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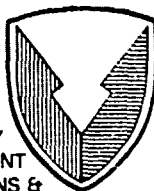
**HIGH PERFORMANCE LIQUID CHROMATOGRAPHY OF PROPELLANTS
PART I - ANALYSIS OF M1, M6, AND M10 PROPELLANTS**

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JEROME HABERMAN

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Reverse phase	Mobile phase	2-nitrodiphenylamine
Diphenylamine	Degradation	2,4 dinitrodiphenylamine
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
The stabilizer content of propellants in the Army stockpile is periodically determined to monitor their remaining safe life. The available standard methods of analysis are time consuming, and there is evidence that they may give misleading information. These methods are being replaced by state-of-the-art, high performance liquid chromatography (HPLC) using reverse phase columns. High performance liquid chromatography permits the differentiation		

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M1

M6

M10

Chromatograms

Dinitrotoluene

Scavengers

20. ABSTRACT (CONTINUED)

Among the stabilizers and their degradation products together with accurate quantitation. This progress report describes work carried out in the analysis of single base propellants containing diphenylamine (DPA) as the stabilizer. Several degradation products have been identified and the routine determination of these compounds is feasible. The degradation of DPA seems to follow a pattern that is unique for M1 and M6's as compared to the pattern for M10's. It is postulated that the ingredients of the propellants, other than the nitrocellulose (NC), may influence the way in which the DPA degradation products are formed. *Key words:*

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INTRODUCTION

Propellants are complex mixtures of nitrocellulose (NC), nitroglycerin, plasticizers, stabilizers, nitroguanidine, and other compounds together with small amounts of inorganic salts. In a surveillance program for stability, a major interest is in the stabilizer content. Nitrocellulose tends to decompose with time and, therefore, diphenylamine (DPA) has been used to stabilize single base propellants for many years. The presumed mode of stabilization is in its reaction with nitrogen oxides released from the decomposing NC. If not removed, these nitrogen oxides act catalytically to accelerate NC degradation, leading to the spontaneous ignition of the propellant. It is necessary, therefore, to periodically monitor the stabilizer content of propellants, assess their remaining "safe shelf" life, and to dispose of those propellant lots which are likely to undergo explosive decomposition.

Propellants in the past have been analyzed periodically to determine their stabilizer content using methods involving alkali digestion and steam distillation followed by spectrophotometric determination (ref 1). These methods are time-consuming and do not always give accurate results, particularly when stabilized derivatives are present which may be partly reconverted to DPA prior to distillation. Therefore, the standard procedure is being replaced with state-of-the-art, automated high performance liquid chromatography (HPLC) using reverse phase columns. High performance liquid chromatography has the capability of resolving many components in a mixture. Using highly sensitive detectors and advanced computer controls, this equipment is capable of precise, simultaneous, and accurate quantitation of various propellant stabilizers and their derivatives. For routine analysis, sample preparation is relatively simple, requiring only dissolution in methanol followed by dilution and filtration into the injection vial. Analysis time will depend upon the number of components to be determined in a sample, the difficulty of separation, and the polarity of the components. For example, when ethyl centralite is being determined, the mobile phase can be made less polar to speed up its elution time. If DPA is being determined, a relatively polar mobile phase is needed to ensure separation from its degradation products.

By determining DPA and its degradation products, a more accurate prediction of the safe life of the propellants can be obtained.

Since its introduction to propellant surveillance, several thousand HPLC analyses were run for the FY84 and FY85 stockpile reliability programs.

This progress report describes work carried out in the analysis of the single base M1, M6, and M10 propellants, and of the identification and quantitation of some of the degradation products.

EXPERIMENTAL

Apparatus

All work was carried out with HPLC equipment manufactured by the Waters Chromatography Division of the Millipore Corporation, Milford, MA. It consisted of Model 510 solvent delivery systems, a Model 481 UV multi-wavelength detector, a Model 710 intelligent sample processor, and a Model 840 data and chromatography control station. The HPLC column was a Radial-Pak reverse phase, 10 micron particle size, C-8 or C18 cartridge (10 cm x 0.8 cm) used in a RCM-100 Radial Compression Module.

The laboratory homogenizer is distributed by TEKMAR of Cincinnati, OH.

Reagents and Standards

Methanol, HPLC grade
Methanol, reagent grade
Water, suitable for HPLC use
Diphenylamine, reagent grade
N-nitrosodiphenylamine, Kodak Laboratory Chemicals
4-nitrodiphenylamine, Aldrich Chemical Co.
2-nitrodiphenylamine, reagent grade
2,4 dinitrodiphenylamine, Eastman Chemicals

CALIBRATION AND STANDARDIZATION

Wavelength of Detector Used: 254 nm
Column Temperature: Ambient

Mobile Phase: Degassed HPLC grade methanol, HPLC water in a ratio that generally depends upon the condition of the column. The average ratio was 60/40 methanol/water with a flow rate of 2 mL/min. A gradient method may also be used. Standards were prepared to contain 0.004 mg/mL each of stabilizer and stabilizer derivatives in one methanol solution.

Procedure: One gram quantities of cut up propellants were accurately weighed into a 125 mL Erlenmeyer flask and about 75 mL reagent grade methanol added. The sample was allowed to stand until the propellant had softened (from a few hours to overnight) and then homogenized at moderate speed with a laboratory homogenizer. The resulting mixture was transferred to a 250 mL volumetric flask and diluted with reagent grade methanol, a 10 mL aliquot was transferred to a 50 mL volumetric flask and diluted with methanol. This gives a nominal concentration of 0.008 mg DPA per mL and is capable of detecting and quantifying down to 0.02%.

About 4 mL of this final dilution was filtered through a 0.45 micron syringe filter into a sample vial. The prepared samples were placed, together with the appropriate standard, into the carousel tray of the sample processor for analysis. A typical analysis time for DPA and its degradation products was 24 minutes.

An alternative method was to extract 5 g of the cut up propellant with methylene chloride overnight in a Soxhlet. The resulting solution was evaporated to ~25 mL and diluted to 250 mL in a volumetric flask with methanol. Analysis can be carried out using this solution or further dilutions can be prepared. This method has the advantage of removing all the NC but the disadvantages of requiring more time for sample preparation and of discarding a chlorinated hydrocarbon.

Attempts to remove NC by precipitating it with water from the methanol solution, and centrifuging, gave lower stabilizer results due to absorption of the stabilizer by the precipitated NC.

RESULTS AND DISCUSSION

The initial phase of this investigation has involved the development of HPLC methods for the determination of DPA in single base propellants. Single base propellants contain NC and the stabilizer DPA, some may contain dinitrotoluene, inorganic salts, carbon black, and a plasticizer.

For maximum accuracy, 1 g samples were extracted by soaking in methanol, allowed to soften, and homogenized. This method gave results comparable to those obtained from propellants that were exhaustively extracted with methylene chloride in a Soxhlet (over 14 hours). The standard deviations (six replicates) for the various components were as follows: N-nitrosodiphenylamine (NNODPA), 0.024; DPA, 0.005; 4-nitrodiphenylamine (4NDPA), 0.006; 2,4 dinitrodiphenylamine (2,4DNDPA), 0.002; and 2-nitrodiphenylamine (2NDPA), 0.002.

A large number of naturally aged single base propellants were analyzed. Typical chromatograms for M1/M6 and M10 propellants are shown in figures 1 and 2. These particular chromatograms were developed with a gradient method, although, a large number were run isocratically. The gradient method saves a little time and yields sharper peaks for those eluting later.

The DPA and its degradation products are fairly well separated and allow good quantitation on the reverse phase C8 column; the NNODPA peak is found associated with the DPA peak; the 4NDPA, 2,4DNDPA, and 2NDPA peaks are well separated. As the amount of DPA found decreases there is an increase in the amount of NNODPA, 4NDPA, and 2NDPA. In cases where DPA is almost depleted, a peak is seen that is tentatively identified as 2,4DNDPA. In these cases, some other unidentified peaks also appear, which probably are other more highly nitrated degradation products. In the overwhelming majority of propellants analyzed where the amount of DPA has not gone below 0.2%, there have been only four peaks found, viz, DPA, NNODPA, 4NDPA, and 2NDPA.

Some representative results of the analysis of M1 and M6 propellants are shown in table 1. Material balances were calculated by converting NNODPA, 4NDPA, and 2NDPA to DPA. In a large number of the cases, most of the original quantity of DPA (nominally 1%) can be accounted for, i.e., from 0.8 to over 1% DPA (from residual DPA and degradation products). There are a few propellants which show a low total DPA and no extra peaks have been found. It is possible that other degradation products are present that do not absorb at 254 nm, or may not be separating. At present, we are investigating the use of other wavelengths to detect these presumed other peaks.

Typical results from the analysis of some M10 propellants are displayed in table 2. In these analyses, calculations of the material balance for total DPA show two propellants in which all of the DPA originally present can be accounted for. There tends to be a relatively large amount of NNODPA present as compared to the quantity present in the M1 and M6 propellants. The ratio of 4NDPA to 2NDPA in the M10 propellants is greater than one, whereas the ratio of 4NDPA to 2NDPA in the M1 and M6 propellants is generally less than one. It is evident that the mechanism of degradation is somewhat different in the M10 as compared to the M1 and M6 propellants. The major difference in the formulation is the presence of about 10% DNT in the M1 and M6 propellants which, therefore, may play a role in the degradation mechanism.

An M10 propellant which was completely devoid of DPA is shown in figure 3. The amount of NNODPA was 0.22%, of 4NDPA, 0.15%, of 2NDPA, 0.04%, and a peak which can be attributed to the 2,4DNDPA, 0.03%. There are three unidentified peaks which are probably higher nitrated DPA's.

A newly manufactured M10 propellant was stored at 65.5°C. As may be seen in table 3, and as expected, there is a decline in the amount of DPA and increases in NNODPA, 4NDPA, and 2NDPA with time. A material balance accounts for all of the DPA originally present so no other degradation products have apparently formed as yet. This propellant will be analyzed at intervals to determine when higher nitrated peaks start appearing. When a sufficient amount of these products have formed, large amounts of this propellant will be aged and extracted, attempts will then be made to isolate sufficient quantities for identification.

A few single base propellants manufactured in 1923, 1928, and 1941 which had been stored under ambient conditions were analyzed. As shown in table 4, there is a little degradation and all of the DPA originally in the propellant can be accounted for via material balances. The pattern of degradation is the same as has been found in the majority of M1 and M6 propellants analyzed in this laboratory.

CONCLUSIONS

When M1, M6, and M10 propellants are stored at ambient or at 65.5°C, three degradation products are formed initially, viz, NNODPA, 4NDPA, and 2NDPA. NNODPA is formed early and in relatively large quantities. When a relatively large amount of DPA has been depleted, other products of degradation may appear and a material balance of DPA and products may be less than the original nominal amount of DPA. At this point, while the presence of higher nitrated degradation products is undoubted, they have not yet been identified with HPLC.

The classic work of Schroeder, et al. (ref 2) presented work on a double base powder which had been aged at 70°C. In these experiments, the first products formed were the same three products found in the single base powder as described above. After 4 to 5 days, higher nitrated products appeared. From this evidence, it can be further concluded that other components of propellants, such as nitroglycerin and dinitrotoluene, may play a part in the degradation process as well as the temperature.

At this point, it would seem that single base propellants should be monitored by determining the quantity of DPA, NNODPA, 4NDPA, and 2NDPA. Since all can act as scavengers for NO_2 , the propellant can be considered safe until such a time as the DPA has been depleted and higher nitrated products start to appear. This type of analysis has the potential of allowing greater insight into the safe life of propellants. In our current studies, the kinetics of the conversion to nitrated products are being followed and will be reported upon in a subsequent report.

Table 1. Analyses of M1 and M6 propellants for DPA and degradation products

<u>Propellant designation</u>	<u>DPA, %</u>	<u>NNODPA, %</u>	<u>4NDPA, %</u>	<u>2NDPA, %</u>	<u>Total as DPA, %</u>
A	0.77	0.11	0.02	0.06	0.92
B	0.48	0.13	0.04	0.10	0.70
C	0.74	0.09	0.02	0.05	0.87
D	0.58	0.14	0.03	0.07	0.78
E	0.66	0.10	0.05	0.12	0.87
F	0.08	0.07	0.16	0.18	0.40
G	0.76	0.13	0.02	0.04	0.92
H	0.67	0.19	0.04	0.08	0.92
I	0.11	0.26	0.15	0.18	0.59
J	0.56	0.24	0.06	0.11	0.91
K	0.70	0.20	0.05	0.08	0.97
L	0.02	0.29	0.17	0.17	0.53

Table 2. Analyses of M10 propellants for DPA and degradation products

<u>Propellant designation</u>	<u>DPA, %</u>	<u>NNODPA, %</u>	<u>4NDPA, %</u>	<u>2NDPA, %</u>	<u>Total as DPA, %</u>
A	0.45	0.48	0.12	0.08	1.02
B	0.12	0.26	0.16	0.12	0.56
C	0.09	0.21	0.20	0.13	0.53
D	0.11	0.28	0.16	0.12	0.57
E	0.00	0.12	0.24	0.10	0.36
F	0.06	0.31	0.24	0.11	0.59
G	0.10	0.36	0.16	0.11	0.62
H	0.63	0.28	0.07	0.04	0.95

Table 3. M10 propellant at 65.5°C

<u>Time exposed days</u>	<u>DPA, %</u>	<u>NNODPA, %</u>	<u>4NDPA, %</u>	<u>2NDPA, %</u>	<u>Total as DPA, %</u>
0	0.92	0	0	0	0.92
23	0.63	0.28	0.07	0.04	0.95
45	0.45	0.52	0.12	0.09	1.06

Table 4. Analyses of old M6 propellants stored at ambient temperature

<u>Year of manufacture</u>	<u>DPA, %</u>	<u>NNODPA, %</u>	<u>4NDPA, %</u>	<u>2NDPA, %</u>	<u>Total as DPA, %</u>
1923	0.79	0.17	0.07	0.11	1.07
1928	0.69	0.20	0.05	0.11	0.99
1941	0.74	0.12	0.04	0.06	0.96

Table 5. Nominal compositions of M1, M6, and M10 propellants

	<u>Propellant</u>		
	<u>M1</u>	<u>M6</u>	<u>M10</u>
Dibutylphthalate, %	5	3	-
Nitrocellulose, %	85	87	98
Potassium sulfate, %	1	1	1
Diphenylamine, %	1	1	1
Dinitrotoluene, %	10	10	-

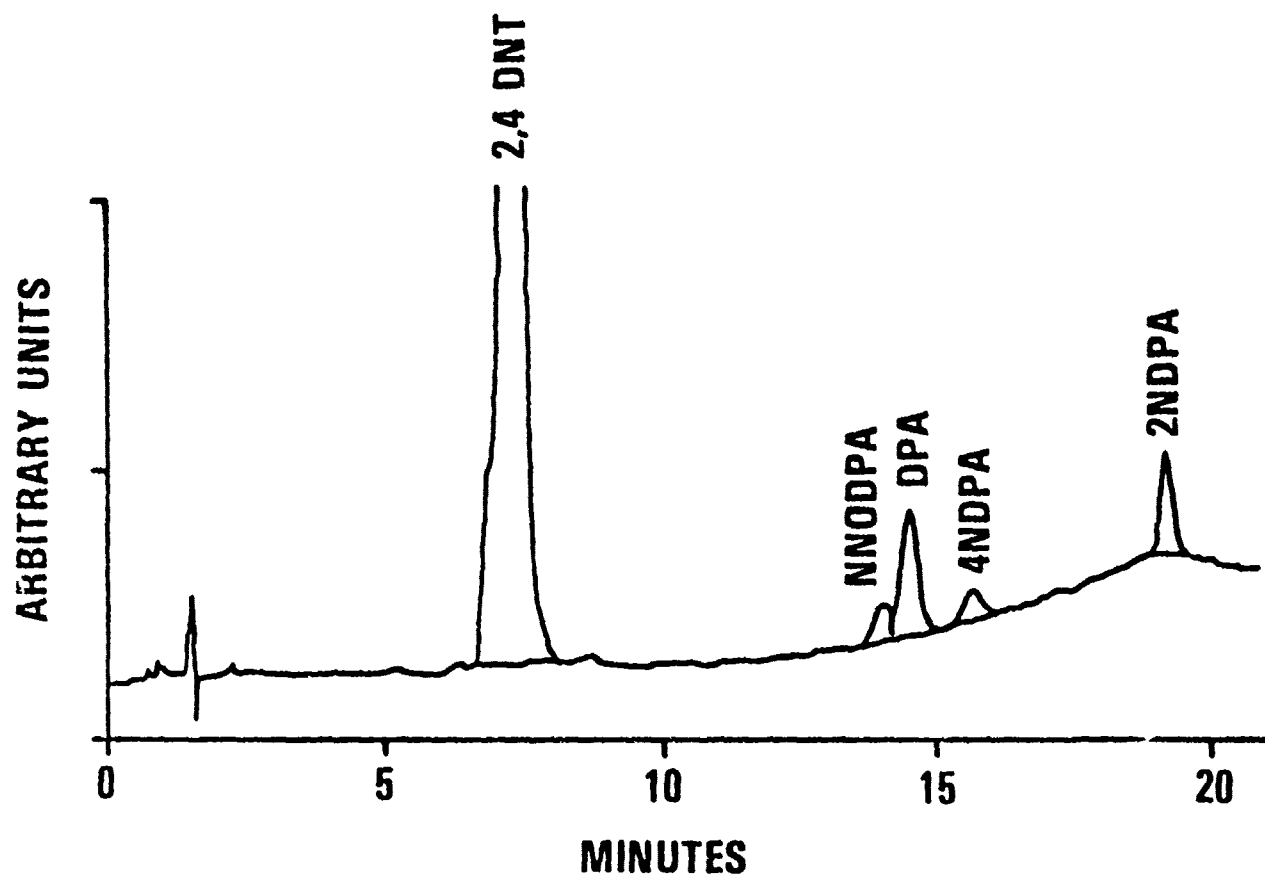


Figure 1. Chromatogram of M1/M6 propellants

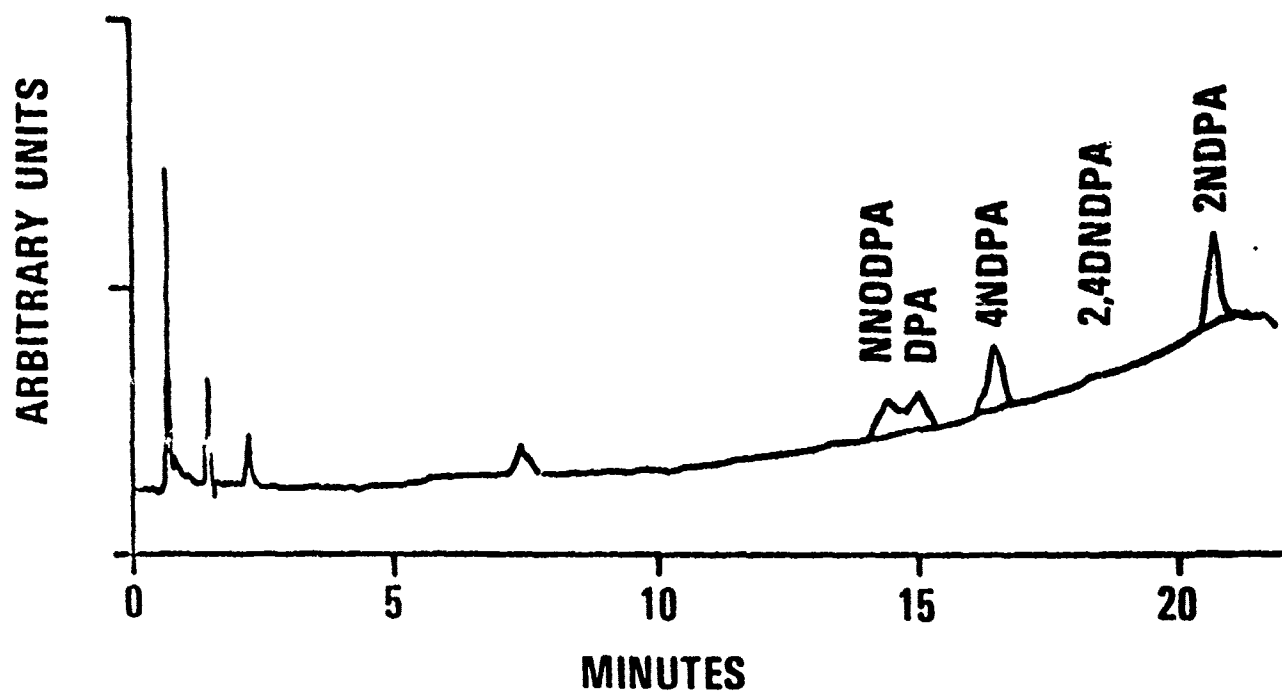


Figure 2. Chromatogram of M10 propellant

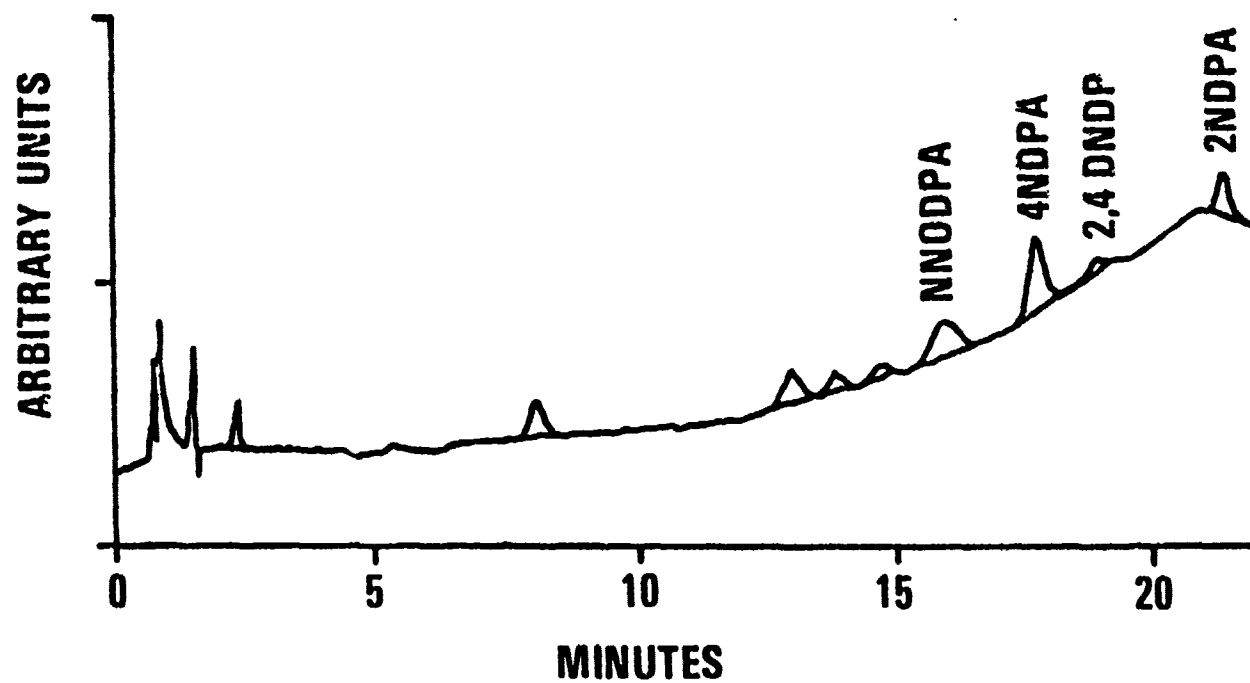


Figure 3. Chromatogram of M10 propellant with depleted DPA

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2. W.A. Schroeder, et al, Ind. Eng. Chem., 41, 2818, 1949.

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