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Variation in the headspace of bulk hexamethylene triperoxide diamine (HMTD): Part II. Analysis of non-detonable canine training aids

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HIGHLIGHTS

- The headspaces of non-detonable commercial HMTD products were compared by SPME-GC/MS.
- Few similarities were found between the headspace of the HMTD training aids.
- Training aids changed over time related to starting materials and substrates used.
- There were some similarities between the training aids and bulk HMTD.

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ABSTRACT

Detection canines are a major source of protection against the powerful peroxide explosive hexamethylene triperoxide diamine (HMTD), as well as other homemade explosives (HMEs). However, HMTD is an extremely unstable molecule, which makes it difficult to safely obtain and use for the purposes of canine training and testing. To address this challenge, several non-detonable canine training aids have been designed for canine training. Bulk HMTD has a complex headspace, as shown by previous studies. This makes it a difficult odor to mimic and, in turn, makes evaluations and comparison of such training aids essential. In this work, five non-detonable HMTD canine training aids that are either commercially available or under development were evaluated with the goal of determining which most accurately represents the headspace of bulk HMTD. Of the five training aids, two were observed to reasonably mimic HMTD. While the remaining three training aids contained similar headspace components as HMTD, they did not exhibit the complexity of the bulk compound headspace. While none of the tested training aids exactly mirrored the bulk HMTD samples, they may have use in maintenance training when no bulk material is available.

1. Introduction

Hexamethylene triperoxide diamine (HMTD) is a homemade explosive (HME) that can be synthesized in clandestine laboratories from commercially-available ingredients [1]. Because the compound is extremely unstable and friction-sensitive, it has no military, industrial, or other legal use. Due to the ease of synthesis, however, it has increasingly been recovered in explosive-related incidents in recent years [2,3]. For example, it was recovered in the 2016 New York and New Jersey attacks as well as the 2005 London subway bombings [1,4].

Molecular HMTD has a very low vapor pressure, making instrumental vapor detection of the HMTD molecule exceedingly difficult, particularly under field conditions [2–7]; however, its unique confirmation and resulting intermolecular ring strain leads to its decomposition under ambient conditions, yielding a number of highly volatile products that can more readily be detected in the vapor phase. Formic acid, acetic acid, formaldehyde, formamide, dimethylformamide, and trimethylamine have been identified in the headspace of the bulk material [5,8–10]. Previous research shows that the presence of these decomposition products and their relative vapor concentrations above HMTD changes drastically based on the manufacturing or synthesis process of the sample, the age of the sample, and storage or environmental factors such as temperature and humidity [5,8–10]. For example, samples from clandestine-type synthesis have been observed to release anywhere from 10 to 100 times more odor than laboratory synthesis [5].

Even with the many advances in instrumental detection, canines are still considered one of the most effective means of real-time, non-

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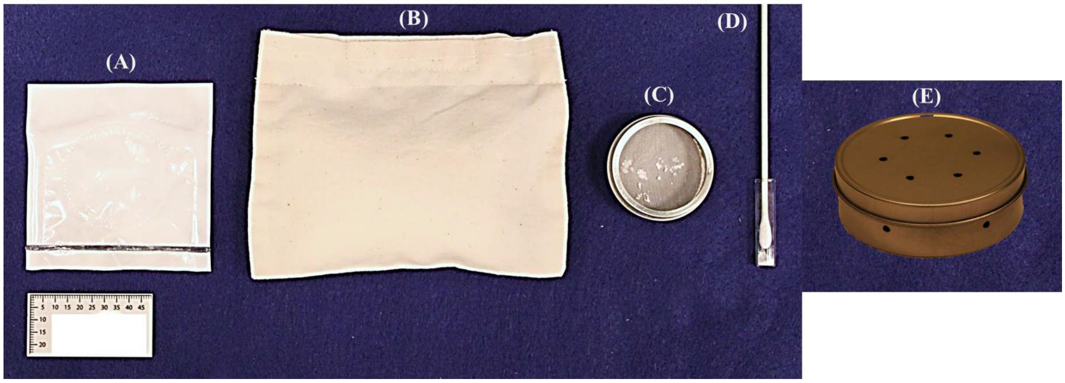

Fig. 1. Images of training aids removed from barrier packaging. Brands are labeled above with their identifying letter. Brand E image is an approximate size for comparison to other training aids.

contact explosives detection [11,12], and thus military and law enforcement canine programs have been at the frontline of the community pursuing an efficient method of detecting most explosives, including HMEs. The complexity of the HMTD headspace as well as the hazardous nature of the bulk material can be problematic for canine training. Due to the associated hazards, training canines on HMTD generally requires the presence of chemists or other trained personnel, which can be time consuming and expensive. Additionally, canine programs often do not have established protocols for training, handling, storing, or transporting bulk HMTD [13]. Those that do train on HMTD often choose to use alternative non-detonable commercial-off-the-shelf (COTS) training aids, of which there are currently five brands available or under development[14–18].

These non-detonable training aids for HMTD use a portion of the authentic material by either imparting solid material onto or into a substrate or capturing the odor extracted directly from the headspace of bulk material to create training aids yielding the same (or a similar) odor as the authentic explosive without the hazards. For example, one COTS training aid uses inert microspheres to encapsulate small amounts of actual HMTD, whose odor is released when the microspheres are heated [19]. Another training aid, not yet commercially available, places HMTD within an enclosure, allowing the explosive vapor to infuse into a polymer substrate and subsequently release the odor of the target through a defined aperture [17]. An alternative method uses the chilled synthetic precursors of HMTD mixed together with an inert substrate matrix, such as diatomaceous earth. The resulting product yields solid HMTD imparted onto said substrate [20,21]. Since previous research of bulk HMTD found that synthesis makes a profound difference on the odor profile of the sample [5,8–10], these various methods likely also play a role in the odor profiles of the training aids.

The use of non-detonable training aids remains a major point of discussion among those in the canine detection training community [22]. Their composition is typically proprietary, which limits opportunities for validation. Third party analysis of these training aids or their headspace rarely exists, and this is the first such evaluation for HMTD training aids. Without such analyses, there may be many important questions left unaddressed, including efficiency and accuracy [22,23] for use in training, as well as headspace composition and odor consistency over time. These factors all affect canine proficiency, especially in the case of complex targets such as HMTD. For these reasons, SWGDOG recommends the strict use of authentic explosives whenever possible [13].

Third party evaluations and validations of the headspace for alternative training aids can help alleviate the stated questions associated with unknown factors. Various COTS training aids for complex targets such as human decomposition have been analyzed and compared [22,24], as well as those for more simple targets including drugs and other explosives [23,25–27]. Studies of simple targets have evaluated canine alerts to certain alternative training aids compared with actual target substance for heroin, marijuana, and a variety of traditional explosives (i.e. TNT, RDX, PETN, detonating cord, nitrate, chlorate, smokeless powders, and C4) [23,27,28]. These studies found that not all of the tested COTS training aids were reliably detected by trained canines. Similar studies have also been completed for human remains, where it has been shown for human decomposition that COTS training aids are neither representative of nor consistent with headspace of authentic samples, and a trained detection canine was unsuccessful in locating the COTS training aids in several double-blind scenarios [22,24]. The headspace of HMTD is similar to human remains in that they are both particularly complex and dynamic due to age and environmental sensitivities [5,22,29].

This information is discussed not to disparage the use of non-detonable or alternative training aids, which have proved to be useful (see for example cocaine and MDMA [30,31]); rather, it is to assert that knowing the headspace composition for various training aids has important implications for subsequent detection canine success. Therefore, this study presents an evaluation of the headspace of HMTD alternative training aids compared to previously identified volatiles in authentic samples, helping to create a safer, more effective environment for detection canine training. A comparison is made between these HMTD training aid samples and the results of DeGreeff et al. [5], who characterized the headspace of both bulk laboratory and clandestine HMTD samples.

2. Materials and methods

2.1. Non-detonable canine training aids

The headspace of five different manufacturers' non-detonable canine training aids for HMTD (identified herein as Brands A–E) were compared (Fig. 1). Table 1 lists manufacturer-provided information on each training aid tested, including the cost for a single aid, recommended total training duration limit (i.e. work time), storage recommendation and resulting storage shelf-life, and a description of the training aid. It should also be noted that only Brands A and D include blank materials, while Brand B offers blank material for purchase.

2.2. Analytical methods

2.2.1. Headspace extraction from training aids

Each training aid was prepared differently by the manufacturer and was provided with unique instructions for use/storage upon receipt (Table 1). For the experiments described herein, the training aids were evaluated under the manufacturer-suggested conditions for canine training, thus specific sampling protocols reflect the individuality of the aids. All training aids intended for repeated use were stored as

Table 1
Information regarding training aids A–E, as provided by the manufacturer. Work time refers to the length of time or training sessions a manufacturer recommends the product to be used. Description of aid is summarized from manufacturer-provided materials.

Brand	Cost per aid	Work time	Shelf-life	Storage recommendation	Description
A	$149.00	Not given	6 months	Freezer	Made from authentic explosives; contains 10 mg of proprietary odor material sealed in breather bag that is subsequently stored in resealable metalized barrier bag
B	$599.99	16 h (or in accordance with SWGDOG guidelines)	Not given	Refrigerator, below 0 °C	Proprietary scent equivalent of target material in fused silica sealed in a cotton bag that is then stored in a resealable metalized barrier bag
C	$535.00	3–8 h	3 months	Not applicable (single-use)	Non-detonable material made from real explosives contained in a metal tin with a mesh cap
D	Not yet established	Not yet established	Not yet established	Not yet established	Encapsulated explosive in microspheres that release odor when heated, which is then collected on steel wool or cotton (requires a microsphere heater); currently under development
E	Not commercially available	Not yet established	Not yet established	Not yet established	Vapor components infused into PDMS, placed in a breather tin; not commercially available

recommended by the manufacturer when not being tested. Blank training aids were tested, when provided by the manufacturer, and for Brand B, which was purchased separately.

Brands A and B were treated the same for analysis since both training aids are intended for multiple use. As such, they were tested upon opening and then periodically for 9 months (270 days), mimicking conditions as if biweekly canine training occurred.

Brand C was designed for single-use training sessions, and was therefore sampled throughout the recommended work time training session (9 h, no storage between sampling) and once on Day 3 (stored closed at ambient temperature following Day 1) to confirm depletion.

Brands D and E are not currently commercially available, but were included in the study. Conversations with the developers provided information for intended use. Brand D has not yet determined the multi-use function of the microspheres themselves, but intended each cotton training aid for single use. It was thus sampled over one working day (7 h). Brand E is intended for repeated use, and was therefore sampled over two months and stored closed, under ambient conditions.

Analysis methods were chosen to closely resemble those of DeGreeff et al. [5]. The headspace of each training aid was analyzed by solid phase microextraction-gas chromatography-mass spectrometry (SPME-GC–MS). For sampling, training aids were removed from the manufacturer's packaging and placed in separate 32 oz. amber septa bottle (ESS Vial, San Leandro, CA) and allowed to equilibrate for an hour. A divinylbenzene/carboxen/polydimehylsiloxane (DVB/CAR/PDMS) SPME fiber (Sigma-Aldrich, St. Louis, MO) was exposed to the headspace above each training aid for one hour at room temperature.

2.2.2. Instrumental analysis

Analytes were desorbed from the SPME fiber at 260 °C for three minutes using an Agilent 6890 gas chromatograph with a 5975 mass spectrometer (Agilent Technologies, Santa Clara, CA) with a 10:1 split. A Rtx-Volatile amine GC column, 30 m × 0.32 mm ID (Restek Co., Bellefonte, PA) was used with a flow of 1.5 mL/min. The GC oven was initially held at 35 °C for 1 min, then ramped to 180 °C at 25 °C/min and then to 240 °C at 40 °C/min, where it was held for an additional 2.2 min. Analytes were transferred to the MS at 250 °C where ions were scanned from m/z 28.5–300. All samples were taken in triplicate and compared to blank training material (as provided) and blank headspace bottles. Any compounds identified in the blank (equal or greater than) were not included in the data analysis.

2.2.3. Quantification

Detected analytes were quantified by comparison to external calibration curves using extracted ion peak areas. Formic acid and acetic acid solutions were prepared in hexane, while dimethylformamide, trimethylamine, ethyl acetate, and propanal solutions were prepared in methanol. Due to poor GC separation and peak shape of formaldehyde and formamide in solution, the quantities of both formaldehyde and formamide were estimated by comparison to calibration curves of the related compounds propanal and ethyl acetate, respectively. The surrogate compounds were chosen based on structural similarity to their respective related compounds, indicating that they therefore have similar chromatographic properties. All chemicals were obtained through Sigma-Aldrich (St. Louis, MO). All solutions were prepared at five concentrations and were run in replicates of five. Limits of detection for each analyte are given in Table 2 and were determined using the mass resulting in a peak with an average signal-to-noise ratio of three.

3. Results and discussion

DeGreeff et al. [5] studied multiple formulations of bulk HMTD under varying storage conditions, and analyzed the decomposition and evolution of headspace products over a 32 week period. In agreement with previous studies [8,9], all compositions and treatments of bulk HMTD were shown to degrade over time, producing a headspace profile

Table 2
The limits of detection (LOD) for the described method for each compound detected calculated based on 3 times the signal-to-noise ratio of the lowest detectable mass, averaged over the course of the experiment.

	LOD (ng)
Formic acid	41.0
Acetic acid	4.8
Trimethylamine	5.4
Formaldehyde	1.8
Formamide	8.0
Dimethylformamide	5.0

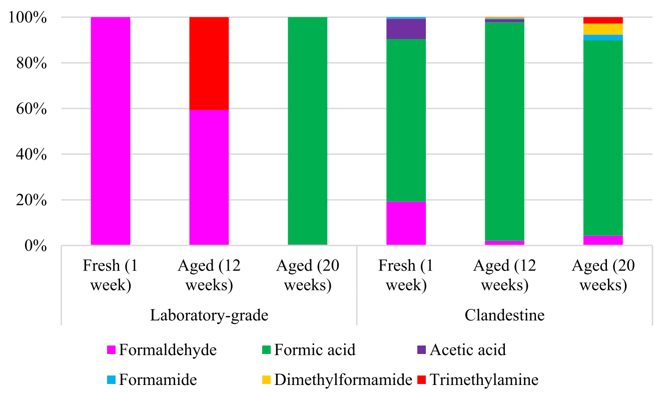

Fig. 2. Relative amounts of compounds detected in the headspace of HMTD of different ages, laboratory-grade and clandestine. Data reproduced from DeGreeff et al. [5].

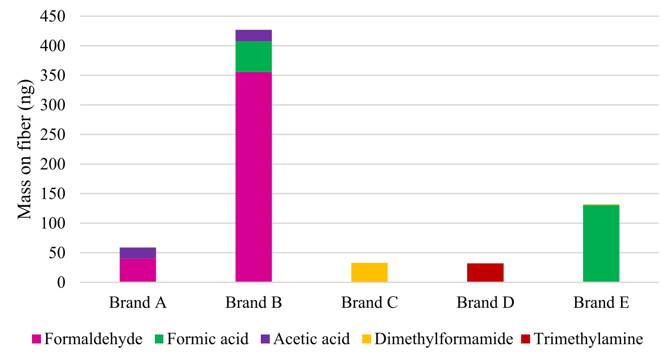

Fig. 3. Comparison of the initial sample upon opening the packaging for each brand of HMTD canine training aid.

that changed in both quantity and quality. Overall, formic acid was the most abundant volatile in the headspace of the bulk material, but was not necessarily detectable in all samples. On the other hand, formaldehyde was found at a lower level, but could be detected in nearly all samples. In addition, acetic acid, formamide, dimethyl formamide, and trimethylamine contributed to the overall headspace profile and varied with the condition of the bulk HMTD being tested (Fig. 2).

A total of six compounds were detected across the tested COTS HMTD canine training aids, though they were present in different combinations. A summary of which compounds were present in each sample can be seen in Table 3. All six compounds were previously observed in bulk HMTD samples, and are headspace decomposition products of the explosive as identified by DeGreeff et al. [5]. No additional volatile compounds that were not detected by DeGreeff et al. in the bulk material were noted in the training aids, with the exception of compounds that could be attributed to the substrate material. As with the previous study, formic acid was the most abundant volatile in the headspace of Brands A and B, and formaldehyde was also detected over time with each brand. These trends were not true for Brands C, D, or E, yet other comparisons to bulk HMTD can be made, and are discussed below.

The initial odor profile of each training aid represents the odor when the training aid is first opened and used, and is compared in Fig. 3. Each brand resulted in a unique odor signature that differed in composition as well as quantity. Considering the compounds of interest identified in Table 3, the sampling of Brand A resulted in approximately 59.0 ng of total odor being detected. Brand B yielded much more odor than any of the other brands (427.0 ng), and also had the most diversity of compounds. Brands C and D had a comparable quantity of odor (approximately 32.0 ng each), and yielded relatively simple headspace compositions. Dimethylformamide was present only in a small amount in Brand E, which was mostly composed of formic acid (with 132.0 ng total odor).

Three (Brands A, B, and E) of the five sampled training aids are intended for multiple use, though the other two training aids (Brands C and D) should have available odor for at least the length of a single training session. As such, the headspace of each training aid was monitored over time, according to its recommend use per manufacturer instructions. Fig. 4 compares the total mass of headspace components collected for each brand over time. Brands A and B (Fig. 4A) gave off significantly more odor than the other brands, and interestingly, the amount of odor from these aids actually increased in the days following the initial measurement. One would suspect that the amount of odor would decrease with time as it is depleted from the substrate; however, this increase in odor suggests a decomposition reaction occurring as the HMTD yields an increasing amount of degradation products, as was seen previously with the bulk sample (Fig. 2). To further support this hypothesis, Figs. 5 and 6, respectively, show that it is specifically formic acid that increases with time in these aids, again similar to that previously measured from the bulk material. In contrast, the highest quantity of odor from Brand E was detected initially upon opening and decreased rapidly after Day 3 (Fig. 4C), as to be expected if the odor was simply being depleted from the substrate over time.

Notably, for both Brand A and the clandestine HMTD samples (fresh and aged; Fig. 2), formic acid dominated the headspace throughout the respective sampling periods. While the aging processes of Brand A and the clandestine HMTD samples do not mirror each other precisely, fresh Brand A appears to better represent the odor profile of fresh clandestine

Table 3
Compounds present in the headspace of each brand of COTS HMTD training aid as well as previous research [5] (Y = presence); *aged = two weeks or more; ** only detected in the Day 17 sample; †data from previous study.

HMTD decomposition products	Brand A	Brand B	Brand C	Brand D	Brand E	Laboratory-grade, fresh†	Laboratory-grade, aged*†	Clandestine, fresh†	Clandestine, aged*†
Formaldehyde	Y	Y			Y**	Y	Y	Y	Y
Formic acid	Y	Y			Y		Y	Y	Y
Acetic acid	Y	Y		Y	Y			Y	Y
Formamide		Y							Y
Dimethylformamide			Y		Y				Y
Trimethylamine				Y			Y		Y

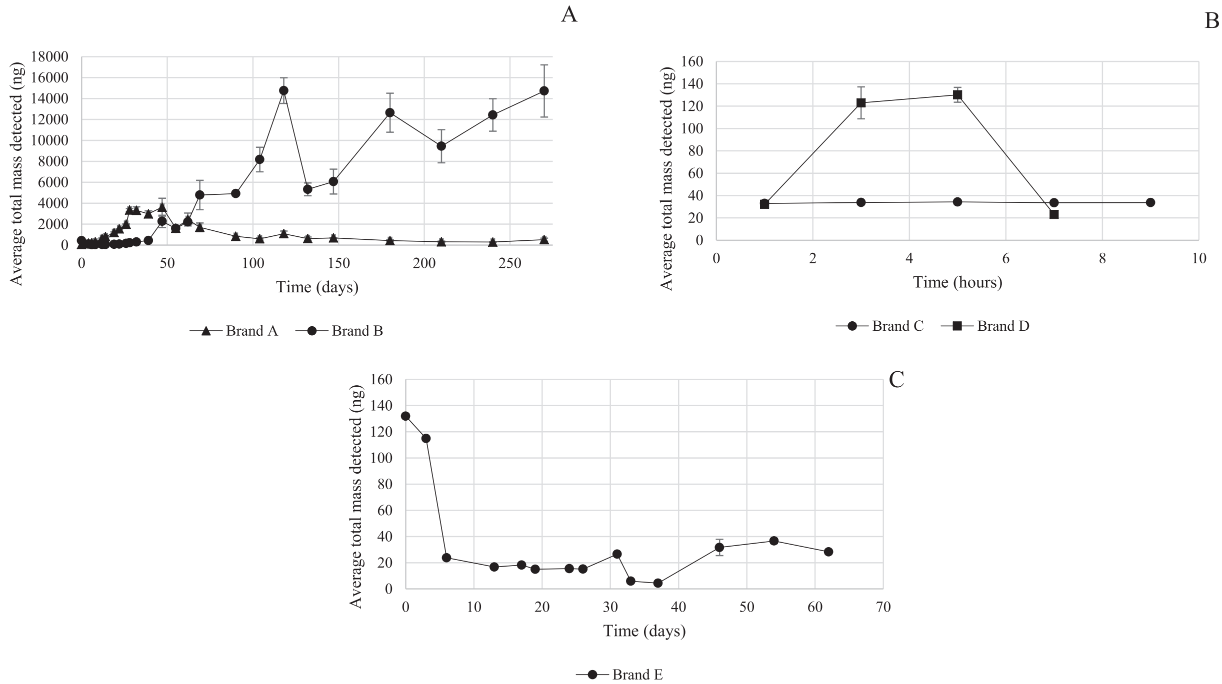

Fig. 4. Comparison of average total mass detected for each training aid; (A) Brands A and B, which were sampled over a period of days; (B) Brands C and D, which were sampled over a period of hours. (C) Brand E (shown separately for clarity of detail). All error bars represent one standard deviation.

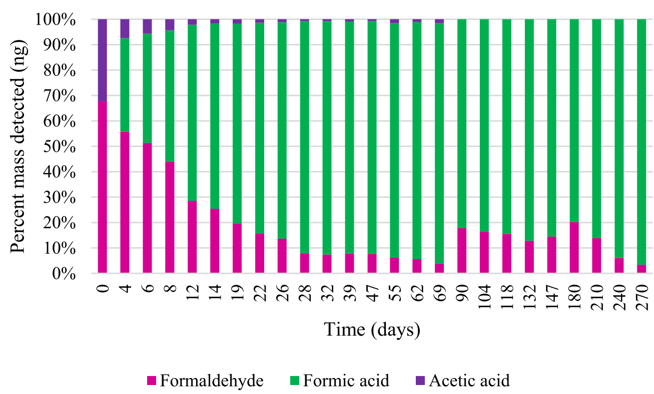

Fig. 5. Percent mass of all compounds detected by day in the headspace of Brand A training aids over 270 days.

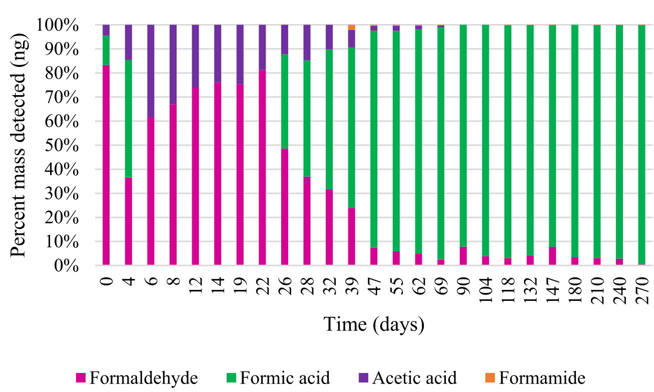

Fig. 6. Percent mass of all compounds detected by day in the headspace of Brand B training aids over 270 days.

HMTD than the other tested COTS training aids.

As mentioned, the previous studies of bulk HMTD odor identified formaldehyde, formic acid, and acetic acid in initial samples of clandestine HMTD (Fig. 2) [5,8]. Each of these compounds is also present in the odor profile of Brand B. While this might indicate that the headspace of Brand B is similar to bulk HMTD, this was not necessarily the case when examining the odor profiles over time (Fig. 6).

Brand E was created using real HMTD, but its odor profile contained only acetic acid and dimethylformamide for the majority of the sampling period (Fig. 7). Of the real HMTD samples, these two compounds were only recovered together from the aged clandestine HMTD (Fig. 2). However, the aged clandestine HMTD also produced four other compounds that were absent (below the instrumental detection limit) from Brand E. The composition of the odor profile of Brand E changed often throughout the sampling period, but the total abundance of odor was stable once formic acid no longer appeared.

Brands C and D were both intended for use over a single training session, and provided detectable odor over a single day (9 and 7 h, respectively) (Fig. 4B). The amount of odor detected was much lower than the other brands initially and had a much simpler odor profile with only dimethylformamide detected in Brand C and trimethylamine and acetic acid in Brand D (Fig. 8). DeGreeff et al. observed neither dimethylformamide nor trimethylamine in initial samples of HMTD; rather the two compounds appeared only in aged samples, and never

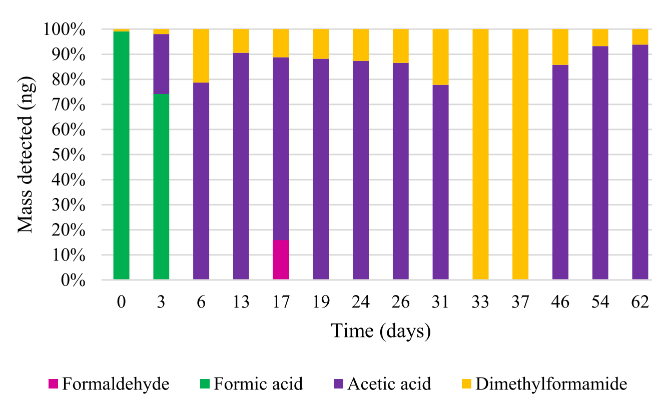

Fig. 7. Percent mass of all compounds detected by day in the headspace of Brand E training aids over 62 days.

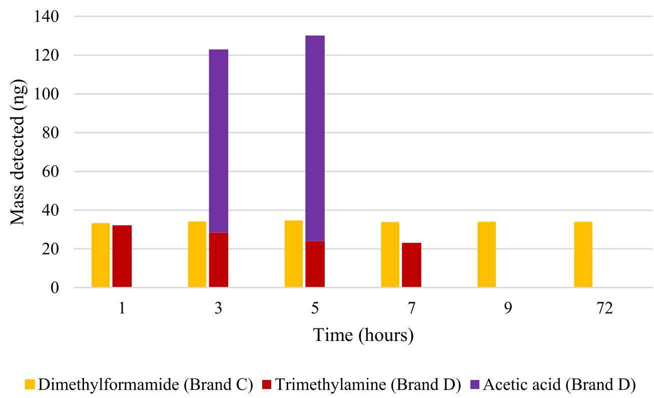

Fig. 8. Average total mass detected (ng) of VOCs in the headspace of Brands C (left bars; dimethylformamide) and D (right bars; trimethylamine and acetic acid) training aids over a work day. Brand C was tested over 72 h, while Brand D was tested over 7 h.

without the presence of other compounds (Fig. 2) [5]. Since Brands C and D are manufactured using real HMTD, it is possible that the solid HMTD contained in the respective training aids reacted or aged while in the training aid, causing the initial odor profile of these COTS training aids to reflect compounds identified in aged samples of bulk HMTD rather than fresh samples of bulk HMTD. Alternatively, it is possible that the training material is unstable when applied to the substrate, causing the observed HMTD decomposition.

Of the variables tested by DeGreeff et al. [5], it was determined that synthesis method, particularly the washing and recrystallization steps, had the greatest effect on headspace composition over time. The laboratory-grade synthesis, having been washed with water and then dried with methanol, exhibited lower levels of volatiles in the headspace initially; while the clandestine formulation, having been washed and not dried exhibited a rapid degradation from its receipt. It was hypothesized that the presence of water and residual acid in the clandestine synthesis, and later formic acid in both formulations, led to degradation and destabilization of the bulk material, promoting additional decomposition [9,10].

Because the observed variations in the headspace of bulk HMTD were likely caused by synthesis, a comparison of the headspace of various training aid syntheses proved to be interesting as well. Unfortunately, since the manufacturing details of each brand of training aid are proprietary, the details of their syntheses are not known. However, certain information can be gleaned from patents and provided marketing information. Brands B and C were made by mixing chilled HMTD precursors. Brand B material was then rinsed with water, sodium bicarbonate, water again, methanol, and a final rinse of water before allowing it to air dry [21]. The Brand C material was rinsed once with water and then vacuum dried [20]. The other brands used premade HMTD (rather than precursors) imparted onto a substrate and the exact synthesis methods were not identified.

Both the clandestine HMTD and Brand B were left to air dry following their respective rinses. Brand B also showed the greatest amount of odor and compound breakdown of all training aids. Previous studies found that the presence of water facilitates the decomposition of HMTD [5,8–10]. It could therefore be suggested that since Brand B was simply air dried following the rinsing procedure during manufacturing, rather than accelerating the drying process chemically, it rapidly began to degrade. Brand C, on the other hand, was dried at the end of the manufacturing process. It produced very low levels of odor and was the most consistent. These results are also supported by previous research, which found that dried samples of HMTD (i.e. the laboratory-grade) degraded far slower than the clandestine synthesis, producing less odor and change over time [5,8,9]. This also agrees with the finding by DeGreeff et al. [5] that clandestine (i.e. air dried) HMTD produced 10–100 times more odor than laboratory-grade (i.e. methanol dried) HMTD. Since the syntheses of the other training aids are unknown, it is difficult to determine if their odor profiles are a result of synthesis, matrix interactions, or both.

Another consideration in odor production is in the matrix itself. Brands A and B both utilize a powder-like material as the substrate, while Brand E consisted of a HMTD dissolved in PDMS, having a rigid gel-like consistency. The pattern of odorant production noted with Brands A and B suggested a degradation reaction occurring within the material, whereas data from Brand E indicated no such reaction. Steinkamp et al. put forth evidence of intramolecular decomposition of HMTD facilitated by the presence of water and residual acid [8]. The rigid gel support of Brand E restricts movement of the HMTD molecules and thus limits interaction between the HMTD molecules with each other and with residual acids and ambient water. Alternatively, the silica powder readily supports interaction between the HMTD molecules and with the surrounding environment. Silica powder is also hydrophilic, and could encourage interactions with ambient moisture, increasing degradation. It can be surmised that the construction of the training aid itself, the synthetic method of the HMTD material, as well as other factors all play a role in how the HMTD training aids perform, both in odor quality, quantity, and duration. The large number of factors effecting training aid performance explains the great variability seen in the five products studied herein.

The odor profile of solid HMTD is complex, changing with the influence of many variables such as temperature, humidity, and time. It is very difficult to mimic such an odor. Fresh samples of Brands A and B were somewhat similar to fresh clandestine HMTD, but were not observed to follow the aging process of bulk HMTD. Each of the five COTS training aids evaluated resulted in simplified versions of HMTD headspace, providing only portions of the odor profile rather than comprehensive representations. Such comparisons of identified compounds are useful, though they are limited by the inability to compare amounts of recovered odor between the training aids and the bulk HMTD, as odor availability does impact canine perception [32,33].

4. Conclusion

In order to best select a training aid for detection canines, it is necessary to understand the odors to which they are being exposed, and therefore trained to detect. Selection of an appropriate aid is made difficult by proprietary manufacturing methods, which thus makes third-party analysis and reporting essential. Each of the tested COTS HMTD training aids produced unique odor profiles initially and over time, never mirroring each other. Additionally, none of the tested COTS HMTD training aids consistently or accurately emulated the headspace of bulk HMTD. However, they may still have use as occasional replacements for real explosives, presenting an acceptable compromise when those are not available due to the regulations and cost associated with extremely hazardous materials such as HTMD.

It is further necessary to understand the odors which canines are more likely to encounter in the field. In the case of HMTD, it is likely that canines will encounter clandestine HMTD rather than laboratory-grade HMTD. Since clandestine HMTD, when aged, produced all six identified compounds in the headspace, it is possible that training with a variety of the available COTS HMTD training aids would be useful. However, to further understand the usability of HMTD COTS training aids, it is necessary to test the aids with detection canines, both previously untrained to HMTD odor, as well as those previously trained to detect the odor. An alternative training aid that reliably provides an odor profile more analogous to that of bulk HMTD would be of great value to the detection canine community to create safer, more efficient detection teams.

Conflict of interest

None.

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Appendix A. Supplementary data

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