Full length articles

Passive delivery of mixed explosives vapor from separated components

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ABSTRACT

Homemade explosive (HME) materials commonly take the form of binary, ammonium nitrate-based explosives, and are a challenge to detect due to the low volatility of ammonium nitrate, the great variation in fuel sources, and the complex environment in which detection takes place. Vapor detection in the form of detector canines overcomes these and other obstacles, and has proven to be a highly effective mode of detection. Due to inherent safety precautions associated with working with HMEs, experienced detector canines often lack the frequency of training on HME material necessary to remain proficient. For this reason, the Mixed Odor Delivery Device (MODD) was designed allowing canines to train on the odor of mixed explosives while keeping the HME components separate and unmixed, thus alleviating the safety requirements for handling, storing, and transporting explosives. Experiments across multiple investigative strategies were carried out to evaluate and characterize the vapor distribution in the MODD including computational modeling, analytical testing, and field trials. All testing indicated the MODD accurately provides uniformly mixed HME vapor at detectable levels from separated HME components.

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1. Background

Improvised explosive devices (IEDs) have been the leading cause of injury and death in recent Middle East conflicts. Approximately two-thirds of all American deaths in combat were by IED attacks, according to the Joint IED Defeat Organization (JIEDDO, now the Joint Improvised-Threat Defeat Organization). From 2003 to 2013 this equaled more than 3000 American military deaths and 33,000 injuries attributed to IEDs [1,2]. IEDs are not only threats abroad, but also pose a great threat to homeland security. Their prevalence at home and abroad is due to both the ease of acquiring the explosive components, as well as constructing the devices.

An IED can be defined simply as any non-industrially produced explosive weapon. The type of explosive material used can vary widely and tends to be made from materials readily available at that time/location [3]. Formerly, during the Iraq conflict, military and commercial explosives were more commonly used in IEDs. Withdrawing Iraqi forces left behind large amounts of unsecured munitions, which, in addition to demolition explosives, were acquired by insurgent groups, and used primarily in roadside IEDs and landmines [2,4]. In Afghanistan and other recent Middle East conflicts, the threat has shifted to homemade explosive (HME) materials most commonly composed of simple binary explosive mixtures, such as ammonium nitrate (AN) or potassium chlorate ($KClO_3$) mixed with various fuel sources [3,5,2].

Many detectors previously developed for the Iraqi conflict are inadequate for current military and homeland security needs. Previous detection capabilities were focused on landmine detection though, attention has broadened to the detection of a range of explosives, including HMEs, in complex and contaminated environments. Thus, versatility is the most important requirement for today's explosives detectors. Remote as well as proximate detection capabilities, detection through packaging or a container, and

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detection of both bulk and trace quantities are also necessary. Additionally, detection systems must be fast, robust, and selective with a low rate of false alarms [3,6,7].

Many current detection strategies for HMEs focus on the collection of explosive residues including direct irradiation of explosive residues, swabbing of residue followed by instrumental detection, or dislodging residue particles by air flow with instrumental detection. These methods are often fast, robust, and selective, but cannot be used or perform poorly in remote and non-contact sampling scenarios. For remote detection, spectroscopic methods, most commonly Raman spectroscopy, are utilized. These methods, however, suffer selectivity and sensitivity issues in complex environments or with certain substrates [6]. Alternatively vapor sampling systems, instrumental or biological (i.e. canines, plants, bees, etc.), may be employed [8]. Instrumental vapor detectors often do not have the sensitivity and selectivity needed for real-world scenarios. Vapor sampling by well-trained canine detectors fulfill all of the above-mentioned needs, and have, thus far, proven to be the most effective tool for HME detection.

Canines can be thought of as an integrated sampling and detection system with the unique ability to follow a vapor trail to its source. Highly efficient sampling with preconcentration occurs in the mucus membranes of the nose. Data collection and processing take place at the olfactory receptors and in the olfactory bulb of the brain. Vapor concentration gradients are used to follow the vapor trail to its source [9]. Canine detection has the benefit of being non-invasive, and has demonstrated improved sensitivity and selectivity compared to most, if not all, field-deployable detectors and sensors [9–13]. With proper and consistent training, a canine detector can identify a wider range of explosives with lower false alert rates than any currently deployable detector [14].

The main challenges to training canines on HMEs are safety and cost. Mixed explosives are difficult and expensive to safely obtain, store, and transport; and for this reason, are frequently limited to same-day production with strict use and disposal oversight by explosives chemists. These safety measures are costly and time-consuming, limiting the frequency of training exercises. In addition, approved training locations are often not realistic to operational setting [15]. For these reasons, many canines are trained on the oxidizer (i.e. AN, $KClO_3$, etc.) alone instead of the explosive mixture. This is less than optimal, as training on single components of these mixtures has been proven inadequate. For example, while testing canines on the detection of AN mixed with aluminum powder (Al), it was observed that canines trained on AN alone did not reliably detect the mixture of AN and Al [16]. Another study testing canine detection of $KClO_3$ and fuel mixtures yielded similar results [17]. In addition to safety challenges, training canines on HMEs may be further complicated by component availability (variable by region), as well as differences in fuel/oxidizer ratios.

The Mixed Odor Delivery Device (MODD) [18] was designed to alleviate the above-mentioned training difficulties. The MODD safely contains and allows for accurate mixing and delivery of vapor from separated explosive components. It offers transportability and ruggedness for field use with minimal sample size requirement, and is easily adaptable for the varied components one might encounter in the field.

In this research, computational modeling of vapor distribution within the device was utilized to aid in developing the design, and laboratory analyses and field evaluations were carried out for confirmation of its efficacy. Also, to lay an analytical foundation for the use of the MODD, headspace analysis of HME components was carried out comparing the vapor signatures of the mixed and separated components.

2. Design

The MODD functions to safely separate up to four explosive components in removable vials. It is separated into upper and lower compartments held together with two metal latches on either side, and an o-ring placed between the upper and lower compartments to ensure an airtight closure (Fig. 1). The MODD is transportable weighing less than five pounds with dimensions $5'' \times 5'' \times 4.5''$. It was designed with a low internal volume to minimize sample size requirements. These features and its ruggedness make it amenable to use in diverse locations.

The goal of the design is for the vapors from the separated vials to meet and diffuse through the device to the outlet of the MODD where they are presented to the canine as a mixture. The pathway of the analyte vapors is shown in Fig. 2 by the white dotted lines. Analyte vapors disperse from the vials, through the neck where separate vapors meet and mix, and then continue to diffuse around a restrictor plug. The analyte vapor escapes as a vapor plume from around the restrictor plug to an area hereafter referred to as the MODD outlet, where the canine inhales a mixture of vapors instead of unmixed vapor.

Vapor diffusion beyond the MODD outlet was also considered in the design and material choice. The design further encourages pooling of the vapor in its bowl-shaped outlet to lessen the effect of large amounts of odor overwhelming the surrounding area. To minimize excessive vapor at the outlet while maintaining its compact size, and thus small internal volume, the MODD was fabricated from PVC with increased surface area to internal volume ratio. In a study of several suitable materials for fabrication, PVC was chosen from due to its ability to adsorb vapor, and the ease in which vapor deposits can be removed by simply cleaning with isopropanol (or similar) wipes [19].

In addition, the vapor plume is limited by the restrictor plug located between the upper and lower portions of the MODD. The restrictor plug (Fig. 3) creates a small gap that acts to limit vapor entering the MODD outlet, thus decreasing the analyte vapor concentration escaping the container. Multiple removable restrictor plugs with varied gap sizes allow different quantities of vapor to diffuse to the outlet of the device, allowing the user to adjust the vapor concentration available to the canine. Further alterations of component vapor concentrations can be made by simply adding or removing individual vials or by placing constricting lids on individual vials. Additionally, the restrictor plug can be removed to allow a greater concentration of vapor to reach the canine, if desired.

Fig. 1. An open MODD, with the interior portion holding a sample vial exposed.

3. Methods

Initial experiments were carried out to lay an analytical foundation for the use of the MODD. As the purpose of the MODD is to deliver representative mixed vapor from unmixed component sources, it was imperative to determine what, if any, effect the physical mixing of the explosive components had on the vapor signature of the mixed product. For this reason volatile components from the headspace of AN-based, mixed explosives were compared to that of the unmixed components. Following these experiments, the design of the MODD was developed with the aid of computational modeling. Models were used to visualize the vapor distribution within the device and at the outlet. Finally, laboratory evaluations and field trials with canine detectors were completed to ensure the model was satisfactory and that the MODD delivers a uniform mixture of vapor at a detectable level.
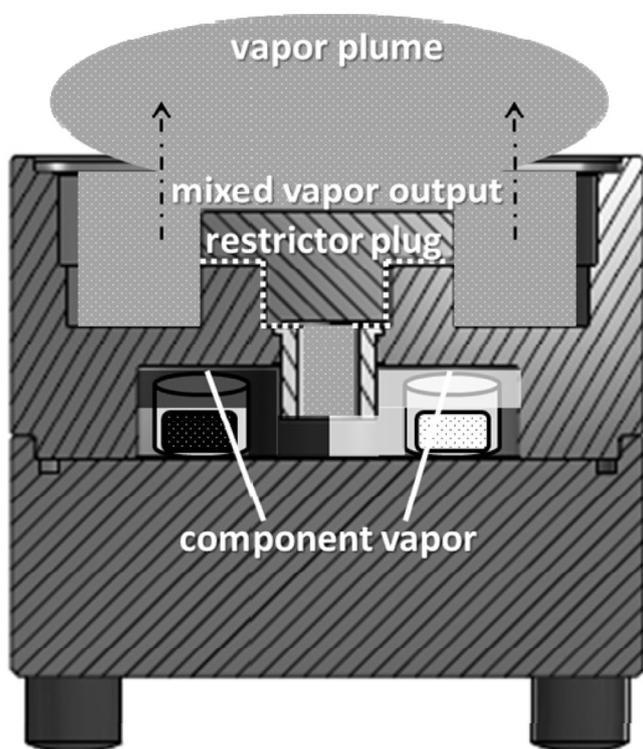
Fig. 2. Diagram of MODD depicting vapor distribution and mixing throughout device.

3.1. Explosive handling

WARNING! Ammonium nitrate mixed with a fuel source can be an explosive material in the proper ratios. Proper handling, storage, and disposal precautions should be taken. AN and fuel materials prepared in the laboratory were weighed and mixed in static dissipative vials using wooden spatulas. All mixing and experimentation was carried out behind Explosives Personnel Shields certified to net explosive weight of 10.0 g. For disposal, the explosive mixture was transferred to a beaker into which 100 mL of water was added to dissolve the AN material. Any solid content or oil was then filtered from the aqueous content, and both were disposed of in the proper locations. Larger quantities of mixed explosives were handled and stored at an alternative outdoor location according to the standard operating procedures at that location.

3.2. Headspace analysis of mixed and unmixed HME components

The headspace of AN and fuel mixtures were analyzed, comparing the headspace of the mixed material to that of the unmixed components. Explosive mixtures included AN (Sigma-Aldrich; St. Louis, MO) with several fuel sources purchased from local grocery and convenience stores, including confectioners' sugar, petroleum jelly, diesel oil, sawdust (made from scrap yellow pine), and aluminum powder (ATA 7100 leafing flake aluminum with stearic acid, Toyal America Inc.; Lockport, IL). All materials were mixed in a ratio of 12:1 AN:fuel to equal 1.3 g of explosive material, and were then transferred to 20 mL glass, volatile organic analysis vials with septa (Thermo Fisher Scientific; Waltham, MA). Masses of the individual components, to equal 1.3 g (i.e. 1.2 g AN and 0.1 g fuel), were also placed in separate glass vials. All samples were prepared in triplicate.

Solid phase microextraction (SPME) with gas chromatography/-mass spectrometry (GC/MS) was utilized for the extraction of volatiles and semi-volatiles from the headspace of AN and fuel samples. The SPME apparatus consists of a fused-silica fiber coated with an absorbent polymer, and analyte extraction was a result of the partitioning of vaporous species between the vapor phase and the fiber coating. A polydimethylsiloxane/divinylbenzene/carboxen (PDMS/DVB/CAR) (Sigma-Aldrich; St Louis, MO) absorbent fiber polymer was used for the extractions throughout all experiments. The SPME fiber was inserted through the septa of the vials and exposed to the headspace for one hour. Analytes were then desorbed from the fiber in the heated inlet (250 °C) of an Agilent 6890 gas chromatograph (GC) for separation with identification by a 5975 mass selective detector (MSD) (Agilent Technologies; Santa Clara, CA). The temperature program of the GC oven began at 60 °C, then was increased to 175 °C at 40 °C/min, increased again to 240 °C at 30 °C/min, and finally held for 5 min. A
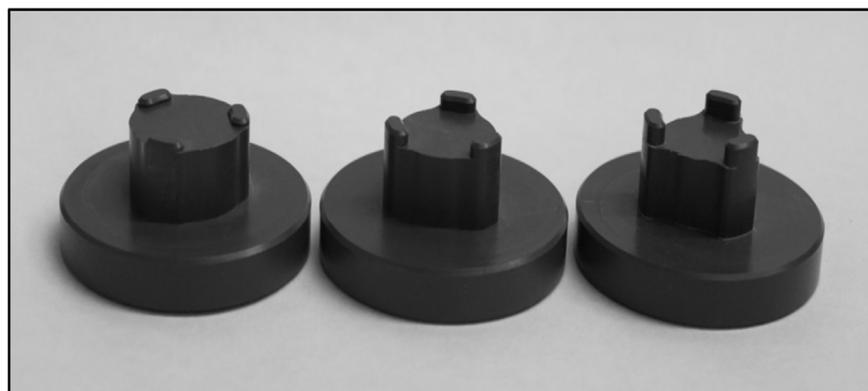
Fig. 3. Restrictor plug used to limit and adjust vapor concentration output in the MODD.

15 m × 0.32 mm i.d. Rtx-Volatiles column (Restek, Inc.; Bellefonte, PA) was used. The column flow was 2 mL/min with an inlet split of 10:1. The mass scan range of the MSD was m/z 30-220.

Ammonium nitrate breaks down into ammonia and nitric acid under ambient conditions. The nitric acid is readily taken up by any water that has absorbed to the bulk AN due to ambient humidity, leaving ammonia as the main headspace component of AN [20]. Passive ammonia samplers (Ogawa Co.; Pompano Beach, FL) were utilized to collect this ammonia vapor from the headspace of the explosive mixtures, as well as AN alone. The passive samplers contained sorbent pads pre-coated for ammonia absorption. Each sampler, containing two sorbent pads, was placed on or near the object of interest for a given amount of time. Ammonia present above the vials of the mixed and unmixed HME components was trapped onto the sorbent pads for 24 h, and then extracted from the pads for 30 min in deionized water.

The extract was analyzed for ammonium by ion chromatography using a Dionex ICS 5000IC (Thermo Scientific; Sunnyvale, CA). For separation, 20 mM methanesulfonic acid eluent was pumped through a Dionex CS12a cation exchange column (Thermo Scientific; Waltham, MA) at 10 μL/min. The injection volume was 0.4 μL, and the separation was performed under isocratic and isothermal (30 °C) conditions. The concentration of ammonium in the extract was determined by comparison to external calibration curves. The mass of ammonia present on the pads was determined using Eq. (1), where C_{NH4}^+ is the concentration of ammonium in the extract, and V is the extract volume. The headspace concentration of ammonia was then calculated taking into account the sampling rate of 32.3 mL/min as determined by Ogawa Co., and using Eq. (2), where C_{NH3} is the concentration of ammonia in the headspace, α is a constant related to the sampling rate, and t is the extraction time [21,22].

$$m_{NH_3} = \frac{C_{NH_4^+} \times V}{MW_{NH_4^+} \times MW_{NH_3}} \tag{1}$$

$$C_{NH_3} = \alpha \times \frac{m_{NH_3}}{t} \tag{2}$$

3.3. Computational modeling

A computational model was used to predict the transport of analyte vapor by diffusion (i.e., passive transport) within the MODD. This distribution was considered at the moment just before the canine sniffs/samples the vapor at the outlet. In other words, the model depicted what the canine would experience upon approaching the MODD. The focus of the analysis was the symmetry of the analyte vapor concentration across the MODD outlet. Assuming a symmetric concentration field at the outlet, the canine would experience the same vapor profile whether it approaches the MODD from the left or from the right, and would not recognize the components in the MODD as separate, but instead as a mixed vapor. The model was used to guide the design of the MODD prior to fabrication.

For diffusion in the model, it was approximated that the analyte vapor was a dilute component of a mixture with air, allowing the diffusion coefficient to be a constant in the model equations. This approximation was valid because the analytes of interest have rather low vapor pressures. The effects of convection, including that caused by active sampling in laboratory experiments, are not included in the model presented in this work as they are outside of the intended scope of the model.

Analyte transport throughout the MODD was predicted by solving a time-dependent, three-dimensional diffusion equation given by Eq. (3) where c represents the concentration of the analyte vapor and D represents the diffusion coefficient of the analyte in air. Numerical solutions were obtained using COMSOL Multiphysics® software (COMSOL, Inc., Los Angeles, CA) with the Chemical Species Transport Module. AUTODESK Inventor® (AUTODESK, Inc., San Rafael, CA) was used to generate the model geometry that was imported into the model.

$$\frac{\partial c}{\partial t} = D\left[\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right] \tag{3}$$

The initial condition for the model included no analyte vapor present in the MODD. At time t = 0, analyte vapor emerged from the sample surface and diffused upward into the MODD (see path indicated in Fig. 2). A fixed-concentration boundary condition was used on the surface of the sample. The air immediately adjacent to the sample was assumed to be in equilibrium with the sample (i.e. the air was saturated with analyte vapor), and the corresponding saturation concentration was calculated from the vapor pressure at 25 °C. Over time, the analyte vapor diffused upward through the MODD coming into contact with its walls. The boundary conditions for all surfaces within the MODD corresponded to zero flux of analyte vapor. It was assumed that there was negligible adsorption of analyte vapor on all surfaces within the MODD; however, there was most certainly adsorption of analyte vapor to some extent on the PVC material surfaces. Since the device was made entirely of PVC, it is unlikely that absorption would affect the symmetry of the analyte vapor concentration at the outlet. Eventually, analyte vapor diffused out of the MODD outlet and emerged into the ambient (laboratory) air. At the outlet, the model included a boundary condition of zero analyte vapor concentration. This boundary condition would likely overestimate the rate of diffusion out of the MODD when surrounded by perfectly quiescent air, but it was not expected such conditions existed during the experiment. For comparison with the zero-concentration boundary condition, a zero-flux boundary condition was used to prevent analyte vapor from escaping the MODD (which was neither the case in the experiments nor the field studies). The zero-flux boundary condition predicted much greater concentrations near the outlet than those measured experimentally.

As one might expect, the initial condition for the model differed from that of the experiment, wherein the sample was contained in the vial for several hours prior to the experiment. Thus, all of the air in the sample-containing vial may have been saturated or nearly saturated with analyte vapor. The model predictions were tested using the initial condition corresponding to all air within the vials being fully saturated with analyte vapor, and it was determined that this change had a negligible effect on the concentration near the outlet (and in the upper chamber) at the times of interest.

As was also done in the experiments, methyl salicylate and limonene were used as representative analytes for model predictions. These compounds were chosen as surrogates as they have appreciable and documented diffusion coefficients and vapor pressures. For methyl salicylate and limonene, the model predictions use the diffusion coefficients of 0.062 and 0.063 cm^2/s, respectively [23], and vapor pressures of 0.343 mmHg and 1.98 mmHg at 25 °C, respectively [24].

Laboratory experiments were conducted for comparison with model predictions; these experiments are discussed in the next section. The experiments involved active sampling of the analyte vapor, but this process was not included in the model. Thus, to compare the model predictions with experimental measurements; it was assumed that the predicted number of moles of analyte near the outlet (i.e. in the upper chamber) was approximately equal to the number of moles that would be experimentally measured by active sampling. This approximation was supported with a comparison, by volume, of the upper chamber compared to that of

the total sample obtained. In the experiments, active sampling occurred for 10 min at a sampling rate of 75 mL/min; thus, a total volume of 750 mL was sampled, which is about 2.5 times greater than the volume (296 mL) of the upper chamber of the MODD. Thus, it was assumed that all of the analyte in the upper chamber was collected during the sampling period.

3.4. Laboratory evaluations of the MODD

The vapor distribution in the MODD was assessed in two separate experiments. First, vapor uniformity was measured across the MODD outlet using static headspace sampling with SPME. Second, the mixing of components in the vapor plume was assessed by active whole-air sampling. Both experiments used surrogate compounds, methyl salicylate, limonene, and decane (Sigma-Aldrich), which were chosen as they have appreciable vapor pressures, good instrumental responses, and, when combined, form stable mixtures.

To evaluate the distribution of individual vapors across the top of the MODD, single sources of methylsalicylate (1 mL) and of limonene (1 mL) in 28.71 mL, instatic-dissipative vials (ESD Plastic Containers; Yorba Linda, CA), were placed in opposite wells in the MODD. The system was then allowed to equilibrate, after which the headspace was sampled using two SPME fibers placed over the MODD outlet, in line with each vial. Equilibration times of both one or four hours were compared. The previously described SPME-GC/MS method was then used for analysis.

The mixing of components in the vapor plume above the MODD was measured using an active sampling technique. One mL aliquots of neat methyl salicylate, limonene, or decane were held in the static-dissipative vials, and were placed into the MODD for a given equilibration time (1 or 4 h). Vapor was then actively sampled from immediately above the device. For comparison purposes, the compounds were also sampled from a 600 mL, Sulfinert-coated (Sulfinert 2000, SilcoTek, Bellefonte, PA), stainless steel, headspace sample chamber (Fig. 4), previously designed at the Naval Research Laboratory [25].

All vapor samples were collected through a heated transfer line (80 °C) at 75 mL/min and onto a cryo-cooled Siltek-coated baffle liner (Gerstel, Inc.; Linthicum, MS) held at −20 °C in a cooled injection system (cIS-4; Gerstel, Inc.), and inline with the GC (Agilent 7890A, Agilent Technologies) and MS (JEOL AccuTOF GCv, JEOL USA Inc., Waterford, VA) (GC/MS). Analytes were desorbed from the cIS-4 liner at 250 °C, and injected onto a 60 m × 0.25 mm i.d. Rtx-5 ms (Restek, Inc.; Bellefonte, PA) GC column at 4 mL/min. The GC column oven was initially heated to 45 °C for one minute. The temperature was then increased to 250 °C at 40 °C/min and held for an additional 1.5 min. Vapor volumes collected from the
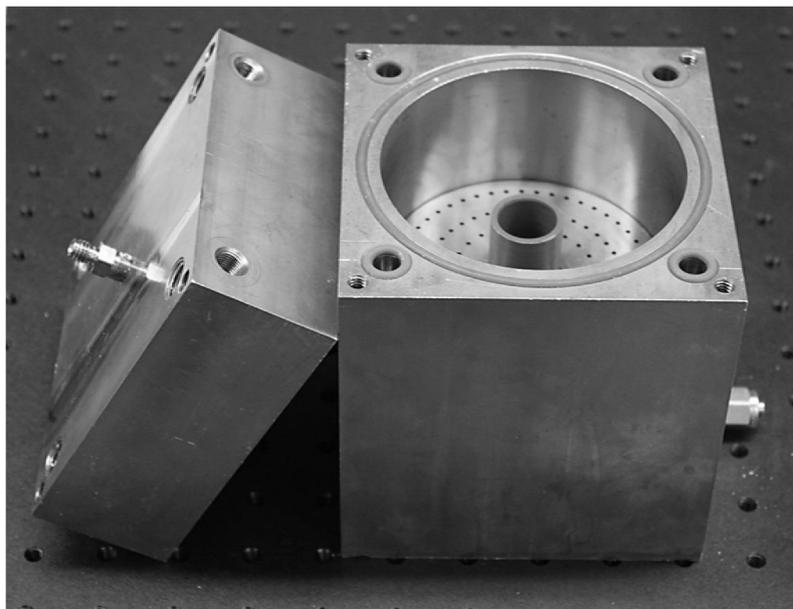
Fig. 4. Headspace sampling chamber [23]. Sample is placed in the holder, the chamber is closed, and air is flowed through the bottom of the chamber to the outlet at the top towards the instrumental transfer line.

Table 1
Canines participating in testing.

K9 ID	Age (yrs)	Dog experience (yrs)	Team experience (yrs)	Experience with components A and B
1	5	3	3	In mixture only
2	7	5	0.5	In mixture only
3	4	2	2	In mixture only
4	5	4	1	In mixture only
5	5	4	0.5	In mixture only
6	7	5	0.5	In mixture only
7	4	2	2	In mixture only
8	8	6	0.5	In mixture only
9	3.5	2	2	A alone and in mixture
10	3	2	2	A alone and in mixture
11	10	9	9	A alone and in mixture
12	8	6	6	A alone and in mixture

MODD and sampling chamber totaled 750 mL and 100 mL, respectively. The masses of analytes collected were determined by comparison to external calibration curves.

For proof-of-concept, actual HME components were placed in the MODD, and the headspace immediately above the MODD was analyzed. Components included AN with diesel fuel, aluminum powder, or petroleum jelly. Three vials each containing AN and a single vial containing fuel to equal 6 g at a 12:1 ratio were placed together in the MODD for four hours. The content of the headspace was then collected by SPME (20 h extraction) or the ammonia samplers (20 h extraction). SPME fibers and ammonia samplers were placed next to the opening of the restrictor plug for extraction. Ammonium was detected by the previously described IC method. Analytes on the fibers were analyzed by GC/MS using the method discussed above, though a 30 m column was used to improve resolution between target analytes and volatiles from the MODD PVC material.

3.5. Canine evaluations

Testing of the MODD by canine detectors was carried out using a binary mixture of unnamed compounds, A and B. Testing was conducted at the Army Blossom Point Research Facility in Welcome, MD using 12 canines. All canines were previously trained and validated on the mixture. Canine information, including age, and dog/team experience is listed in Table 1. Training practices were varied amongst the canine participants as to not influence the overall results. The canines' prior experience with A and B alone or in a mixture was noted.

Prior to MODD testing, validation testing was carried out to ensure reliable detection of the hidden mixture of A and B in several scenarios. Validation testing was conducted outdoors and consisted of search scenarios containing the target mixture and other distractors. Scenarios included vehicles searches, odor recognition testing, parcels (nylon bags) searches, and a field search. 113 g of the mixture was used in the odor recognition test, and 226 g was used in the other scenarios. The mixture used in the validation phase was contained in cotton bags (Pacific Midwest; Grainger, Lake Forest, IL). Distractor materials included empty vials, nitrile

Table 2
Contents of all MODDs used in canine trials, including targets, distractors, and blanks.

MODD #	Contents
1	Blank (contained clean vials only)
2	A (3 vials × 1.88 g) and B (0.36 g)
3	A (3 vials × 1.88 g)
4	B (0.36 g)
5	Blank (contained clean vials only)
6	Distractor – cotton bags
7	Blank (contained clean vials only)
8	Distractor – isopropanol wipes
9	A/B mixed (3 vials × 2 g)
10	Distractor – nitrile gloves
11	Blank (contained clean vials only)

Table 3
Targets used in each testing scenario.

Scenario number	Target
1	A/B mixed
2	A and B unmixed
3	A
4	B
5	No target

gloves, and isopropyl wipes. The canines were required to locate at least 90% of the targets with minimal false alarms to be included in the following MODD testing phase.

The MODD testing phase was held in a steel Quonset hut containing miscellaneous furniture and equipment. Eleven MODDs were used, and the content of each MODD is given in Table 2. The mixture of A and B, as well as unmixed A and B components were placed into 22 mL PFA vials (Savillex, Eden Prairie, MN) which were then placed into the MODD. Distractor materials included cotton bags (previously used in validation testing), isopropanol wipes (used for cleaning the MODD), and nitrile gloves (used for handling MODD and all explosive materials). All material, including distractors and targets, were enclosed in the MODDs for a minimum of 1.5 h prior to testing. Each run utilized a total of five MODDs including four containing blanks or distractors, and one MODD containing either a target odor (i.e. A/B mixture, A and B in separate vials, A alone, or B alone) or an additional blank. The location of the target amongst the five MODDs was chosen using a random number generator and was changed for each canine. The blank/distractor MODDs were also chosen at random and were rotated throughout the testing. All MODDs were cleaned with isopropanol wipes between runs.

For testing, the MODDs were concealed from view in various locations throughout the testing area. In all cases, the MODDs were positioned in such a way that the canines were able to sniff at or very near the top of the outlet. Each canine was given five scenarios (Table 3). The order of the scenarios was previously chosen by a random number generator for each canine. The hiding locations and position of the target were changed at random for each scenario and each canine.

All testing was double-blind, meaning neither the canine/handler team nor the impartial assessor knew the correct location of the target. To maintain test integrity, canine/handlers waiting to be tested were not allowed to observe the testing. A positive response from a canine was identified by the handler. Canine "interest" in a target, distractor, or blank was noted by the handler and/or the assessor. After the canine either correctly located the target or thoroughly sampled all MODDs, the canine/handler was dismissed from the scenario.

Correct response rates to the mixed and unmixed components were compared, as were positive response rates to the mixture and the individual components in the MODDs. False alert rates were considered using the positive predictive value (PPV), the probability that a true response was correct by comparison to the rate of false positives as given by Eq. (4).

$$PPV = \frac{True\ positive}{True\ positive + False\ positive} \qquad (4)$$

4. Results and discussion

4.1. Headspace analysis of mixed and unmixed HME components

As the purpose of the MODD is to represent mixed odor from unmixed component sources, it is imperative to determine if the physical mixing of these components alters the presentation or make up of the vapor profile. The results of the headspace analyses of mixed vs. unmixed AN-based binary explosives are given as overlaid chromatograms (Fig. 5). The diesel fuel contained a number of characteristic peaks. A few of these, noted on the chromatogram in Fig. 5A, include toluene, *p*-xylene, and trimethylbenzene. The presence and abundance of these and other volatiles in the chromatogram did not appear to be affected by mixing the diesel fuel with AN. The main headspace component of petroleum jelly is phenylethyl alcohol, giving petroleum jelly its pleasant

Fig. 5. Chromatograms representing the headspace of fuel components alone overlaid with the headspace of the fuel component mixed with AN, including A) diesel fuel, B) petroleum jelly, C) sugar, D) sawdust, E) aluminum.

floral odor. The abundance of this compound was slightly increased with mixing, though not significantly (*t*-test, 95% confidence) (Fig. 5B). All other components in the chromatogram were present and in similar quantities in both samples. Few components were detected in the headspace of either sugar (Fig. 5C) or sawdust (Fig. 5D), although butyl acetate, a sweet smelling compound, and α-pinene could be identified in each, respectively. The amount of butyl acetate in both sugar samples was nearly identical, as was the quantity of α-pinene in the sawdust samples. There were some discrepancies in other compounds in the chromatograms of the sawdust samples. This could be due to the low abundance of all volatile species decreasing the sample-to-sample reproducibility. Acetic acid, the most abundant component of the headspace of aluminum coated with stearic acid, was present in both the mixed and unmixed samples (Fig. 5E), though the amount was greater in the mixed sample. This could be due to the increased separation of the Al particles when in the mixture liberating a greater amount of volatiles from the Al. Overall, with each AN/fuel set, the same characteristic peaks from the headspace of the fuel were present and most in similar quantities. No additional compounds that could be produced by a reaction were identified from any pair. The vapor signatures of the fuels were not significantly altered by physical mixing with the AN.

Similarly, changes in the quantities of ammonia vapor from AN when mixed with the fuels were measured and reported as headspace concentration (ppb) (Fig. 6). The average headspace concentration of ammonia in AN alone was 1.9 ± 0.51 ppb. The concentrations of ammonia from AN and fuel mixtures ranged from 1.3 ppb to 2.4 ppb. Using a *t*-test (95% confidence) to compare the concentration of ammonia from AN alone to each mixed samples, it was determined that there were no statistical differences between the amount of ammonia liberated from AN mixed or alone. Overall, the physical mixing of explosive components did not significantly alter the vapor signatures of the individual components, thus the use of the separated components of AN-based HMEs in the MODD was supported.

4.2. Vapor distribution within MODD

A computational model was used to predict the analyte-concentration field within the MODD. The modeled vapor distribution near the outlet of the MODD after a one-hour equilibration period is depicted in Fig. 7, using limonene as the analyte. Observe that the concentration field was symmetric. It may seem counter-intuitive that the concentration field starts as highly asymmetric at the base of the MODD and emerges highly symmetric around the restrictor plug and nearly uniform across the MODD outlet. However, the concentration field becomes symmetric due to the small central channel separating the upper and lower chambers. The diameter of the central channel is smaller than its length (length/diameter = 1.3); thus, horizontal diffusion occurred on a shorter time scale than vertical diffusion. This acted to reduce any horizontal concentration gradients before the vapor diffused through the entire vertical length of the central channel. The symmetry predicted by the model indicated that the vapor profile at the MODD outlet was approximately the same for any direction that a canine chooses to approach the MODD for sampling.

Further, from this it can be concluded that a symmetric profile will emerge near the MODD outlet when multiple samples are placed in the vials at the base of the MODD so long as their vapor concentrations within the MODD are dilute. Note that this model prediction involved only a single analyte; in other words, the simultaneous diffusion of both methyl salicylate and limonene in the air within the MODD was not simulated. This was not necessary, as the analyte concentrations were too dilute to affect each other's transport.
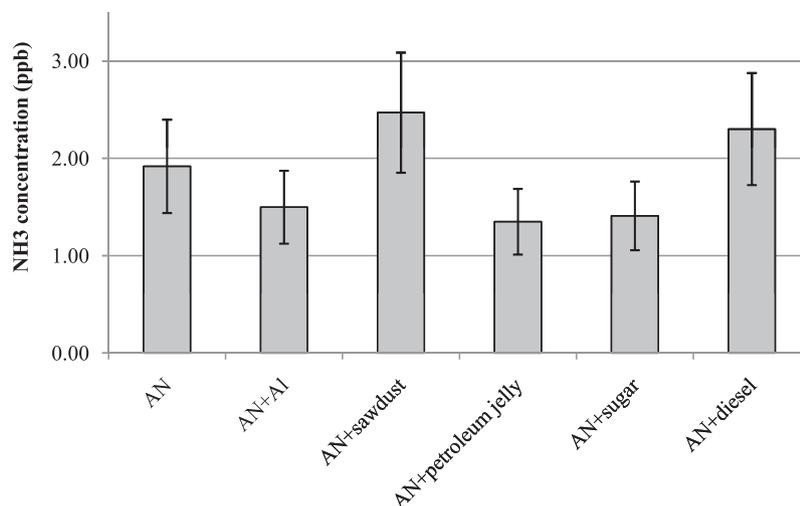
Fig. 6. Headspace concentrations of ammonia above AN alone and mixed with fuel sources, to include aluminum, sawdust, petroleum jelly, sugar, and diesel fuel.
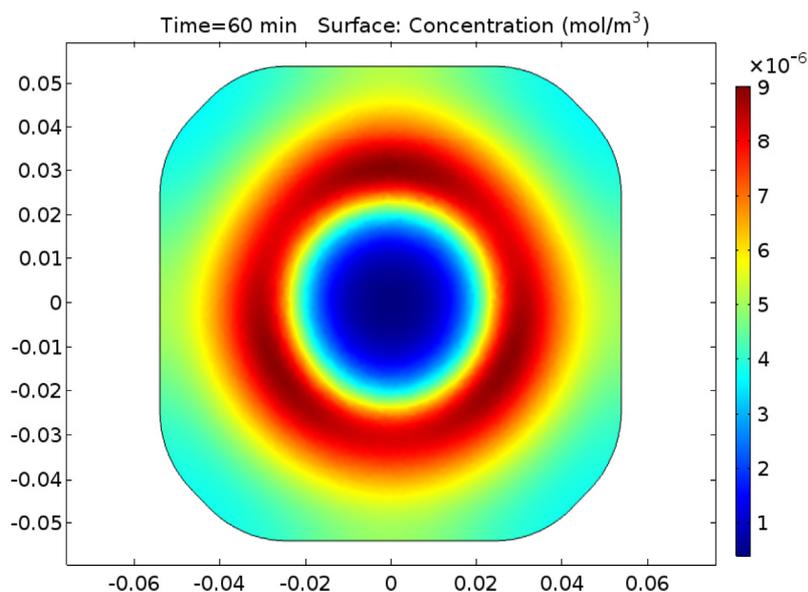
Fig. 7. Predicted molar concentration of limonene on horizontal surface located 2 mm beneath the top of the MODD. Prediction shown at t = 1 h. *(reproduce in color)*

Laboratory experiments measuring the distribution of mixed vapor at the top of the MODD were used for comparison with the predicted vapor distribution. Methylsalicylate and limonene were placed separately in opposite wells in the MODD and allowed to equilibrate for one and four hours. The relative amounts of these compounds were measured using two SPME fibers positioned directly above the wells where the compounds were placed (Fig. 8). The reproducibility was less than desirable due to sampling in an open environment. The ratio of methylsalicylate to limonene collected from either fiber was statistically similar (*t*-test, 95% confidence), meaning there was little asymmetry at the MODD outlets. This data is in agreement with the predictions of the vapor distribution model and further indicates both that the individual vapor sources mix thoroughly and that a canine would be unlikely to recognize the output vapor as originating from individual sources. There was some difference between the one hour and four extractions indicating the limonene was still increasing over this time period. This change, however, did not affect the mixing of the compounds at the top of the MODD.

In Table 4, the predicted number of moles of analyte in the upper chamber of the MODD was compared with the measured number of moles sampled in the experiments at two equilibration times of one and four hours, and for both analytes, limonene and methylsalicylate. The predictions showed reasonable agreement between the measurements, which were within a factor of about 2–8. These experimentally measured values were consistently less than the predicted values. Factors that could contribute to the over-prediction by the model include adsorption of analyte vapor on the surfaces of the MODD, or loss of vapor due to diffusion away from the sampling point. However, it is unlikely that these over-prediction factors will affect the symmetry of the vapor profile at the outlet.

In additional analytical experiments, the mixing of vapors in the MODD was explored. Pairs of compounds of varying vapor pressures and functionalities were placed in the MODD or sampling chamber, and the vapors were collected and quantitated using active sampling. The ratio of analyte vapors collected from the MODD outlet were compared to those calculated using known
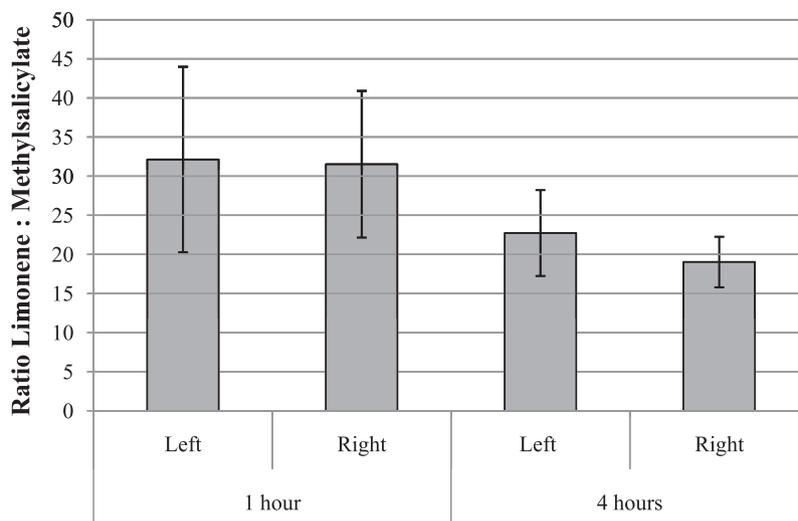
Fig. 8. Ratio of limonene and methylsalicylate masses collected by SPME above two locations (left and right) above the MODD following equilibration times of 1 and 4 h.

Table 4
Measured and predicted quantities of methyl salicylate and limonene from above the MODD in moles after one hour and four hours equilibration.

	Methyl salicylate (mol)		Limonene (mol)	
	1 h	4 h	1 h	4 h
Measured (Average)	3.6E-11	9.1E-11	6.9E-09	8.1E-09
Standard Deviation	*1.8E-11*	*3.9E-11*	*1.3E-09*	*1.2E-09*
Predicted	2.72E-10	5.30E-10	1.11E-08	2.19E-08
Magnitude difference (predicted/measured)	7.6	5.8	1.6	2.7
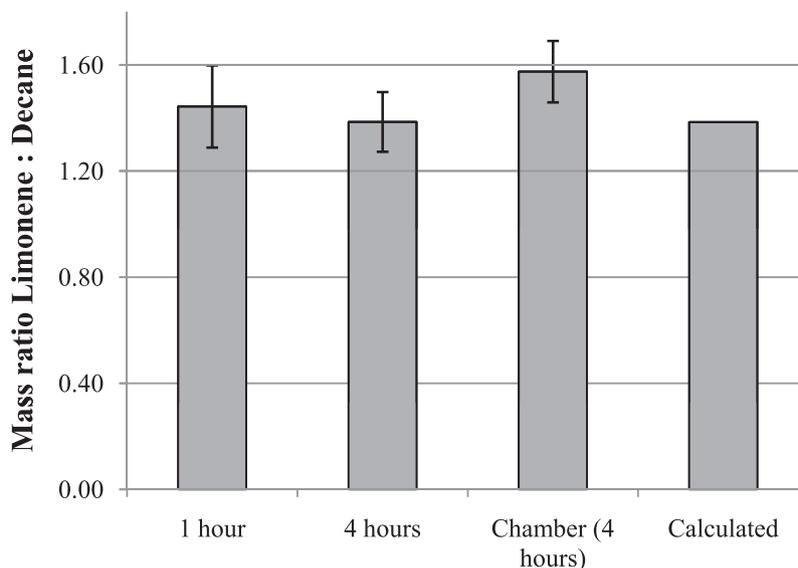
Fig. 9. Averaged ratios of limonene to decane detected from above the MODD following 1 and 4 h equilibration times, and compared to that from the headspace sampling chamber and to the predicted value.

vapor pressures values, and those collected from an alternative container. Assuming that neither the MODD structure nor material impedes vapor mixing, the ratios determined experimentally should be the same as the calculated values and those sampled from another container. The first pair of compounds, limonene and decane, have similar vapor pressures and diffusion coefficients but dissimilar functional groups. The ratios of limonene to decane showed no statistical difference between either equilibration times

or in comparison to the sampling chamber or calculated values (Fig. 9). Limonene and methylsalicylate have similar functionalities but dissimilar vapor pressures. The ratios of these in the MODD were statistically similar (*t*-test, 95% confidence) to one another and to the calculated value (Fig. 10). Both sets of data indicate no alteration of the vapor profiles from the MODD outlet, and based on this data, it can be concluded that the MODD accurately portrays the mixed odor of these separated compounds.
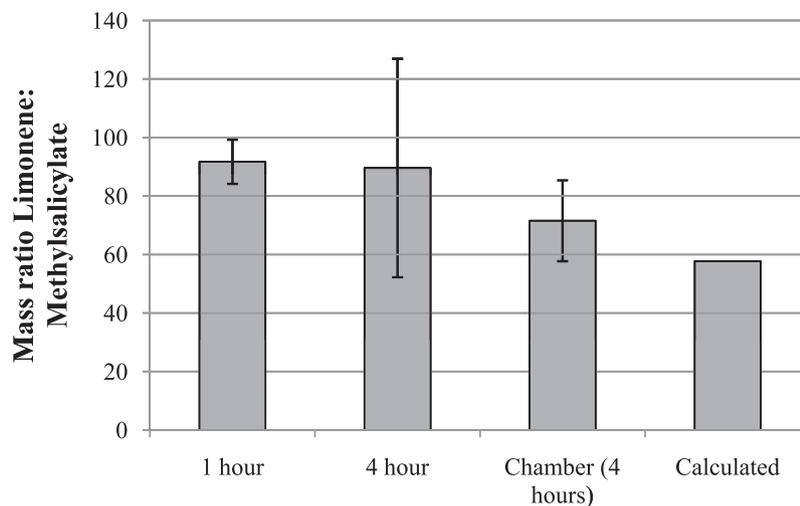
Fig. 10. Averaged ratios of limonene to methylsalicylate detected from above the MODD following 1 and 4 h equilibration times, and compared to that from the headspace sampling chamber and to the predicted value.
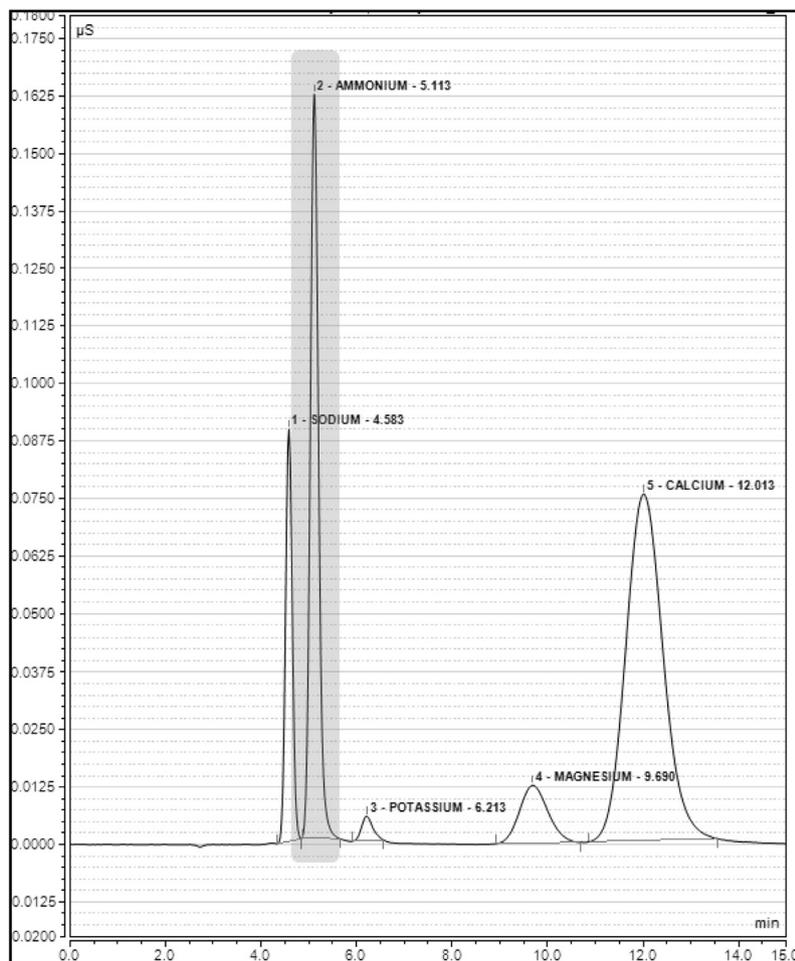
Fig. 11. Chromatogram of ions from sorbent pads placed in MODD containing explosive components. The peak attributed to ammonium is highlighted.

4.3. Proof-of-concept

Finally, explosive components were placed inside of the MODD, where they were held for 4 h prior to sampling. The vapor concentration of ammonia from the AN component was measured at the MODD outlet. An ammonia concentration of 7–10 ppb was estimated from a single vial containing 2 g of AN. An example ion chromatogram from this analysis is given in Fig. 11. The vials of AN were placed in the MODD in combination with several fuel sources, including diesel fuel, aluminum powder, and petroleum
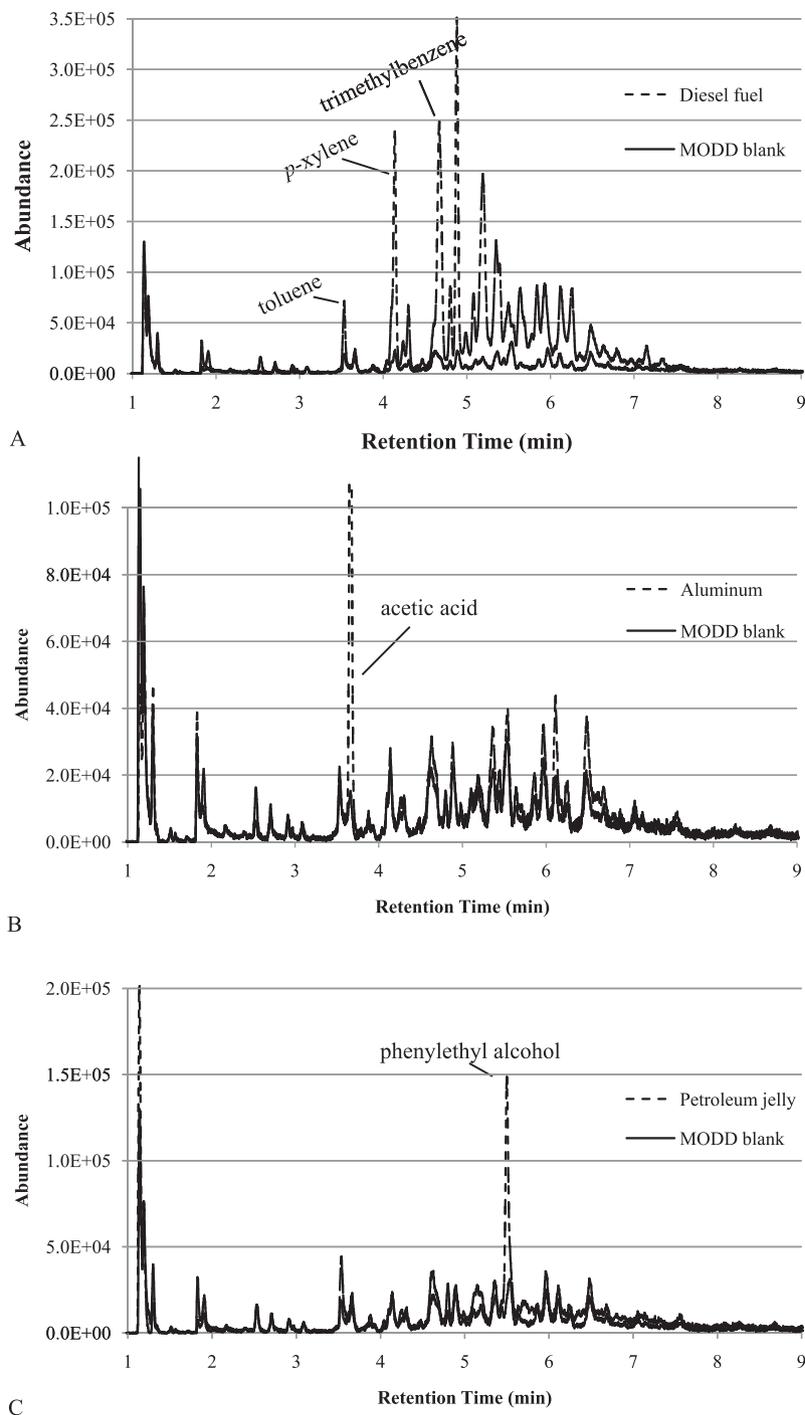
Fig. 12. Chromatograms representing the headspace at the MODD outlet when containing HME components, AN and; A) diesel fuel, B) aluminum, C) petroleum jelly.

jelly. Chromatograms representing the headspace at the MODD outlet are given below (Fig. 12). In all cases, the main volatile components of the compounds could be detected at the outlet.

4.4. Canine field trials

Results from field trials using canine detectors are given in Table 5. The numbers of true and false responses out of total number of responses possible are listed for each target material. A true response was deemed a correct response to target material (i.e. A/B mixture, A + B unmixed, A alone, or B alone), while a false response

was judged as a response to any MODD containing material other than the targets (i.e. blanks or distractors). All responses, true or false, were recorded by the assessor with concurrence from the handler. Interest in a target, blank, or distractor without a final response was noted by the assessor, and is included in Table 5.

Eleven of the twelve canines tested passed the validation tests (K9 4 did not pass the validation section and was not included in the final data). Of these eleven canines, nine correctly responded to both the mixed and unmixed materials. The same two canines that did not respond to the unmixed material, also did not respond to the mixed material, thus the tabulated response rates to the

Table 5
Results from canine testing on MODDs. The number of true responses and false responses out of the total possible number of responses are reported. Underlined numbers indicate interest with no final response. *Canines did not perform last run of the day, which, in this case, was the scenario with no target.

		No Target	A/B mixed	A + B unmixed	A	B	Comments
K9 1	True response	0/0	1/1	1/1	0/1	1/1	
	False response	0/5	0/4	1/4	0/4	0/4	
K9 2	True response	n/a*	1/1	1/1	<u>1</u>/1	<u>1</u>/1	
	False response	n/a*	0/4	0/4	0/4	0/4	
K9 3	True response	n/a*	1/1	1/1	0/1	0/1	
	False response	n/a*	0/4	0/4	2/4	1/4	
K9 5	True response	0/0	1/1	1/1	0/1	0/1	Canine corrected from responding to all MODDs
	False response	4/5	0/4	0/4	0/4	2/4	
K9 6	True response	0/0	1/1	<u>1</u>/1	0/1	<u>1</u>/1	Canine corrected from responding to all MODDs
	False response	3/5	¼	0/4	2/4	2/4	
K9 7	True response	0/0	0/1	<u>1</u>/1	0/1	0/1	
	False response	1/5	0/4	1/4	0/4	0/4	
K9 8	True response	0/0	0/1	<u>1</u>/1	0/1	1/1	Canine responding to cotton bags → corrected
	False response	0/5	2/4	1/4	0/4	1/4	
K9 9	True response	0/0	1/1	1/1	1/1	0/1	Canine responding to cotton bags → corrected
	False response	1/5	0/4	0/4	0/4	1/4	
K9 10	True response	0/0	1/1	1/1	1/1	**1**/1	
	False response	0/5	0/4	0/4	0/4	0/4	
K9 11	True response	0/0	1/1	1/1	0/1	1/1	Canine corrected from responding to all MODDs
	False response	3/5	0/4	0/4	0/4	0/4	
K9 12	True response	0/0	1/1	1/1	1/1	1/1	Canine responding to nitrile gloves → corrected
	False response	2/5	0/4	0/4	2/4	0/4	
Totals	**True response**	**n/a**	**9/11**	**9(11)/11**	**3(4)/11**	**4(7)/11**	
	False response	**14/45**	**3/44**	**3/44**	**6/44**	**7/44**	
% of total	**True response**	**n/a**	**82%**	**82% (100%)**	**27% (36%)**	**36% (64%)**	
	False response	**31%**	**6.8%**	**6.8%**	**14%**	**16%**	
Positive Predictive Value		*n/a*	*75%*	*75%*	*33%*	*36%*	

mixed and unmixed components were identical. The PPV were 75% indicating that the rates of true responses to the A/B mixture and A + B unmixed were significantly greater than chance.

A greater rate of false responses was recorded when neither vapor mixture was present in the testing scenario (i.e. blank, A alone, or B alone). It appeared as though many of these false alerts were due to the canine responding to the MODD itself instead of locating a target odor. While the rate of false positives was high at these times, once the behavior was recognized, it was corrected by the handler. Other false responses were on clean cotton bags similar to those used in the validation runs, and clean nitrile gloves due to a previous encounter with training materials that had been exposed to nitrile gloves. These behaviors were also quickly extinguished by the handlers. Though some false alert rates were initially higher than a deployable instrumental detector, these unwanted behaviors were modified by the handlers through brief retraining, a benefit that cannot be ascribed to common instrumental detectors.

Four of the 11 canines were previously trained on A alone, and 3 of these 4 canines positively responded to component A. None of the other canines responded to component A alone. Though none of the canines had been trained on B alone, four canines did indicate to it, although this true response rate was not greater than chance (PPV = 36%). The true response rates of the canines to A and B (mixed or unmixed) were compared to both individual components (A alone or B alone) using a chi-square test (95% confidence level; one degree of freedom). The results of the chi-square test ($\chi^2 = 6.78$ and $\chi^2_{crit} = 3.84$) indicate there were significantly less true responses to the individual components than to the mixed and unmixed A and B, and thus, the canines were significantly less inclined to locate the individual components over the mixed odor. These results support the previous research on canine detection of binary explosives [17]. Overall, results of the canine trials suggest the presence of A and B vapor mixture at the outlet whether they were actually mixed or unmixed in the MODD. Furthermore, there was no evidence, from either the canine trials or the analytical

testing, that the mixed vapor was altered in such a way to affect canine detection as it moved through the MODD.

5. Conclusions

A device was designed to hold separated HME components while allowing for the detection of mixed HME vapor during canine training, and preliminary work was completed to validate the this device. In agreement with computational modeling of the vapor distribution across the top of the MODD, evaluations indicated that single, separated HME component vapors distribute symmetrically around the restrictor plug at the MODD outlet. This implies that when multiple components are placed in the MODD, their vapors will be mixed at the outlet and the canine detectors will be presented with the vapors as a mixture and not individual components. Furthermore, laboratory testing confirmed that physical mixing of the HME components tested does not significantly alter the vapor profile, and thus the vapor coming from the separated components is statistically similar to that from the mixed material.

Further analytical assessments and canine field-testing showed that the MODD design accurately portrays the vapor profile of mixed materials from separated components. The data validated the use of the MODD for training canines to detect mixed materials. The MODD can now be used to present HME vapor to canines for training, and will thus support more regular training on HMEs as safety, storage, and disposal restrictions are lifted. Training will also benefit from the ease in which training materials and material quantities can be adjusted within the MODD, improving the overall proficiency of canine detection on these threat materials.

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