees

Library Match Table

#	Match1 Angle	Match1 Thresh.	Match1 Flag	Match1 Ideal	Match1 Spect. Name	Match1 Lib. Name
1	0.781	2.024		Yes	4-NDPA	Stabilizers

Peak Purity Passes Table

#	Purity Angle	Purity Threshold	Purity Flag	Maximum Impurity
1	1.018	2.719		5.997
2	0.941	2.681		6.197
3	0.904	2.607		5.930
4	0.852	2.548		6.063

Figure 5. Peak purity and library match report of compound 4-NDPA (peak #2) 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).

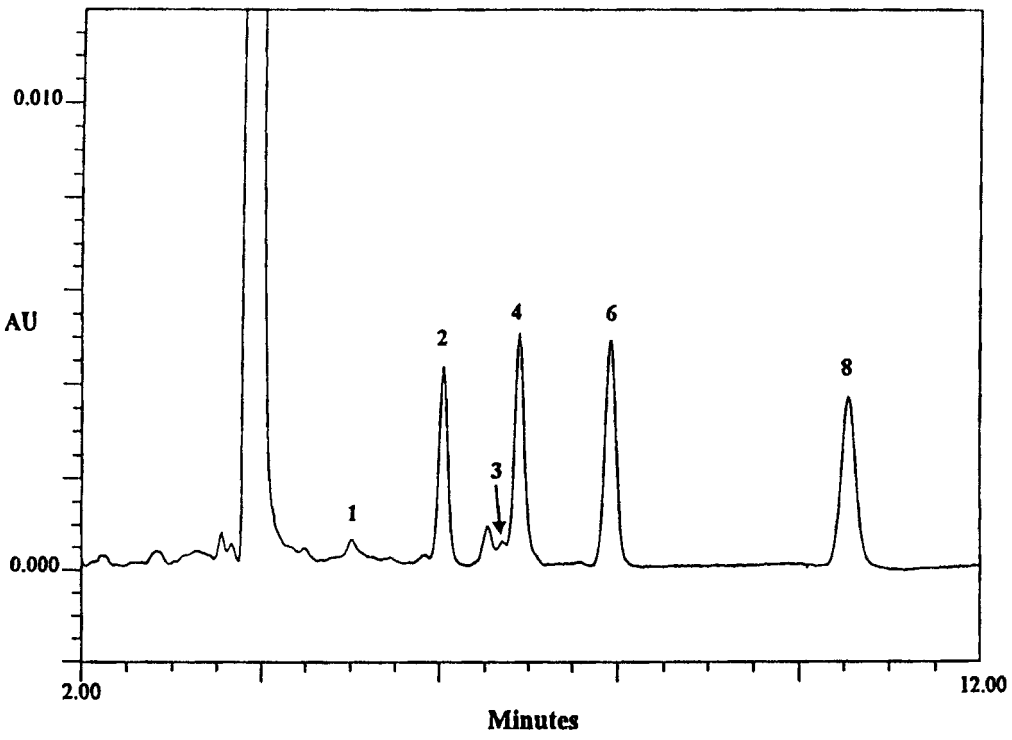


Figure 6. Chromatogram of IMR propellant sample (0.0296 gram extracted in 10.0 mL of acetonitrile) at 254 nm. Peaks were identified using library searching routine. Amounts in solution are in parenthesis. Peaks: **1**: 4,4'-DNDPA (0.13 mg/L), **2**: 4-NDPA (1.25 mg/L), **3**: 2,4'-DNDPA (0.09 mg/L), **4**: NNO-DPA (4.38 mg/L), **6**: DPA (3.58 mg/L), **8**: 2-NDPA (1.27 mg/L).

Peak: 6.90 min. Purity Angle: 0.37 degrees Threshold Angle: 1.24 degrees

Library Match Table

#	Match Angle	Match Threshold	Spectrum Name	Library Name	Match Flag	Ideal
1	0.367	1.242	NNO-DPA	Stabilizers		Yes
2						
3						

Peak Purity Passes Table

#	Purity Angle	Purity Threshold	Purity Flag	Maximum Impurity
1	1.169	1.356		6.745
2	0.925	1.351		7.045
3	0.354	1.340		6.812
4	0.279	1.338		6.962

Figure 7. Peak purity and library match report of compound NNO-DPA (peak #4) from figure 6. The top match, #1, is considered the best match of the spectra in the libraries searched. In this case the best match is NNO-DPA and the match angle (0.37 degrees) is less than the threshold (1.24 degrees) which is considered a good match.

TABLE I

Analyte	Sample 1	Sample 2	Sample 3
4,4'-DNDPA	0.13	0.27	0.17
4-NDPA	1.25	2.38	1.66
2,4'-DNDPA	0.09	0.23	0.24
NNO-DPA	4.38	8.02	14.06
2,2'-DNDPA	ND	ND	0.06
DPA	3.58	6.79	0.38
2-NDPA	1.27	2.17	2.42

Amounts are in mg/L
ND=None Detected

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