Evaluation of non-detonable canine training aids for explosives by headspace analysis and canine testing

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Highlights

- Commercially-available non-detonable canine training aids lack third-party testing
- Headspace analysis of non-detonable explosives canine training aids was carried out
- Training aids for nitroaromatics and peroxide explosives were tested
- The explosives training aids had poor inter- and intra-batch reproducibility
- Canines did not spontaneously generalize between the TATP aid and the true material

Abstract

There is a need for non-detonable training aids to enable training of canines when access to true material is limited. A disadvantage of non-detonable training aids is the lack of third-party independent verification and validation to certify the efficacy of the aid to yield a detection capability to true material. The goal of this research is to guide the development of a pipeline for the evaluation of commercial or novel training aids by using both analytical analysis as well as canine olfactory testing. Headspace analysis was carried out for nitroaromatic explosive training aids, RDX and PETN, as well as peroxide explosives, HMTD and TATP. Batch-to-batch reproducibility and usage lifetime mimicking operational usage, were also assessed for peroxide explosive aids. As a result of the analytical analysis, various issues were identified such as limitations of explosive component detection, presence of extraneous odors, dynamic headspaces, and both inter- and intra- batch variability. A single TATP training aid was selected to be tested in a proof-of-concept canine assessment which compared canines trained using true material in their ability to detect the training aid in question and a set of canines trained solely with a commercial training aid in their ability to detect true material. It took nearly 21 trials of exposures to true TATP before all canines trained with the non-detonable training aid were able to detect the true TATP with a 100% detection rate, highlighting the importance of analytical characterization of non-detonable training aids paired with canine validation studies.

1 Introduction and Background

One of the many questions that arises when training odor detection canines relates to the efficacy of the training aid material used during the training process, as the quality of the aid may correlate to detection capability in the field. While true target material is considered optimal [1], there is a need for non-detonable alternative training aids to enable the training of detection canines in locations where true explosives are not permitted, and for certain explosives which are considered too sensitive to be stored in traditional explosives training aid kits. The explosive sensitivity of the peroxide explosives, triacetone triperoxide (TATP) and hexamethylene triperoxide diamine (HMTD), is such that many detection canine teams must work with outside agencies to gain brief and limited access to these materials. The validation of non-detonable alternative explosive training aids would enable more frequent access and proper maintenance training for this class of explosives.

Existing commercially-available, as well as novel and homemade, non-detonable explosive training aids can be divided into several categories based on their method of preparation [2], [3]. Mimic Aids, which have also been referred to as “pseudos” or “pseudo-scent”, are created by impregnating a substrate with chemicals chosen to imitate or mimic the actual odor of a targeted material [4], [5], and are based on the premise that canines often alert to an odorant associated with the target of interest as opposed to the target itself [5], [6], and may include a single dominant odorant or a mixture of relevant odorants. The development of Mimic Aids requires knowledge of the main odorants associated with the target material. This necessitates both analytical measurements to determine the volatile compounds in the headspace of the target, as well as canine testing to determine the odorants important to olfactory detection of the target. Dilution Aids are fabricated by placing a trace amount of the actual target materials (e.g., explosive material) onto a substrate rendering it non-detonable. The purity of material used in the fabrication of Dilution Aids is highly important, as any impurity in the target material will be transferred to the Aid and will affect the odor given off by said Aid. Finally, Sorption Aids are made by soaking a sorbent material in the headspace of the true material. This method of training aid fabrication is used by commercial training aid manufacturers using proprietary substrates and source material, or may be made by

the end user by soaking a common substrate, such as cellulose filter paper [7], cotton balls, gauze [8], or other novel polymer materials [9]–[11]; also commonly referred to as a "soak". The amount of odor available from a Sorption Aid will be dependent on the type of substrate, target material type, amount and condition of the target material, and the environmental conditions (e.g., time, temperature, humidity) during the sorption process. Because of these many variables, it may be challenging to create batches of Sorption Aids with reproducible odor availability. Furthermore, like Dilution Aids, the use of impure source material may alter the odorants present. The development and testing of commercial aids is often proprietary to the manufacturer, and little or no testing may be done for more novel or homemade training aids. As such, the efficacy of the materials as training aids is often essentially unknown to the end user making third-party evaluation of the aids critical [2], [3].

In general, when evaluating a canine training aid, many factors should be considered, such as cost (e.g., lifecycle cost, cost per use, up-front cost, etc.), legal requirements (e.g., special licensing and permits), storage considerations (e.g., infrastructure requirements such as explosives magazines, narcotics safes, temperature regulation, etc.), potential safety concerns associated with handling, storing, and transporting the training aid, and ease of use in training (e.g., form factor, odor availability, and usage lifetime). Use of alternative training aids may be advantageous as they typically do not require special permits and licenses, are safe to handle/store/transport, and do not require a magazine or safe. These advantages reduce training burden on handlers, thus saving time and money. The major disadvantage has been the lack of third-party independent verification and validation (IV&V) to certify the efficacy of the training aid to yield a detection capability on the true material [2].

Ideally, a training aid should produce an odor profile that is comparable to the parent source [12], [13] and provide a reproducible odor profile and consistent odor concentration amongst individual training aids, as well as for the given usage lifetime of the aid. When developing an aid, one must also consider what odor profile of the threat one wants to capture. Is there a difference between fresh and aged material or laboratory-grade and clandestine-produced, and, if so, which should the training aid represent [14]? Additional considerations should include the presence of non-target odors. These may be present due to the training aid fabrication process, such as solvents used in manufacturer of Dilution Aids, odor from the substrate, contamination present on the source material, or cross-contamination between aids of different kinds made in close proximity.

In addition to analytical measurements to assess the volatile compounds that make up the odor profiles of the training aids, it is imperative that canine testing be carried out to best understand the true efficacy of the aids [2], [14], [15]. Analytical analysis alone is not enough to tell the full story, due to instruments and canines being different sensing/detecting platforms and thus will have different affinities for and sensitivities to various compounds as well as interpret the incoming signals from the headspace compounds differently. Thus it is important to conduct testing with detection canines in addition to analytical analyses [16]. The ultimate test of a canine training aid for the purpose of initial odor learning is a canine validation study in which the test demonstrates that detection canines trained using a given training aid perform equally or better to those trained using a different aid by more than a small margin. These studies must utilize "green" canines (i.e., canines naïve to the odor in question) so that the detection data can be attributed to the training aid and training and not odor generalization from a previous learned odor to the new experimental odor. For this purpose, the research herein employed a double cross-over study design, where two groups of canines were utilized, one group being trained on the true explosive

and the other group using an alternative training aid. The ability of all of the canines to then detect both the true and alternative aids were then measured.

While reported anecdotal experiences with alternative training aids tend to be mixed, past peer-reviewed research has shown limited utility of many commercial training aids both by analytical comparison of the volatile components and testing of canines in their ability generalize from the true material to the non-detonable aid and vice versa [3], [6], [17]. A limited number of previous research studies have assessed non-detonable canine training aids using headspace analysis. In an early study in 1998, Auburn University, in collaboration with the Federal Aviation Administration (FAA; predecessor for the Transportation Security Administration [TSA]), assessed the XM NESTT TNT (trinitrotoluene) training aids in comparison to military-grade TNT [12]. XM NESTT training aids are Dilution Aids made from purified explosives diluted to 4-8% in silica powder or petroleum jelly [18]. The researchers found that, while both contained the major vaporous compounds 2,4-dinitrotoluene (2,4-DNT) and TNT, the concentration of these in each material were statistically different. This begs the question – do such differences in compound ratios affect detectability and the ability of the canine to generalize from the training aid to the true material? The authors also discussed the importance of understanding changes in the odor signatures of both materials over time, as well as batch-to-batch variations [12]. Furthermore, research by Harper et al. (2005) indicated that XM NESTT TNT and RDX (1,3,5-trinitro-1,3,5-triazinane) aids were not recognizable to operational explosive detection dogs (EDDs) (n = 6) in a double-blind study. The RDX aid had no explosive-related compounds, which would be expected from purified RDX given the very low vapor pressure of the material. Headspace analysis of the XM NESTT aids yielded a significant background of hydrocarbons for the petroleum-based variations. The dominant compound in the TNT was TNT itself with small contributions from 1,3-dinitrobenzene (1,3-DNB) and 2,6- and 2,4-DNTs [6]. The discrepancies between these two studies may be due to variation in training aid lots or differences between analytical methodologies. The limited headspace components emanating from these aids in combination with high background odor are likely explanations as to why the trained EDDs did not recognize these materials.

The need to detect homemade explosives (HMEs) has become increasingly important in today's threat landscape. In particular, there is a significant need to train canines for the detection of peroxide explosives, namely TATP and HMTD, which can be synthesized by a novice chemist from commercial materials [19] [20]. However, these explosives are highly shock and friction sensitive [20], making their use, transport, and storage restricted, significantly limiting the use of the true material as training material. TATP is highly volatile compared to many other explosives, including the nitroaromatics. As such, it is readily detectable in the vapor phase and is amenable to be used in creation of Dilution or Sorption Aids. The first to publish on the creation of a TATP Sorption Aid was Oxley et al. (2004), where cotton balls were placed in the headspace of 0.5 g of TATP housed in a 1 L glass jar for 48 hours. Canine testing data (n = 2) indicated that, while the odor from the TATP-impregnated cotton balls was recognizable to the trained canine tested, they were only viable for 20 minutes. Nonetheless, the two canines trained using the cotton ball Sorption Aids were shown to readily detect 0.3 g of neat TATP [21]. Similarly, Moore et al. (2011) and later Simon et al. (2021 and 2022) characterized polydimethylsiloxane (PDMS) as a sorbent for TATP vapor. The headspace analysis indicated that the main volatile compound detected from the TATP-PDMS aid was TATP itself [13][22][23], and, like the impregnated cotton ball, when left open to the environment, the abundance of TATP vapor available dropped rapidly [23]. GetXent tubes are proprietary polymer sorbent material that have recently entered the market and

are advertised as able to ab- or adsorb and then release the odor of any target material that one wants to detect [11]. Like other Sorption Aid substrates, the amount of odor collected and subsequently released by the tube is dependent on the amount of odor from the true material and the soak time [11] [23]. In a study, the GetXent tube was shown to have minimal background odorants compared to the TATP abundance following soaking for 24 and 48 hours, though, like many other Sorption Aids, the TATP vapor was nearly depleted after 8 hours open in the environment [23].

Dilution Aids have also been prepared from trace quantities of TATP. Wilhelm et al. (2022) coprecipitated TATP and HMTD on activated charcoal yielding desensitized materials. Headspace measurements indicated that the activated charcoal/TATP material provided TATP vapor and the background odor from the activated charcoal itself was minimal. Operational canine teams (n = 6) previously trained in the detection of TATP and HMTD, correctly located the TATP training aid in 100% of operational search scenarios which included boxes and vehicles, while ignoring activated charcoal alone and other distractor odors [24]. Additionally, the odor from several commercial Dilution Aids, TrueScent® and TA-SPOT®, were also characterized by headspace analysis. Both contained the target odorant, TATP, in addition to acetone, likely remaining from synthesis of the true material, and diacetone diperoxide (DADP). The quantities of TATP vapor in the two aids were significantly different, with the amount of TATP measured from the TA-SPOT® being nearly two orders of magnitude greater than that from the TrueScent® material. No canine testing was carried out to assess the efficacy of these materials [23].

Finally, Jeunieau et al. (2022) compared common filter paper and gauze-based training aids made by both dilution and sorption. The Dilution Aid was made by pipetting TATP in a methanol solution onto the filter paper substrate, while the Sorption Aid was fabricated by placing filter paper or gauze in the headspace of the true material. The analyses of the training aids found that the amount of TATP on the Sorption Aids (filter paper and gauze) decreased rapidly during the first hour of exposure to the environment, and then more slowly with additional time, with only 40% of the original abundance being present after six hours. In agreement with the Oxley et al. study, this indicated that these Sorption Aids were not viable for long periods of time. The Dilution Aids were prepared solely from the filter paper substrate. At time zero, there was poor reproducibility in abundance of TATP measured between the replicates; however, the amount of TATP on the filter paper decreased more slowly with time, with 88% of the TATP remaining after 10 days left in the open air. The drawback to the measurements made in this work was that the mass of TATP remaining on the substrate was measured by extraction into solution, and the actual abundance of vapor emanating from the aids was not measured, nor were undesirable volatile compounds, such as acetone and DADP. The training aids were also tested using eight canines previously trained in the detection of true TATP. Both the Sorption and Dilution Aids were presented to the canines. All of the canines alerted to the TATP Sorption Aids, while initially not all of the canines correctly indicated to the Dilution Aids, with increasing time and exposure to the Aids, eventually seven of the eight canines recognized the Dilution Aids [7]. Without headspace analysis to understand the volatiles associated with each type of aid, it is not possible to hypothesize why the Dilution Aids were more challenging than the Sorption Aids, though one might speculate that a high amount of residual methanol that evaporates off with time could have been a contributor.

Significantly less research has been published on HMTD training aids, which, like TATP, is a peroxide explosive that can be synthesized in a clandestine lab using commercially-available ingredients, and is even more shock sensitive than TATP [25]. Unlike TATP, molecular HMTD

has a very low vapor pressure and is not readily detected in the headspace of bulk material [26], nor has it been previously detected from commercial training aids [14]. Under ambient conditions, HMTD readily degrades into vaporous components that can be detected from both the bulk material and training aids. The vaporous analytes related to HMTD include formic acid, formaldehyde, formamide, dimethylformamide, trimethylamine, and hexamine [27] [28]. In the bulk materials, the number and ratio of these compounds are known to change with time as the HMTD continues to decompose. Depending on the purity of the starting HMTD, the type of substrate, and the manufacturing process of the training aid, the presence and generation of the compounds is variable initially and as the training aids are used over time [27].

As mentioned, Wilhelm et al. (2022) coprecipitated HMTD on activated charcoal to create a Dilution Aid. Known HMTD degradation products including formamide, formic acid, acetic acid, and dimethylformamide were detected in the headspace of the HMTD aids. The canine teams readily located the activated charcoal/HMTD aids hidden in a desk container, locker, and vehicle, indicating that the odor from the aids was indeed recognizable to the canines [24]. Currently, there are Sorption, Dilution, and Mimic Aids available commercially for HMTD, though there are no peer-reviewed or third-party testing publications related to their efficacy as training aids. Simon and DeGreeff (2019) published a study examining the odor from HMTD training aids available in 2017, including five commercial and novel aids. Of those tested, it was found that each training aid produced unique volatile profiles both upon initial "use" (i.e., removal from the storage vessel) and over time with continued "use" (i.e., regular removal from storage vessel and exposure to ambient surroundings). Not only did volatile profiles not mirror one another, they also did not present a similar odor compared to previous research with true HMTD material [14][27]. No canine testing was carried out, thus the significance of these variations in the odor to canine detection is still unclear.

The goal of this research is to move towards the development of a guideline for testing and evaluation of commercial or novel training aids, using both analytical analyses, as well as canine olfactory testing. In this research, headspace analysis was carried out for nitroaromatic explosives training aids, RDX and PETN, which have not been widely explored in existing literature, as well as peroxide explosives, HMTD and TATP. For the peroxide explosives, batch-to-batch reproducibility and usage lifetime mimicking operational usage, which has not previously been examined, were also assessed. Moreover, a single TATP training aid was selected to be tested in a proof-of-concept canine assessment. The cross-over study design for this assessment tested two sets of "green" canines (i.e., canines with no prior odor detection training); one set trained using the true material in their ability to detect the TA in question, and a second set trained on the COTS TA in their ability to detect the true material.

2 Materials and methods

2.1 Materials

The training aids tested in this study are listed in Table 1 and included aids representing military explosives, RDX and PETN, as well as homemade peroxide explosives, TATP and HMTD. The TW and PDMS aids are categorized as Sorption Aids, SL RDX and PETN are categorized as Mimic Aids, and TS, OP, and GL, as well as SL TATP and HMTD, are considered Dilutions Aids. All aids were purchased through commercial vendors with the exception of the PDMS aid which was made for this study by researchers at the National Institute of Standards and Technology (NIST) using methods described by MacCrehan et al. (2012) [29].

*Table 1.Explosives training aids listed by manufacturer and explosive target. *Included tagged and untagged varieties.*

Training aid manufacturer code	RDX	PETN	TATP	HMTD	Blank	Recommended storage by manufacturer (temperature stored)
SL	X*	X	X	X		Freezer (-4 °C)
TS	X	X	X	X	X	Freezer (-4 °C)
OP	X	X	X	X	X	Not listed (room temp., 20-24 °C)
GL			X	X		Not listed (room temp., 20-24 °C)
TW			X	X		Refrigerator (4 °C)
PDMS			X		X	Refrigerator (4 °C)

All materials were tested immediately out of the package. Only the peroxide explosive aids were subjected to further usage-lifetime studies. All aids were stored at the manufacturer recommended temperatures in their original containment. When no storage recommendations were available, the aids were stored under ambient conditions. Blank training aids were analyzed when provided, though not all manufacturers provided blanks, as indicated in Table 1. All training aids were purchased initially in duplicate allowing for within batch comparisons. Based on these results, several manufacturers were selected for purchase of a third replicate aid, approximately 1.5 – 2 years later, to allow for batch-to-batch comparisons. It should be noted that the substrate for the OP aids changed over this time period likely resulting in a disparity in vapor release between the two batches.

2.2 Analysis of canine training aids for nitroaromatics

Two sampling and analysis methods were used – collection onto thermal desorption tubes with analysis by gas chromatography with electron capture detection (TD-GC-ECD), as well as solid phase microextraction with gas chromatography-mass spectrometry (SPME-GC-MS). The TD-GC-ECD method was used due to its extremely low detection limits for compounds containing nitro- groups, with previous research showing detection limits for RDX and PETN vapor in the parts per trillion vapor concentration range [30]. The SPME-GC-MS method was used to supplement the TD-GC-ECD, allowing for identification of additional headspace components by MS identification.

For both methods, training aids were placed inside 500 mL perfluoroalkoxy (PFA) jars with lids having two ¼" outer diameter (OD) sample ports (Savillex) allowing for duplicate samples. Initially, the sample ports were closed off with caps for 1 hour prior to sampling allowing the volatile compounds from the training aids to enter the headspace of the jars. The sampling ports were then temporarily opened to allow SPME or Tenax-TA TD tubes to be inserted into the jars. A SKC Pocket Pump was used to pull the headspace into the tubes at 100 mL/min for 30 min. The TD tubes were removed and placed into a Gerstel TDS-A tube autosampler. Analytes were thermally desorbed by the Gerstel Thermal Desorption System (TDS) and then collected onto the Gerstel CIS-4 PTV inlet. Analysis was carried out using an Agilent 7890 GC equipped with a 15 m, 0.25 mm (inner diameter) ID, 0.25 µm df Restek RXi-5MS and a µ-ECD for detection. The desorption and analysis parameters can be seen below (Table 2), with methods varying slightly between the analysis of RDX or PETN. For identification of RDX and PETN by retention time, external calibration curves were prepared from RDX and PETN in acetonitrile solution (purchased from AccuStandard).

Table 2. TDS desorption and GC-ECD analysis parameters for RDX and PETN training aids.

	RDX	PETN
Desorption flow	450 mL/min	500 mL/min
TDS initial temperature	20°C	20 °C
TDS desorption parameters	40 °C/min to 250 °C, hold 2 min	180 °C/min to 200 °C, hold 3 min
CIS initial inlet temperature	0 °C	0 °C
CIS temperature parameters	12 °C/sec to 250 °C, 5 min hold	10 °C/sec to 175 °C, 6 min hold 12 °C/sec to 250 °C, 0.1 min hold
GC oven starting parameters	40 °C for 2 min	50 °C for 0.25 min
GC oven Ramp parameters	20 °C/min to 210 °C, 1 min hold 40 °C/min to 250 °C, 1 min hold	20 °C/min to 175°C, 1 min hold
GC column flow	4 mL/min	5 ml/min
ECD temperature	270 °C	270 °C
Makeup gas (N2) flow	60 mL/min	60 mL/min

Analysis by thermal desorption was always conducted first, and then returned to their appropriate storage location. SPME-GC-MS was conducted between one and seven days later. For analysis by SPME-GC-MS, the training aids were again placed inside the jars this time fitted with a Swagelok fitting containing a GC inlet septum on each sample port which was used to close off the jar to allow for the headspace to equilibrate while still allowing the SPME fibers to be inserted into the jar for sampling. The samples were allowed to equilibrate for 1 hour, followed by a 1-hour sample time using divinylbenzene / polydimethylsiloxane / carboxen (DVB/PDMS/CAR) SPME fibers. Analysis of the fiber was performed on an Agilent 7890 GC coupled to a 5975 MS. Analytes on the fiber were thermally desorbed in a standard split/splitless inlet heated to 260 °C. The GC oven was set at 35 °C for the start of the run for 0.5 min, followed by a 40 °C/min ramp to 240 °C with a final hold of 1 min. The GC column used was 15 m, 0.25 mm ID, 0.25 µm df Restek RXi-5MS, with a flowrate through the column of 2 mL/min and a 10:1 split. The MS was operated under standard conditions, with a scan range of *m/z* 40-400. The resulting chromatograms were analyzed qualitatively, and any compounds not also in the blank were tentatively identified by the NIST mass spectral library.

2.3 Analysis of canine training aids for peroxide explosives

For the analysis of both target compounds, the TATP and HMTD training aids were placed in PFA jars. On the first occasion the samples were tested (Day 0), individual aids were placed in the jars for 1 hour to equilibrate, followed by a 1-hour SPME extraction for the HMTD aids and 5 min extraction for the TATP aids. After the initial headspace sampling, to simulate regular usage in the field, all training aids were opened twice a week for four hours. Sampling occurred once a week during the first of the two weekly four-hour sessions. On the day of sampling, the training aids were first opened to the laboratory atmosphere for one hour, after which the jars were closed for two hours – one hour for the headspace to accumulate and one hour for sampling, though the actual SPME sampling time for the TATP aids was 5 minutes, and for the HMTD aids, 1 hour sampling time. Finally, the jars were left open for one final hour, to total four hours of the aids removed from storage. On days when sampling did not occur, the training ais were simply placed in the open PFA jars and left on the lab bench for four hours before they were returned to the appropriate storage.

The GC-MS analysis parameters for both TATP and HMTD training aids can be seen below (Table 3) and was performed on an Agilent 7890 GC coupled to a 5975 MS for TATP and an

Agilent 6890 GC coupled to a 5975 MS for HMTD. An external liquid calibration curve of TATP in methanol (Accustandard) was used to determine the quantity of TATP on the SPME fiber. The abundance of the individual analytes detected from the HMTD were normalized by comparison to an internal standard (methyl anthranilate, >98%, Sigma-Aldrich), sampled for 5 seconds in a 4 mL headspace vial prior to exposure to the training aids. The changes in headspace for each training aid were analyzed over time, as well as quantitative and qualitative comparisons between the different training aids for the same analyte.

Table 3. GC-MS Analysis parameters for TATP and HMTD training aids

	TATP	**HMTD**
Inlet Temp	260 °C	260 °C
GC oven starting parameters	35 °C for 0.5 min	35 °C for 1 min
GC oven ramp parameters	40 °C/min to 240 °C, 1 min hold	25 °C/min to 180 °C, 1 min hold 40 °C/min to 240 °C, 2.2 min hold
Column flowrate	2 mL/min	3 mL/min
Inlet split	10:1	10:1
Column	15 m, 0.25 mm ID, 0.25 µm df Restek RXi-5MS	15 m, 0.32 mm ID, 5 µm df Restek RTX-VolatileAmine
MS scan range	*m/z* 40-400	*m/z* 50-550

2.4 Odor recognition training and testing by canine

While it was beyond the scope of the project to test all canine training aids included in the analytical study, a single training aid, the OP TATP aid, was chosen to explore the potential role a non-detonable training aid could play in the imprinting and/or maintenance training of odor detection canines. In this portion of the study, 11 canines not previously trained in odor detection (referred to as "green") were initially trained to detect the Universal Detector Calibrant (UDC), 1-Bromooctane (CAS# 111-83-1). The UDC was used as an initial training tool to teach the canines search mechanics, provide a non-target odor during maintenance training, and to serve as a vigilance and motivation aid during testing. After all canines were proficient at the detection of the UDC (defined as consistent 90%+ detection rate), the 11 canines were separated into two groups. The Experimental Group (n = 6) was imprinted and trained using the OP non-detonable TATP training aids and the Control Group (n = 5) was imprinted and trained using 1 gram of true TATP material synthesized by the Federal Bureau of Investigations (FBI) on August 23, 2021 (approximately 3 months prior to training). After the canines were proficient at the detection of their training aids (defined as consistent 90%+ detection rate), both groups were tested on both sets of training aids (non-detonable and true material), as indicated in Figure 1. Additional information about the training of the canines can be found in Appendix A.

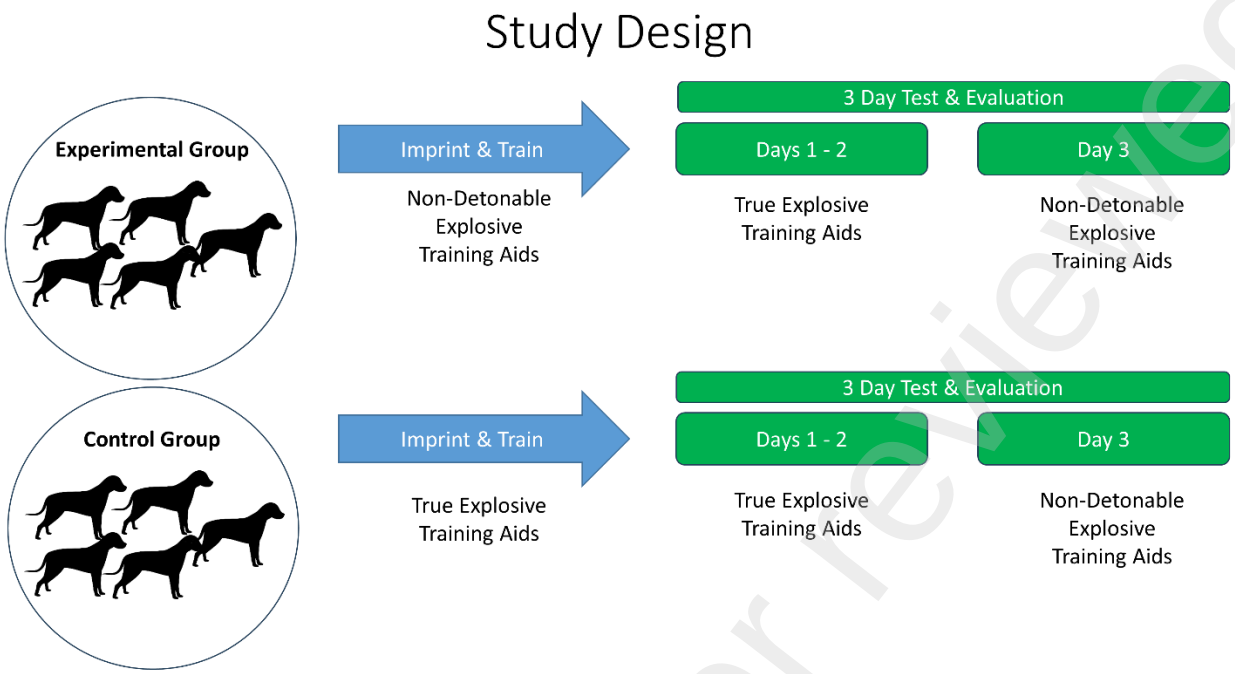


Figure 1: Illustration of the design utilizing two groups of canines, one trained using the non-detonable explosive training aid (experimental group) and one trained using the true explosive material (control group). Both groups were then tested on both the non-detonable and true explosive material.

Testing took place at Tactical Directional Canine Systems (TDK9) in Smithsburg, MD from 10-13 January 2022 where the canines were trained and housed for the duration of the study. For the Odor Recognition Test (ORT), the targets (actual TATP or OP TATP training aid) and non-target items (distracter odors and negative controls) were concealed within discrete sample locations, specifically four ammo cans held within a custom wooden lineup (Figure 2). Holes were added to the lid of each ammo can to allow for the odor to be released, and customized wooden inserts were fabricated to hold test items steady within each ammo can.

Figure 2: (Above) odor recognition trial lineups and (Below) custom ammo cans with holders for anti-static vial (left) and TADDs (right).

Test items included target odors, controls, and distracters (Table 4). Target items used include new (i.e., unused and previously unopened) 1 g sample of TATP, provided by the FBI (synthesized on 8/23/21 – the same batch/date as the training sample), within an anti-static vial, an OP TATP training aid within a Training Aid Delivery Device (TADD; SciK9), as well as the Universal Detector Calibrant (UDC) [31] used in the canine training (see Appendix A) also within a TADD. TATP and OP aids were presented to both groups of canines as indicated previously by the study design of the ORT. The UDC was utilized as the target prior to the start of the ORT to allow each canine a chance to become acclimated to the format of the ORT before starting data collection on OP and TATP targets. Data was not collected during the acclimation sessions with UDC. During the data collection portion of the ORT with TATP and OP aids, the UDC was provided as an additional opportunity for a canine to be rewarded for the act of searching the trials prior to leaving the session, but was not included in the data collection. It was noted that certain canines demonstrated diminished search vigilance during the test scenarios if they were not rewarded as regularly as they were accustomed to in training, therefore utilizing the UDC allowed the handler an opportunity to reward the canine prior to leaving a session to keep each canine motivated to continue to search in upcoming sessions.

Table 4: Test items used in the ORT.

Test Item Type	ID	Description
Target	T-1	1 g TATP in Anti-Static Vial
	T-2	OP TATP in TADD
	T-3	UDC + Cellulose in TADD
Control	C-1	OP Blank in TADD
	C-2	Anti-Static Vials
	C-3	TADDS + Cellulose
	C-4	Anti-Static Vials + Cellulose
	C-5	Empty TADDs
Distracter	D-1	Gloves
	D-2	DI Wipes
	D-3	Mylar Bags

Non-target items included negative controls and distracter odors (Table 4). Negative controls included a blank OP aid, as provided by the manufacturer, in a TADD, empty anti-static vials, TADDs with cellulose, anti-static vials with cellulose, and empty TADDs. The presence of

these materials required the canines to discriminate between target odors, materials they may associate with the target (i.e., controls), and novel odors (i.e., distracters). Distracters included nitrile and polyethylene gloves, deionized (DI) water wipes, and mylar bags as those items came into contact with test articles. Inclusion of these materials also helped ensure that the activity of placing items into the test did not become a cue for the canine.

Each lineup of four ammo cans contained a single target material within an ammo can and the rest of the ammo cans within the lineup contained negative controls and distracters chosen randomly. A minimum of one blank lineup was also used each session and included no target material, only negative controls and distracters. To avoid cross-contamination of the various target materials used in the testing, test items were maintained in dedicated, labeled containment devices and sealed inside a quality, secondary container for all transport and storage prior to the event. All materials were handled while wearing clean nitrile gloves, and new, clean nitrile gloves were used when handling each type of material. Previously unused ammo cans were dedicated to each type of control, target, or distracter.

A search of each lineup containing four ammo cans constituted one trial. A search of all five lineups, placed in separate areas and searched sequentially, is referred to as one session. A total of 37 sessions over the course of 3 days across all dogs were conducted. All testing materials were allowed a minimum 30-minute equilibration time prior to the first team beginning their search. After completing the session, the canine team left the testing area, and the outer surface of the ammo cans were each cleaned with a new deionized water wipe to remove saliva and hair which could inadvertently cue subsequent canine teams to the location of target items.

2.4.1 Canine Handling, Execution, and Scoring

A single handler was used for all canines to minimize handler effect on the results. The order of the trials and the items within the trials were randomized for each canine being tested. Testing was conducted with the canine 'on-lead' due to the hazardous nature of the TATP. Each canine searched the trial and the handler made a determination whether the canine alerted to presence of a target material (or if they felt the trial was blank) prior to moving on to the next trial. The handler was allowed to re-send the dog to previously visited containers until the handler indicated a response on a container or whether the trial was a "blank". Once the handler terminated a search, the team proceeded to the next trial within the session; they were not allowed to return to the completed trial. The final outcome (position of an alert or a "blank") was scored in addition to whether alert occurred on the first sample of a container or after one or more

The test administrator was visually segregated and concealed from the handler and canine using a Schutzhund blind to eliminate administrator-influenced bias. When the handler believed they had a final response, the handler signaled to the test administrator with a thumbs up. The test administrator would respond with showing either a thumbs up (to indicate a positive alert) or thumbs down (to indicate a false alert) to the side of the blind. In the case of a correct response to TATP or the OP TATP training aid, the canine was scored with a detection and the handler rewarded the canine. In the case of an incorrect response, the canine was scored with a non-productive response and the handler either directed the canine to continue searching the trial or move on to the next trial. If the canine failed to respond to a target, the handler was not notified or corrected; the canine simply was scored with a miss. The test administrator electronically recorded the outcome (detection/miss/false alert) of each test item on a Microsoft Surface tablet with Canine Assessment Tool (CAT) software previously developed by Excet, Inc. The CAT software was pre-loaded with the test matrix prior to the start of the ORT.

3 Results and Discussion

3.1 Analysis of training aids for nitroaromatics

Duplicate RDX and PETN training aids were obtained from three commercial manufacturers. Brands TS and OP provided the RDX and PETN aids in addition to a blank, which was the training aid substrate and packaging sans odorants or explosive material. SL provided two types of RDX training aids, "tagged" and "untagged", referring to the addition of the taggant, 2,3-dimethyl-2,3-dinitrobutane (DMNB). A true SL blank was not available, instead the outer training aid packaging that housed the powder substrate alone and not including the substrate material was provided.

The main headspace components found in the SL RDX training aids were octane (1), cyclohexanol (2), cyclohexanone (3), and 2-ethyl-1-hexanol (4), all compounds known to be associated with C-4 plasticizers and not the RDX explosive itself [32], as well as DMNB (6) in the tagged aid (Figure 3A). The compounds were found in similar amounts for all replicates. The PETN training aid had small quantities of octane, as well as toluene and an unknown branch alkane noted as #5 in Figure 3A. There were no compounds with abundances near or above the explosive-related odorants found in the backgrounds or the blank aid.

Though purchased on the same occasion, the two OP RDX training aids were very distinct from one another. Octane (1), cyclohexanol (2), cyclohexanone (3), and 2-ethyl-1-hexanol (4) were detected in Sample 1, but not Sample 2 (Figure 3B). Penta- (5) and hexanedioic acid dimethyl ester (6), were also detected at lower levels in both the PETN and RDX training aids (Figure 3B). The origin of these compounds is unknown, as they were not detected in the blank. The PETN training aids had no other compounds present, and no RDX or PETN was detected in the vapor phase from any of the OP training aids. No other compounds that were greater than the main explosive-related odorants were found associated with the blank aid. A comparison of the SL and OP RDX training aids can be seen below (Figure 3D). The total amount of explosive-related odorants is approximately an order of magnitude higher for SL compared to OP. Indeed, it was noted that upon opening the SL aid from the manufacturer storage container, the odor experienced by the researcher was quite intense, if not overwhelming.

The TS RDX and PETN aids differed from SL and OP aids. The TS training aids had a number of lower-level compounds in the headspace that were not found in the blank provided by the manufacturer (Figure 3C). The majority of these compounds were branched and straight chain alkanes. No compounds commonly reported as being associated with explosives were detected, although it should be noted that the same unknown branched alkane at 2.24 min was found in the SL PETN aid was also a major component in the headspace of the TS PETN aid.

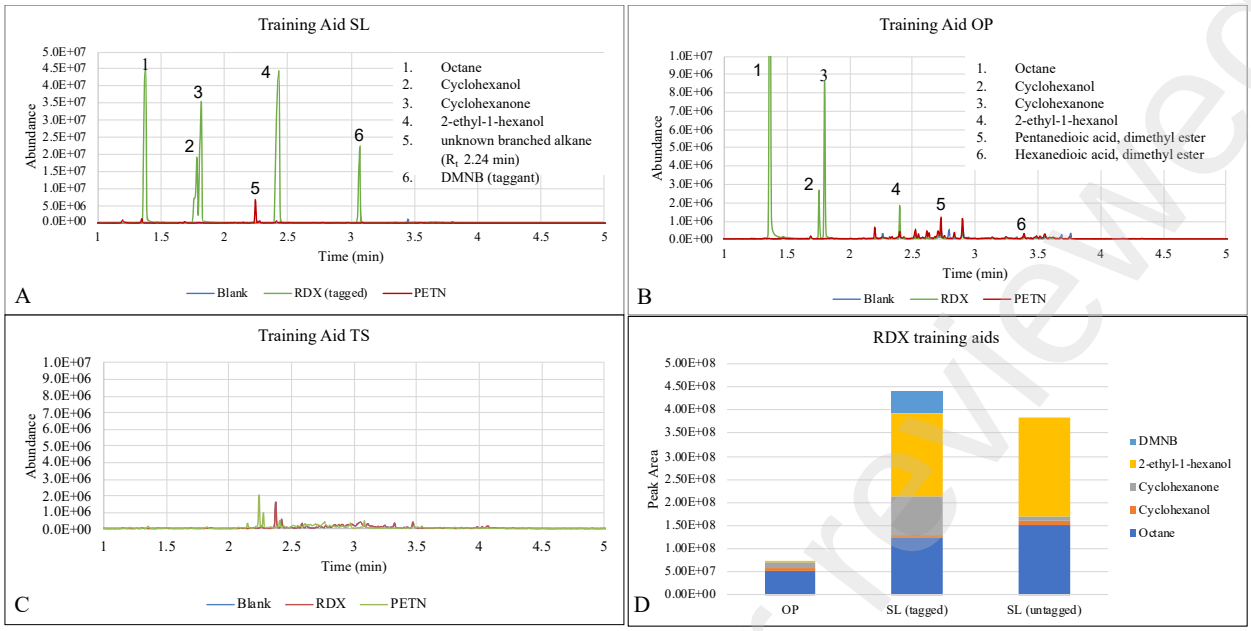


Figure 3. (A-C) Chromatograms representing the headspace of blank, RDX, and PETN training aids from Brands SL, OP, and TS, respectively. Some major headspace components are labeled. (D) Stacked bar graphs representing the relative peak areas of major explosive-related headspace components in RDX training aids from Brands OP and SL (tagged and untagged).

While most of the training aids tested had some distinct odorants, PETN and RDX were undetectable in all the training aids in the vapor phase by both the TD-GC-ECD or SPME-GC-MS methods. Though this does not imply that those compounds were not present in the training aids, it does indicate that, if present, they are at very low vapor concentrations owing to the extremely low vapor pressures of those compounds. While detection of these low volatility analytes by canines may be possible, the presence of other, much more volatile compounds, are likely more readily detected by canines. In particular, octane, cyclohexanol, cyclohexanone, and 2-ethyl-1-hexanol were present in several of the RDX training aids, and can be associated with plasticizers used in RDX based explosives. These have very high vapor pressures ranging from around 0.14 torr for 2-ethyl-1-hexanol to 14 torr for octane, compared to vapor pressures of RDX (3.3E-09 torr) and PETN (1.16E-08 torr) [33]. Additionally, an unknown branched alkane compound was found in several PETN training aids, although the association with PETN explosives is unknown.

3.2 Analysis of training aids for peroxide explosives – HMTD

3.2.1 Initial headspace profile and inter- and intra-lot variability of HMTD training aids

Figure 4 compares the headspace components of the commercially-available HMTD training aids at Time 0, or immediately after being removed from the packaging. Overall, the TW aids had the greatest amount of odor which was dominated by formic acid, a product of HMTD decomposition that increases with age or impurity of the sample [27]. The headspace profiles of the TS, SL, and, to a lesser extent, GL aids were also dominated by formic acid. All training aids also had formaldehyde in at least one sample, which has been identified as a primary compound found in fresh HMTD [27]. Other compounds indicative of HMTD decomposition could be seen

as well, including acetic acid in SL B and TW A and B, and formamide in SL B, GL A and B, and TW A and B.

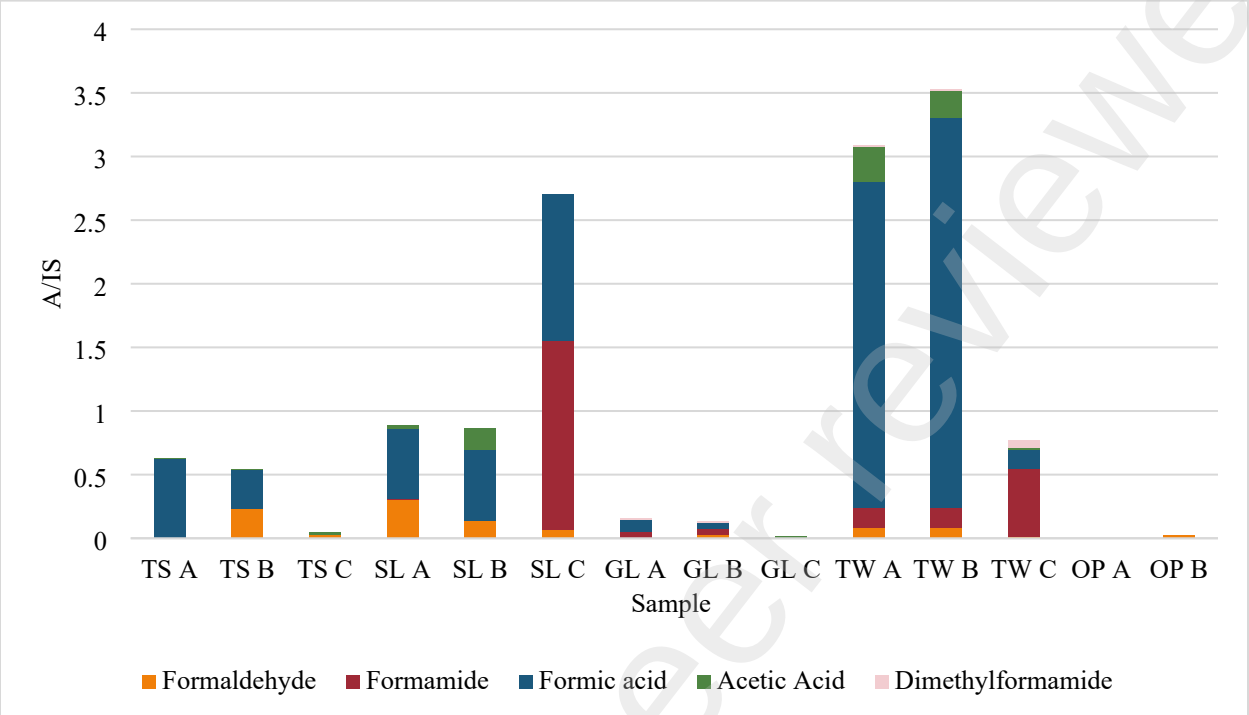


Figure 4. Volatile compounds detected from the headspace of HMTD training aids, measured upon removal from the manufacturer packaging (Time 0). Data is given as the ratio of analyte (A) to internal standard (IS) peak abundance and are averages of duplicate measured for each sample. Replicates A and B were purchased at the same time, while replicate C was purchased approximately 1.5. years later.

Samples A and B were duplicate samples purchased at the same time. Of these, no pair were identical, but most did emit similar total amounts of odor. Sample C was purchased for a subset of these aids approximately 1.5 years later. It was assumed that because Samples A and B were purchased at the same time, they were likely from the same batch, while Sample C was from a different batch being purchased at a much later date. Because the headspace profile of HMTD is highly dynamic and variable, it was hypothesized that there could be significant variation between lots of HMTD training aids. Indeed, this was found. The TS C and GL C aids had much lower relative quantities of odorants compared to Samples A and B, which could be accounted for in several ways. Because these materials are Dilution Aids utilizing small amounts of actual explosive material on a substrate, the quality and age of the HMTD used in fabrication would affect the resulting odor. Thus, it was possible that the HMTD used to fabricate these aids was more pure or fresher, or, though seemingly less likely, simply less physical material was added to the substrate. On the other hand, both SL and TW C training aids had notable increases in formamide compared to their earlier batches, and TW C had significantly less formic acid. These differences may be due to a number of factors that affect the decomposition of HMTD.

In addition to the headspace compounds indicated in the figure above, some additional non-HMTD-related compounds were noted (Figure 5). At Time 0, acetonitrile was noted in the TS HMTD aids at quantities much higher than the even the most abundant HMTD-related volatiles, although a similar quantity of acetonitrile was also found in the blank material, and evaporated off after the second use (Week 1). Isopropyl alcohol was noted in SL and GL aids at Time 0, though

is far lower quantities. In addition to the presence of solvents, a notable nitromethane peak was found in SL A and B (but not SL C), which can likely be attributed to cross-contamination with other aids fabricated in similar area at a similar time.

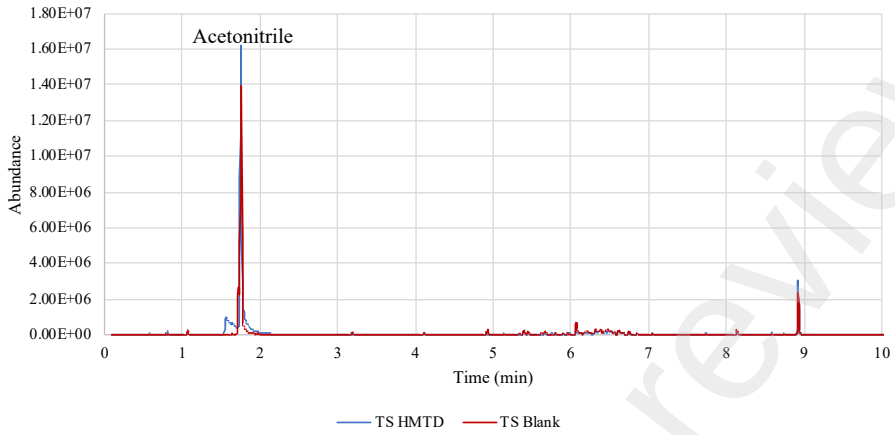
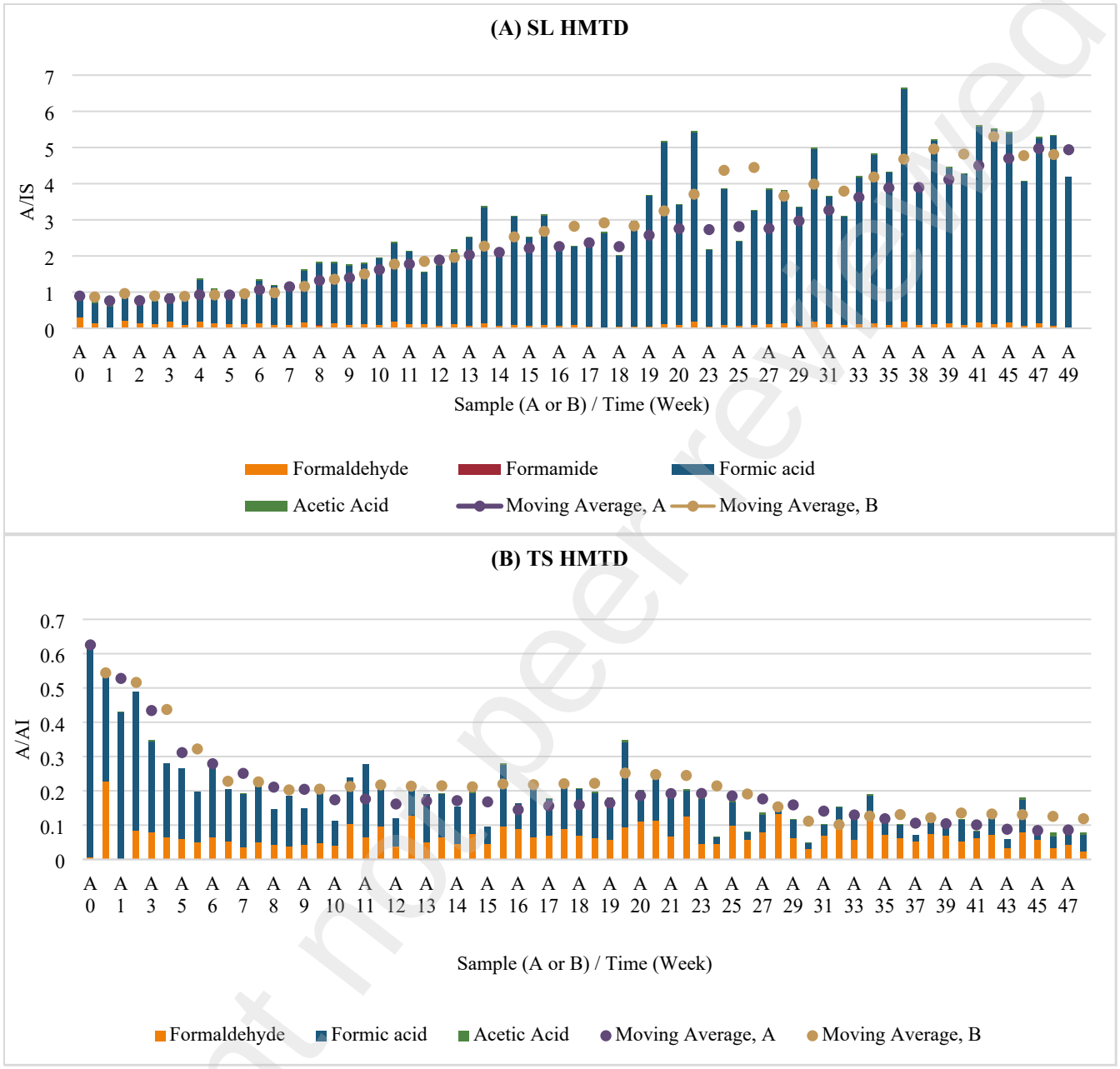


Figure 5. Chromatogram of TS HMTD C overlaid with TS Blank C training aids, Time 0. Acetonitrile peak is identified.

3.2.2 *Headspace profile of HMTD training aids over time*

The headspace profiles from Samples A and B were assessed over time. For this purpose, the training aids were removed from the suggested storage location (freezer, refrigerator, or ambient), brought to room temperature, and then removed from their outer packaging in which they were received (all were metalized, resealable bags) and sampled as described above. The figures below display the changes in headspace profiles over time. All aids tested showed unique patterns of HMTD depletion and decomposition over time yielding odor profiles that varied both qualitatively and quantitatively, as can be seen in Figure 6. Three of the four aids (TS, GL, and TW) decreased in the total abundance of odorants overtime, as would be expected as the odorants on the substrate become depleted. The total abundance of odorants in the SL training aid, on the hand, increased over time, specifically in the abundance of formic acid, indicating active decomposition of the HMTD material on the substrate [27].



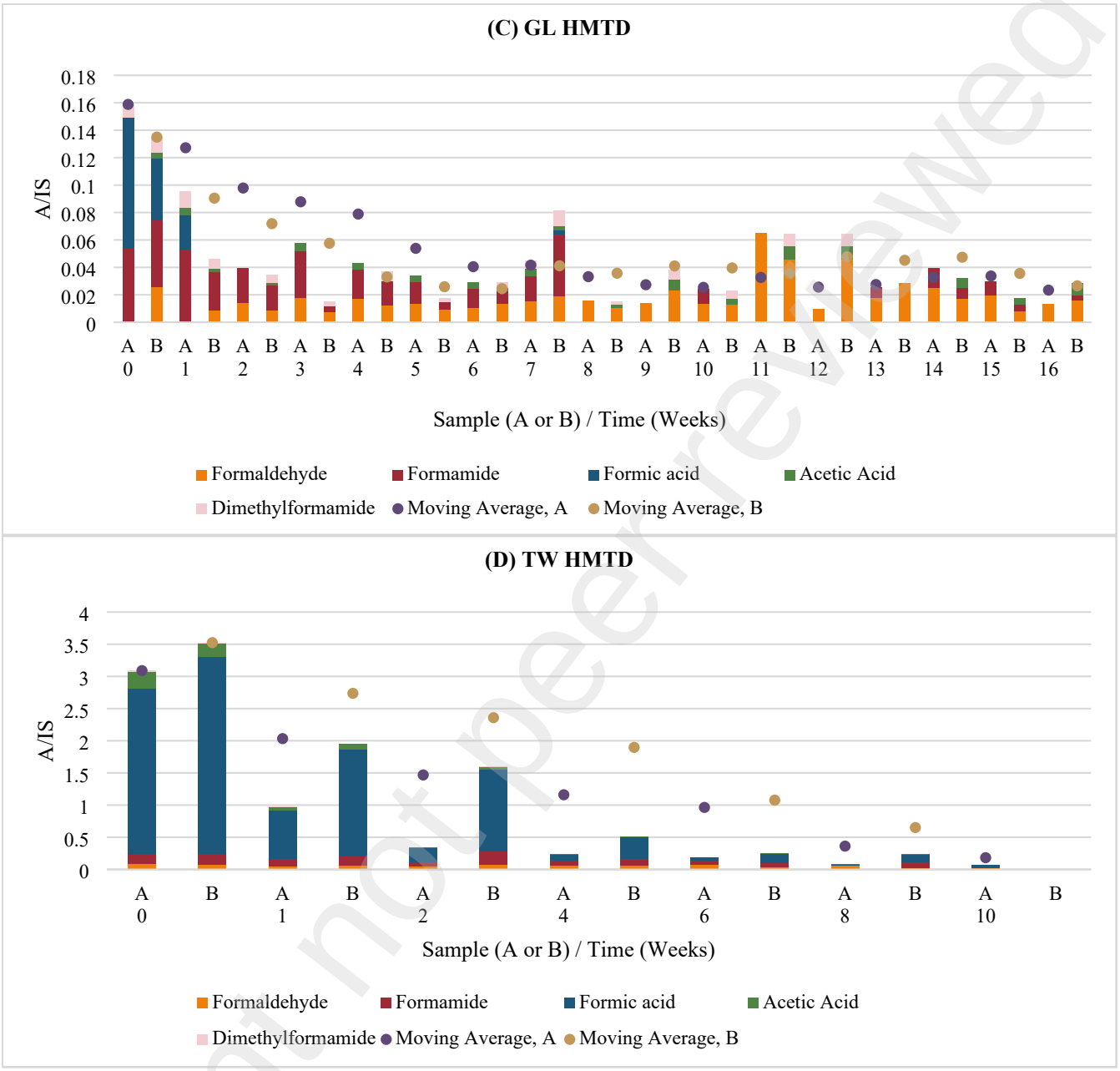


Figure 6. Comparison of the headspace profiles detected from HMTD training aids Samples A and B over time for training aids (A) SL, (B) TS, (C) GL, and (D) TW. Data are reported as a ratio of analyte (A) to internal standard (IS) peak abundance and are the averages of duplicate SPME-GC/MS analyses for each sample. Each point on the graph is the average total A/IS abundance of the five previous data points.

The odor emitted from the SL aid primarily consisted of formic acid and was still increasing after 49 weeks of testing. No new HMTD-related compounds were noted during this time period; however, the ratio of formic acid compared to the formaldehyde, the other main headspace component at Time 0, increased over time (Figure 6A). The main odorants in the TS aids were formic acid and formaldehyde. While the total abundance of odorants from the TS HMTD aid decreased over time, odorants could still be readily detected after 47 weeks. The decrease in the total abundance was correlated to a decrease in the formic acid, as the formaldehyde levels remained similar over the duration of the experiment, again resulting in a change of ratio of these

odorants (Figure 6B). The GL aids initially had formic acid, like the other aids, and formamide, as well as contributions from acetic acid and dimethylformamide, although the total abundance of these compounds was much lower than the other aids tested (Figure 4). The total odorant abundance decreased significantly after the first day of use, which was to be expected as the aid is said to last 4-8 hours by the manufacturer; however, HMTD-related odorants could be detected through Week 16. After Day 1, the formic aid was no longer detectable and the headspace profile was predominantly made up of formamide (until Week 7) and formaldehyde (Figure 6C). HMTD-related odorants were detected from the headspace of the TW aids for the least amount of time, with odorants being detected in both Sample A and B only through Week 8. The main headspace compound was formic acid, and this decreased over time, while smaller quantities of formaldehyde and formamide remained through Week 8 (Figure 6D).

3.3 Analysis of training aids for the detection of peroxide explosives – TATP

3.3.1 Initial headspace profile and inter- and intra-lot variability of TATP training aids

The initial quantity of TATP vapor measured from each commercial TATP training aid is given in Figure 7. The quantities measured initially upon opening the aid is given in comparison to that from 790 mg of bulk TATP (provided by the Federal Bureau of Investigation, Explosives Unit) sampled in the same manner. The quantity of TATP odor from the SL (Sample A), GL (Sample B), and PDMS training aids were significantly higher than that from OP and TS, while no TATP was detected from the TW devices.

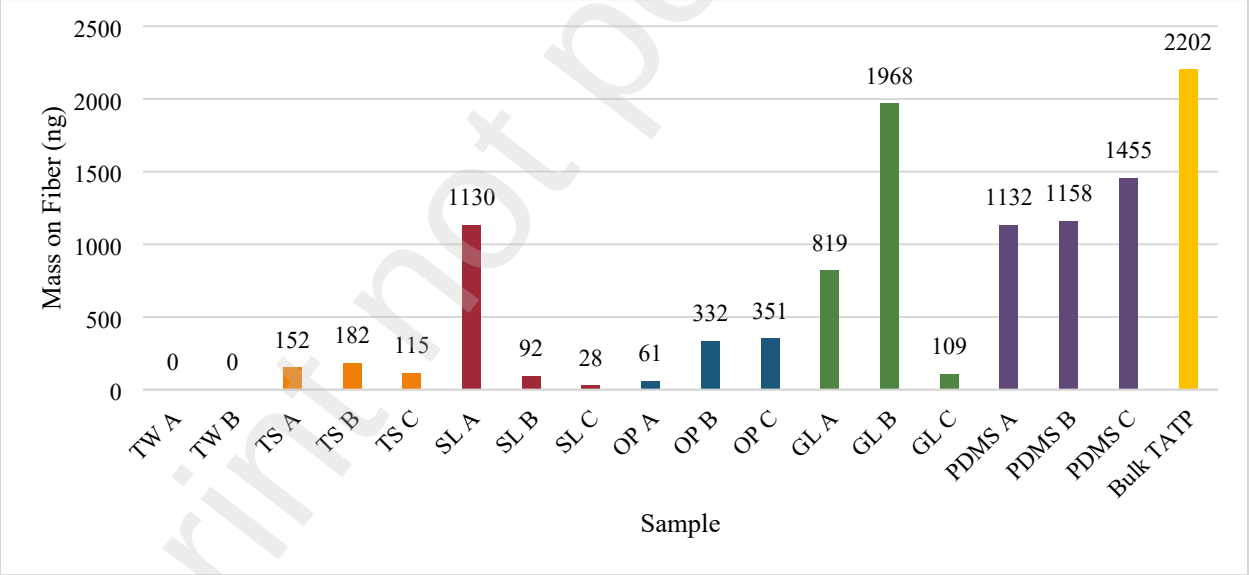


Figure 7. Relative quantity of TATP detected in the headspace of TATP training aids, measured immediately upon removal from the manufacturer packaging (Time 0). The data are reported as an average of duplicate measurements in mass (ng) collected on the SPME fiber. Replicates A and B were purchased at the same time, while replicate C was purchased approximately 1.5 years later.

As with HMTD, the Samples A and B were purchased at the same time, presumably from the same manufacturer lot, while Sample C samples were purchased 1.5 years later. The PDMS aids were made by NIST over several months, and A and B were from the same lot at the same time, while C was made from a different lot of bulk TATP several months later. The TS and PDMS

aids were the only aids to produce similar intra- and inter-batch TATP vapor quantities. The other aids showed much larger discrepancies, not just between batches but also within a single batch.

While none of the training aid substrates were wholly free of VOCs, the majority were many orders of magnitude lower in abundance than the TATP peak. The only significant non-target compounds detected from any of the training aids was acetone, which was detected in all but the PDMS and TW aids. From the chromatograms shown in Figure 8, one can see the relative abundances of acetone and TATP in the headspace of the aids. TATP was the dominant peak in the GL and OP TATP aids, with the peak being more than an order of magnitude in excess of the acetone peak. However, acetone and TATP were of similar abundance in the TS TATP aid, and, in the SL TATP aid, the acetone peak was larger than the TATP peak. It should be noted that the TS blank also had a similar amount of acetone as the TS TATP aid, as shown in the chromatogram. No acetone was detected from either the SL or OP blanks, as seen in Figure 3A and B.

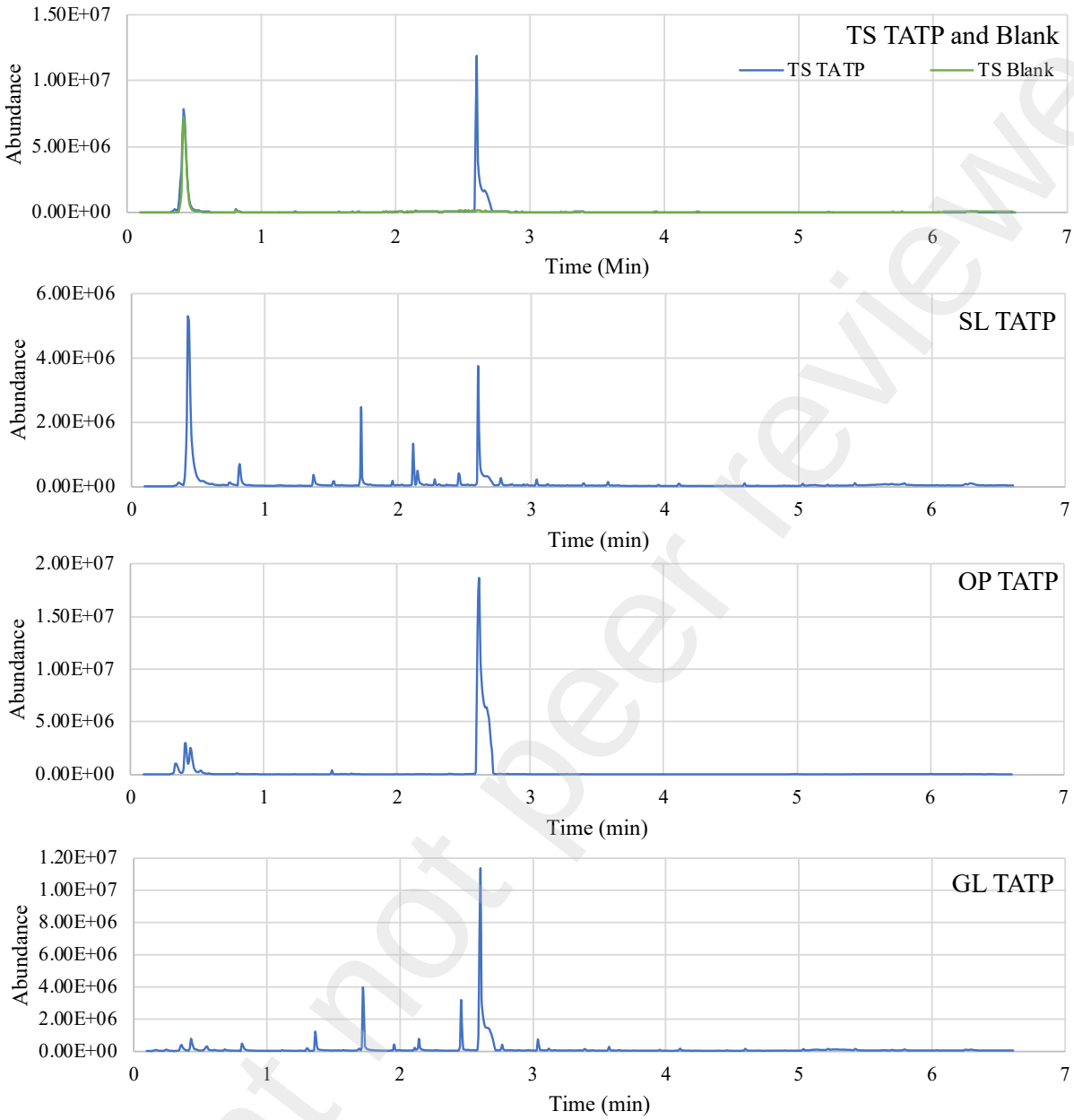


Figure 8. Representative chromatograms from TATP training aids, (A) TS, (B) SL, (C) OP, (D) GL. Acetone (0.45 min) and TATP (2.6 min) peaks are highlighted.

3.3.2 *Relative quantities of TATP vapor in training aids over time*

Figure 9 gives the relative abundance of TATP collected from the TATP training aids over time. The TW aid was not included in this data set, as no TATP was detected at Time 0. The data in Figure 9 are reported as the percent of the starting amount of TATP measured at Time 0. The replicate samples from each manufacturer performed relatively similar to each other over time, with the exception of GL TATP. The abundance of TATP in most training aids trended downward, as to be expected as the source of TATP was depleted. However, GL A actually increased up to

more than 250% of its original value. It is unclear what caused this additional release of TATP as both training aids were sampled on the same day and treated in the same manner. SL TATP, Sample B also had a temporary influx in TATP vapor detected.

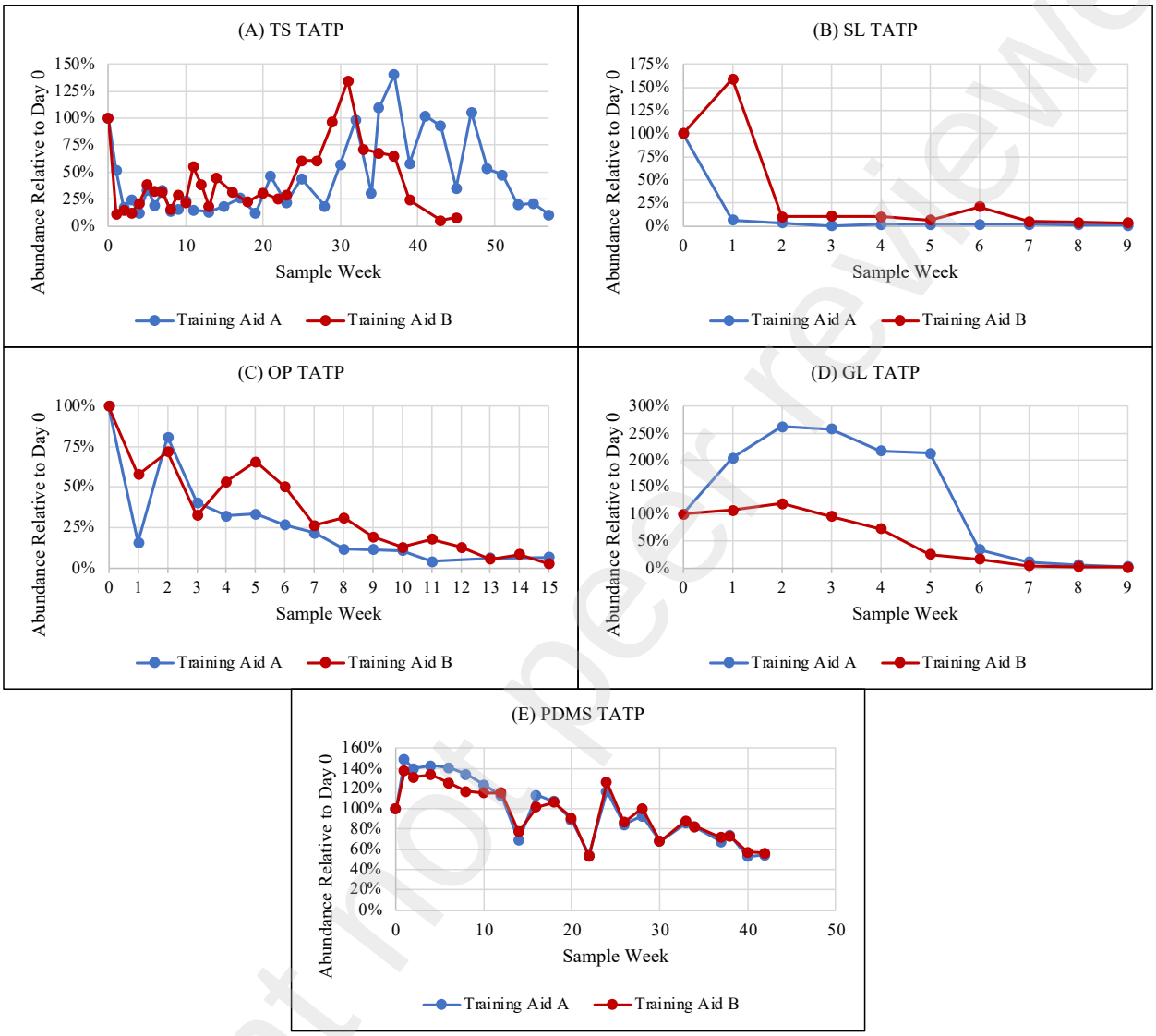


Figure 9. Comparison of the headspace profiles detected from TATP training aids Samples A and B over time for training aids (A) TS, (B) SL, (C) OP, (D) GL, and (E) PDMS. Data are reported as the percent abundance relative to Day 0 and are the averages of duplicate SPME-GC/MS analyses for each sample.

More notably, the amount of TATP from the TS aid initially dropped after Time 0, but then increased after Week 24 (Figure 7A). The largest amount of TATP detected was 214 ng and 245 ng mass on fiber for Training Aids A and B, occurring on Week 37 and 31, respectively. While there is no visible evidence of wear on the devices, it is possible that the materials used to contain the loaded substrate become more permeable over time due to handling, or it is possible that the substrate within the devices changed, allowing for greater release of the sequestered TATP analyte over time. Regardless of the mechanism for this increase in TATP released, the amount detected remained elevated until approximately Week 31 (Training Aid B) and Week 37 (Training Aid A)

when the TATP vapor began to deplete. Sampling ceased when the total amount fell below 10% of the initial abundance (Week 45, Sample B and Week 57, Sample A).

The TATP vapor from the SL aid (Figure 9B) rapidly decreased to below 10% of their original abundance after the first or second use, Time 0 (Sample A) or Week 1 (Sample B), respectively. The OP (Figure 9C) and PDMS (Figure 9E) aids yielded a steadier decrease in TATP abundance over time. The OP TATP aid reached below 10% of the original measured amount of TATP vapor by Week 13. The usage lifetime of the GL aid, under the given conditions, was estimated to be 7 weeks (Figure 9D). The PDMS was the longest lasting aid, still at above 50% of the original concentration through Week 42. Overall, the lifetime of the PDMS aids is likely to be significantly longer than the current testing period based on the consistent behavior of the devices, and despite some variability in the weekly data the overall trend of the headspace appears to be fairly consistent, with the relative abundance decreasing at a rate of 1.7% and 2.1% per week for Samples A and B, respectively.

3.4 Odor recognition tests by canine

Error! Reference source not found. shows the proportion of trials in which the dogs made a correct response (alerts to the TATP or the OP training aid) for the dogs trained with TATP (TATP-trained) and dogs trained with the OP training aid (OP-trained). Both groups of dogs showed similar responses to the OP training aid, but lower detection accuracies were observed for the OP-trained dogs. A logistic mixed effects model was fit in which trial accuracy (0 or 1) was predicted by the training aid material (TATP or OP) for detection of the OP material and TATP material (separate models). A random intercept was fit for each dog for each model. Overall, there was no difference in detection of the OP material between the OP-trained and TATP-trained dogs (X^2=0.66, p=0.42). There was, however, a difference for detection of TATP in which TATP-trained dogs outperformed OP-trained dogs (X^2=37.39, p<0.001).

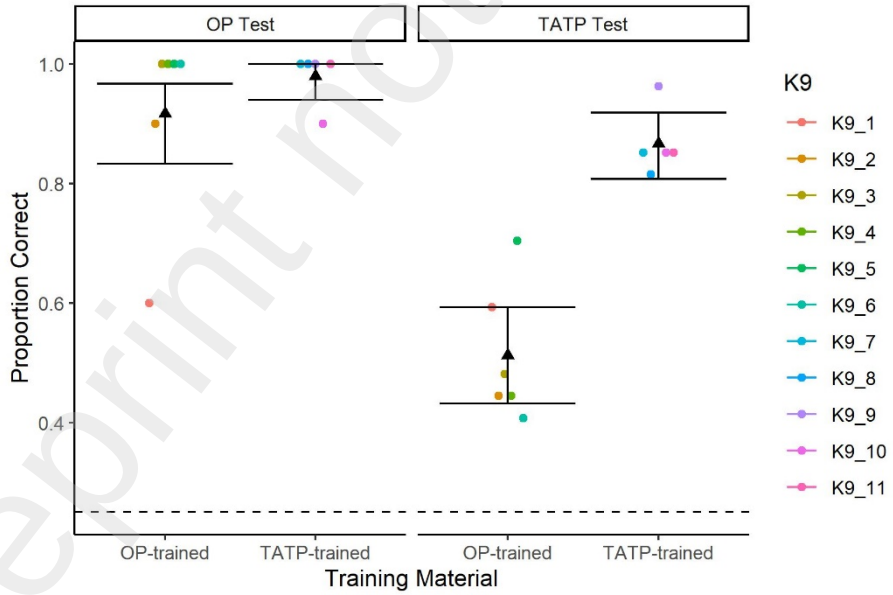


Figure 10. Proportion Correct in Detection. Triangle shows the mean and error bars shows the 95% bootstrap estimated confidence interval. Dashed line indicates chance performance, 25%.

Figure 11 further breaks down the difference in TATP detection between the TATP-trained dogs and OP-trained dogs on a trial-by-trial basis. This highlights that dogs showed substantial within-session training to the TATP test material. On Trial 1, no OP-trained dogs made a correct response to the TATP test material, whereas 60% of TATP dogs showed a response. Nonetheless, this still indicates a decrement from the training criterion prior to test (90% accuracy), indicating that the unopened TATP material was perceptually different than the trained target for TATP trained dogs. Similarly, Figure 11B shows the same data for trials in which the TATP was present but restricting a correct response to dogs' first evaluation of each odor container. This analysis is a more conservative evaluation of canine performance by scoring a response as correct, only if the dog alerted when first investigating the target container. An incorrect response was scored if a dog had to sample all containers, then return to a previously sampled container to indicate a target (e.g., the dog passed the target on the first investigation). Nonetheless, similar results are observed, where both groups of dogs show poor initial recognition of the TATP used during testing, but TATP dogs learned more rapidly to detect the testing TATP.

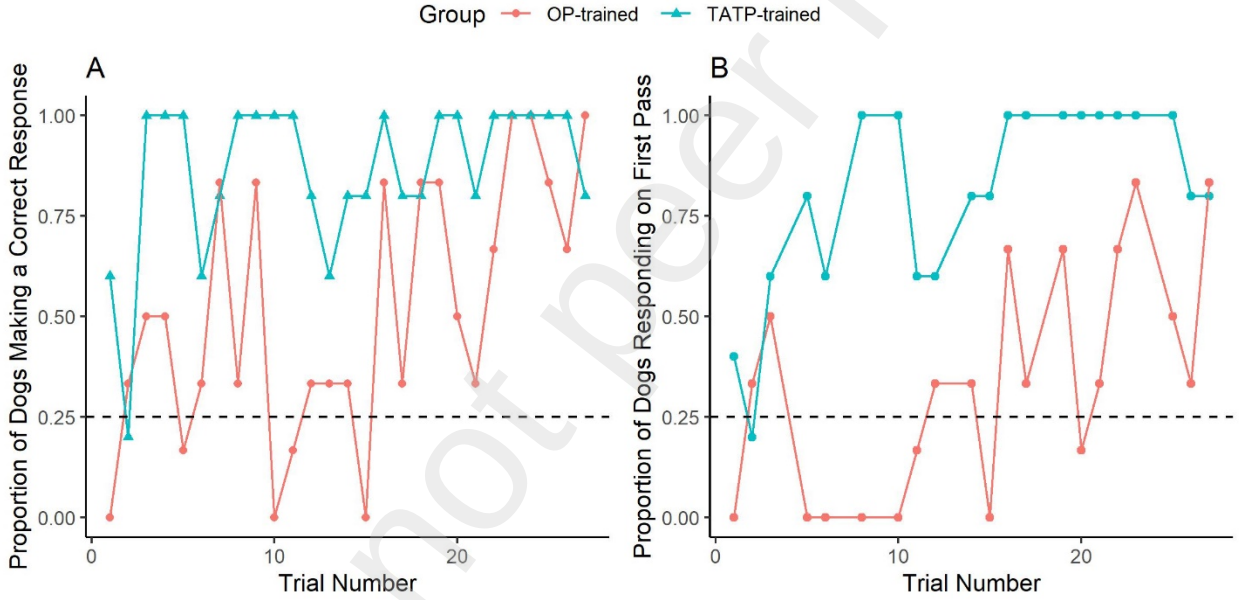


Figure 11. Acquisition of response to the testing TATP material. A: Proportion of dogs responding correctly by trial number. B: Proportion of dogs correctly responding to the TATP test material on the first investigation of the test material within the trial.

Lastly, to evaluate stimulus control of the dogs, we calculated the probability of alerting to all the odors (including distractors and controls). Figure 12 shows the proportion of trials in which a response was made to an odor, which was defined as the number of trials a response was made to an odor divided by the number of trials in which that odor was presented to the dog. Looking at individual dog patterns, OP trained dogs such as K9_3 and K9_4 showed excellent responses to the OP with little to no false alerts, but nonetheless failed to respond to the TATP test material. In contrast, K9_1 showed poor performance across all odors.

A logistic mixed effect model was fit to the response data (response or no response) and was predicted by odor identity and training group (OP-trained or TATP-trained). A random intercept was fit for each dog and Tukey adjusted least square means post hoc test were used to compare response probability between groups for each odor. Overall, TATP-trained dogs showed higher response rates to TATP compared to OP-trained dogs ($z=-5.38$, $p<0.001$), but there was no

difference in response to the OP test material (z=1.15, p=0.19). All distractors were similar between groups, except that OP-trained dogs showed a higher probability of responding to DI wipes (z=2.38, p=0.02).

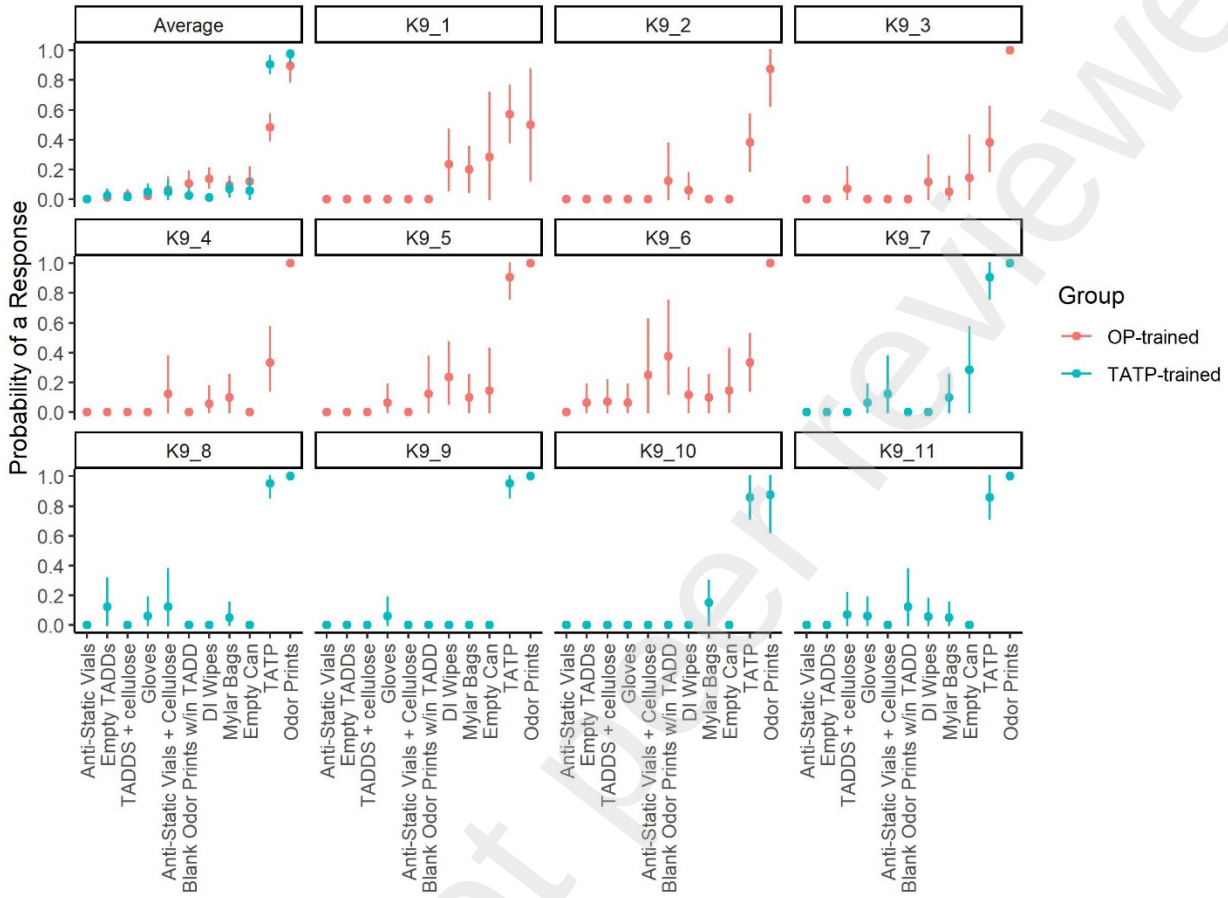


Figure 12. Probability of response to each odor. Shows the number of trials a dog responded to each odor divided by the number of trials in which that odor appeared. Average shows the mean across all dogs. Error bars show the bootstrap estimated 95% confidence intervals.

4 Discussion

4.1 Chemical analysis of Training Aids

An ideal training aid should present an odor that is identical to the true material having no or minimal extraneous odors, such as solvents, and provide a blank aid that produces the same extraneous odors for canine "proofing". The key odorants used for olfactory detection of each target is currently unknown for the explosives in this research. While some research has been conducted to determine the odorants of interest for explosives, the data are limited. Testing with a statistically relevant number of trained canines is necessary to make such a determination. The detection of the nitroaromatic compounds remain in a debate in the field with some believing that the canines detect the explosive itself, while others argue that it is the more salient compounds associated with that explosive.

Unlike TATP, the explosives HMTD, PETN, and RDX, have very low vapor pressures, thus it is unlikely to detect the presence of these compounds in the headspace by common instrumental detection methods. As such, compounds related to the degradation or manufacturer of the explosives are more likely the to be the volatile compounds present in the headspace. For instance, the vapor pressure of RDX has been estimated at 4.85×10^{-12} atm under normal conditions, while 2-ethyl-1-hexanol is 1.79×10^{-4} atm, or approximately 100 million times higher. This accounts for the non-detection of RDX in the vapor signature by our instrumentation even if solid RDX used in the production of the aid was very nearly pure [34].

For all of the non-detonable PETN training aids considered, few volatiles were found in the headspace. Likewise, the TS RDX aid also had few volatiles present, potentially indicating the use of purified RDX in the Dilution Aid. Similarly, in Harper et al. (2005), no compounds other than those associated with the substrate were detected from the headspace of the NESTT RDX aid [6]. The other RDX aids (SL, a Mimic, and OP, a Sorption), on the other hand, had a number of volatiles present that are often associated with the plasticized explosive, C4, of which RDX is the main component. These common compounds included octane, cyclohexanol, cyclohexanone, and 2-ethyl-1-hexanone. In an effort to determine the key odorants for the detection of C4 (RDX-containing plastic explosive), Harper et al. tested 12 operational explosive detection canines from local law enforcement agencies and indeed found that the majority of the canines (70%) hit on 2-ethyl-1-hexanol, while 8.3% alerted to the cyclohexanone [6]; however, use of a larger population of canines as well as green canines would be more conclusive.

Based on the chemical analysis conducted of the RDX and PETN aids herein, it is impossible to know which aid would be the most effective, though we do know that all but the TS aid contain VOCs associated with the C4 explosive in high abundance. It is also important to choose an aid free from non-target-related compounds. Neither the OP or the SL aids had significant contributions from extraneous odors. Finally, abundance of the odor should be considered. Too low and the canine would have difficulty in detecting the odor; however, research has also shown that too high of a concentration could be perceived as an entirely different odor [35], [36], which should be considered given the over-powering abundance of compounds on the SL aids. In the end, the only way to know the true utility of the aids is by testing with green canines, as done in the proof-of-concept dross-over study discussed herein.

Of the explosives examined in this research, TATP has the simplest VOC profile, with TATP vapor itself being the dominant compound. All of the training aids tested, with the exception of the TW TATP aid, had a high abundance of this analyte in the headspace. In addition to TATP, diacetone diperoxide (DADP) is a possible product of the synthesis of acetone and hydrogen peroxide. A number of factors affect the yield of DADP versus TATP, which include reaction temperature, purity and ratios of the acetone and hydrogen peroxide, and ratio of hydrogen peroxide to the acid catalyst [37]. With a higher vapor pressure than TATP, DADP is also likely to be found in the headspace if present in the bulk sample [26]. None of the training aids tested had evidence of DADP present. Residual acetone from synthesis may also be found in the headspace of TATP. As acetone is a highly volatile solvent with a vapor pressure of 3.0×10^{-1} atm at 25 °C compared to that of TATP, 6.31×10^{-5} atm [38], thus a very small amount of residual acetone left in the bulk product can still produce a large peak abundance compared to the TATP peak abundance. Acetone was found in abundance similar to or higher than the TATP in the TS and SL TATP aids, as well in lower amounts in the GL and OP aids. Without fully understanding how canines perceive acetone versus TATP vapors, it is currently unknown whether significant levels of acetone in the training material would encourage the canine to alert to commercial acetone

products, such as nail polish remover. Though Oxley et al. (2004) showed that canines trained on pure TATP and TATP Sorption Aids did not give an indication in the presence of acetone [21], the influence of acetone when present in a TATP training aid on canine efficacy would be a recommended avenue of future research.

Choosing the "correct" odor profile for an HTMD training is highly complicated. There are a variety of factors that may alter the rate of HMTD decomposition, such as age, storage temperature, and presence of residual solvents or precursors making determining the odorants and odorant ratios that should be in the training aids challenging [27]. The majority of HTMD training aid manufacturers synthesize their own HMTD, and as such these factors will affect the quality of the aid produced. For instance, the greater abundance of HTMD-related compounds found in the TW aids, could indicate an older or less pure starting material, while those with lower starting abundances of these odorants could indicate a fresher or more pure starting material, though, it is also possible that simply less HMTD odor was transferred to the substrate.

It should be noted that trimethylamine, a particularly odorous, fish-smelling compound, that is commonly found in aged HMTD, was not detected in any of these samples. While it is not known if this is true for canines, the human olfactory threshold (i.e., minimum level of an odorant that can be detected) for trimethylamine is very low, regularly measured below one part per billion. Few other compounds are known to have such a low olfactory threshold [39]. For example, the odor thresholds for formaldehyde was measured in the range of 0.5 to 1 ppm [40] and 21 ppm for formic acid [41]. As such, it could be surmised that the absence of trimethylamine from an HMTD training aid could potentially cause the emitted odor of the training aid to be perceived quite differently than actual HMTD material that does contain trimethylamine.

Simon and DeGreeff (2019) conducted a similar study. The compounds identified from the aids in both studies were similar; however, in the former study, the total odor abundance from TS HMTD aid increased over usage time while the SL HMTD aid remained steadier. The GL aid was also dissimilar; in the former study the only volatile detected was dimethylformamide and it only persisted for several hours [14]. At the time of the former study, the GL aids were very new to the market, and thus likely changed in form or manufacturing process. Furthermore, TW and OP HMTD aids did not exist in 2019 at the time of the previous study, and thus cannot be compared.

An ideal training aid would also retain the same odor, in quality and quantity, for a given amount of time determined to be that aid's usage lifetime. This would ensure that the canine or canines experience the same odor quality and abundance every time they trained with this aid. The dynamic nature of HMTD makes this goal particularly difficult compared to other target materials. All training aids had headspace profiles that were dynamic over time, with TS, GL, and TW decreasing over time as headspace components were depleted, and SL increasing over time as the HMTD on the substrate continuously decomposed. The ratio of the headspace compounds changed overtime, as well, though no additional compounds were noted. These results do not necessarily allow for the estimation of a usage lifetime, as there is no period of time that the odor profiles are consistent for any of the aids. The differences between the replicate aid further exacerbates this problem.

For this study, the usage lifetime of the TATP aids was arbitrarily defined as when the relative quantity of TATP dropped below 10% of its original value. By this definition, the usage lifetimes of the TATP training aids tested varied from less than 2 weeks (SL TATP) to more than 45 (TS TATP and PDMS TATP) for our particular experimental setup, where the aid was removed from its packaging twice a week for four hours under ambient conditions, and which equates to 16 (or less) – 360 (or more) hours out of the package. This is not to say that if the aid was left out for

360 hours straight, the TS TATP aid would reach the 10% depletion limit at this same time. On the contrary, it would likely be depleted much faster, as repeatedly returning the aid to storage in its original containment system allowed for a modest replenishment of the odor, and meaning a change in the experimental setup would likely result in a different outcome. It would be ideal to compare the results of this study to other experimental setups to determine how much deviance there is in usage lifetime based on the ratio of time in and out of the packaging and the environmental conditions.

A previous study also assessed the headspaces of non-detonable TATP training aids over time, though in this study, the aids were left exposed to the environment and were not returned periodically to their packaging, as would be done operationally, meaning their odor was likely depleted much more quickly. Indeed, the TATP vapor was depleted from the headspace of these aids in as little as four hours and up to two weeks. It should be noted, however, that these times to depletion were estimated and each aid in the former study were not sampled in consistent increments with no measurements being taken between in the range of Day 4 or 5 to Weeks 2 or 3. In the current study herein, the PDMS TATP aid lasted the longest, in agreement with the former study, followed by the TS, OP, GL and SL TATP aids (the TW aid had no detectable TATP at Time 0). Interestingly, this order was quite different in the former study, where after PDMS, the SL and GL TATP aids were next, followed by TS, TW and OP TATP aids [23]. The discrepancies between the two studies are interesting, and may be attributed to the inconsistency between manufacturer lots. As such, lot-to-lot reproducibility should be further studied.

Finally, an ideal training aid would present an identical odor each time it was purchased with limited inter- or intra-batch variability. This was the most challenging aspect for the commercial training aids purchased for this research. There was limited batch-to-batch consistency in any of the aids, with the exception of the TS aids. Surprisingly the intra-batch uniformity was similarly inconsistent. Given that the aids were all made in different manners, Sorption, Mimic, or Dilution, and that the researchers were not privy to manufacturing or QA/QC procedures used, it is difficult to pinpoint reasons for this. It would have been ideal if many within batch and between batch replicates could have been purchased to better understand the variance, though this was not possible due to the high costs of the aids. These inconsistencies, however, could have dire consequences on canine outcomes. If a commercial training aid is chosen following proper validation by a third party, by both chemical analysis and green canine testing, but the end user receives a different variation of this aid, the validation is no longer applicable and it will not be known whether or not the product used for training is indeed effective.

4.2 Canine odor recognition testing

As described above, the TATP aids have the simplest VOC profile, with TATP being the prominent odorant, which should imply that making a training aid to represent the odor of true TATP should be more straightforward than with other types of explosives. However, setting a target detection threshold of >80% to indicate high proficiency, as modeled in Aviles-Rosa et al. (2022) [42], canines trained with the commercial TATP training aid designated "OP" did not spontaneously generalize and to true TATP when first presented with that material. Over the course of two days the OP-trained canines were exposed to true TATP and then became proficient in the detection of true TATP. As a result, our data suggests that imprinting a canine with this non-detonable form of a training aid may not produce canines proficient in finding the corresponding true material the first time they are introduced to it.

An important limitation and note to this finding is that dogs even trained to the true TATP material still showed a substantial decrement in the initial detection of the test TATP (~60%

detection). This indicates that there were sufficient differences from the TATP used throughout training to the unopened TATP used for testing to cause a performance decrement. This suggests that the use of the training material alone may lead to sufficient differences from the original material, leading to a generalization decrement. This highlights the potential need for more than a single example of TATP to be included in a training program.

Interestingly, although OP-trained dogs did not immediately respond to TATP, all dogs, including TATP trained dogs did show a response to the OP TATP training aid. This suggests that non-detonable training aids, such as the OP aid, could potentially be used as a bridge to assist in learning and maintenance when the true material is not available. Interestingly, the canines trained with true TATP took approximately six days of training on the initial training with the true material whereas OP-trained canines were nearly 100% proficient on true TATP in just two days of training during the test period with true TATP. This suggests that it is possible that training aids such as OP may help reduce the time necessary to train dogs to true TATP when it is available, although it may not alone be a replacement for training to the true material. Additional studies would be required to indeed determine if such non-detonable training aids could potentially give canines a head start prior to training on the true material.

Due to the dogs' low response rate to TATP during the testing phase, reward rate was reduced compared to training. As a result, some canines lost motivation during the trials. After the second session on the first day of the ORT, a separate lineup was set up outside the test area that contained UDC. The handler was then able to use that lineup to reward their canine prior to them leaving the session, and therefore was able to keep the canines interested and invested in completing each session.

Another important consideration to the canine testing is that dogs were reinforced for all responses to the true TATP and training aid (i.e., a continuous rate of reinforcement). This helps maintain canine performance and motivation, but does mean that the only true instance of spontaneous generalization that occurs is the first trial a canine is exposed to the target material. After the first reinforced (or even non-reinforced) trial, the canine can learn the contingency in effect and begin responding to the new odor. This was clearly observed within our data, where dogs showed substantial learning/improvements in responding across reinforced trials. Although we saw no responses from OP-trained canines and 60% responses from TATP trained canines, this difference is difficult to compare statistically with only 11 dogs. An alternative approach for future work could be to use an intermittent schedule of reinforcement allowing for multiple non-reinforced assessments of responses to a novel odor sample. Aviles-Rosa et al. (2022) demonstrated that the reinforcement schedule can be reduced to a rate as low as 50%, while still maintaining a high proficiency rate (>80%) on target items [42]. By utilizing a reduced reinforcement schedule, the ORT could have been conducted in such a way to minimize learning during the test, therefore making data from replicate target exposures more valuable.

One potential reason for the poor response to TATP from the OP-trained dogs is that the OP training aid did not sufficiently replicate the concentration of TATP from bulk material. Research has shown that if an odor concentration is more than 10 times different, it is challenging for a canine to spontaneously generalize to the new odor [43], [44]. Indeed, chemical analysis of TATP vapor from the OP TATP training aid was approximately one order of magnitude (10 times) lower than that of the true TATP (~ 1 g) that was tested (Figure 7). Although the headspace of the materials used during testing was not analyzed, it is likely that there was a similar difference in headspace concentration which could have influenced the ability of canines to spontaneously

generalize. In future studies it would be advantageous to both train and test utilizing targets that contained similar odorant concentrations.

The canine testing performed in this study can be used as both an example to conduct similar studies with other types of aids, but also serves to highlight some lessons learned and limitations to conducting canine testing. When conducting canine testing, it is best to use green canines which have not been trained to detect the true material for a corresponding non-detonable training aid. Because these canines had not learned the mechanics of odor detection training, it was beneficial to have access to a UDC to train the canines on the basics of odor recognition before gaining access to more limited sessions with the target material. This allowed the canines to already understand the method of odor detection training and in the sessions with target material, they only had to focus on learning the new odor. The UDC also was useful in the data collection portion of the odor recognition testing to keep the canines invested in the search when the frequency of positive reward on odors significantly decreased from what they were exposed to in training. In future studies, the canines would be trained to detect their target odor to a certain level of proficiency. The reward schedule in which they are reinforced for successfully identifying targets would be reduced to minimize the amount of learning within the odor recognition trial. This would allow for more of the data in each odor recognition trial to be used to discern whether the canines were spontaneously generalizing to new targets or learning to detect new targets over the course of the study.

5. Conclusions

In summary, the aim of this study was to highlight the importance of the chemical analysis of non-detonable alternative training aids, and confirmation of efficacy via canine testing. Chemical analysis was carried out for alternative training aids representing, the explosives, RDX, PETN, TATP and HMTD. For the nitroaromatic explosives, the majority of the RDX aids contained volatile components associated with C4, a RDX-containing plastic explosive, while few headspace components were detected from the PETN aids. The parent explosives were not detected in the headspaces of any of these aids, as to be expected due to the low vapor pressures of both RDX and PETN. Like the nitroaromatics, no HMTD was detected in the headspace, though known HMTD decomposition products were found in abundance in the headspace of all aids. Formic acid was found it the greatest abundance for most aids, in addition to formaldehyde and formamide. The headspace profiles of these aids changed both quantitatively and qualitatively over time. Finally, TATP aids had readily detectable TATP vapor, with the exception of one brand, which had no detectable TATP. In addition to TATP, acetone was also detected in abundance for many of the aids tested. When opened repeatedly over time, the acetone dissipated quickly, and TATP vapor was detected for as little as 2 weeks (16 hours open) or more than 45 weeks (more than 360 hours open), depending on the manufacturer. For all aids tested, batch-to-batch and within batch variability was high, particularly for certain manufacturers.

A single manufacturer of an alternative non-detonable TATP aid was also tested with canines. Two groups of canines were trained to detect either the alternative aid or the true material. The true TATP-trained group generalized to the alternative aid at a rate of approximately 87%, while the alternative aid-trained group only generalized to the true material at a rate of approximately 51%, though it was shown that this group quickly learned the true TATP odor after a short period of time.

Out of the three types of non-detonable training aids (sorption, dilution, and mimic), only sorption and dilution aids use the true material in the manufacture of the aids, therefore these types of aids are likely to have headspaces with a closer representation of the true material. However,

this also implies that for sorption and dilution aids, which use true material in their manufacture, the composition and quality of the true material can influence the resulting training aids. Mimic aids, on the other hand, are made based on what odorants are believed to be critical in canine detection, though proper canine validation testing is required to ensure that these types of aids include the critical elements canines recognize in the corresponding true material. This is particularly critical when extraneous odors associated with the manufacture or formulation of the explosive change. If the canine has been trained with an aid that includes extraneous odors there is the potential for that canine to not be able to recognize an explosive with a different chemical composition, synthesis, or manufacturer. Independent verification and validation is a critical component of evaluating a training aid because it is important to understand the composition of the odors of the training aid along with the expected usage lifetime and shelf-life to know the unique usage case for each brand or type of training aid. Without knowing if a training aid is consistently produced without major batch-to-batch variability, it is challenging to discern what a canine is being trained to detect and with what certainty. This is particularly worrisome when a trainer is using a non-detonable training aid in lieu of the true material. There are also limitations to analytical testing of training aids due to factors such as a target material having a low vapor pressure or the limits of detection of instrumentation, therefore analytical testing in combination with canine testing is the most comprehensive way to understand the efficacy of a training aid.

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