



## Effect of Water Vapor to Explosives and Their Use for Improvised Explosive Devices \*

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**Abstract.** This report examines the stability of TNT and dinitronaphthalene and their mixtures after their thermal extraction from the shells of artillery munitions by means of water vapor and their use for improvised explosives with high power. The comparison of the baseline explosive mixture with the samples acquired after the water vapor extraction showed no significant differences in their characteristics. Similarly, each of the explosive mixture components (TNT and DNN) after the water vapor extraction, examined separately, did not show significant differences from the original TNT and DNN characteristics.

**Keywords:** explosives, TNT, DNN, munitions, water vapor

### 1. INTRODUCTION

The detection and disposal of improvised explosive devices, unfortunately, will be a serious problem for a long time. Thus the range of most commonly used explosives can be limited to individual compositions or explosive mixtures prepared from readily available commercial components.

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The aim is to obtain high explosives with powerful characteristics, usually stolen from artillery munitions storage or unexploded ordnance. The extraction of explosive substance from the body of the shells is usually made through heated water vapor.

The objective of the report is to explore changes in mixtures of TNT and dinitronaphthalene before and after the extraction with water vapor and to conclude on their suitability for use in improvised explosive devices.

The analysis of mixtures used in different explosives has been the aim of many works. According to a publication on the subject, "*Gas Chromatography Analysis of Nitroaromatics and Nitro – polycyclic Aromatic Hydrocarbons by Capillary Gas Chromatography with the Agilent 6890 Micro*" [1], it is described that 2,4,6-trinitrotoluene (TNT) has a peak with a retention time of 9.2 min; 1,5-dinitronaphthalene (DNN) – 13 min, 1,3-DNN – 14 min, where the three of them were obtained through gas chromatography analysis (GCA). The authors of the article "*Modern Methods and Analysis of Explosives*" [2] summarized the information for different methods of GCA: analysis of isomers of TNT on page 49, application of thermal energy analyzer detector on page 66, application of electron – capture detector on page 76, application of supercritical fluid extraction and capillary high permission liquid chromatography (HPLC) with different detectors on page 140. All these methods were carried out with special equipment and the analysis was very expensive. It is important to point out that the results of the analysis depend on the used analytical method. For example on page 76 of the same book, the retention time of 2,4,6-TNT here is measured as 12.26 min.

This value is different from the value given in the publication [1] – 9.2 min. In certain cases, the explosive samples for analysis must be prepared by means of special methods. For example in the *Handbook of GC/MS: fundamentals and application* [3] three different extraction methods were described: methanol soxhlet (1), methanol flow (2), and with diethyl ether (3). It is interesting, that the level of extraction of DNN and TNT from raw materials with all of these methods were different respectively: 56% and 6% with first method, 80 and 70% with the second and 95 and 85% with the third method. In this way, the accuracy of the analysis depends mainly on the preparation of the samples. In the article „*Determination of mono-, di- and trinitronaphthalenes in soil samples*” [4], T. Bausinger compared layer and gas chromatography with infrared (IR), ultraviolet (UV) and x-ray – phase analysis.

The aim of this work is to find a quicker and cheaper method for the analysis of TD-50 with UV-VIS and FTIR analysis and to mark the most suitable peaks for UV and FTIR quantitative analysis of waste mixtures of water dispersions of this explosive.

## 2. EXPERIMENTAL

Waste water dispersion of explosives, obtained from disposed weapons, which were made in 1983 in Bulgaria, was analyzed. The dry content of the dispersion was determined according to the standard method. The samples for UV-VIS analysis were obtained by the addition of acetone (p.a., products of *Merck*) to the water dispersion through stirring. The clear solutions were obtained and were analyzed with apparatus Cary 100 Scan UV-Vis spectrophotometer, manufactured by *Varian* in Germany. Samples from TNT and TD-50, technical grade, produced in Russia, were measured within an accuracy of 0.0001 g and were dissolved in solvents such as acetone or toluene, products of *Merck* to clear the diluted solutions. Diluted solutions with different concentrations  $C$  (mg/ml) and a respective absorbance  $A$  were made (eq. 1).

$$A = a \cdot C + b \quad (1)$$

The average values of the coefficient „a” and „b” from equation 1 stand for coefficients of correlation  $R$  and  $R^2$  for all maxima in the spectra of the solutions of TNT and TD -50, which were calculated from the obtained results. From the values of the absorbance  $A$  of the solutions of TD-50 and TNT, the values of  $\Delta_1 = A_{TD-50} - A_{TNT}$  for the wavelength ( $\lambda$ ) with maximal values of  $R$  and  $R^2$  of DNN were calculated. In this way, the most suitable maxima for quantitative UV-VIS analysis were determined.

Dry material and pellets of KBr were obtained from the samples of the TNT/DNN mixture after the evaporation of the water. FTIR spectra were made with apparatus Spectrum GX, FT, IR System Perkin Elmer, made in USA. The absorbances  $A$  of the maxima were calculated (eq. 2)

$$A = (\lg 100 - i) / I \quad (2)$$

where  $i$  was the distance between the 100% absorbance and the cross point of the basic line of the analyzed maximum and the perpendicular line passing through the peak;  $I$  was the distance from the perpendicular line passing through the peak to the 0% absorbance. [5]

These maxima values of  $-\text{NO}_2$  groups were compared with the maxima values of  $-\text{CH}_s$  groups like internal standard (i.s) and the values of  $A^* = A/A_{i.s}$  were calculated. The differences  $\Delta_2$  between these values were obtained and in this way the most suitable maxima for quantitative IR analysis was determined.

## 3. RESULTS AND DISCUSSION

The investigated waste water dispersion consists of an amount of explosive TD-50 – mixture of TNT: DNN = 50 : 50 [6]. It is well known, that 2,4,6-TNT (CAS Number 118-96-7) has a melting point of 80.35°C and a boiling point of 295°C.

The melting points of different isomers of DNN (1,2-, 1,3-, 1,4-, 1,5-, 1,6-, 1,7-, 1,8-, 2,3-, 2,6- and 2,7-) are between 145°C and 279°C [7]. According to the article “*Current trends in the detection of peroxide – based explosives*” [8], the determination of non-volatile compounds in the examined material was made by heating them to 105°C. During the heating of the sample of the dispersion, the possibility to lose some amount of the investigated compounds was very small because the temperature is less than the boiling points of TNT and the different isomers of DNN. The result was 0.459 weight % (4.59 mg/ml) of the mixture TNT/DNN. A sample of well mixed (stirring) waste water dispersion was taken and a clear solution was obtained by the addition of acetone, a product of *Merck*. The solution was investigated with UV-VIS apparatus. From the obtained spectrum, it became evident that some of the values of absorption  $A$  were bigger than the value of 4 and in this way it was impossible for quantitative analysis to be applied. Only the values of the wavelength under 220 nm were suitable for quantitative analysis.

In order to assess whether the treatment with water vapor had some influence, the infrared spectra of pure trinitrotoluene model, sample 1 (before treatment) and sample 2 (after treatment), were compared. The results for the main characteristic bands due to vibrations of nitro groups, benzene nucleus and the methyl group, are shown in Table 1:

Table 1. Main characteristic bands (in  $\text{cm}^{-1}$ ) of pure trinitrotoluene, sample 1 and sample 2

oscillations	trinitrotoluene	sample 1	sample 2
$\nu_{NO_2}^s$	1530	1538	1538
$\nu_{NO_2}^{as}$	1352	1351	1352
$\nu_{C-N}$	906	907	907
$\delta_{CNO}$	638	636	637
$\nu_{=C-H}^{Ar}$	several bands most intense in 3094	several bands most intense in 3096	several bands most intense in 3097
$\nu_{C=C}^{Ar}$	1601 and 1615	1604 and 1617	1603 and 1618
$\nu_{CH_3}^s$	2876	2850	2877
$\nu_{CH_3}^{as}$	2951	2955	2955
$\delta_{CH_3}^s$	1379	1380	1384
$\delta_{CH_3}^{as}$	1464	1465	1465

A band at  $1600\text{ cm}^{-1}$ , due to skeletal vibrations of the benzene nucleus is split, which according to research in this scientific field, is evidence that the nucleus is conjugated with some unsaturated bonds.

The other two bands that should be around  $1500$  and  $1450\text{ cm}^{-1}$  overlap with bands of the nitro group and the methyl group. Moreover, in  $1650\text{--}2000\text{ cm}^{-1}$  benzene and its derivatives have a series of overtones and compound frequencies that are more selective to the type of substitution in the core of  $\gamma_{=C-H}^{Ar}$ . The trinitrotoluene has two such bands at  $1810\text{ cm}^{-1}$  and  $1840\text{ cm}^{-1}$  in which a sample is at  $1809\text{ cm}^{-1}$  and  $1844\text{ cm}^{-1}$  and in sample 2 – in  $1811\text{ cm}^{-1}$  and  $1843\text{ cm}^{-1}$ . The absorption in the low frequency spectral area (below  $900\text{ cm}^{-1}$ ) is determined by the interplay between non planar deformation vibrations of the nitro groups ( $\gamma_{NO_2}$ ) and the aromatic C – H-bonds ( $\gamma_{=C-H}^{Ar}$ ) so not used that often to identify the type of substitution in aromatic nitro compounds. Therefore, despite the presence of several intense bands between  $700\text{ cm}^{-1}$  and  $800\text{ cm}^{-1}$ , they were not treated to  $\gamma_{=C-H}^{Ar}$  and were not put in Table 1. Moreover, often in the area  $710\text{--}675\text{ cm}^{-1}$  a band appears due to non-planar deformation vibrations of the core, which further complicates the interpretation of the spectrum in this area.

The comparison shows that the main characteristic bands in sample 1 and sample 2 have the similar values as in the pure trinitrotoluene, indicating that it is present in both samples and that it did not change during heat treatment.

In a similar manner dinitronaphthalene was examined. It is known that the dinitronaphthalene is obtained as a mixture of isomers, the greatest practical importance are the 1.5- and 1.8-isomers. We examined the spectra of 1.5-, 1.8-, 1.3-dinitronaphthalene, the model shown for comparison with the samples and samples 1 and 2 themselves (sample 1 is again the pretreatment with water vapor and sample 2 after treatment). Their spectra comparison results are shown in Table 2.

Condensed aromatic compounds have bands of valence vibrations of relations C–H ( $\nu_{=C-H}^{Ar}$ ) and skeletal vibrations of the nuclei ( $\nu_{C=C}^{Ar}$ ) in the same areas as mononuclear compounds. The most characteristic bands in them are related to non-planar deformation vibrations of the bonds – H ( $\gamma_{=C-H}^{Ar}$ ), located in  $900\text{--}675\text{ cm}^{-1}$ . There is a good correlation between the research results and the literature data, but due to an interaction with non-planar deformation vibrations on trinitrotoluene we will not identify these bands.

Table 2. Main characteristic bands (in  $\text{cm}^{-1}$ ) for dinitronaphthalene, sample 1 and sample 2

oscillations	1.5-	1.8-	1.3-	model	sample 1	sample 2
$\nu_{NO_2}^s$	1520	1524	1537	1515	1538	1538
$\nu_{NO_2}^{as}$	1352	1353	1341	1349	1347	1352
$\nu_{C-N}$	891	958	928	954	938	937
$\nu_{=C-H}^{Ar}$	3102	3094	3090	3082	3096	3097
$\nu_{C=C}^{Ar}$	1605, 1504	1602, 1500	1607, 1509	1599, 1629	1604, 1617	1603, 1618

#### 4. CONCLUSION

The comparison between the water vapor extracted explosive substances and the original ones did not show any significant differences in their properties. We can therefore conclude that the heat treatment in the water vapor extraction of DT-50 and their substances (TNT, DNN) from artillery munitions does not affect their stability. Therefore, it is possible to use those explosives to prepare improvised explosive devices with high power.

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