Comparative Analysis of the Vapor Headspace of Military-grade TNT versus NESTT™ TNT Under Dynamic and Static Conditions

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ABSTRACT

The Institute for Biological Detection Systems (IBDS) has developed a quantitative vapor delivery system that can aid in characterizing dog's sensitivity and ability to recognize odor signatures for explosives and contraband substances. Determining of the dog's odor signature for detection of explosives is important because it may aid in eliminating the risk of handling explosives and reducing cross-contamination. Progress is being made in the development of training aids that represent the headspace of the explosives. NESTT™ TNT materials have been proposed as an approach to developing training aid simulates. In order for such aids to be effective they must mimic the headspace of the target material. This study evaluates the NESTT™ TNT product with regard to this criterion. NESTT™ TNT vapor was generated by the IBDS vapor delivery system, which incorporates a vapor generation cell that enables the user to control the conditions under which a substance is tested. The NESTT™ TNT vapor was compared to the headspace of military-gradeTNT. The findings identify and quantify major vapor constituents of military-gradeTNT and NESTT™ TNT. A comparative analysis evaluated the degree to which the NESTT™ TNT mimics the headspace of an actual TNT sample.

Keywords: explosives, TNT, NESTT™ TNT, vapor analysis, headspace, thermal desorption, static, dynamic

1. INTRODUCTION

The Institute for Biological Detection Systems (IBDS) is conducting canine olfactory research to determine sensitivity and detection odor signatures on explosives and other contraband materials. Conducting dog-handler training in explosives detection is becoming increasingly time and labor intensive due to the challenges of handling and storing explosives while avoiding cross contamination. Within the last couple of years, these issues have been approached by developing training aids intended to mimic the vapor headspace for an explosive, potentially eliminating the need to have bulk explosives on site for training.

In order to study the dog's olfactory capabilities, IBDS developed quantitative vapor delivery systems (olfactometers) capable of generating and delivering odors to the dog under controlled conditions[1,2,3]. The vapor generation cell of the olfactometer (Figure 1) allows airflow through the sample to create a concentrated vapor source. With this approach, it is possible to generate a meaningful headspace by controlling the conditions to which the sample is subjected, thereby avoiding the need to reach equilibrium.

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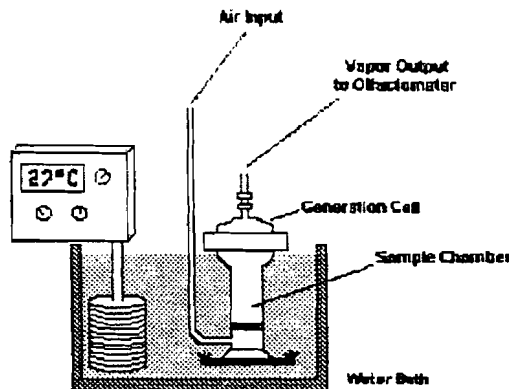SPIE Vol. 3392 • 0277-786X/98/$10.00

Figure 1 Design schematic of the vapor generation cell

The objective of this study was to compare: (1) the output of the vapor generation cell (dynamic system) in terms of the components delivered from military-grade TNT (Trinitrotoluene) and NESTT™ TNT, (2) component analysis of both materials under "static conditions", and (3) relative ratios of 2,4-DNT to that of TNT for all samples. Vapor signatures of both materials were examined under static and dynamic conditions. In this study, we defined the "dynamic system" as the high-flow vapor generation cell used during olfactometer operation. The "static system" was defined as collection of vapor in an open-air environment at ambient temperature, although it is acknowledged that air turbulence associated with sample collection exists within this static system.

2. METHODS

2.1 Dynamic vapor generation

The odorant source was kept in a water bath at 30°C. The water bath was made of 0.125 in. stainless steel (153/8 in. x 153/8in. x 7 in.) and fitted with a hinged lid. The walls were 1.5 in. thick and filled with foam insulation to provide thermal stability. The odorant sample vessel (Figure 1) was made of borosilicate glass (ca. 100 mL). The top of the vessel was fitted with a 65-40 ball joint sealed with a Viton O-ring and a fritted glass disc was fused 0.5 in. from the bottom. Inlet and outlets ports (0.25 in., OD) were fitted to the top and bottom of the vessel. Inlet air was purified by pressure swing adsorption (PG-030, Peak Scientific, Chicago, IL). The input flow rate was maintained at 250 ml/min by a mass flow controller (Teledyne-Hastings Instruments).

2.2 Static vapor generation

The odorant sample was placed at ambient temperature in a 30 mL beaker. The beaker was covered by a layer of lint-free tissue paper to allow free air exchange while minimizing external flow currents. The tissue paper prevented contaminating particulates from entering the system. Vapor collection was performed through a small slit in the tissue paper.

2.3 Dynamic vapor collection

The odorant sources used for this study were military-grade TNT that has been in the possession of IBDS for 10 months and NESTT™ TNT (RKN-01-A-01 Lot # 1030T batch #3) material that has been in IBDS possession for the same time period. The exact age of both samples was unknown. For each experiment,

approximately 25 g of the materials were placed in the vapor generation cell. An adsorbent bed consisting of 65 mg Tenax TA (35-60 mesh, Tekmar-Dohrmann, Cincinnati, OH) was packed within a quartz inlet liner (Tekmar-Dohrmann, Cincinnati, OH). Vapor from the vapor generation cell was passed through the adsorbent trap at a rate of 20 mL/min for duration of 30 minutes. Triplicate samples were collected directly from the output port of the vapor generation cell and each dynamic experiment was duplicated.

2.4 Static vapor collection

The odorant sources used were the same as in the dynamic study. For each experiment 10g of the materials was placed in a 30 mL beaker. The same absorbent bed was used as previously described in the dynamic study. The adsorbent trap was placed 5 mm above the surface of the material and the vapor was collected at a rate of 20 mL/min for the duration of 30 minutes. Triplicate samples were collected for each experiment and each static experiment was duplicated.

2.5 Vapor analyses

Analyses were performed by gas chromatography/ mass spectrometry (GC/MS) on a GCD-1800A system (Hewlett-Packard, Palo Alto, CA). The GC was fitted with 0.25 mm x 30 m column with a film thickness of 0.25 um 5% phenyl substituted methylpolysiloxane (DB-5, Restek, Bellefonte, PA). The quadrupole mass spectrometer used in this study was configured with electron impact ionization source. The selected scan for measurements made in this study was m/z 29 to 425. Adsorbent packed inlet liners previously described were placed in a temperature programmable injection port (Optic, Tekmar-Dohrmann, Cincinnati, OH) and thermally desorbed onto the guard column. The 0.53-mm phenyl-methyl deactivated guard column (Restek, Bellefonte, PA) was utilized for the on-column cryogenics (Scientific Instruments Services, Ringoes, NJ). The cryo unit was set at –60°C during desorption then ramped to 150°C after desorption was completed. The carrier gas (He) flow rate was 1 mL/min. The injection port temperature was programmed to desorb the Tenax® from 40°C to 280°C (hold) at 1 ° C/s and the detector temperature was 250°C. The oven temperature was programmed from 40° C to 220° C (5 min) at 10°C/min. Observed analytes were identified by mass spectral fragmentation patterns and statistical comparison with NIST/EPA/NIH library mass spectra.

2.5 Vapor quantification

A standard solution of 2,4-Dinitrotoluene, and 2,4,6-Trinitrotoluene in acetonitrile was obtained (Radian International, Austin, TX) at a nominal concentration of 1000 ug/mL for each. The two standards were then quantitatively diluted in acetone (UltimAR, Mallinckrodt) from 1000 ug/mL to 100 ng/uL. Standards were injected directly onto the adsorbent trap and analyzed by the methods previously described for vapor analysis. The final method yielded >90% recovery for each analyte compared to a standard injection onto a blank injection liner.

Signal intensities from standard injections of 2,4-Dinitrotoluene, and 2,4,6-Trinitrotoluene (Table 1) indicated linear responses for each component tested. The responses for both components were found to be linear up to 500 ng (on column). Desorption temperature was optimized in order to minimize thermal decomposition products and optimizing for collection flow in order to prevent analyte break through.

Table 1. Summary of GC/MS calibration data

	t_r(min)	N	slope	%SEM	y-intercept	R	p
2,4 DNT	13.7	3	3.5×10^4	5.7%	-2.0×10^6	0.998	0.0360
2,4,6-TNT	15.7	3	1.4×10^4	1.3%	0	0.999	0.0028

N = number of data points
SEM = Standard error of mean
R = Correlation coefficient
p = percent probability

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3. RESULTS AND DISCUSSION

3.1 Military-grade TNT

Vapor samples were collected directly from the output port of the vapor generation cell for the dynamic study and from the beaker for the static study. Representative chromatograms of the "dynamic" and "static" military-grade TNT are presented in Figures 2 and 3 respectively. Representative chromatograms of the "dynamic" and "static" of NESTT™ TNT are presented in Figures 4 and 5 respectively. The identification of the 1,4-DNT can also be named 2,5-DNT based on the assumption that the methyl group is number 1 position. The rationale for the "static" sampling was to determine whether the generated vapor of the NESTT™ TNT is a valid representation of the military-grade TNT sample. A previous study indicated that the dynamic vapor generation provides similar vapor profile of that of static vapor generated system[4].

For the first collection of the military-grade TNT, only dynamic conditions were observed (Figure 2). In the second evaluation of the military-grade TNT, the ratios of 2,4-DNT to TNT were 39:1 in the static collection and 23:1 in dynamic collection. Besides 2,4-DNT and TNT, other DNT isomers, 1,3-DNB was observed in both static and dynamic collections. Traces of toluene were detected but were not consistent from sample to sample.
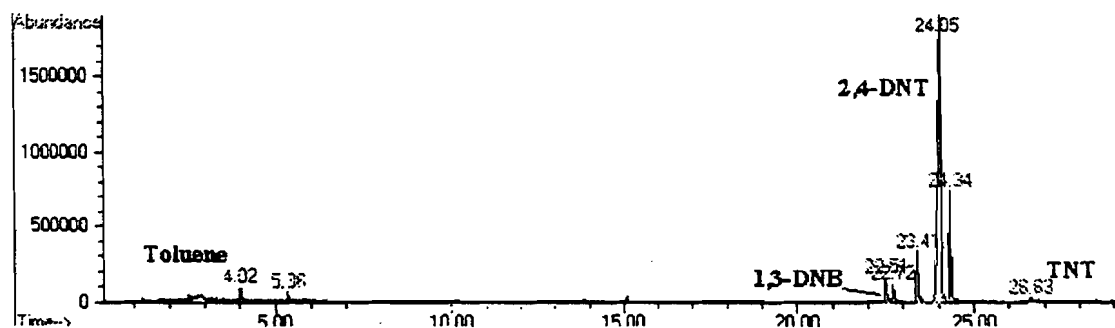

Figure 2. Military-grade TNT – Dynamic Conditions

Based on standard injections (Table 1), responses of selected analytes were quantified to yield ppb levels of 2,4-DNT and 2,4,6-TNT as summarized in Table 2 for the military-grade TNT and Table 3 for NESTT™ TNT. Variability within experimental trials was found to be relatively low. Table 4 represents the differences in the relative ratios between the military-grade TNT compared to the NESTT™ TNT material.
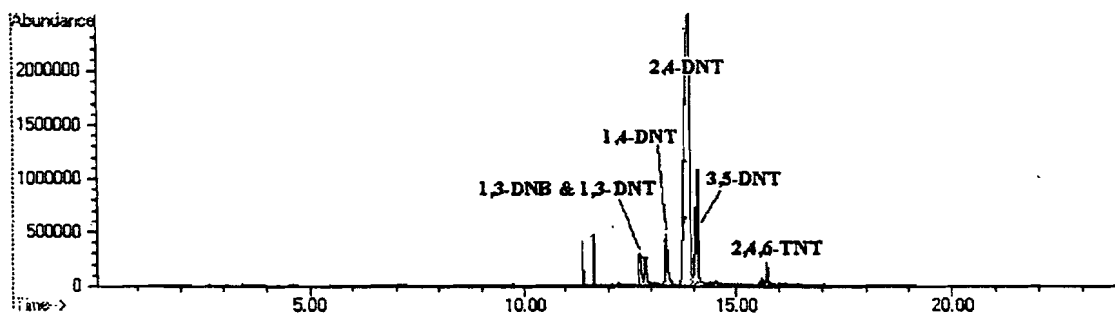

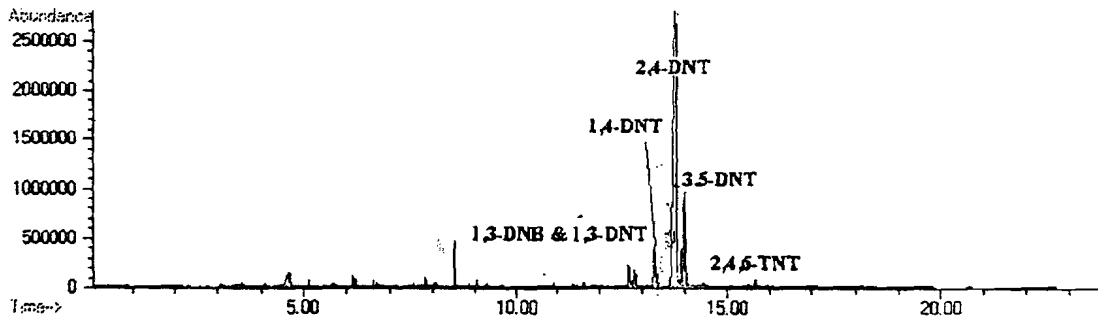Figure 3A. Military-grade TNT – Dynamic Conditions

Figure 3B. Military-grade TNT – Static Conditions

3.2 NESTT™ TNT

The first collection of the NESTT™ TNT was taken only in the "static" conditions (Figure 4). This evaluation was made to see if a correlation of this product matches the vapor headspace of a military-grade TNT sample. The initial findings showed that there were constituents in the vapor from NESTT™ TNT not found in the military-grade TNT. The second finding was that the TNT abundance was higher than that 2,4-DNT constituent in the NESTT™ TNT was. This has not been observed in the previous analysis of the military-grade TNT. This comparison was not direct because the samples were collected in different conditions. Therefore, a further comparison between those samples was conducted under identical vapor generated methods.
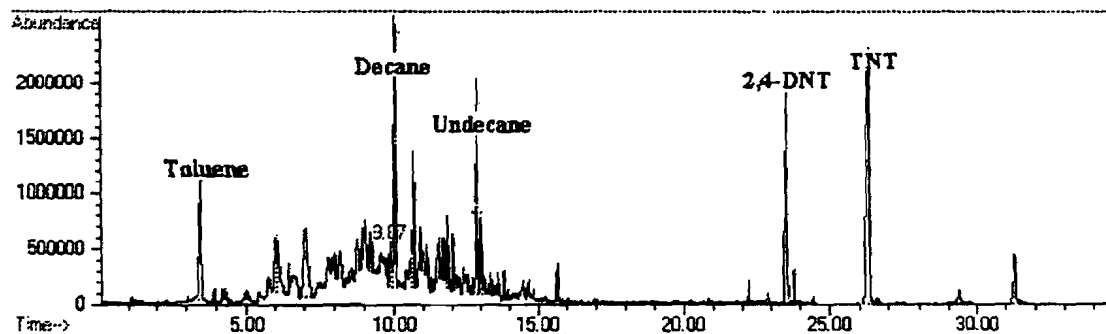

Figure 4. Headspace NESTT™ TNT under Static Conditions

The second evaluation of the "static" and "dynamic" condition of the NESTT™ TNT material yielded yet another different vapor headspace (Figure 5A and 5B). The sample seemed to off gas the solvents and hydrocarbons and now depicting a chemical vapor signature that could appear to mimic the military-grade TNT in terms of constituents present. The ratio of 2,4-DNT to TNT was 8:1 in the static collection and 4:1 in dynamic collection (Table 4). Other vapor constituents identified that were present were DNT isomers, quinone, hexanal, and cyclohexanone in the static collection, whereas, DNT isomers, quinone, and nonanal were present in the dynamic samples. Cyclohexanone was identified as an artifact because of the daily use within our laboratory, therefore, it is more than likely that this is contributory to the air within the room. Table 3 correlates the concentrations of 2,4-DNT and TNT for both the static and dynamic collections.
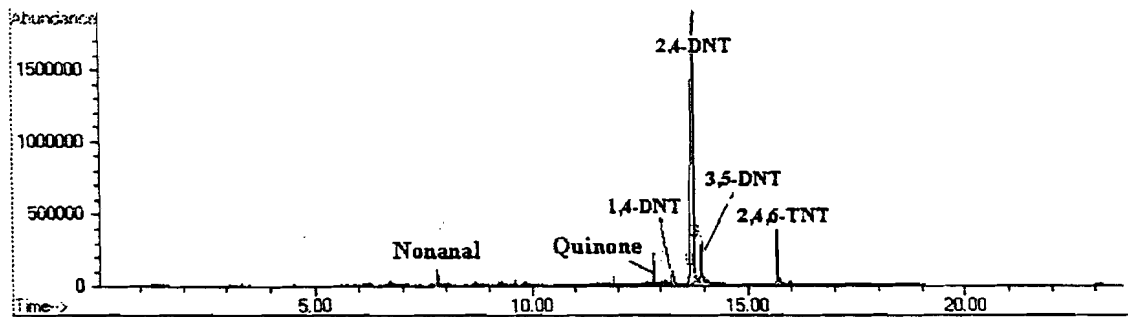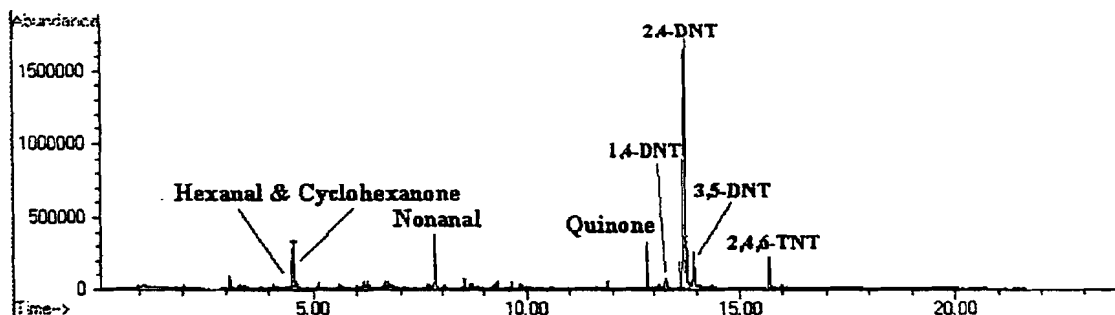
Figure 5A. NESTT™ TNT under Dynamic Conditions

Figure 5B. NESTT™ TNT under Static Conditions

Table 2. Summary of concentrations from military-grade TNT

	Static		Dynamic	
	ppb+/-SEM	%SEM	ppb+/-SEM	%SEM
2,4-DNT	251 +/- 14	5	362 +/- 12	4
2,4,6-TNT	6.5 +/- 0.8	13	15.8 +/- 2.6	16

Table 3. Summary of concentrations from NESTT™ TNT

	Static		Dynamic	
	ppb+/-SEM	%SEM	ppb+/-SEM	%SEM
2,4-DNT	120 +/- 4	3	128 +/- 7	5
2,4,6-TNT	15.9 +/-4.7	29	36.4 +/- 10.0	27

Table 4. 2,4-DNT versus TNT Ratios of the NESTT™ TNT and Military-grade TNT

	Static		Dynamic	
	NESTT™ TNT	Military Grade	NESTT™ TNT	Military Grade
2,4-DNT (ppb)	120	251	128	362
TNT (ppb)	16	7	36	16
Ratio DNT:TNT	8:1	39:1	4:1	23:1

4.0 CONCLUSIONS

The static-to-dynamic comparison showed that the vapor from the NESTT™ TNT material and military-grade TNT are not similar. However, the static-to-static and the dynamic-to-dynamic comparison showed that the vapor from each were similar in terms of the identity major vapor constituents. In reviewing the concentrations and the ratios of 2,4-DNT to TNT, there is a statistically significant difference between the two. The question remains whether these differences in the ratios are important relative to using this NESTT™ TNT material in replacing bulk explosives in canine training. Answering this question requires further analyses of the NESTT™ TNT material to better understand the extent of possible differences of the headspace signature of this material versus that of military-grade TNT. These analyses should evaluate chemical vapor signature changes over time and determine the extent to which analytes are not characteristic of the military-grade TNT appear in the headspace of the NESTT™ TNT. The possibility of variations between batches of NESTT™ should be evaluated before a general conclusion can be drawn on the efficacy of the NESTT™ TNT as a training aid in lieu of bulk explosive. The present work addresses only the chemical characteristics of the headspace of NESTT™ TNT and does not predict its value as a training aid.

5.0 ACKNOWLEDGEMENTS

6.0 REFERENCES

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