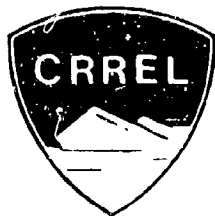


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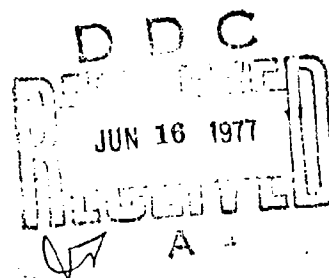
Special Report 77-16

COMPOSITION OF VAPORS EVOLVED FROM MILITARY TNT AS INFLUENCED BY TEMPERATURE, SOLID COMPOSITION, AGE, AND SOURCE

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20. Abstract (cont'd)

✓ for the vapor pressure of TNT, and the partial pressure of DNT was related to its concentration in the solid by a Henry's constant. Age and source of the TNT were found to have little or no influence on these relationships. The reasons for finding a relatively high DNT partial pressure are discussed, as is its implication for TNT detection by trace gas methods.

PREFACE

This report was prepared by D. C. Leggett, and T. F. Jenkins, Research Chemists in the Earth Sciences Branch, Research Division, U. S. Army Cold Regions Research and Engineering Laboratory, and by Dr. R. P. Murrmann, formerly of CRREL and currently Assistant Area Director, Agriculture Research Service, Starkville, Mississippi. The work was sponsored by the U.S. Army Mobility Equipment Research and Development Command under USAMERDC Order No. A5021, Task A5466DAD421, *Mine Detection by Trace Gas Analysis*. The report was technically reviewed by Dr. K. Sterrett, CRREL, and Dr. M. Odell, USAMERDC.

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EFFECTS OF AGE, SOURCE, AND SOLID COMPOSITION
ON VAPORS EVOLVED FROM MILITARY TRINITROTOLUENE

INTRODUCTION

Mine warfare, which was used as early as 1350 A.D. by the Chinese¹¹ remains a mainstay in conventional military tactics and is used by the United States and all of its potential foes. Since it is not anticipated that military tactics will change dramatically in the near future, the U. S. Army needs to update current equipment capable only of detecting metallic mines to the capability of detecting emplaced mines fashioned from a wide range of materials. While many novel detection concepts have been considered to solve this problem, no detector superior to all others has emerged. It now appears that no single device which does not suffer a significant number of false alarms will be found. It seems more likely that future detection systems will be based on two or more concepts whose individual capabilities complement one another, thus increasing reliability of detection.

One of the advanced concepts which has been considered for multi-detector systems is trace gas detection. The trace gas concept relies on the ability to sense vapors emanating above ground from the mine explosive itself or from hardware associated with the emplaced mine. In order to design sensors capable of providing real-time detection, the concentrations of pertinent vapors at the ground level above emplaced mines must be known. Because of the large number of natural and man-made substances which can now be detected in the atmosphere, it might be concluded that the contribution of vapors originating from the mine would be obscured by those emanating from other sources. However, the problem has been overcome using the separating power of gas chromatography, and vapors emanating from emplaced military mines have been detected above ground level, demonstrating the feasibility of the concept^{6, 8, 15}.

While a number of explosive formulations are used in different countries to charge military mines, TNT (trinitrotoluene) is known to be the most universal component. For this reason researchers at CRREL have focused their attention on determining concentrations and characteristics of vapors associated with TNT and TNT-based mines. While 2,4,6 TNT has obviously been considered a likely signature, its concentration in the vapor phase above the solid at ambient temperatures was still not known with certainty^{2, 3, 10, 18}. An earlier study identified both 2,4-dinitrotoluene (2,4 DNT) and 2,4,6 TNT as potentially detectable effluvia of military TNT¹⁴. In particular, 2,4 DNT, which is a minor component in the solid phase, was shown to be a major component of the vapors in equilibrium with the solid¹⁴ and in fact is generally present at concen-

trations exceeding that of 2,4,6 TNT by a factor of 10. This finding has important implications since it identifies 2,4 DNT as a potentially easier signature for detection of military explosives. In addition, the vertical migration of 2,4 DNT through a soil column has been shown to be faster than migration of 2,4,6 TNT¹.

Encouraged by the results obtained to date, we have undertaken to determine the flux rates of DNT/TNT through the surface layer above emplaced mines. It is not clear at this point whether existing pre-concentration techniques and detection devices are adequate for this purpose. However, if direct measurement fails, numerical simulation^{13,16} can be used to predict the concentrations of vapors at the surface above emplaced mines. This approach, however, requires that the concentrations of vapors entering the soil matrix be known as a boundary condition. The study reported here was undertaken with the following objectives in mind:

1. To determine the universality of 2,4 DNT and 2,4,6 TNT as components of vapor emanating from domestic and foreign military explosives, and their concentrations in the emitted vapor at equilibrium.
2. To determine the effects of source, age, temperature and solid composition of the explosives on the equilibrium vapor composition.

MATERIALS AND METHODS

Samples of military explosives were provided by USAMERDC. Their characteristics are given in Table I. The isomeric composition of the solid phase of U. S. military TNT samples was determined by gas chromatography of 0.5 μ l of a chloroform solution containing 20 μ g TNT/ μ l. Chromatographic conditions are shown in Table II. Standard solutions of 2,4,6 TNT and 2,4 DNT were prepared in chloroform from Eastman White Label materials without further purification. Quantitative analyses for DNT and TNT isomers were made by taking the ratio of peak areas of unknowns and standards, respectively, as determined by manual triangulation. The detector responses for 2,4 DNT and 2,4,6, TNT were used to calculate the concentrations of the other DNT and TNT isomers, respectively, as this is generally considered to be an accurate practice in flame-gas chromatography.

Vapor phase analysis was performed on both the foreign and domestic explosives by a headspace technique. Portions of the samples were placed in individual 125-ml hypo vials (Pierce Chemical Co.) stoppered with silicone rubber septa. The solids were allowed to equilibrate in

Table I

Characteristics of U.S. military explosives, 1945-1971.

<u>SAMPLE NO</u>	<u>TYPE</u>	<u>DATE MANUF.</u>	<u>PROCESS</u>	<u>SOURCE</u>
1	Tetrytol, Cast (Composition Tetryl 80% TNT 20%)	1945	Batch, 1-stage mixture	US Mil. Lot KOP 18-35
2	TNT, Cast	1951	Batch, 3-stage nitration	French Mine
3	TNT, Cast	1953	Batch, 3-stage nitration	US Mil. Lot KNK 3-450
4	TNT, Cast	1955	Batch, 3-stage nitration	U.S. Mil. Lot KNK 5-143
5	TNT, Flake, Grade 1	1966	Batch, 3-stage nitration	U.S. Mil. Lot HOL C-263
6	TNT, Crystalline, 1966 Grade 1		Batch, 3-stage nitration	US Mil. Lot BC 3-476
7	TNT, Crystalline, 1971 Grade 1		Batch, 3-stage nitration	US Mil. Lot JOL 2C-957
8	TNT, Crystalline, 1971 Grade 1		Continuous nitration	US Mil. Lot

Table II

Chromatographic conditions for TNT
solid and vapor analyses.

	<u>Solids</u>	<u>Vapors</u>
column	1.8 m (1/8 in. o.d.) stainless steel, 10% Dexsil 300GC on 100-120 mesh Anakrom ABS (Analabs, Inc.)	
carrier gas	helium	nitrogen*
flow-rate	50 ml/min	40-60 ml/min
temperature column	200°C for 16 min, then programmed to 250° at 4°/min	190°C
injector	225°C	225°C
manifold	230°C	230°C
detector	190°C	190°C
detector	flame ionization	tritium source electron capture pulsed with 50 V at 100 usec intervals

*pre-scrubbed with ascarite, Oxy-trap (Analabs, Inc.) and Linde 5-A
molecular sieve at -90°C

the closed vials at the desired temperature for a period of at least 2 weeks. Preliminary experiments to determine the length of time required for equilibration have been described in a previous report⁴. For temperatures other than room temperature, a water bath controlled to $\pm 0.5^{\circ}\text{C}$ (Forma Scientific Co.) was used to maintain the sample temperatures. Bath temperatures were determined by three mercury thermometers, which agreed to better than $\pm 0.5^{\circ}\text{C}$. Samples of equilibrium vapor (0.5-2.5 ml) were withdrawn from the vials with gas-tight syringes (Hamilton Co., Inc.) and injected into a gas-chromatograph. Chromatographic conditions for vapor analysis are shown in Table II.

Particular attention was paid to the method of sampling TNT vapors with gas-tight syringes. In the first approach, the syringe was filled several times with the equilibrium vapor and the vapor expelled in an effort to circumvent any adsorption to the syringe parts, which would lead to erroneously low concentrations in the vapor. Erratic, and what appeared to be erroneously high, results were in fact obtained by this technique. This led to the finding that the syringe needle rather efficiently sorbed both TNT and DNT isomers from the vapor phase. This explained the erroneously high values which were reported earlier (Leggett et al., Progress Report to MERDC, June 1972, unpublished). For the vapor composition reported in this study it was found that all the DNT and TNT components were essentially 100% adsorbed by the stainless steel needle; thus in the final method no consideration needed to be given to adsorption on the glass barrel. This simplified matters and the body of the syringe was then just a convenient metering device which had no chance of interacting with the sample components. Also, the components were completely desorbed from the needle during injection of the syringe contents into the hot (200°C) injection port of the gas chromatograph. No decomposition of 2,4,6 TNT was observed at these temperatures in the inert nitrogen carrier gas, which confirmed the observation of others⁵.

In the technique finally adopted for this work, the syringe was filled slowly (ca. 0.25 ml/s) with the equilibrated vapor and the outside of the needle wiped with a tissue lightly wetted with acetone before injection into the chromatograph. This eliminated any vapors sorbed to the outside of the needle during sampling. Also for sample volumes of less than 2 ml, the syringe was filled (2.5 ml) with lab air to ensure adequate flushing of the needle during injection into the chromatograph.

Chromatographic peaks were qualitatively identified as in our previous study⁴ by their relative retention times compared to known reference materials. The identities of chromatographic peaks determined on the Dexsil analytical column were confirmed on both DC 200 and OV-17. In addition, 2,4 DNT and 2,4,6 TNT were confirmed on Carbowax 400.

Retention times of DNT and TNT isomers relative to 2,4,6 TNT on the Dexsil analytical column are presented in Table III. Reference standards for 2,4 DNT were prepared from Eastman White Label material without further purification. For 2,4,6 TNT a recrystallized military sample was used (US mil. lot BC 3-476, purified in 1970 at Picatinny Arsenal). This material was the most chromatographically pure available, showing no significant peaks in chromatograms obtained using either a flame ionization or electron capture detector. Standards in the range of 10^{-9} to 10^{-12} g/ul were prepared by dilution in benzene (Nanograde, Mallinckrodt), which was chromatographically free of interfering impurities. From 0.5-3 ul of these solutions was injected into the chromatograph. The working range was generally between 0.01 and 0.3 ng as larger quantities were outside the linear range of the detector. An appropriate quantity of standard was generally injected before and after each vapor injection, and the average detector response factor was used for quantitation purposes. Peak areas were measured manually by triangulation. This was found to be a highly reproducible technique, the variability between successive measurements being $< 2\%$. The detector response factor was expressed in units of mm^2/s determined by multiplying the peak area by the amplifier attenuation factor. The ratio of the sample response (peak area x attenuation factor) to the detector response factor gave the quantity per injection in grams. The following expression of the ideal gas law was then used to calculate partial pressures, p_a , of the components of interest:

$$p_a = \frac{mRT}{MV}$$

where m is the mass per injection determined as above M the molecular weight, V the volume injected in liters, T the absolute temperature of the sample in kelvins, and R the molar gas constant. For calculation of p in torrs (millimeters of mercury) $R = 62.36$ liter-torr/mole K. Some sample chromatograms are shown in Figure 1. Detection limits using this technique were generally on the order of 10^{-14} g for both 2,4,6 TNT and 2,4 DNT.

RESULTS AND DISCUSSION

I. Composition of Military TNT Vapors.

A. General Observations

The results of the solid phase analysis of the eight U. S. military TNT samples used in this study are shown in Table IV. Unknowns 1 and 2 in this table appear to be identical to the ones detected in the vapor (Table III). Unknowns 3, 4, and 5 had longer retention times than the 2,3,6 isomer of TNT and were not detected in the vapors. Note that

Table III

Relative retention times for components
observed in vapor analyses

<u>Peak No.</u>	<u>Component</u>	<u>Relative Retention*</u>
1	2,6 DNT	0.35
2	Unknown #1	0.41
3	2,5 DNT	0.44
4	Unknown #2	0.49
5	2,4 DNT	0.58
6	2,3 + 3,5 DNT	0.64
7	3,4 DNT	0.86
8	2,4,6 TNT	1.00
9	2,3,6 TNT	1.11

*Relative to 2,4,6 TNT on a 6-ft x 1/8-in. column containing 10% Dexsil 300GC on Anakrom ABS operated at 190°C and at a flow rate of 50 ml/min of nitrogen.

Table IV

Concentration¹ of DNT and TNT isomeric impurities in solid production grade military TNT.

Compound	Sample							
	<u>1²</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>
2, 4, 5 TNT	0.010	0.422	0.014	0.008	0.012	0.033	0.014	0.033
2, 3, 4 TNT	0.028	0.543	0.143	0.207	0.154	0.254	0.122	0.176
2, 6 DNT	t ³	0.002	n.d.	n.d.	n.d.	0.002	n.d.	0.004
2, 5 DNT	n.d. ⁴	0.001	0.004	0.004	t	0.006	0.003	0.004
2, 4 DNT	0.022	0.099	0.083	0.088	0.061	0.089	0.064	0.110
2, 3 and 3, 5 DNT ⁵	t	0.002	0.016	0.020	0.013	0.030	0.018	0.029
3, 4 DNT	n.d.	t	t	t	t	0.002	t	t
unknown 1 ⁶	0.002	0.002	0.007	0.004	0.002	0.080	0.001	t
unknown 2 ⁶	0.043	0.009	0.009	0.011	0.018	0.031	0.018	0.031
unknown 3 ⁷	0.025	0.242	0.108	0.144	0.079	0.129	0.085	0.092
unknown 4 ⁷	0.036	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
unknown 5 ⁷	<u>0.073</u>	<u>0.269</u>	<u>0.297</u>	<u>0.348</u>	<u>0.302</u>	<u>0.358</u>	<u>0.278</u>	<u>0.288</u>
Total	0.239	1.591	0.681	0.834	0.641	1.014	0.603	0.734

¹In percent by weight; average of 2 determinations²Tetrytol (19.4% TNT)³t - trace⁴n.d. = not detected⁵Isomers not well resolved but appear to be mostly 3, 5 DNT⁶Calculated as DNT⁷Calculated as DNT

the significant vapor components elute from the chromatographic column before 2,4,6 TNT (Fig. 1). This is expected, as vapor pressure is roughly related to chromatographic retention time as:

$$\log \frac{P_1}{P_2} = \frac{R_2}{R_1}$$

where P_1 and P_2 represent the vapor pressures of two components and R_1 and R_2 their respective retention times when polarity effects are minimized, in this case by use of a nonpolar column. Of particular interest is the 2,4 isomer of DNT which appears always to be an impurity associated with the manufacture of military TNT and is the most abundant component eluting before 2,4,6 TNT in the chromatograms. This is quite evident in the vapor analyses shown in Tables V-VIII. The partial pressure of 2,4 DNT often exceeds that of TNT by an order of magnitude (i.e. it is 10 times more abundant in the vapor). The other DNT isomers were also often more abundant in the vapor than the TNT species. The 3,4 isomer was not determined at any of these temperatures but was found to be an insignificant vapor component in all of these samples.

B. Foreign Explosives

In addition to the domestic TNT samples, a number of explosives of foreign manufacture were analyzed. In this work the vapors were analyzed at only one temperature, since the main interest was in qualitative comparison with domestic samples to see if the signatures were significantly different. The analyses are presented in Table IX, and typical chromatograms in Figure 2. The vapor analyses are qualitatively similar, although the relative concentrations of the various components differ somewhat between U. S. and foreign and among foreign samples. The two unknowns tend to be higher in the foreign samples. These differences are probably due to impurities in the starting material (dinitroxylenes are one possibility)¹ and/or to different processes used by the foreign manufacturers. Again 2,4 DNT is the major vapor phase component in most cases. The reason it was not detected in one of the samples (VC) and barely detectable in two others is not clear. It is conceivable that these samples underwent some additional treatment since their manufacture which caused the 2,4 DNT to be lost.

II. Effect of solid phase impurities on composition of the vapor above military TNT samples.

A. Evaluation of vapor composition in terms of Raoult's and Henry's laws.

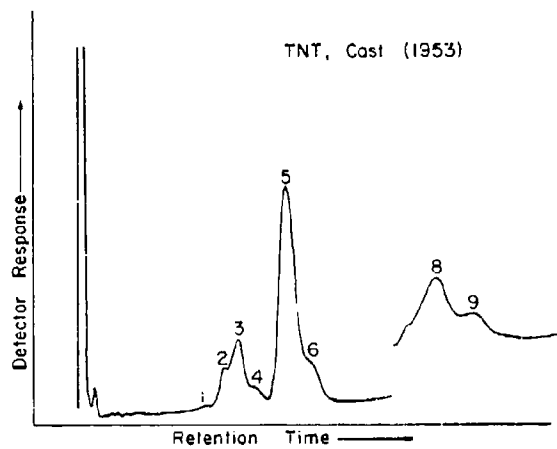
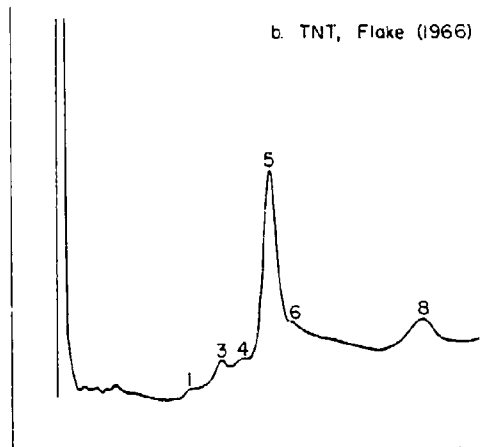
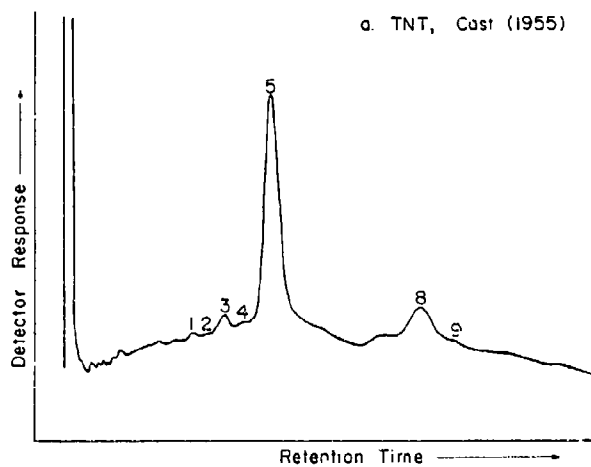


FIGURE 1. Typical chromatograms of domestic explosive headspace vapors.

Table V

Analysis of headspace vapors at 2°C
partial pressure (torr x 10⁶).

<u>Sample</u>	<u>Component</u>					
	<u>2, 6</u>	<u>2, 5</u>	<u>2, 4</u>	<u>2, 3 + 3, 5</u>	<u>3, 4</u>	<u>2, 4, 6</u>
1	n.d.	0.13	1.07	0.18	n.a.	0.07
2	0.09	0.28	3.28	0.37	n.a.	0.09
3	n.d.	0.70	3.40	0.58	n.a.	0.11
4	n.d.	0.26	3.28	0.57	n.a.	0.12
5	0.09	0.10	1.52	0.09	n.a.	0.08
6	0.26	n.a.	1.94	0.46	n.a.	0.22
7	n.d.	0.84	3.91	0.70	n.a.	0.07
8	0.15	0.57	5.05	0.68	n.a.	0.07

n.d. not detected n.a. no analysis

Table VI

Analysis of headspace vapors at 12°C
partial pressure (torr x 10⁶)

<u>Sample</u>	<u>Component</u>					
	<u>2, 6</u>	<u>2, 5</u>	<u>2, 4</u>	<u>2, 3 + 3, 5</u>	<u>3, 4</u>	<u>2, 4, 6</u>
1	n.d.	0.15	3.16	0.53	n.a.	0.24
2	0.17	0.47	12.5	1.46	n.a.	0.18
3	n.d.	1.36	12.5	2.09	n.a.	0.34
4	n.d.	0.47	13.6	2.09	n.a.	0.31
5	n.d.	n.d.	3.24	0.61	n.a.	0.19
6	0.41	5.32	6.68	1.15	n.a.	0.41
7	n.d.	1.67	13.6	2.92	n.a.	0.35
8	0.38	1.04	14.6	2.09	n.a.	0.14

Table VII

Analysis of headspace vapors at 20°C
partial pressure (torr x 10⁶)

<u>Sample</u>	<u>Component</u>					
	<u>2, 6</u>	<u>2, 5</u>	<u>2, 4</u>	<u>2, 3 + 3, 5</u>	<u>3, 4</u>	<u>2, 4, 6</u>
1	0.08	0.88	5.75	0.49	n.a.	0.87
2	0.70	1.61	33.3	n.d.	n.a.	1.28
3	0.13	4.74	24.2	3.36	n.a.	1.47
4	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
5	n.d.	0.54	6.31	0.70	n.a.	1.52
6	0.43	2.86	16.9	2.79	n.a.	0.93
7	n.d.	4.80	21.8	4.24	n.a.	1.26
8	2.44	5.83	32.5	7.29	n.a.	1.03

Table VIII

Analysis of headspace vapors at 32°C
partial pressure (torr x 10⁶)

<u>Sample</u>	<u>Component</u>					
	<u>2, 6</u>	<u>2, 5</u>	<u>2, 4</u>	<u>2, 3 + 3, 5</u>	<u>3, 4</u>	<u>2, 4, 6</u>
1	0.10	1.79	22.5	2.96	n.a.	10.9
2	1.44	2.86	71.4	4.43	n.a.	6.97
3	0.02	10.7	103.5	6.50	n.a.	7.57
4	0.02	3.38	99.2	4.19	n.a.	7.46
5	0.37	2.75	31.8	3.49	n.a.	10.4
6	2.74	n.a.	38.2	6.09	n.a.	16.3
7	0.02	7.40	61.6	7.64	n.a.	6.07
8	4.09	10.05	121.4	6.26	n.a.	9.31

Table 10

Comparison of domestic and foreign TNT explosive
headspace vapors at 22°C (1).

Sample Description	2,6 DNT	Unknown 1 (3)	2,5 TNT	Partial Pressure (P) of Vapor Component (%)		2,4 DNT	2,5 + 4,5 DNT	3,4 DNT	2,4,6 TNT	2,3,6 DNT
				Unknown 2	2,5 TNT					
US38 130 mm	2.9	25	b	13	17	t	t	a	1.8	t
Bulgarian 100 mm	2.0	49	c	26	27	t	t	t	1.6	t
USSR 100 mm	1.5	18	b	13	11	t	t	t	1.6	t
Poland 120 mm	0.5	10	c	1.9	13	t	t	t	1.5	t
Hungary Grenade	1.7	15	c	15	24	t	t	t	1.9	t
Czech 82 mm	0.8	b	11	2.1	22	t	t	t	2.0	t
China 100 mm	1.3	20	c	12	31	t	t	a	1.9	t
USSR 122 mm	1.5	c	17	8.9	28	c	c	t	1.9	t
VC (Vietnamese)	a	a	a	b	a	b	b	a	1.3	b
NGA 50	a	a	a	c	t	b	b	a	3.2	b
TNT + A	t	a	t	b	2.8	t	t	a	1.1	b
TNT + 50% A, China	4.9	t	9.2	t	56	b	b	a	1.9	1.1
TNT + Tetrayl	a	a	a	t	t	b	b	a	1.5	b
TNT Russian	a	a	a	1.6	1.1	b	b	a	1.5	0.4
1951, 1 Stage, Batch, French	0.4	1.2	a	0.5	22	b	b	b	1.7	0.3
1915, 1 Stage, Batch, Tetrayl (4)	0.1	1.3	0.3	0.6	5.8	0.7	0.7	b	1.3	t
1952, 3 Stage, Batch, Cust	a	2.4	2.1	0.8	20	2.6	2.6	0.2	2.0	t
1955, 3 Stage, Batch, Cust	0.1	t	0.3	t	13	0.9	0.9	b	1.3	t
1946, 3 Stage, Batch, Flake	t	a	0.2	t	5.9	0.6	0.6	b	1.3	a
1966, 3 Stage, Batch, Crystal	b	10	b	4.8	20	3.6	3.6	b	1.4	t
1971, 3 Stage, Batch, Crystal	t	a	0.6	a	7.7	1.1	1.1	b	1.1	t
1971, 3 Stage, Continuous, Crystal	0.3	t	2.9	a	30	3.6	3.6	0.4	1.9	t

(1) Temperature variability $\pm 1.0^\circ\text{C}$

(2) Expressed in : mm^3/h^3

(3) Calculated as 2, 4 DNT

(4) Mixture of 20% TNT and 80% Tetrayl

a None detected

b Not determined

c Detected but unable to quantitate due to poor separation of unknown #1 and 2, 5 TNT

t Traces detected

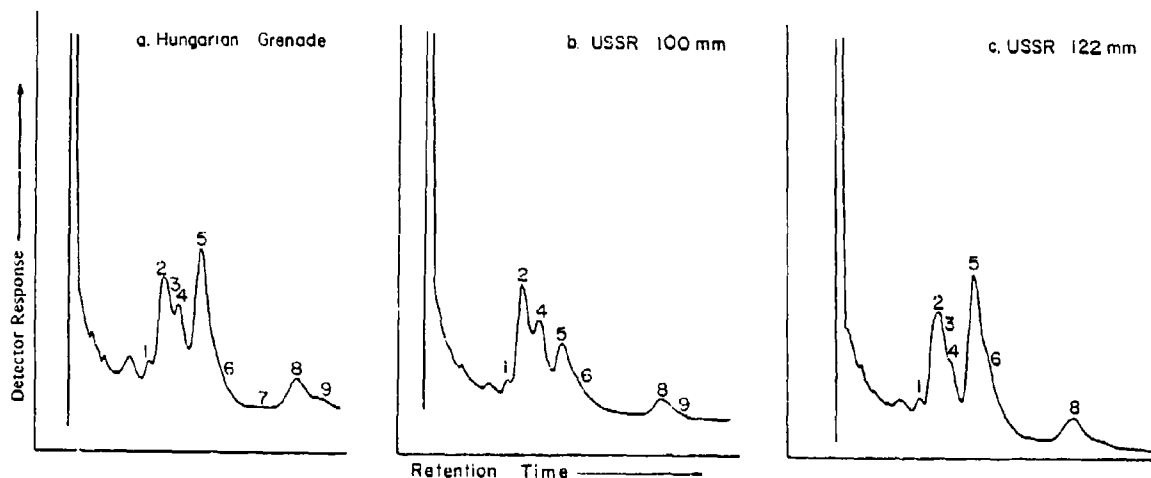


FIGURE 2. Typical chromatograms of foreign TNT headspace vapors (peak numbers refer to Table III).

As would be expected, the presence of more-volatile impurities in the solid phase of TNT greatly influences the composition of the emitted vapors. Impurities ideally exhibit behavior in the gas phase which is related to the amount of impurity present in the solid. In the simplest case this relationship is given by Raoult's law: $p_a = p_a^\circ X_a$ where p_a° is the vapor pressure of the pure substance (e.g. 2,4 DNT) and X_a is the mole fraction of the substance in solution (in this case TNT). Raoult's law is the limiting law relating the behavior of ideal solutions. In reality there are very few cases where Raoult's law is followed, as ideality in solution implies: 1) complete uniformity of cohesive forces on the solute molecules over the entire concentration range, and 2) independence of these forces from solute-solvent interactions, a condition which is seldom if ever met even at extreme dilution. Henry's law is an empirical relation describing the behavior of solutions in which the second condition has been removed. This relation can be expressed as $p_a = K_a X_a$ where the constant of proportionality K_a is no longer the vapor pressure of the pure solute but an empirical constant. This law *does* hold for all solutions at extreme dilution, as the condition of uniformity of chemical environment is met even though it is not the same as in the pure solute.

For the moment, if we consider TNT to be an ideal solid solution, the partial pressures of the various impurities over solid TNT at equilibrium should be given by $p^0 X_a$. Thus, all that is needed to calculate the equilibrium vapor composition is a knowledge of the vapor pressures of the individual impurities and their concentrations in the solid phase. To test Raoult's law for TNT it was necessary to know the vapor pressures of the various impurities of interest. These include the various isomers of dinitrotoluene (DNT), particularly the 2,4 DNT isomer, as it was found to be the principal component in the vapors detected by electron capture gas chromatography*.

A review of the literature revealed that the vapor pressure of 2,4 DNT is not known with any certainty^{2,10}, making a test of Raoult's law impossible. In fact, experimental data in the ambient temperature range have not been reported. Extrapolation of data obtained at higher temperatures yielded values of from 1.2×10^{-5} torr (ref. 10) to 1.6×10^{-2} torr (ref. 2) at 20°C. After an error was discovered in reference 10, the data were recalculated yielding a value of 1.2×10^{-4} torr. Since the discrepancy between the two published data sets was still large, the vapor pressure of 2,4 DNT was determined experimentally according to the methods reported here, yielding a value of 2×10^{-4} torr at 20°C. This value agrees well with the recalculated data of reference 10 and chromatographic retention data; thus it was accepted for evaluation purposes. The ratios of p_0/X_a for the eight military TNT samples were calculated from the electron capture chromatographic analyses of the headspace vapors for 2,4 DNT at 20°C (Table VII) and the solids analysis (Table IV). This ratio is the Henry's constant of proportionality K_a at 20°C, which under the condition of ideality described earlier would be equal to the vapor pressure of 2,4 DNT. Although individual values varied, most fell between 2×10^{-2} and 3×10^{-2} (Table XII). The average value for the Henry's constant was 2.09×10^{-2} , two orders of magnitude greater than the vapor pressure of pure 2,4 DNT at 20°C. Thus the actual partial pressure of 2,4 DNT in equilibrium with solid TNT was found to be 100 times higher than that predicted by Raoult's law for ideal solutions. Whether this is due to matrix interactions or lack of true solution is not known at this time.

Volatile impurities in military grade TNT other than 2,4 DNT have been detected in all the equilibrium headspace vapors tested, namely the other isomers of DNT: 2,5; 2,6; and 2,3 + 3,5. The partial pressures of these impurities were always found to be lower than that of the 2,4 isomer (Fig. 5-8). Nor were significant amounts of mono-nitro toluenes detected in the headspace vapors, a result which is in agreement with

* Since electron capture gas chromatography responds specifically to the nitro-containing compounds in the TNT samples, the presence of undetermined impurities was not entirely ruled out; however, significant amounts of other volatile impurities have not been detected using a flame ionization detector¹⁴ or mass spectrometer¹⁵.

previous investigations by us and others^{1,5,14}. Several non-nitro compounds have been reported¹; however, these have not been shown to be characteristic of all TNT samples, whereas some 2,4 DNT is always found. Isomers of TNT other than 2,4,6, which are also found as impurities in the solid TNT samples, are insignificant components of the vapors. This is reasonable in view of their lower vapor pressures (i.e. longer gas chromatographic retention times).

B. Effect of Solid Phase Impurities on the Vapor Pressure of TNT

The concentration of 2,4,6 TNT in the equilibrium headspace vapor is ideally equal to its vapor pressure. To see if the presence of impurities has an effect on the actual value of the equilibrium pressure above solid military grade TNT, the measured partial pressures of 2,4,6 TNT above the military TNT samples were compared with the vapor pressure of pure 2,4,6 TNT. Again there were no actual data at ambient temperatures for the vapor pressure of TNT. Therefore the equilibrium concentration was determined experimentally at 20.0°C using the gas chromatographic headspace technique and converted to partial pressure using the ideal gas law. The results of nine determinations using purified TNT (Eastman Kodak, lot no. 268 and Military lot BC 3-476, recrystallized) were compared with single analyses of seven military production samples. As shown in Table X the military grade averaged slightly higher, although the difference does not appear to be significant. Thus the concentration of TNT in equilibrium headspace vapor at this temperature was relatively unaffected by the presence of impurities normally found.

Table X. Vapor Pressure of TNT at 20°C.

<u>Sample description</u>	<u>No. detns.</u>	<u>Pressure (torr x 10⁶)</u>	
		<u>Mean</u>	<u>s.d.*</u>
Eastman Kodak	4	1.02	0.12
Recrystallized military	5	1.04	0.19
Military production grade	7	1.20	0.26
Overall	16	1.10	0.22

*Standard deviation

III. Effect of Temperature on Composition of the Vapor Above Military TNT Samples

A. Vapor Pressure of TNT

The concentration of vapors above a solid at any temperature is simply the sum of the partial pressures of the individual components

that are present. In the case of military TNT samples, the TNT component of the total pressure is equal to its vapor pressure as discussed previously. To resolve the disagreement among several investigations of the vapor pressure of TNT^{3,9,10,18} and to obtain reliable data for the vapor pressure at ambient temperatures, experimental measurements were made in the range of 12-40°C using the equilibrium headspace technique. These data are presented in Table XI and plotted in Figure 2 along with the data in the range of 23-63°C of from other investigators. Fairly good agreement exists between the data of Edwards, those of Lenchitz and Velicky* and those presented here, the curve representing these three sets of data. The data of Wood appear to be high, possibly due to sample purification problems, and the one point given by Dravnieks and cited in reference 9 is low. Plots of this type are expected to be nonlinear, due to the change in heat of sublimation ΔH_s with temperature^{2,14}. However, it is customary to apply the Clausius-Clapeyron equation over short temperature ranges; that is: $\ln p = -\Delta H_s/RT + B$, which is the equation of a straight line. Inspection of the data (Fig. 3) shows that the points between 12° and 30°C lie nearly in a straight line of the form $\log p = A/T + B$, the least squares equation of best fit over this range being $\log p = -7371.46/T + 19.2533$.

Table XI. Vapor pressure of 2,4,6 TNT vs temperature.

<u>T(°C)</u>	<u>No. of Detns.</u>	<u>Mean</u>	<u>p(torr x 10⁶)</u>	
			<u>s.d.^a</u>	<u>l.s.^b</u>
12.0	9	0.27	0.09	0.252
20.0	16	1.10	0.22	1.28
21.5	14	1.72	0.42	1.72
25.5	4	3.98	0.19	3.75
30.0	13	8.82	0.29	8.61
40.0	13	42.4	3.10	

^aStandard deviation

^bLinear least squares fit of $\log p$ vs $1/T(K)$ for mean values

Solving for ΔH_s gives a value of 33.7 kcal/mole in this temperature range, and a value of 1.28×10^{-6} torr for the vapor pressure of TNT at 20.0°C, which is in excellent agreement with the value of 1.27×10^{-6} torr given by Coates et al.² from a nonlinear least squares fit and extrapolation of Edwards data³.

* The data of reference 10 have been corrected for some minor discrepancies which were discovered.

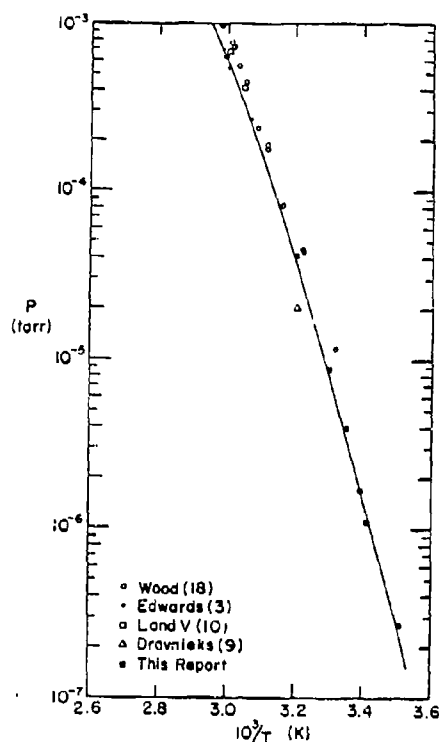


FIGURE 3. Vapor pressure of TNT.

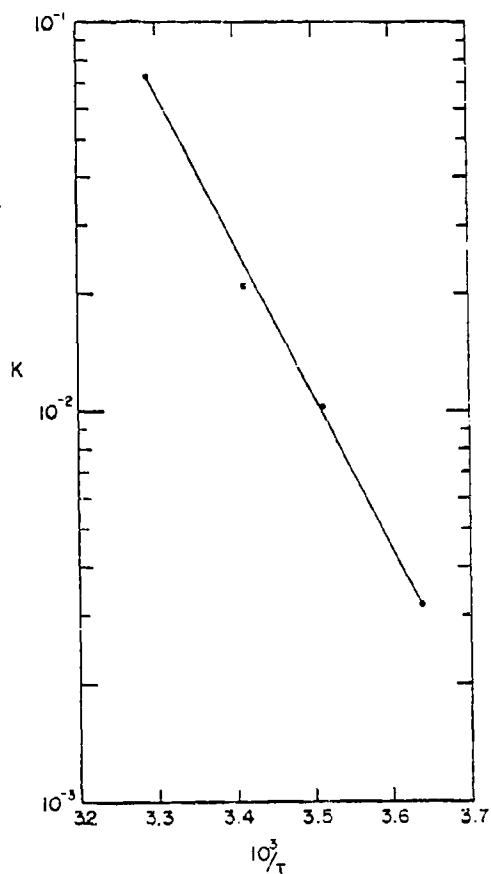
It was indicated in the previous section that the vapor pressure of 2,4,6 TNT did not appear to be affected by the presence of the more volatile impurities normally found in military grade TNT. This is a major advantage of the headspace method over effusion methods, which measure total weight loss through a small aperture as a function of time. The disagreement among previous determinations of the vapor pressure of solid TNT using effusion methods^{3,9,10,18} is probably due to: 1) difficulty in obtaining pure material, 2) failure to maintain equilibrium, and/or 3) surface diffusion effects¹⁷. All these effects are overcome in the headspace method, as volatile impurities are chromatographically separated from the substance of interest and the sample can be allowed to equilibrate for as long as is necessary prior to analysis. In addition the method is more sensitive and requires rather simple experimental apparatus available in most modern laboratories.

B. Partial Pressure of 2,4 DNT

If the logarithm of Henry's constant for 2,4 DNT is plotted against $1/T$, a curve analogous to the vapor pressure curve is obtained. ($K_a = p_a/X_a$,

where p_a is the observed partial pressure of 2,4 DNT in the headspace and X_a the mole fraction of 2,4 DNT in solid TNT.) The data for the eight military TNT samples are presented in Table XII. The mean values were used in a plot of $\log K_a$ vs $1/T$ in order to cancel the effects of other variables, which will be discussed separately. As shown in Figure 4, a good linear fit was obtained. The equation for the best fit determined by least squares analysis of the data is $\log K_a = -3749.91/T + 11.1397$.

Since $K_a = p_a/X_a$, the partial pressure p_a of 2,4 DNT above TNT for any sample can be calculated by $\log p_a = -3749.91/T + 11.1397 + \log X_a$ where X_a is the mole fraction of DNT in TNT determined from analysis of the solid. As shown in Table XIII the agreement between predicted and experimental values is quite good. As an example consider the partial pressure of 2,4 DNT above TNT containing 0.1-mole-% 2,4 DNT. At 20°C the equilibrium vapor concentration would be 2.2×10^{-5} torrs or nearly 20 times higher than the vapor pressure of 2,4,6 TNT in the same sample.



The heats of sublimation of 2,4 DNT from the 8 U.S. military TNT's were calculated from the slope of $\log K_a$ vs $1/T$ (Table XIV). The average value was found to be 17.1 kcal/mole which is less than the value of 24 kcal/mole reported for pure 2,4 DNT¹⁰. This is indicative of a lower energy required to volatilize 2,4 DNT from the TNT matrix compared to the pure substance. The data thus seem to suggest the existence of weaker intermolecular forces in the TNT matrix than in pure 2,4 DNT.

FIGURE 4. Henry's constant vs $1/T$ for 2,4 DNT in solid TNT.

Table XII.

Partial pressure of 2,4 DNT and
Henry's constant K_a for military TNT.

Sample No.	2°C		12°C		20°C		32°C	
	$p_a (x10^5)$	$K_a (x10^2)$	$p_a (x10^5)$	$K_a (x10^2)$	$p_a (x10^5)$	$K_a (x10^2)$	$p_a (x10^5)$	$K_a (x10^2)$
1	.11	.40	.30	1.10	.58	2.12	2.25	8.21
2	.33	.27	1.25	1.01	3.33	2.70	7.14	5.78
3	.34	.33	1.25	1.21	2.42	2.34	10.34	9.99
4	.33	.30	1.36	1.24	a	-	9.92	9.05
5	.15	.20	.32	.42	.63	.83	3.18	4.20
6	.20	.18	.67	.60	1.68	1.51	3.82	3.44
7	.39	.49	1.36	1.70	2.18	2.73	6.17	7.71
8	.51	.37	1.46	1.06	3.26	2.38	12.14	8.85
Mean	.295	.32	0.996	1.04	2.01	2.09	6.87	7.23
by least squares ^b		.33		0.97		2.23		7.12

^a-inadvertently not determined

^b $\log K_a = \frac{A}{T} + B$ where A and B are constants

Table XIII. Predicted vs experimental values for partial pressure of 2,4 DNT above solid TNT at 20°C.

No.	p_a (torr $\times 10^5$)	
	Predicted	Experimental
1	.61	.58
2	2.75	3.33
3	2.31	2.42
4	2.41	a
5	1.69	.63
6	2.47	1.69
7	1.78	2.18
8	3.06	3.27

^anot determined

C. The Partial Pressure of Other Impurities

The equilibrium concentration of 2,4,6 TNT above military explosives can be predicted from its vapor pressure curve. In the majority of cases and in all the U.S. TNT samples, the major contributor to the equilibrium vapor concentration was 2,4 DNT (Table IX). However, in several foreign samples the concentrations of unknown electron capturing components exceeded the 2,4 DNT concentrations. It would be useful to identify these components; however, they were not prevalent in U.S. TNT and were not as frequently detected as 2,4 DNT.

Table XIV. Henry's constants and heats of sublimation of 2,4 DNT in military TNT samples at 20°C.

Sample No.	K_a^*	ΔH_s^*
1	2.44	16.6
2	2.14	17.2
3	2.69	18.6
4	2.67	18.7
5	1.08	16.7
6	1.27	16.5
7	2.89	14.9
8	2.51	17.6
avg.	2.22	17.1

*calculated from least squares analysis of $\log K_a$ vs $1/T$.

IV. Effect of Source and Method of Manufacture

As discussed earlier the partial pressure of 2,4 DNT above military TNT samples at 20°C is higher than that predicted by Raoult's law for ideal solutions by approximately two orders of magnitude (2×10^{-5} vs 2×10^{-7} torr). The measured vapor pressure of 2,4 DNT at 20°C was 2×10^{-4} torr, a difference of one order of magnitude, indicating that the system behaves more like a mixture of DNT in TNT; i.e. each component exhibits a partial pressure equal to its own vapor pressure. The degree to which TNT behaves like a solution thus determines what the vapor composition at equilibrium will be. It seems likely that such factors as rate of crystallization from the melt and final form (crystalline structure, etc.) resulting from the manufacturing process would determine the vapor equilibria and sublimation kinetics. Other matrix effects such as aging (date of manufacture) might also be expected to affect the final equilibrium concentrations of impurities due to their preferential depletion or enrichment at the surface.

However, the high Henry's constant for 2,4 DNT in TNT compared to its vapor pressure (i.e. 2×10^{-2} vs 2×10^{-4}) argues against surface depletion on aging, as that would lead to the opposite effect. The data presented in Table XII support the contention that age has no effect on the equilibrium partial pressure of 2,4 DNT above military TNT based on these eight samples, since there is no discernible trend in K values with date of manufacture. In this regard, data on the sublimation kinetics of impurities would be useful. These factors were beyond the scope of this work; however, earlier work in this laboratory¹⁴ indicated that 2,4 DNT reaches equilibrium in a closed system faster than does 2,4,6 TNT. In an open system this might lead to more rapid loss of 2,4 DNT, lowering its concentration in the bulk solid and presumably its partial pressure. As changes in the mole fraction of 2,4 DNT in TNT with time were not studied, this question is open to speculation. While the flux of DNT away from TNT explosives is not known, there is no evidence from these data (Tables I and IV) to suggest that the mole fraction of 2,4 DNT in military TNT has changed significantly over a span of more than 30 years (since 1945). Furthermore, preliminary data indicated that the rate of vaporization of 2,4 DNT from buried explosives is rapid, compared to the rate at which the vapors reach the soil surface^{7,14,16}, so that such changes have no bearing on the problem of vapor detection above ground.

In two of the domestic TNT samples, both manufactured in 1966, the Henry's constants appear to be significantly different from the mean (Table XII). The reason for this is not apparent as we have no evidence to suggest that a different manufacturing practice was employed at that time (Table I). For whatever reason, the difference is small relative to the deviation in ideality present in all samples (a factor of 2 as opposed to 100). If the ranges in 2,4 DNT concentrations and K_a values of these military TNT samples are representative, i.e. 0.0008 to 0.0014 moles per mole of TNT, and 10^{-2} to 2.7×10^{-2} , respectively, we can be confident that the uncertainty of predicting the concentration of 2,4 DNT in the vapor above military TNT at ambient temperature without any prior knowledge of 2,4 DNT concentration in the solid is less than a factor of 5.

CONCLUSIONS

The following results of this study are considered to be the most significant findings:

1. The most universally detected vapor component above foreign and domestic military explosives was 2,4 DNT.
2. The concentration of 2,4,6 trinitrotoluene in the headspace of both domestic and foreign military explosives containing TNT can be predicted from its vapor pressure curve.

3. The vapor pressure of TNT in the ambient range (12-30°C) is given by $\log p = -7371.46/T + 19.2533$.

4. The concentration of 2,4 DNT in the vapor above domestic military grade TNT (and presumably foreign TNT as well) cannot be predicted from its vapor pressure alone using Raoult's law. It can, however, be predicted reasonably well using an experimentally determined Henry's constant and the mole fraction of 2,4 DNT in the solid phase.

5. An empirical relationship for the partial pressure of 2,4 DNT based on eight domestic TNT samples was $\log p_a = -3749.91/T + 11.1397 + \log X_a$ where X_a is the mole fraction of 2,4 DNT in the solid phase.

6. The source and method of manufacture did not significantly influence this relationship.

7. The concentration of 2,4 DNT at equilibrium with TNT explosives generally exceeds that of 2,4,6 TNT by at least one order of magnitude.

8. The vapor signatures of foreign TNT samples were qualitatively similar to those of domestic samples.

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