

AD-F500059

12

AD A119397

NSWC TR 81-123

# ANALYSIS METHODS FOR EXPLOSIVE MATERIALS - I. POLYNITRO COMPOUNDS

BY ELEONORE G. KAYSER  
RESEARCH AND TECHNOLOGY DEPARTMENT

3 MARCH 1982

Approved for public release, distribution unlimited.

DTIC  
ELECTE  
SEP 20 1982  
S D  
B

DTIC FILE COPY



## NAVAL SURFACE WEAPONS CENTER

Dahlgren, Virginia 22448 • Silver Spring, Maryland 20910

82 08 30 001

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NSWC TR 81-123	2. GOVT ACCESSION NO. 92-A 119 397	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) ANALYSIS METHODS FOR EXPLOSIVE MATERIALS - I. POLYINITRO COMPOUNDS	5. TYPE OF REPORT & PERIOD COVERED Final Report	
	6. PERFORMING ORG. REPORT NUMBER	
7. AUTHOR(s) Eleonore G. Kayser	8. CONTRACT OR GRANT NUMBER(s)	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Surface Weapons Center White Oak, Silver Spring, Maryland 20910	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS OR11;Rj;N01	
11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE 3 March 1982	
	13. NUMBER OF PAGES 29	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report) UNCLASSIFIED	
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Polynitro Aromatics Thermally Stable Explosives Explosives		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A high pressure liquid chromatography method was developed for rapid and quantitative chemical analysis of the following thermally stable explosive materials: DATB, DINA, DIPAM, DNT, DODECA, HNAB, HNBIB, HMX, HNBP, HNS, NONA, ONT, PA, PETN, PYX, RDX, TATB, TETRYL, TNA, TNB, TNN, TNS, TNT, and TPT (see glossary). Additional chemical characterization of the above materials was carried out by Nuclear Magnetic Resonance Spectroscopy and by Thin Layer Chromatography. Dimethylsulfoxide was used as the common solvent for all the compounds in this investigation.		

DD FORM 1473

1 JAN 73

EDITION OF 1 NOV 65 IS OBSOLETE  
S/N 0102-014-6601

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

## FOREWORD

This report describes quantitative analytical techniques that can be used for several thermally stable explosives (e.g. TATB, HNS, ONT, NONA, DODECA, TNN, PYX, TPT, etc.) and related compounds. This work is currently being sponsored by the Lyndon B. Johnson Manned Spacecraft Center, Task NASAR12RB, and the Strategic Systems Projects Office, Task B00035B001, R12GC. The identification of vendors and/or products implies neither endorsement nor criticism by the Naval Surface Weapons Center.

*J. F. Proctor*  
 J. F. PROCTOR  
 By direction



Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
<b>A</b>	

## CONTENTS

	<u>Page</u>
INTRODUCTION . . . . .	1
EXPERIMENTAL . . . . .	3
MATERIALS AND SOLUTIONS. . . . .	3
CALCULATIONS . . . . .	3
HPLC CONDITIONS. . . . .	3
NMR CONDITIONS . . . . .	3
TLC CONDITIONS . . . . .	4
RESULTS AND DISCUSSION . . . . .	4

## ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	HPLC CHROMATOGRAM OF A 14 COMPONENT MIXTURE . . . . .	5
2	HPLC CHROMATOGRAM OF A FOUR COMPONENT MIXTURE . . . . .	6

## TABLES

<u>Table</u>		<u>Page</u>
1	HPLC DATA OF EXPLOSIVE COMPOUNDS. . . . .	7
2	HPLC DATA OF EXPLOSIVE COMPOUNDS. . . . .	8
3	HPLC DATA OF EXPLOSIVE COMPOUNDS. . . . .	9
4	$^1\text{H}$ -NMR DATA OF EXPLOSIVE COMPOUNDS. . . . .	10
5	TLC DATA OF EXPLOSIVE COMPOUNDS . . . . .	11
6	MELTING POINT DATA OF EXPLOSIVE COMPOUNDS . . . . .	12

## INTRODUCTION

The importance of heat resistant and insensitive high explosive compounds is increasing, since new weapons warheads are being sought that can withstand a higher degree of aerodynamic heating and that have a lower vulnerability to accidental initiation. A series of high temperature resistant explosives, most of which were first prepared or evaluated at NSWC, are shown in the glossary. Typical examples are: TATB, PYX, ONT, DATB, HNS, NONA, DODECA, AND TPT. Relatively few of the presently used common explosive materials can withstand temperatures above 200°C without melting and/or decomposition, whereas the compounds of this investigation are stable and can be used in the temperature range of 230°-350°C.

In the past, there has not been any single chemical analysis method for all of these relatively insoluble heat-resistant explosives. However, this report describes a practical high performance liquid chromatographic (HPLC) analysis procedure that provides good accuracy and reproducibility. Additional information is provided on the chemical characterization of these explosive compounds by nuclear magnetic resonance spectroscopy (NMR) and by thin layer chromatography (TLC). The melting points of all of the materials are also reported.

The HPLC method described in this report uses the Waters Associates Radial Compression Separation System (RCSS). The RCSS consists of two components: a radial-Pak cartridge containing reverse phase C-18 column packing and a Model RCM-100 module that compresses the Radial-Pak cartridge. Using this system, a quantitative assay ( $\pm 2\%$ ) is achieved for all of the twenty-four explosive compounds investigated.

Previously reported assay methods for the insensitive high explosive TATB include spectrophotometric determinations using ethylenediamine (EDA)<sup>1</sup>, tetraethylammoniumhydroxide (TEAH)<sup>2,3</sup>,

---

<sup>1</sup> Glover, D. J. and Kayser, E. G., Anal. Chem., Vol. 40, 1968, p. 2050.

<sup>2</sup> Sawicki, E. and Stanley, T. W., Analyt. Chem. Acta, Vol. 23, 1960, p. 551.

<sup>3</sup> Selig, W., "Spectrophotometric Determination of Some Nitro and Nitroso Derivatives of Diphenylamine in N,N-Dimethylformamide," Lawrence Livermore Laboratory (LLL) Report, UCRL-6903, May 1963.

dimethylsulfoxide (DMSO)<sup>4</sup>, and sulfuric acid<sup>5</sup>, as well as a liquid chromatography-spectrophotometric method<sup>6</sup>. Spectrophotometric methods of analysis<sup>1,7</sup> have also been reported for HNS, DODECA, NONA, ONT, HNBP, TNN, TNB, HNBiB, TPT, PYX, and DNT as well as HPLC procedures<sup>8-14</sup> for HNS, HNBiB, TNT, TNB, RDX, HMX, PA, TNA, DNT and TATB.

- 
- <sup>4</sup> Selig, W., "Photometric Determination of 1,3,5-Triamino-2,4,6-Trinitrobenzene (TATB) in Dimethylsulfoxide (DMSO)," Lawrence Livermore Laboratory Report, UCID-17542, July 1977.
  - <sup>5</sup> Ungnade, H. E., "1,3,5-Triamino-2,4,6-Trinitrobenzene (TATB) - Preparation and Purification," Los Alamos National Laboratory (LANL) Report, GMX-2-R-64-1, 1963, pp. 10-11.
  - <sup>6</sup> MacDougall, C. S., "A Liquid Chromatographic-Spectrophotometric Assay for TATB in TATB," in Quarterly Progress Report, Mason & Hanger-Silas Mason Co., Inc., Pantex Plant (MHSMP), MHSMP-77-18, Jan-Mar 1977.
  - <sup>7</sup> Kilmer, E. E., "A Characterization Study of Several Heat Resistant Explosives," NOLTR 74-177 Oct 1974.
  - <sup>8</sup> Kayser, E. G. and Burinson, N. E., "Analysis of Water and Soil Samples from 'Fate of <sup>14</sup>C Labelled Explosive Compounds in Soil Study," Final Report from the Naval Surface Weapons Center, White Oak, submitted to the U.S. Army Medical Bioengineering R & D Lab. (USAMBRDL), Fort Detrick, Md., MIPR No. 9952, Jan-Dec 1979.
  - <sup>9</sup> Kayser, E. G., "Analysis of 2,2',4,4',6,6'-Hexanitrostilbene (HNS) by High Performance Liquid Chromatography," NSWC/WOL TR 77-154, 14 March 1978.
  - <sup>10</sup> Kayser, E. G., "An Investigation of the Shipp Hexanitrostilbene (HNS) Process," NSWC TR 80-111, 25 Aug 1980.
  - <sup>11</sup> Schaffer, C. L., "HNS Analysis," Mason & Hanger-Silas Mason Co., Inc., Pantex Plant, MHSMP-75-50, Oct-Dec 1974.
  - <sup>12</sup> Stanford, Jr., T. B., "Determination of Tetryl and 2,3-,2,4-,2,5-,2,6-,3,4-, and 3,5-Dinitrotoluene Using High Performance Liquid Chromatography," Final Report, from Battelle Columbus Laboratories, Columbus, Ohio, submitted to the U.S. Army Research and Development Command, Washington, D.C., Contract No. DAMD-17-74-C-4123, 31 Jan 1977.
  - <sup>13</sup> Schaffer, C. L., "Analysis of TATB by HPLC," Mason & Hanger-Silas Mason Co., Inc., Pantex Plant, MHSMP-78-65, 1978.
  - <sup>14</sup> Krull, I. S. and Camp, M. J., American Laboratory, May 1980, pp. 63-73.

EXPERIMENTAL

MATERIALS AND SOLUTIONS. Most of the explosive compounds used in this investigation are not commercially available and were therefore synthesized in the Synthesis and Formulations Branch. The exceptions were PYX and DIPAM which were obtained from Los Alamos National Laboratory (LANL) and from Northrop Carolina Co., Inc. respectively.

The solubility<sup>15</sup> of the less soluble compounds such as TATB, HNS, DODECA, NONA, PYX, TPT, and HMX was quantitatively determined in methanol, dimethylsulfoxide, dimethylformamide, and n-methylpyrrolidone. Although the dimethylformamide and n-methylpyrrolidone proved to have a greater solvent capacity for several of the explosive materials (TATB, HMX, and TPT), all of the compounds had sufficient solubility in DMSO at ambient temperature so that HPLC, NMR, and TLC data could be accurately obtained with this solvent. An HPLC trace of several neat DMSO samples indicated the presence of two small impurity peaks with a retention time of approximately 3.0-3.2 minutes (methanol: water, 70:30) which could have interfered with the peak height calculations of several of the explosives at the low concentration limits. Therefore all the DMSO used in this study was passed through a column of activated charcoal which removed over 95% of the impurities.

CALCULATIONS. The concentration of each explosive material was initially determined by peak area as well as peak height. Using the RCSS unit, the percentage accuracy of the area method was found to be equivalent to that of the peak height method, therefore for simplicity reasons, the latter method was used for all the analyses.

HPLC CONDITIONS. A high-performance liquid chromatograph (Waters Associates Model ALC 202) equipped with a 254 nm wavelength detector, a solvent delivery system (Model 6000), and a U6K high pressure loop injector was used with a Model RCM-100 module containing a reverse-phase C-18 Radial-Pak cartridge. Sample solutions were eluted isocratically at ambient temperature. Column flow was 2.0 ml/minute, with a mobile phase consisting of the following mixtures of HPLC grade methanol and distilled water: 40:60 (v/v), 50:50 (v/v), and 70:30 (v/v). The solvent mixtures were not degassed prior to use in the HPLC and sample injections of 2 to 10 microliters were used.

NMR CONDITIONS. Proton NMR spectra were obtained on a Varian XL-200 spectrometer. The chemical shift values ( $\delta$ ) were determined relative to the reference compound tetramethylsilane (TMS). The NMR solvent used was dimethylsulfoxide-d<sub>6</sub> (99.5 atom % D), since it proved to be the best general solvent for all twenty-four compounds investigated.

---

<sup>15</sup> Sitzmann, M. E., Foti, S. and Misener, C. C., "Solubilities of High Explosives- Removal of High Explosive Fillers from Munitions by Chemical Dissolution," NOLTR 73-186, 21 Nov 1973.

TLC CONDITIONS. Thin layer chromatographic analyses of all the compounds reported used benzene as the developing solvent. In several cases where the samples did not chromatograph (e.g. HMX, PETN, TATB, TNN) methanol was also tried as the developing solvent.

The adsorbent used was Merck Silica Gel HF-254 coated on glass plates. A short wave UV lamp (2537Å) was used for spot visualization.

## RESULTS AND DISCUSSION

For the quantitative analysis of the explosive compounds by HPLC, DMSO solutions were used. Figure 1 shows the separation of a fourteen component synthetic mixture. Ten of the materials RDX, TATB, TNB, DATB, TETRYL, TNN, TNT, DNT, HNS, and DIPAM are completely resolved, two components HMX and PYX are partially resolved, and only TPT and HNB1B remain unresolved. Another HPLC chromatogram of a four component synthetic mixture containing three of the impurities<sup>9-11,16</sup> (TNB, TNT, HNB1B) found in several production grade samples of HNS-I is shown in Figure 2. The average retention time (minutes), average response factor (mm/mg), solution concentration (Molar), and approximate limit of detection (micrograms/ml) for all the explosive compounds studied are given in Tables 1, 2 and 3. From the peak height responses reported in Tables 1, 2 and 3, the detection limit for all the materials was calculated to be 15 mm on scale 0.005 absorbance units full scale ( $3 \times 10^{-4}$  AUFS). This limit was set assuming a signal to noise ratio of 5.

The <sup>1</sup>H NMR spectra of all the compounds were determined using DMSO-d<sub>6</sub> as the solvent. Deuterated benzene (C<sub>6</sub>D<sub>6</sub>) was also used as a sample solvent since peak overlap in the case of DATB, and H→D exchange of the OH in PA was noted in the DMSO. The pulse sequence was repeated four times and the signals time-averaged for all the compounds with the exception of TATB. In the case of TATB, the pulse sequence was repeated 5000 times, because of the low solubility, and the resulting signals time-averaged. The NMR data are reported in Table 4.

For the thin layer chromatographic analyses the glass plates were prepared according to the method of Hoffsommer<sup>17</sup> using Merck Silica Gel HF 254 as the adsorbent. This material contains a fluorescent indicator which allows location of the developed spots with 2540Å light. The developing solvents used were benzene and methanol R<sub>f</sub> values were obtained for all the explosive compounds with the exception of HMX, TATB, PETN and TNN. The data are recorded in Table 5.

The melting points of most of the explosive compounds of this investigation were determined with a Thomas Hoover Capillary Melting Point Apparatus, with a heating rate of approximately 20/minute. All temperatures measured are uncorrected. In addition, melting point data from the literature are cited. The melting points are listed in Table 6.

<sup>16</sup> Stull, T. W., "Synthesis of High Purity Hexanitrostilbene," Mason & Hanger-Silas Mason Co., Inc., Pantex Plant, MHSMP-75-37, Sep 1975.

<sup>17</sup> Hoffsommer, J. C. and McCullough, J. F., J. Chromatog., Vol. 38, 1968, p.508.

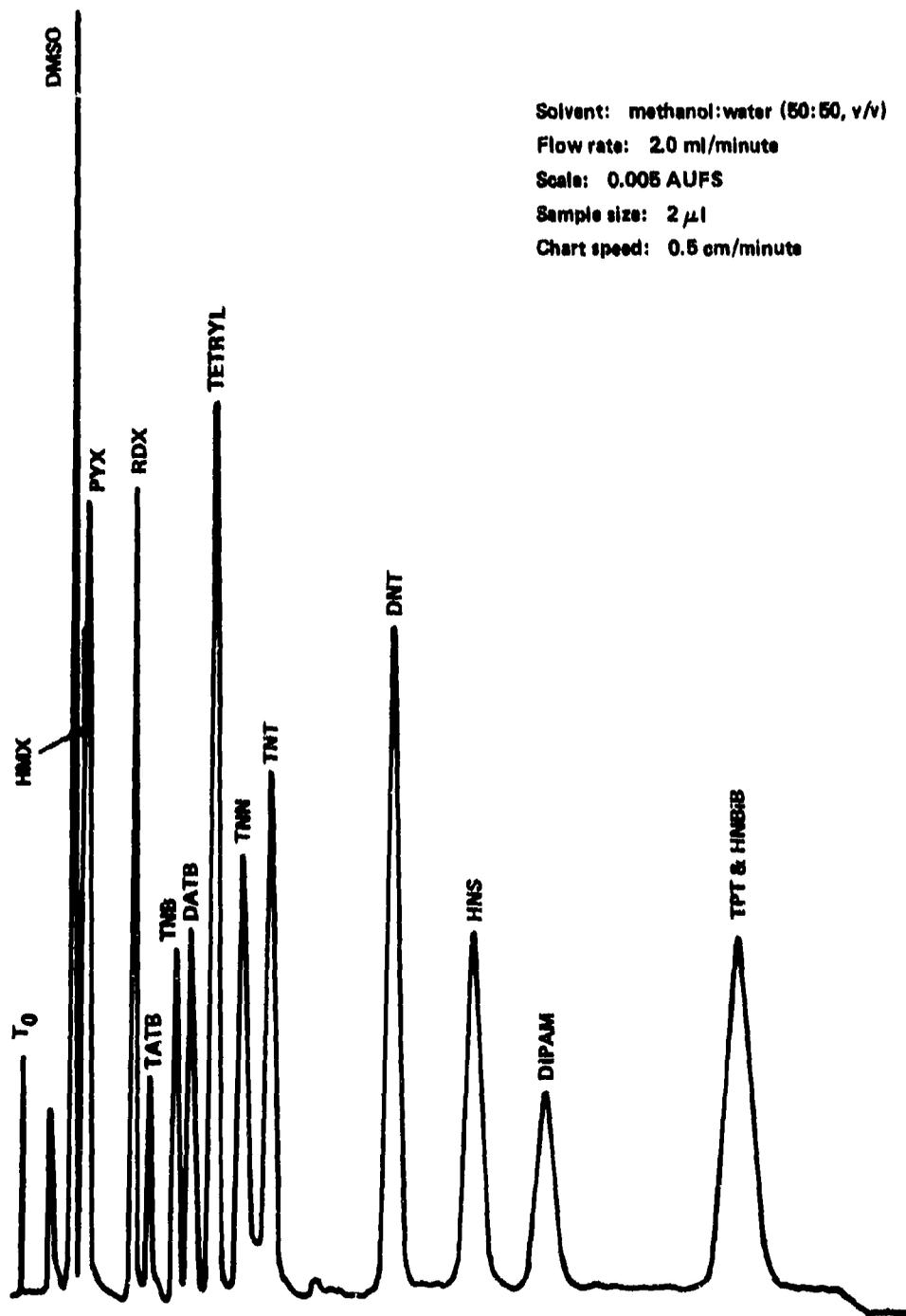


FIGURE 1 HPLC CHROMATOGRAM OF A 14 COMPONENT MIXTURE

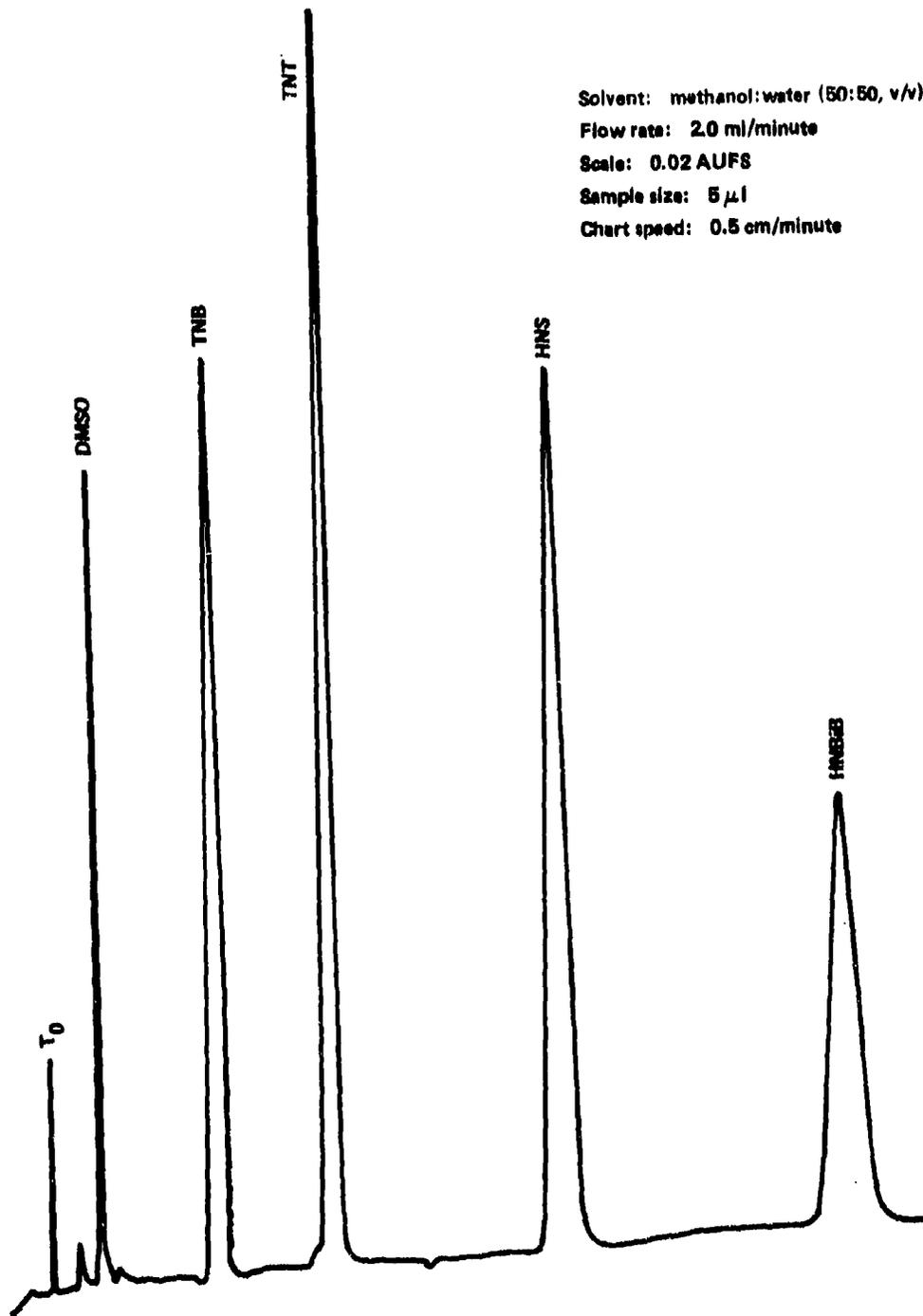


FIGURE 2 HPLC CHROMATOGRAM OF A FOUR COMPONENT MIXTURE

TABLE 1 HPLC DATA OF EXPLOSIVE COMPOUNDS

COMPOUND	AVERAGE RETENTION TIME (minutes)	AVERAGE RESPONSE FACTOR (peak height mm/mg)	DMSO SOLN CONC (moles/liter)	APPROX LIMIT OF DETECTION <sup>a</sup> (micrograms/ml; ppm)
DMSO	1.8	—	—	—
HMX	2.8	—	—	—
PETN	21.2	$4.5 \times 10^3$	$10^{-2} - 10^{-3}$	3332
PYX	9.6	$1.1 \times 10^6$	$10^{-4} - 10^{-6}$	13.4
RDX	5.8	—	—	—
TATB	7.4	—	—	—
TPT	80.0	$1.7 \times 10^5$	$10^{-4} - 10^{-5}$	87.5

## CONDITIONS:

Isocratic elution

Detector wavelength, 254 nm

Column: Radial-PAK A with the RCM-100 Radial Compression Module

Flow rate: 2.0 ml/minute

Mobile phase: 40% MeOH/60% H<sub>2</sub>O by volume

Chart speed: 0.5 cm/minute

- <sup>a</sup> From the peak height responses given, the detection limit for all the explosive compounds was calculated to be 15 mm on scale 0.005 absorbance units full scale ( $3 \times 10^{-4}$  AUFS). This limit was set assuming a signal/noise ratio of 5.

TABLE 2 HPLC DATA OF EXPLOSIVE COMPOUNDS

COMPOUND	AVERAGE RETENTION TIME (minutes)	AVERAGE RESPONSE FACTOR (peak height mm/mg)	DMSO SOLN CONC (moles/liter)	APPROX LIMIT OF DETECTION <sup>a</sup> (micrograms/ml; ppm)
DATB	5.5	$2.77 \pm 0.01 \times 10^6$	$10^{-4} \cdot 10^{-5}$	5.4
DINA	4.1	$1.82 \pm 0.04 \times 10^6$	$10^{-4} \cdot 10^{-6}$	8.2
DMSO	1.6	—	—	—
DIPAM	16.1	$1.55 \times 10^6$	$10^{-4} \cdot 10^{-6}$	9.7
DNT	11.6	$4.37 \times 10^6$	$10^{-4} \cdot 10^{-6}$	3.4
HNAB	9.2	$9.5 \pm 0.06 \times 10^5$	$10^{-4} \cdot 10^{-6}$	~ 15
HNBIB	22.8	$2.41 \times 10^6$	$10^{-4} \cdot 10^{-6}$	9.9
HNS	14.2	$2.31 \times 10^6$	$10^{-4} \cdot 10^{-6}$	6.5
HMX	2.0	$4.77 \times 10^6$	$10^{-4} \cdot 10^{-6}$	3.1
PA	0.8	$8.98 \pm 0.05 \times 10^7$	$10^{-4} \cdot 10^{-6}$	0.2
PETN	12.0	$1.31 \pm 0.03 \times 10^4$	$10^{-2} \cdot 10^{-3}$	1236
PYX	2.1	$4.04 \pm 0.06 \times 10^6$	$10^{-4} \cdot 10^{-5}$	3.7
RDX	3.4	$4.35 \pm 0.04 \times 10^6$	$10^{-4} \cdot 10^{-6}$	3.5
TATB	4.0	$3.62 \pm 0.04 \times 10^6$	$10^{-5} \cdot 10^{-7}$	4.1
TETRYL	5.8	$4.42 \times 10^6$	$10^{-4} \cdot 10^{-6}$	3.4
TNA	6.8	$2.6 \pm 0.04 \times 10^5$	$10^{-4} \cdot 10^{-6}$	5.8
TNB	5.3	$4.97 \times 10^6$	$10^{-4} \cdot 10^{-7}$	3.0
TNN	7.0	$2.12 \pm 0.08 \times 10^6$	$10^{-3} \cdot 10^{-5}$	7.3
TNT	7.8	$4.74 \times 10^6$	$10^{-4} \cdot 10^{-6}$	3.1
TPT	22.9	$1.32 \pm 0.01 \times 10^6$	$10^{-4} \cdot 10^{-5}$	11.4

## CONDITIONS:

Isocratic elution

Detector wavelength, 254 nm

Column: Radial-PAK A with the RCM-100 Radial Compression Module

Flow rate: 2.0 ml/minute

Mobile phase: 50% MeOH/50% H<sub>2</sub>O by volume

Chart speed: 0.5 cm/minute

- <sup>a</sup> From the peak height responses given, the detection limit for all the explosive compounds was calculated to be 15 mm on scale 0.005 absorbance units full scale ( $3 \times 10^{-4}$  AUFS). This limit was set assuming a signal/noise ratio of 5.

TABLE 3 HPLC DATA OF EXPLOSIVE COMPOUNDS

COMPOUND	AVERAGE RETENTION TIME (minutes)	AVERAGE RESPONSE FACTOR (peak height mm/mg)	DMSO SOLN CONC (moles/liter)	APPROX LIMIT OF DETECTION <sup>a</sup> (micrograms/ml; ppm)
DIPAM	3.3	$7.36 \pm 0.06 \times 10^6$	$10^{-4} - 10^{-6}$	2.0
DMSO	1.5	—	—	—
DNT	3.7	$1.19 \times 10^7$	$10^{-4} - 10^{-6}$	1.3
DODECA	6.7	$4.81 \pm 0.03 \times 10^6$	$10^{-5} - 10^{-7}$	3.1
HNBIB	3.9	$9.72 \pm 0.03 \times 10^6$	$10^{-4} - 10^{-6}$	1.9
HNBP	3.6	$1.14 \pm 0.02 \times 10^7$	$10^{-4} - 10^{-7}$	1.3
HNS	2.9	$9.71 \pm 0.03 \times 10^6$	$10^{-4} - 10^{-6}$	2.1
NONA	4.7	$8.03 \pm 0.06 \times 10^6$	$10^{-4} - 10^{-6}$	1.9
ONT	5.3	$7.56 \pm 0.04 \times 10^6$	$10^{-4} - 10^{-6}$	2.0
PETN	3.3	$5.37 \times 10^4$	$10^{-2} - 10^{-3}$	1000
TNN	2.3	$6.32 \pm 0.01 \times 10^6$	$10^{-4} - 10^{-5}$	2.4
TNS	5.2	$5.48 \pm 0.04 \times 10^6$	$10^{-4} - 10^{-6}$	2.7
TNT	2.9	$1.07 \times 10^7$	$10^{-4} - 10^{-6}$	1.4
TPT	3.1	$7.86 \pm 0.07 \times 10^6$	$10^{-4} - 10^{-7}$	1.9

## CONDITIONS:

Isocratic elution

Detector wavelength, 254 nm

Column: Radial-PAK A with the RCM-100 Radial Compression Module

Flow rate: 2.0 ml/minute

Mobile phase: 70% MeOH/30% H<sub>2</sub>O by volume

Chart speed: 0.5 cm/minute

- <sup>a</sup> From the peak height responses given, the detection limit for all the explosive compounds was calculated to be 15 mm on scale 0.005 absorbance units full scale ( $3 \times 10^{-4}$  AUFS). This limit was set assuming a signal/noise ratio of 5.

TABLE 4 H<sup>1</sup> - NMR DATA OF EXPLOSIVE COMPOUNDS

COMPOUND	SOLVENT <sup>a</sup>	NMR SPECTRUM <sup>b</sup>
DATB	DMSO-D <sub>6</sub>	9.10 (s, Ar-H)
		9.10 (s, 2NH <sub>2</sub> )
DATB	BENZENE-D <sub>6</sub>	8.91 (s, Ar-H)
		8.61 (s, 2NH <sub>2</sub> )
DINA	DMSO-D <sub>6</sub>	4.76 (t, 2CH <sub>2</sub> )
		4.17 (t, 2CH <sub>2</sub> )
DIPAM	"	9.08 (s, 2Ar-H)
DNT	"	8.68 (s, 2NH <sub>2</sub> )
		8.68 (d, Ar-H)
		8.42 (q, Ar-H)
		7.87 (d, Ar-H)
DODECA	"	2.62 (s, CH <sub>3</sub> )
		9.39 (s, 2Ar-H)
		9.24 (s, 2Ar-H)
		9.20 (s, 2Ar-H)
HNAB	"	10.19 (s, 4Ar-H)
HNBIB	"	9.08 (s, 4Ar-H)
		3.39 (s, 2CH <sub>2</sub> )
HNBP	"	9.27 (s, 4Ar-H)
HNS	"	9.07 (s, 4Ar-H)
		7.11 (s, 2CH)
HMX	"	5.98 (s, 8R-H)
NONA	"	9.26 (s, 5Ar-H)
CNT	"	9.26 (s, 6Ar-H)
PA	"	8.56 (s, 2Ar-H)
PA	BENZENE-D <sub>6</sub>	8.07 (s, 2Ar-H)
		11.00 (s, OH)
PETN	DMSO-D <sub>6</sub>	4.65 (s, 4CH <sub>2</sub> )
PYX	"	8.85 (s, 5Ar-H)
		9.10 (s, 2NH)
		9.10 (s, 2NH)
RDX	"	6.06 (s, 6R-H)
TATB	"	10.00 (s, 3NH <sub>2</sub> ) <sup>c</sup>
TETRYL	"	9.28 (s, 2Ar-H)
		3.63 (s, CH <sub>3</sub> )
TNA	"	9.04 (s, 2Ar-H)
		8.88 (s, NH <sub>2</sub> )
TNB	"	9.13 (s, 3Ar-H)
TNN	"	8.80 (s, 4R-H)
TNS	"	9.14 (s, 2Ar-H)
		8.08 (d, Ar-H)
		7.86 (d, 2Ar-H)
		7.68 (m, Ar-H)
		7.54 (d, CH)
		7.09 (d, CH)
TNT	"	8.99 (s, 2Ar-H)
		2.52 (s, CH <sub>3</sub> )
TPT	"	9.23 (s, 6Ar-H)
DMBO-D <sub>6</sub> (neat)		2.48 (m, 2CH <sub>3</sub> )
BENZENE-D <sub>6</sub> (neat)		7.18 (s, 6Ar-H)

- a The solvents used were: benzene C<sub>6</sub>D<sub>6</sub> - 99.5 atom % D; dimethylsulfoxide DMSO-D<sub>6</sub> - 99.5 atom % D. A water peak @ 3.30 (s, 2H) was noted in the DMSO samples.
- b s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, Ar = aromatic, R = ring protons. Chemical shifts are in  $\delta$  units downfield from internal TMS with line multiplicity and relative intensity in parentheses. Spectra were determined on a Varian XL-200 Spectrometer. The pulse sequence was repeated 4 times and the signals time-averaged.
- c The TATB pulse sequence was repeated 5000 times, and the resulting signals time-averaged.

TABLE 5 TLC DATA OF EXPLOSIVE COMPOUNDS

COMPOUND	R <sub>f</sub> <sup>a</sup>	SOLVENT <sup>b</sup>
DATB	0.32	C <sub>6</sub> H <sub>6</sub>
DINA	0.38	"
DIPAM	0.20	"
DNT	0.78	"
DODECA	0.63 <sup>c</sup>	"
HNAB	0.67	"
HNBIB	0.58	"
HNBP	0.76	"
HNS	0.38	"
HMX	0.00	"
HMX	0.00	MeOH
NONA	0.69 <sup>c</sup>	C <sub>6</sub> H <sub>6</sub>
ONT	0.14 <sup>c</sup>	"
PA	0.09 <sup>c</sup>	"
PA	0.96	MeOH
PETN	0.00	C <sub>6</sub> H <sub>6</sub>
PETN	0.00	MeOH
PYX	0.00	C <sub>6</sub> H <sub>6</sub>
PYX	0.96 <sup>c</sup>	MeOH
RDX	0.17	C <sub>6</sub> H <sub>6</sub>
TATB	0.00	"
TATB	0.00	MeOH
TETRYL	0.52	C <sub>6</sub> H <sub>6</sub>
TNA	0.43	"
TNB	0.75	"
TNN	0.00	"
TNN	0.00	MeOH
TNS	0.62	C <sub>6</sub> H <sub>6</sub>
TNT	0.86	"
TPT	0.40	"

a R<sub>f</sub> taken from leading edge of spot. A short wave U V lamp (2537 Å) was used for spot visualization. The adsorbent used was Merck Silica Gel HF-254 coated on glass plates.

b The solvents used were: benzene (C<sub>6</sub>H<sub>6</sub>) and methanol (MeOH).

c Streaking or tailing to origin.

TABLE 6 MELTING POINT DATA OF EXPLOSIVE COMPOUNDS

COMPOUND	MELTING POINT (°C)
DATB	287 <sup>a</sup> , 290 <sup>18</sup> , 286 <sup>19</sup>
DINA	52 <sup>a</sup>
DIPAM	306 dec <sup>a</sup> , 304 <sup>19</sup>
DNT	71.5 <sup>a</sup> , 71 <sup>18</sup>
DODECA	> 425 <sup>a</sup>
HNAB	220-221 <sup>20</sup>
HNBIB	218 <sup>a</sup> , 218-220 <sup>21</sup>
HNBP	239.3-240.8 <sup>a</sup>
HNS-I	318 dec <sup>a</sup>
HNS-II	318 dec <sup>a</sup>
HMX	280 dec <sup>a</sup> , 273 <sup>18</sup>
NONA	440 <sup>19</sup>
ONT	> 400 <sup>7</sup>
PA	121.8-122.4 <sup>a</sup>
PETN	141.3 <sup>20</sup>
PYX	380 <sup>7</sup>
RDX	204 dec <sup>a</sup> , 204 <sup>20</sup>
TATB	> 370 <sup>a</sup> , > 360 <sup>18</sup> , ~ 460 dec <sup>19</sup>
TETRYL	130 Dec <sup>a,18</sup> , 129.5 <sup>20</sup>
TNA	188 <sup>a,20</sup>
TNB	121 <sup>a</sup> , 121.3 <sup>20</sup>
TNN	450 <sup>19</sup>
TNS	180-181 <sup>a</sup>
TNT	80.7 <sup>a</sup> , 80.8 <sup>20</sup>
TPT	352 <sup>7</sup> , 352-353 <sup>19,22</sup> , 349-351 <sup>23</sup>

<sup>a</sup> Melting points determined on a Thomas Hoover Capillary Melting Point Apparatus, using a heating rate of approximately 2°/minute. All measured temperatures are uncorrected.

<sup>18</sup> Headquarters, U.S. Army Material Command, Engineering Design Handbook, AMCP 706-177.

<sup>19</sup> Shipp, K. G., ed., "Properties of Selected Thermally Stable Explosives," NOLTR 70-95, May 1970.

<sup>20</sup> Bennett, ed., Chemical & Technical Dictionary, 3rd ed., (New York, New York: Chemical Publishing Co., Inc., 1974.

<sup>21</sup> Shipp, K. G. and Kaplan, L. A., J. Org. Chem., Vol. 31, 1966, p. 857.

<sup>22</sup> Dacons, J. C. and Sitzmann, M. E., J. Heterocyclic Chem., Vol. 14, 1977, p. 1151.

<sup>23</sup> Dacons, J. C., "2,4,6-Tripicryl-s-Triazine, TPT; Crystallization and Crystal Density Determination," NSWC/WOL/TR 76-16, Mar 1976.

## REFERENCES

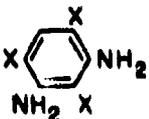
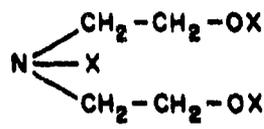
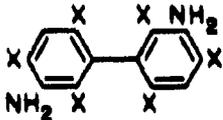
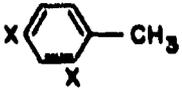
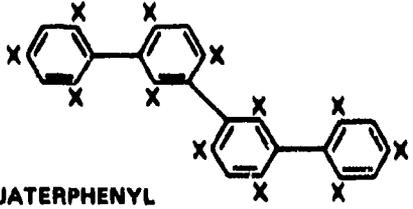
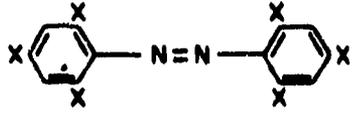
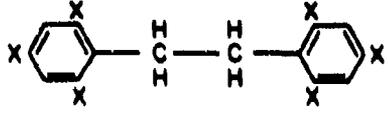
1. Glover, D. J. and Kayser, E. G., Anal. Chem., Vol. 40, 1968, p. 2050.
2. Sawicki, E. and Stanley, T. W., Analyt. Chem. Acta, Vol. 23, 1960, p. 551.
3. Selig, W., "Spectrophotometric Determination of Some Nitro and Nitroso Derivatives of Diphenylamine in N,N-Dimethylformamide," Lawrence Livermore Laboratory (LLL) Report, UCRL-6903, May 1963.
4. Selig, W., "Photometric Determination of 1,3,5-Triamino-2,4,6-Trinitrobenzene (TATB) in Dimethylsulfoxide (DMSO)," Lawrence Livermore Laboratory Report, UCID-17542, July 1977.
5. Ungnade, H. E., "1,3,5-Triamino-2,4,6-Trinitrobenzene (TATB) - Preparation and Purification," Los Alamos National Laboratory (LANL) Report, GMX-2-R-64-1, 1963, pp. 10-11.
6. MacDougall, C. S., "A Liquid Chromatographic-Spectrophotometric Assay for TATB in TATB," in Quarterly Progress Report, Mason & Hanger-Silas Mason Co., Inc., Pantex Plant (MHSMP), MHSMP-77-18, Jan-Mar 1977.
7. Kilmer, E. E., "A Characterization Study of Several Heat Resistant Explosives," NOLTR 74-177 Oct 1974.
8. Kayser, E. G. and Burlinson, N. E., "Analysis of Water and Soil Samples from 'Fate of  $^{14}\text{C}$  Labelled Explosive Compounds in Soil Study," Final Report from the Naval Surface Weapons Center, White Oak, submitted to the U.S. Army Medical Bioengineering R & D Lab. (USAMBRDL), Fort Detrick, Md., MIPR No. 9952, Jan-Dec 1979.
9. Kayser, E. G., "Analysis of 2,2',4,4',6,6'-Hexanitrostilbene (HNS) by High Performance Liquid Chromatography," NSWC/WOL TR 77-154, 14 March 1978.
10. Kayser, E. G., "An Investigation of the Shipp Hexanitrostilbene (HNS) Process," NSWC TR 80-111, 25 Aug 1980.
11. Schaffer, C. L., "HNS Analysis," Mason & Hanger-Silas Mason Co., Inc., Pantex Plant, MHSMP-75-50, Oct-Dec 1974.

REFERENCES (Cont.)

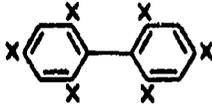
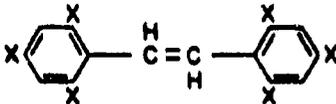
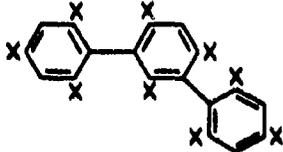
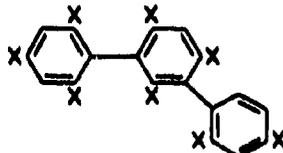
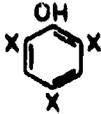
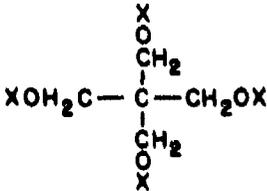
12. Stanford, Jr., T. B., "Determination of Tetryl and 2,3-,2,4-,2,5-,2,6-,3,4-, and 3,5-Dinitrotoluene Using High Performance Liquid Chromatography," Final Report, from Battelle Columbus Laboratories, Columbus, Ohio, submitted to the U.S. Army Research and Development Command, Washington, D.C., Contract No. DAMD-17-74-C-4123, 31 Jan 1977.
13. Schaffer, C. L., "Analysis of TATB by HPLC," Mason & Hanger-Silas Mason Co., Inc., Pantex Plant, MHSMP-78-65, 1978.
14. Krull, I. S. and Camp, M. J., American Laboratory, May 1980, pp. 63-73.
15. Sitzmann, M. E., Foti, S. and Misener, C. C., "Solubilities of High Explosives- Removal of High Explosive Fillers from Munitions by Chemical Dissolution," NOLTR 73-186, 21 Nov 1973.
16. Stull, T. W., "Synthesis of High Purity Hexanitrostilbene," Mason & Hanger-Silas Mason Co., Inc., Pantex Plant, MHSMP-75-37, Sep 1975.
17. Hoffsommer, J. C. and McCullough, J. F., J. Chromatog., Vol. 38, 1968, p.508.
18. Headquarters, U.S. Army Materiel Command, Engineering Design Handbook, AMCP 706-177.
19. Shipp, K. G., ed., "Properties of Selected Thermally Stable Explosives," NOLTR 70-95, May 1970.
20. Bennett, ed., Chemical & Technical Dictionary, 3rd ed., (New York, New York: Chemical Publishing Co., Inc., 1974).
21. Shipp, K. G. and Kaplan, L. A., J. Org. Chem., Vol. 31, 1966, p. 857.
22. Dacons, J. C. and Sitzmann, M. E., J. Heterocyclic Chem., Vol. 14, 1977, p. 1151.
23. Dacons, J. C., "2,4,6-Tripicryl-s-Triazine, TPT; Crystallization and Crystal Density Determination," NSWC/WOL/TR 76-16, Mar 1976.

## GLOSSARY

NOTE: X = NO<sub>2</sub>

COMPOUND	STRUCTURE	CODE
1,3-DIAMINO-2,4,6-TRINITROBENZENE		DATB
DIOXYETHYLNITRAMINE DINITRATE		DINA
DIPICRAMIDE		DIPAM
2,4-DINITROTOLUENE		DNT
2,2',2'',4,4',4'',6,6',6'''.DODECANITROQUATERPHENYL		DODECA
2,2',4,4',6,6'-HEXANITROAZOBENZENE		HNAB
2,2',4,4',6,6'-HEXANITROBIBENZYL, DIPICRYLETHANE		HNBIB

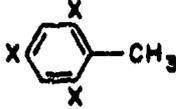
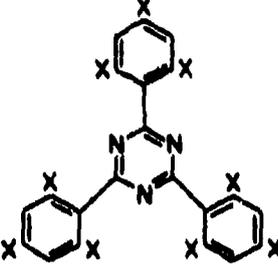
## GLOSSARY

COMPOUND	STRUCTURE	CODE
2,2',4,4',6,6'-HEXANITROBIPHENYL		HNBP
2,2',4,4',6,6'-HEXANITROSTILBENE		HNS
1,3,5,7-TETRANITRO-1,3,5,7-TETRAAZACYCLOOCTANE		HMX
2,2',2'',4,4',4'',5,6',6''-NONANITROTERPHENYL		NONA
2,2',4,4',4'',6,6',6''-OCTANITRO-m-TERPHENYL		ONT
2,4,6-TRINITROPHENOL, PICRIC ACID		PA
PENTAERYTHRITOLTETRANITRATE		PETN

## GLOSSARY

COMPOUND	STRUCTURE	CODE
2,6-BIS(PICRYLAMINO)-3,5-DINITROPYRIDINE		PYX
1,3,5-TRINITRO-1,3,5-TRIAZACYCLOHEXANE CYCLO-1,3,5-TRIMETHYLENE-2,4,6-TRINITRAMINE, CYCLONITE		RDX
1,3,5-TRIAMINO-2,4,6-TRINITROBENZENE		TATB
2,4,6-TRINITROPHENYLMETHYLNITRAMINE		TETRYL
2,4,6-TRINITROANILINE, PICRAMIDE		TNA
1,3,5-TRINITROBENZENE		TNB
1,4,5,8-TETRANITRONAPHTHALENE		TNN
2,4,6,2'-TETRANITROSTILBENE		TNS

## GLOSSARY

COMPOUND	STRUCTURE	CODE
2,4,6-TRINITROTOLUENE		TNT
2,4,6-TRIPICRYL- <i>s</i> -TRIAZINE		TPT

## DISTRIBUTION

	<u>Copies</u>
Lyndon B. Johnson Space Center National Aeronautics & Space Administration Attn: Technical Library T. Graves (EP4) 2101 Webster-Seabrook Road Houston, TX 77058	1 1
George C. Marshall Space Flight Center National Aeronautics & Space Administration Attn: Technical Library Robert White (EP-14) Huntsville, AL 35812	1 1
University of California Lawrence Livermore National Laboratory Attn: Milton Finger Walter Selig P.O. Box 808 Livermore, CA 94550	1 1
Chemtronics Attn: Technical Library Heather Hudson Old Bee Tree Road Swannanoa, NC 28778	1 1
Ensign Bickford Company Attn: B. Boggs 660 Hopmeadow Street Simsbury, CT 06070	1
General Dynamics Attn: W. Early (MZ2843) K. Monroe P.O. Box 748 Fort Worth, TX 76101	1 1

## DISTRIBUTION (Cont.)

	<u>Copies</u>
Grumman Aerospace Corporation Attn: J. Hopkins South Oyster Bay Road Bethpage, NY 11714	1
U.S. Army Aviation Research and Development Command Attn: J. Boen M. L. Baucchio 4300 Goodfellow Boulevard St. Louis, MO 63120	1 1
Teledyne McCormick Selph Attn: R. Richards P.O. Box 6 Hollister, CA 95023	1
Lockheed Missiles & Space Co., Inc. Attn: F. Chapman P.O. Box 504 Sunnyvale, CA 94086	1
Los Alamos National Laboratory Attn: Dr. L. Smith Harry Flaugh P.O. Box 1663 Los Alamos, NM 87544	1 1
McDonnell Douglas Corporation Attn: M. Schimmel P.O. Box 516 St. Louis, MO 62166	1
Commanding Officer U.S. Armament Research & Development Command Attn: T. Castorina W. Fisco Dover, NJ 07801	1 1
Sandia Corporation Attn: Dr. N. Brown P.O. Box 5400 Albuquerque, NM 87115	1
Space Ordnance Systems, Inc. Attn: Dr. N. Zable 375 Santa Trinita Sunnyvale, CA 94006	1

## DISTRIBUTION (Cont.)

	<u>Copies</u>
Langley Research Center National Aeronautics & Space Administration Attn: L. Bement	1
W. Kellier	1
R. Brooks	1
Hampton, VA 23665	
Mason & Hanger-Silas Mason Company, Inc. Pantex Plant Attn: Dr. Clyde Alley	1
Ted Stull	1
P.O. Box 30020 Amarillo, TX 79177	
McDonnell Douglas Astronautics Company Attn: H. W. Fairchild	1
5301 Bolsa Avenue Huntington Beach, California 92647	
Commanding Officer Naval Weapons Support Center Crane, IN 47522	1
Director Strategic Systems Projects Office Attn: M. Baron (SSPO-2731)	1
Department of the Navy Washington, D.C. 20376	
Commander Naval Air Systems Command Attn: AIR-1116	1
Washington, D.C. 20361	
Commanding Officer Ballistics Research Laboratory Attn: Technical Library	1
Aberdeen Proving Ground Aberdeen, MD 21005	
Commanding General Army Materiel Command Department of the Army	1
Washington, D.C. 20316	
Commander Army Rocket and Missile Agency Redstone Arsenal	1
Huntsville, AL 35809	

## DISTRIBUTION (Cont.)

	<u>Copies</u>
Director Defense Technical Information Center Attn: TIPCR Cameron Station Alexandria, VA 22314	12
Commander Systems Engineering Group Attn: RTD Wright-Patterson Air Force Base, OH 45433	1
Chief of Staff U.S. Air Force Attn: AFORD-AR Washington, D.C. 20350	1
Explosive Technology Attn: F. Burkdoll P. Posson P.O. Box KK Fairfield, CA 94533	1 1
Commander Naval Sea Systems Command Attn: SEA-62R32 SEA-64E SEA-99612 (Technical Library) Washington, D.C. 20362	1 1 1
Office of Naval Research Attn: ONR-175 (Technical Library) ONR-473 (R. Miller) 801 N. Quincy Street Arlington, VA 22217	1 1
Chief of Naval Operations Washington, D.C. 20350	1
Commander Naval Weapons Center Attn: Technical Library L. Smith T. Joyner C. Heller China Lake, CA 93555	1 1 1 1
Commanding Officer Naval Ordnance Station Attn: W. Carr Indian Head, MD 20640	1

## DISTRIBUTION (Cont.)

	<u>Copies</u>
Commanding Officer Naval Academy Attn: Hd. Weps Dept Annapolis, MD 21402	1
Superintendent Naval Postgraduate School Monterey, CA 93940	1
Commanding Officer Naval Weapons Station Attn: Technical Library	1
W. McBride	1
S. C. Hogge	1
E. Cousins	1
L. Carlton	1
Yorktown, VA 23491	
Library of Congress Washington, D.C. 20540	4