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Development of an Alternative Mixed Odor Delivery Device (MODD) for Canine Training

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14. ABSTRACT

A device for training canines on binary explosive materials, the Mixed Odor Delivery Device (MODD) was previously developed by the Naval Research Laboratory. Interest in the device from the law enforcement and military canine handlers led to an appeal for a second prototype and motivated the design, fabrication, and testing of a large-scale MODD (LS-MODD). The LS-MODD holds a greater quantity of materials, such as those that cannot easily be divided into smaller amounts. In this work, a prototype was designed maintaining the features of the original MODD, and similar to the original MODD, the LS-MODD was evaluated by three techniques: computational modeling, headspace analysis, finally, field trials with trained detection canines.

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EXECUTIVE SUMMARY

A device for training canines on binary explosive materials, the Mixed Odor Delivery Device (MODD), was previously developed by the Naval Research Laboratory. Interest in the device from the law enforcement and military canine handlers led to an appeal for a second prototype and motivated the design, fabrication, and testing of a large-scale MODD (LS-MODD). The LS-MODD holds greater a quantity of materials, such as those that cannot easily be divided into smaller amounts. In this work, a prototype was designed maintaining the features of the original MODD, and, similar to the original MODD, the LS-MODD was evaluated by three techniques: computational modeling, headspace analysis, and finally, field trials with trained detection canines.

Following completion of the design of the new LS-MODD, a three-dimensional, time-dependent diffusion model to predict transport of 2,4-DNT vapor within the device was developed. Variation in the concentration along the diffusion path through the device was predicted, and showed that the concentration field was highly asymmetric in the lower portion of the device, but became symmetric at the olfaction outlet where the canines sample the vapor. The development of symmetry appeared primarily to occur within the neck, a central channel connecting the lower and upper portions. This result was likely due to a fast diffusion time scale along the horizontal cross section of the neck as compared to that of diffusion along the vertical axis.

Headspace analyses of the volatile components emanating from the LS-MODD outlet was carried out with volatile extraction by solid phase microextraction (SPME) and analysis by gas chromatography / mass spectrometry (GC/MS). Like the computational modeling, the laboratory analyses examined the symmetry of the vapor concentration around the LS-MODD outlet. This was accomplished by placing a single odor source in the device and measuring the vapor at differing locations in the outlet. Like the vapor distribution model, results suggested that the vapor distribution was symmetrical around the restrictor plug and that the upscaling of the design of the original MODD to that of the LS-MODD did not qualitatively affect the symmetry of the vapor distribution at the outlet.

In a second set of experiments, vapor mixing in the LS-MODD was explored by placing two components, either mixed or separated, in the LS-MODD, and measuring vapor at the outlet. Similar to experiments carried out with the original MODD, there were no statistical differences

between the ratios of the vapors at the outlet, mixed or unmixed, and thus, the design of the new device did not appear to affect the delivery of the vapor mixture.

In final proof-of-concept experiments, characteristic volatile compounds from the diesel fuel with ammonium nitrate, separated in the LS-MODD, were measured at the outlet. Such compounds were, in fact, detected at the outlet, and comparing these results to that of actual explosive mixture, it was found that the same compounds were present at similar ratios from both the individual components in the LS-MODD and the HME mixtures. Thus, the LS-MODD emitted the same vapor signature from separated components as from the actual explosive mixture.

For field evaluations, both TNT and explosive components, ammonium nitrate and diesel fuel, were (separately) placed in the LS-MODDs. Certified explosive detection canines were directed to locate the LS-MODD containing the explosive material from a series of three devices. The canines easily located both targets, confirming that vapor from the explosive materials were accurately portrayed at the outlet of the device.

BACKGROUND / MOTIVATION

In recent years, the types of explosive threats recovered in Middle East conflicts have shifted from traditional, military-type explosives, such as TNT and RDX, to homemade explosive (HME) materials. HMEs are most commonly composed of simple binary explosive mixtures of an oxidizer, such as ammonium nitrate (AN) or potassium chlorate ($KClO_3$) mixed with a fuel source. When not mixed, the components are safe and non-explosive, and often commercially available. The ease of acquiring and mixing the components make the use of HMEs particularly appealing to terrorists and criminals, not only in the Middle East but also domestically [1, 2].

Though many devices exist for the detection of explosives, canines are currently the most effective tool for the detection of HMEs. Canine detection has demonstrated superior sensitivity and selectivity over most, if not all, field-deployable detectors and sensors for explosive materials [3, 4, 5, 6, 7], and, unlike instrumental detectors, canines are easily trained to new threats as they arise. With proper and consistent training, canine detectors are capable of locating a wider range of explosives with lower false alert rates than any currently deployable detector [8]. However, regular access to HMEs to support consistent training is often limited. This is because mixed explosives are difficult to safely obtain, store, and transport. Training frequency is restricted by same-day production limitations and the requirement for an explosive chemist to be present during operations. These necessary safety measures are costly and time consuming, and for this reason many handlers choose to train the canines on the oxidizer alone (i.e. AN or $KClO_3$) instead of the explosive mixtures. Training on a single component of a mixture has shown to be insufficient. Several studies have revealed that regular training with the actual explosive mixtures, and not solely single components, improves detection proficiency on HMEs [9, 10].

The Mixed Odor Delivery Device (MODD) [11, 12] was designed to alleviate the above-mentioned training difficulties. The MODD safely contains and allows for accurate presentation of the vapor mixture without the physical mixing of the components. The MODD also offers transportability and ruggedness for field use, and is easily adaptable for the varied components one might encounter in the field.

DESIGN OF MIXED ODOR DELIVERY DEVICE / PREVIOUS RESEARCH

The MODD (Figure 1) functions to safely separate up to four explosive components in removable vials. The vials are placed securely in a lower compartment. An upper compartment, where the canine sniffs, or "samples", the odor is placed on top of the lower compartment, and is held in place by two metal latches. An o-ring sits between the compartments to ensure an airtight closure. The design allows vapors from the separated vials to diffuse to the base of a neck, centered between the vials, where the vapors meet and mix, and then continue around a restrictor plug above the neck. The analyte vapor escapes from around the neck and restrictor plug to the MODD outlet as a plume of mixed vapor. The outlet is a bowl-shaped area around the restrictor plug in the upper compartment where the canine places its snout for sampling. The canine samples a mixture of vapors instead of separated component vapor at this outlet.
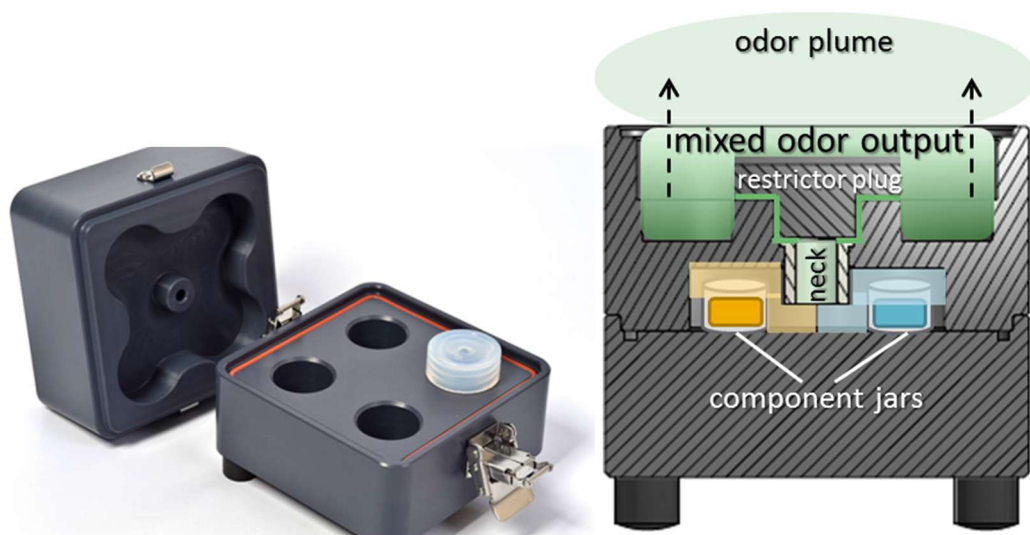
Figure 1. (left) The MODD, opened with lower portion holding a sample vial exposed; (right) Diagram of MODD depicting vapor distribution and mixing throughout device.

The MODD was previously evaluated to assess the distribution of vaporous analytes at its outlet by three approaches. The methodologies included computational modeling, headspace analysis, and canine field-testing [11]. Computational modeling of the vapor distribution within the device was utilized in developing the design of the device, and laboratory analyses and field-testing using certified explosive-detection canines were carried out for confirmation of its efficacy.

The vapor distribution was considered using a model that depicts undisturbed odor residing in the MODD outlet following a given equilibration time. This scenario mimics what the canine would experience upon initially approaching the MODD. The focus of the analysis was the symmetry of the analyte vapor concentration across the MODD outlet. A symmetrical distribution would signify that 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. Results of the modeled vapor distribution for a single component in one corner of the MODD after a one-hour equilibration period, was, indeed, shown to be symmetric around the restrictor plug (Figure 2).
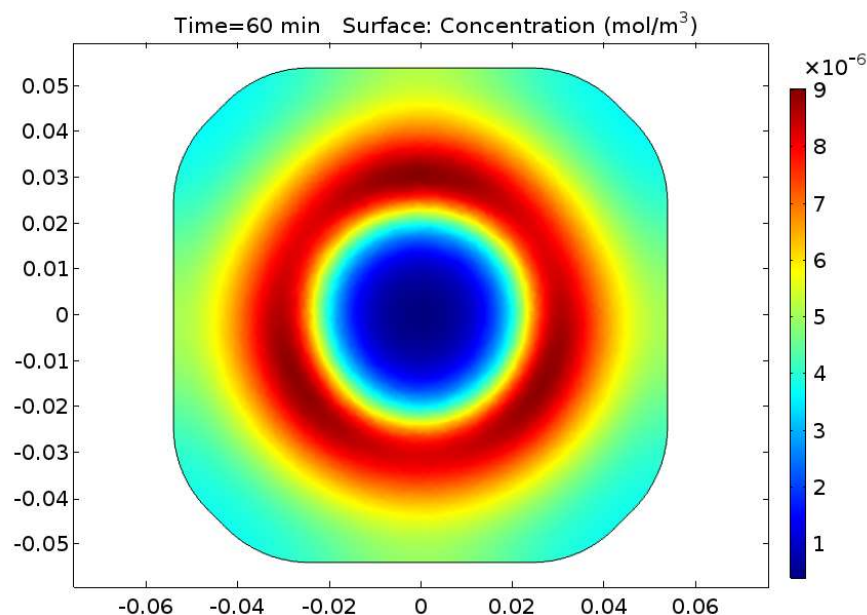
Figure 2. Predicted molar concentration of limonene on horizontal surface located 2 mm beneath MODD. Prediction shown at t = 1 hour [13].

In agreement with the computational modeling, headspace analysis also indicated that single, separated component vapors do distribute symmetrically around the restrictor plug at the MODD outlet. Further analytical assessments, in addition to canine field-testing with HMEs, demonstrated that the MODD design does accurately portrayed the vapor profile of mixed materials from separated components. In field trials with mixed and separate HME components, canines were shown to correctly locate MODDs containing separated HME components at the same rate as MODDs containing actual HME, and headspace analysis from above the MODD outlet indicated

the presence of key volatile HME vapors [11]. These results validated the use of the MODD for training canines to detect mixed materials.

In this current, follow-on research, a large-scale MODD (LS-MODD) was designed to hold greater quantities of training materials, as recommended by law enforcement and military canine handlers. To do this, the current MODD design was altered to house larger glass containers (16-oz jars), already commonly used by canine handlers to store training aids. As done previously, the vapor distribution within the device was modeled to ensure even distribution and proper mixing of the component vapors prior to fabrication. Upon satisfactory results, devices were fabricated and validated by laboratory analyses and canine field-testing.

DESIGN OF LARGE-SCALE MIXED ODOR DELIVERY DEVICE

The LS-MODD was designed to house four 16-oz jars, similar to those used by canine handlers for the storage of training materials. As depicted in Figure 3, the basic design of the original MODD was maintained. The jars were again contained in the lower chamber of the MODD, into which a Teflon neck extends to promote mixing of vapors. Vapors from the jars disperse and mix in the neck as they move into the upper chamber for sampling by the canine. Like the original design, the LS-MODD has a restrictor plug creating a gap above the neck around which the vapors diffuse as they move to the upper chamber. Restrictor plugs of different sizes were fabricated, allowing more or less vapor to reach the sampling chamber in a given amount of time.
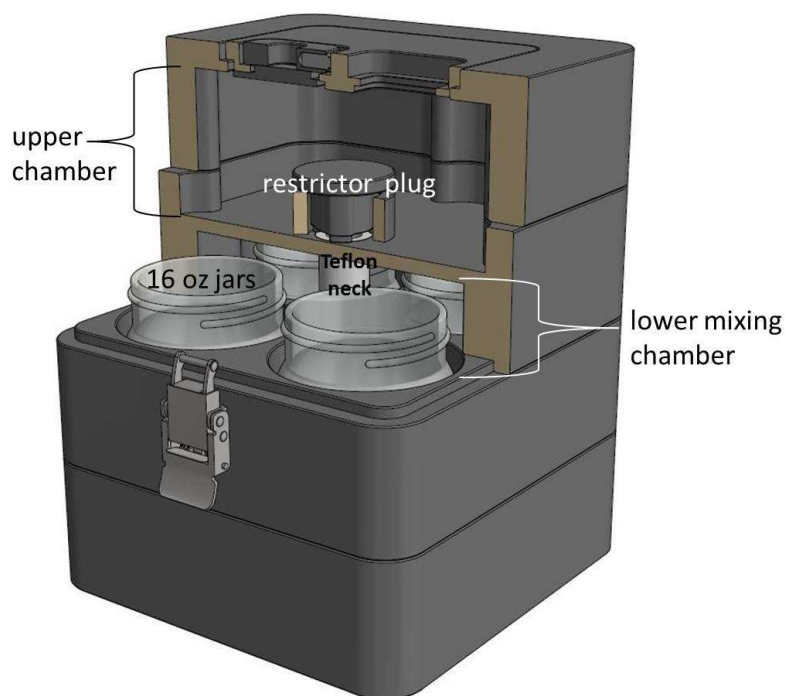
Figure 3. Diagram of LS-MODD containing four 16-oz glass jars with cut-away to expose lower mixing chamber, upper chamber and restrictor plug.

COMPUTATIONAL MODELING

Vapor distribution models were created to assist in the design and characterization of the LS-MODD. The model predicts the analyte concentration field within the device and its evolution over time. A goal for the LS-MODD was to present a symmetric concentration field of mixed vapors to ensure that, in the absence of external forces, the vapor mixture that the canine samples is independent of the position of the explosives in the lower portion of the device. Since the LS-MODD outlet has a square cross section, it was desired to achieve (at least to a very good approximation) four-fold symmetry of the concentration profile at the outlet. A possible setback for achieving such symmetry was that the placement of samples in the base of the device was not symmetric. Up to four *different* samples can be placed in the device, which will certainly lead to asymmetric concentrations in the lower chamber immediately above the samples. Thus, symmetry of analyte concentrations must develop as the vapors transport within the LS-MODD, from the lower chamber to the outlet.

Modeling schematic of LS-MODD

The schematic of the LS-MODD used for model predictions is shown in Figure 4. Note that the geometry shown represents the interior of the LS-MODD, wherein analyte vapor can transport. Figure 4 (left) shows a side view with four slots that hold the jars. The slots are also seen from the bottom view (Figure 4, lower right). The shorter slot of the four in the image depicts a slot containing a single sample. As vapors diffuse from the sample surfaces and out of the jars, they begin to mix in the lower chamber above the slots. From here the vapors diffuse into the neck, which is partially capped with the restrictor plug to reduce analyte vapor transport to desired levels. The area above in the neck the upper chamber is open to the ambient environment and accessible for sampling by the canine. The top view of the device (Figure 4, upper right) depicts the outlet, a 5" by 5" square opening where the canine samples the mixed vapor.
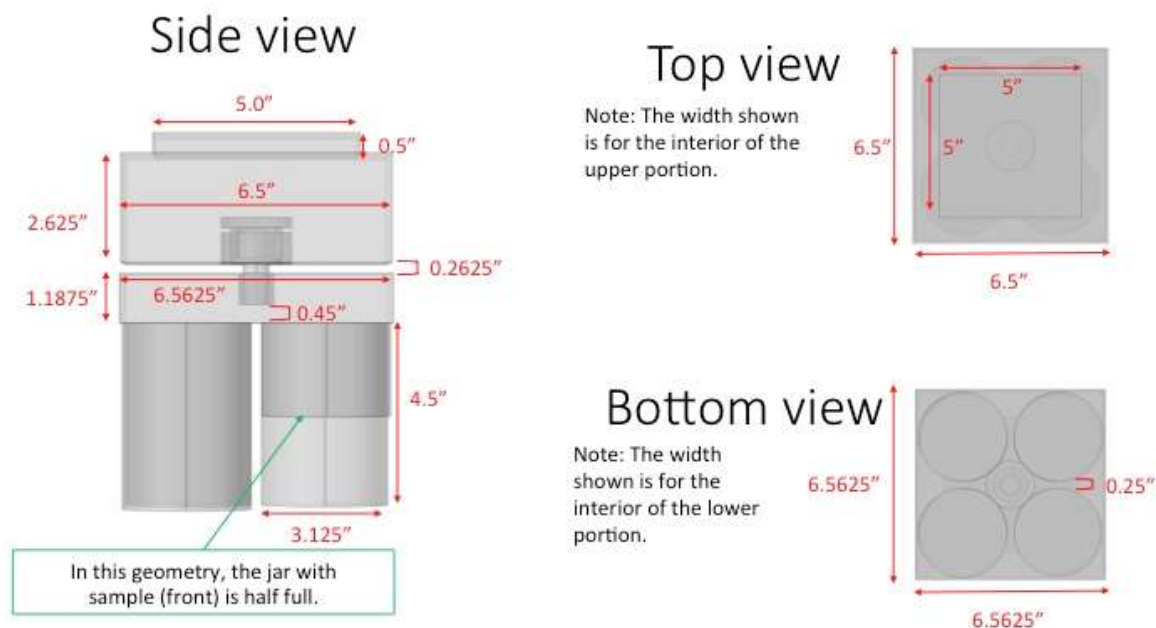
Figure 4. External views of geometry used for preliminary modeling studies that approximates the increased-scale MODD.

The geometry of the neck and restrictor plug excluding the rest of the LS-MODD are shown in Figure 5. Note that there are upper and lower regions of the neck, each having a different diameter. The lower region of the neck has an inner diameter of 0.625" and a length of 1". The material bounding the neck is a PTFE insert, whereas the rest of the device is composed of PVC. The upper region of the neck has an inner diameter of 1.25" and a length of 0.75", but can be capped with a

restrictor plug to reduce vapor transport. Four restrictor plugs of different sizes were fabricated. As depicted in Figure 5, each plug has a characteristic length scale, δ, that corresponds to the distances between the plug and the base of the upper portion of the neck (Figure 5, right). Also, the maximum radial opening along the length of the upper region of the neck and the opening between the top of the neck and that of the plug are depicted in Figure 5, right and left, respectively. The values of δ for the four plugs are 0.0625", 0.125", 0.1875", and 0.9375". Each plug has three wedges, through which vapor cannot pass, that are used to secure the plug within the upper region of the neck. Blocks are used in the model schematic to approximate the plug wedges, though the outer surface of the actual plugs is smoother than that of the approximation.
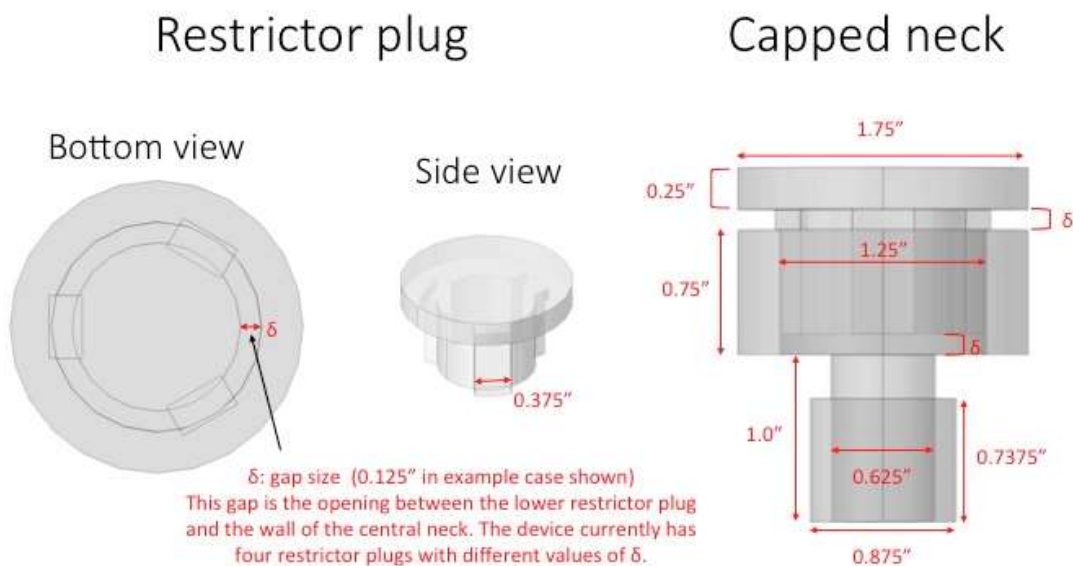
Figure 5. Internal views of geometry used for preliminary modeling studies that approximates the LS-MODD.

The computational domain for the model includes the schematic shown in Figure 4 and Figure 5, as well as a large cylinder above the outlet. The large cylinder represents the space above the device and allows vapors to transport out and away from it into the open environment.

Vapor transport model

The model aimed to predict transport of analyte vapor starting from the surface of a sample and progressing through and out of the LS-MODD. The following assumptions were used in the model:

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- Convection was negligible; thus, the model did not describe the effect of fluid flow such as wind, canine sniffing, etc. Convection from such external sources may likely affect the concentration field, but describing their effects on the concentration field would require a model with much greater complexity to be developed.

- Molecular adsorption (i.e., "sticking") of the analyte on the device had a negligible effect on symmetry of concentration field at the outlet [11], though neglecting adsorption in the current model for the LS-MODD may over-predict the actual amount of analyte vapor diffusing through the device. This model is only intended for qualitative predictions, specifically for the symmetry of the concentration field in the device.

The model solves for three-dimensional, time-dependent diffusion of analyte vapor within the computational domain. The equation solved is given by

$$\frac{\partial C}{\partial t} = D\left[\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right], \tag{0.1}$$

where C is the analyte (molar) concentration and D is its (isotropic) diffusivity.

The initial condition for the simulation at t = 0 was no analyte present; i.e., C = 0 everywhere. Two different boundary conditions were used in the model; one for the analyte sample surface, and the other for the walls of the device/computational domain. In this model, the analyte sample surface was represented as a flat horizontal surface at the middle height of a single jar slot (see the shortest slot on the bottom of the device in Figure 4). The air immediately surrounding the sample was treated as saturated with analyte vapor, where the saturation concentration was obtained from the analyte vapor pressure. Thus, the boundary condition on the sample surface was that of a constant vapor concentration. With the exception of the sample surface, it was specified that no vapor entered or exited the domain from all other surfaces of the computational domain. Thus, a zero-flux boundary condition was used on both the device walls and the large cylinder above the device.

Similar to previous modeling efforts with the original design, calculations were performed with the analyte 2,4-dinitrotoluene (2,4-DNT). At 25 °C, 2,4-DNT is a solid with a vapor pressure of 2.9 x 10^{-2} Pa, and its vapor has a diffusivity of 6.7 x 10^{-6} m^2/s in air (Table 1). Previous research

with the MODD indicated that this analyte had the tendency to adsorb on the PVC walls of the device; as discussed previously, the current model does not account for such adsorption.

Table 1. Properties used in the model for analyte 2,4-DNT (at 25 °C).[1]

System	Vapor pressure (Pa)	Saturated concentration in air (mol/m³)	Diffusivity (m²/s)
2,4-DNT	0.029	1.2×10^{-5}	6.7×10^{-6}

The COMSOL Multiphysics software package was used to numerically solve Eqn. (0.1). COMSOL can automatically generate a mesh to discretize the computational domain subject to the desired level of accuracy specified by the user. A mesh tailored for fluid dynamics calculations was utilized at an "extremely fine" setting, giving the greatest accuracy obtainable from the default mesh-generation options.

Results and comparison to original device

In this report, modeling was focused on the symmetry of the concentration field along the diffusion path of the analyte within the LS-MODD. The results showed that a theoretical equilibration time of one hour was a sufficient amount of time for vapor to diffuse through and out of the device. Although the concentration of vapor within the device continued to rise via diffusion for times beyond 1 hour, the symmetry of the concentration field did not appear to change over time based on visual inspection of the results carried out for a total duration of 4 hours. The example calculations shown were conducted using a restrictor plug with characteristic length δ = 0.125".

Figure 6 depicts the concentration field within the computational domain at t = 1 hour. The space indicated in the figure is the open space into which vapor can diffuse. In Figure 6a it is apparent that an asymmetric concentration field developed in the lower portion of the device containing the sample. For the device to work as desired, this asymmetry needed to be eliminated along the diffusion path to the outlet. In Figure 6b, slices of the concentration field were shown; the middle slice includes a profile of the concentration field within the neck above the lower chamber. It was clear from this profile that the variation in the concentration across the neck was small relative to that seen in the mixing chamber below, which indicates a reduction in the asymmetry of the concentration as the vapor progresses through the diffusion path.

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[1] Ravikrishna, R., Valsaraj, K.T., Thibodeaux, L.J., Price, C.B., Brannon, J.M., "The efficiency of capping to control air emissions from exposed contaminated seidments and dredged material." *Journal of Air and Waste Management*, vol. 54, pp. 1525-1533, 2004.
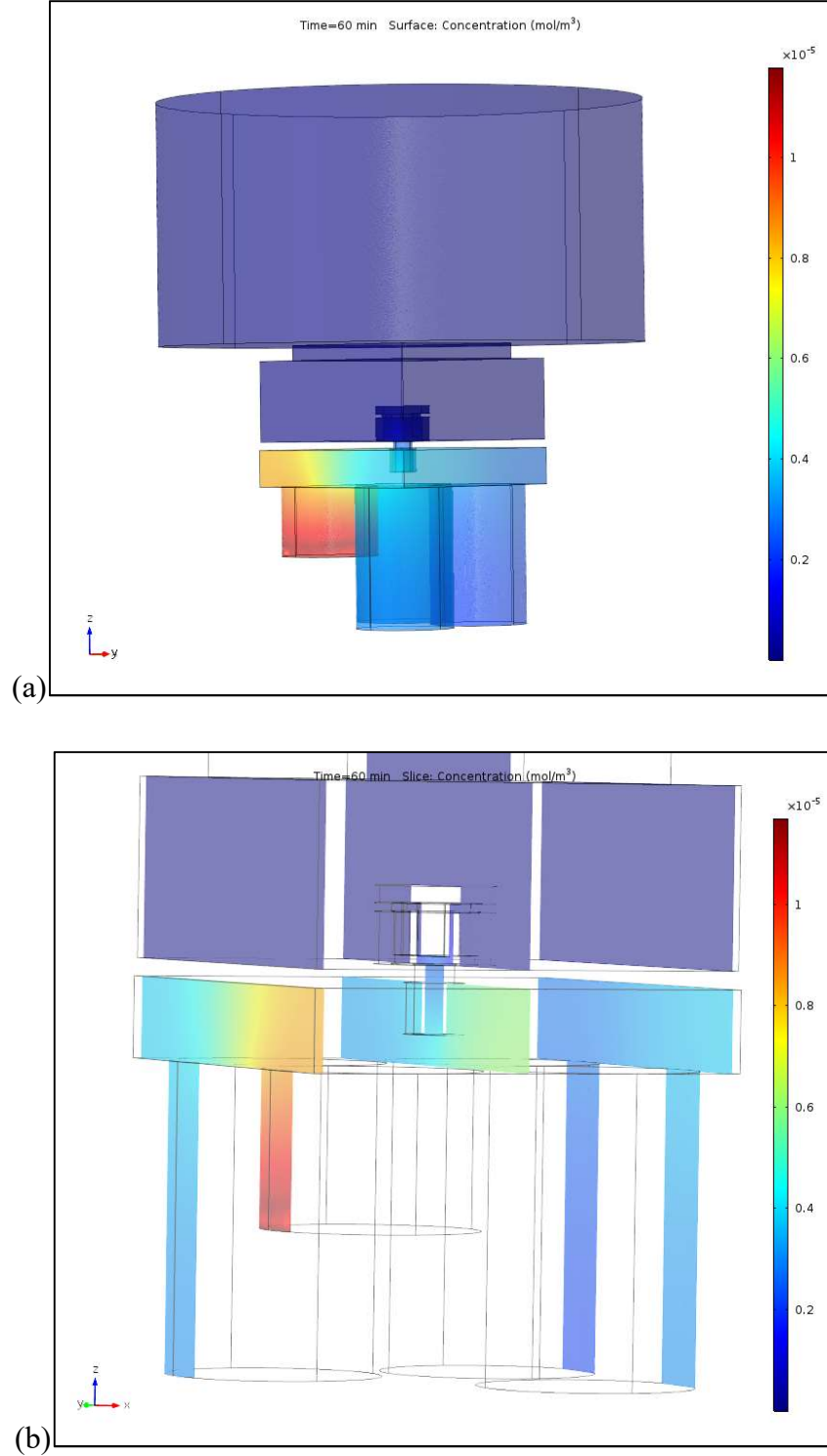
Figure 6. Space inside of the LSMODD into which vapor can diffuse; (a) Side view of analyte concentration field within full computational domain at 1 hour. (b) View of sliced surfaces of concentration field within full computational domain at 1 hour.

A closer look at the concentration in the neck is shown in Figure 7. Figure 7a displays the location within the neck for which the concentration was plotted in Figure 7b. This surface was a cross

section of the lower neck area just below the (capped) upper neck. The concentration became symmetric at the top of the lower neck area, as horizontal diffusion within the neck significantly reduced any horizontal concentration gradients before the vapor diffused through the entire vertical length of the neck. This belief is supported by noting that the diameter of the neck (0.625") is appreciably smaller than its length (1.0").

Figure 7. (a) Cross-sectional surface of the lower portion of the neck and (b) corresponding analyte concentration at 1 hour.
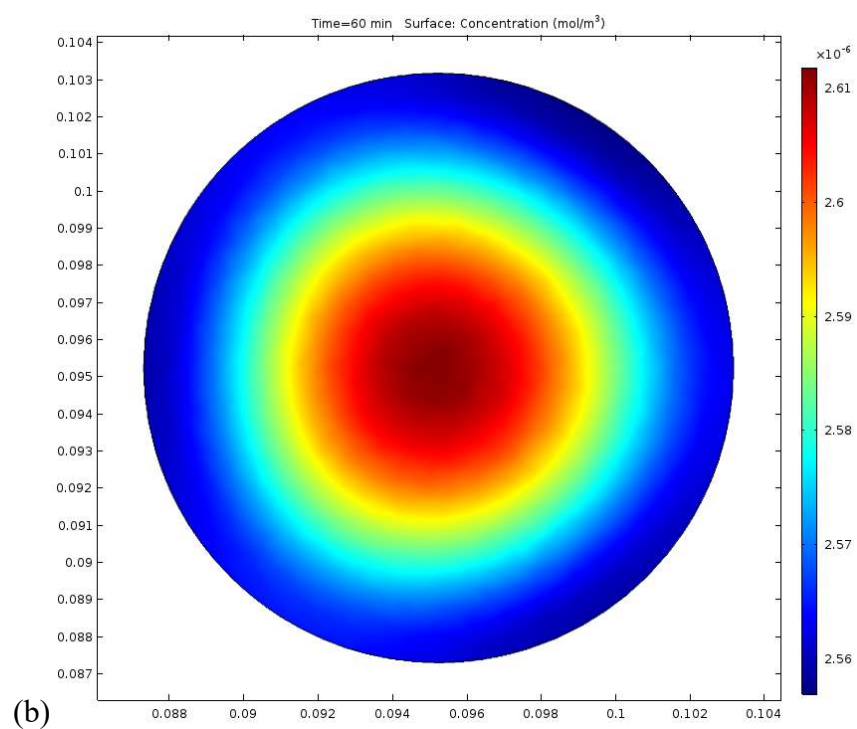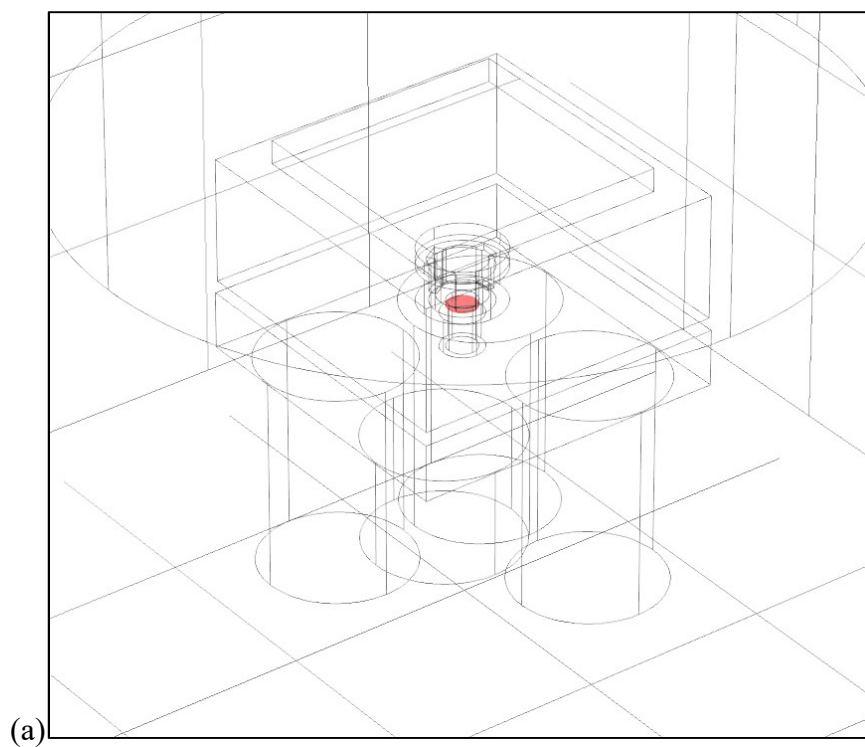
As the analyte vapor diffused upward and out of the neck, it encountered a wedged plug (Figure 5) that disturbed the symmetry of the concentration field. The vapor diffused through the openings between the plug, its wedges, and the neck. The effect of the wedged plug on the concentration field is shown in Figure 8. The surface on which the concentration was plotted as shown in Figure 8a and the corresponding concentration was plotted in Figure 8b. In Figure 8a, the horizontal surface for the plot slices through the gap between the top surface of the upper neck and the bottom surface of the cylindrical upper plug. As one might expect, the wedges were obstacles along the diffusion path of the analyte; thus, there was a reduction in the concentration immediately outside the wedges, as shown in Figure 8b. The wedges caused concentration gradients to develop in the immediate surroundings of the plug. Diffusion occurring beyond the plug reduced these gradients as the analyte vapor continued to diffuse upward through the device. It is reasonable to expect that the asymmetry caused by the wedges would not persist to the outlet, as the length scale of any gradient caused by the wedges is likely similar to the width of the wedges (0.375”), which is appreciably smaller than the vertical length that the analyte vapor must diffuse to reach the outlet (1.5”).

(a)

(b)
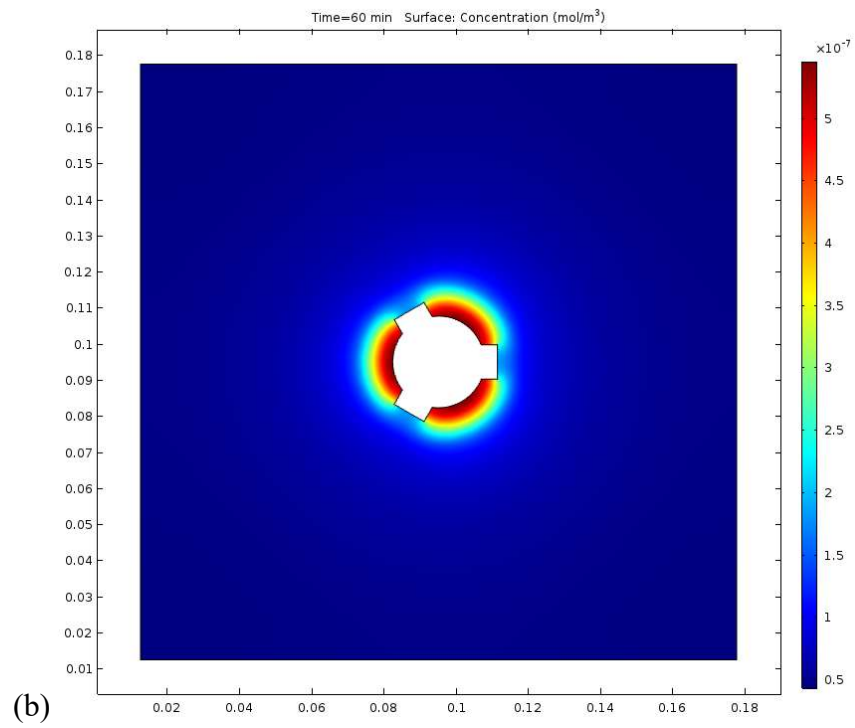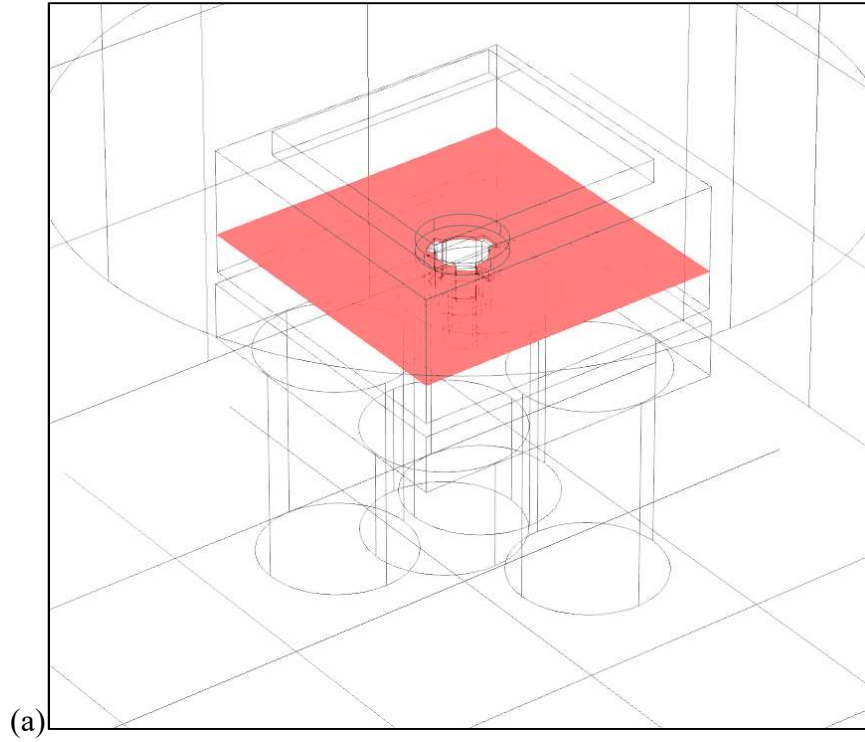
Figure 8. (a) Cross-sectional surface through capped outlet and (b) corresponding analyte concentration at 1 hour.

The symmetry of the concentration at the surface of the LS-MODD outlet is important as this location represents where the canine samples the analyte vapor. The concentration profile at this outlet is given in Figure 9. The surface itself is shown in Figure 9a, and the corresponding concentration is plotted in Figure 9b. The analyte vapor concentration was highly symmetric at the outlet.

(a)

(b)
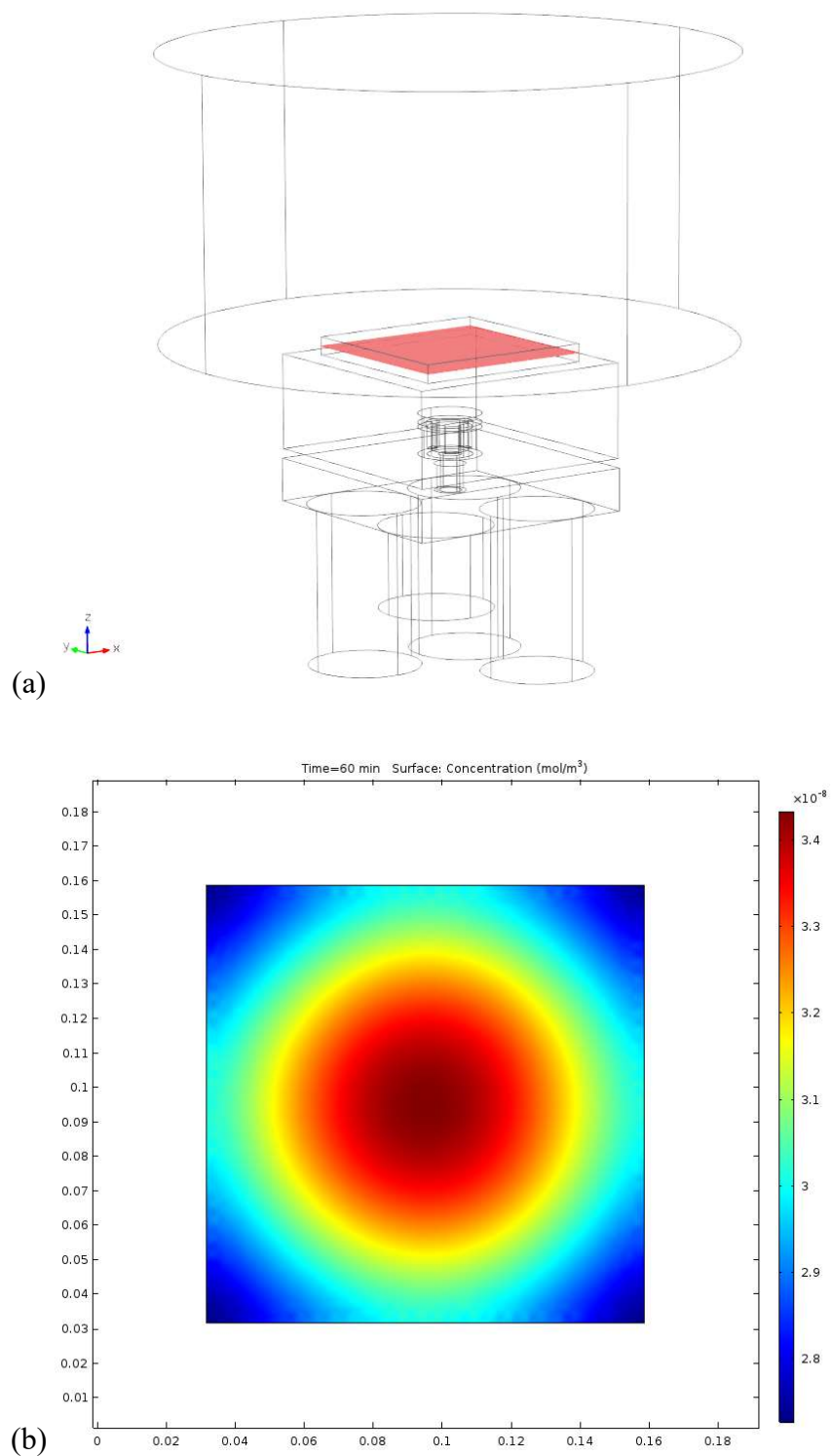
Figure 9. (a) Cross-sectional surface through olfaction orifice and (b) corresponding analyte concentration at 1 hour.

Vapor concentration predictions between the LS-MODD and the original were not compared. The two devices likely differ in the concentrations at the outlet; however, the variation in restrictor

plug size can be used to suppress the diffusion of analyte vapors (in either device) if the concentration is greater than desired. Both devices, however, show approximate radial symmetry in the vapor concentration across the outlet.

ANALYTICAL EXPERIMENTS

Symmetry of vapor distribution

As mentioned previously, one factor that was considered when evaluating the MODD was the symmetry of the vapor output, i.e. if a single vapor source is placed in one corner of the MODD, the vapor output should be evenly distributed around the restrictor plug at the outlet.

Symmetry in the original MODD design was tested by both computational modeling and laboratory experiments, and, both evaluations concluded that the vapor evenly distributes concentrically around the restrictor plug, as depicted in Figure 2. The modeling of the LS-MODD, discussed above, also predicted a symmetrical vapor output.

For corroboration of the current model, laboratory analyses of the LS-MODD evaluated the vapor output from a single source within the device. A single 16-oz glass jar containing approximately 10 mL of methyl salicylate (Sigma-Aldrich) was placed in the lower chamber of the device. The LS-MODD was then closed for equilibration times of one and four hours. Following equilibration, the methyl salicylate vapor at the LS-MODD outlet was measured in two locations: one in line with the jar and one above the opposite location (Figure 10). It was hypothesized that if the plume were perfectly symmetric then the amount of methyl salicylate on each fiber would be indistinguishable at each location.

Figure 10. Diagram of experimental set-up with a single odor source in the lower portion of the LS-MODD (left) and two SPME fibers (one above from the odor and one across) at the device outlet (right).

The headspace at the LS-MODD outlet was extracted by solid phase microextraction (SPME) and analyzed by gas chromatography with mass spectrometry (GC/MS). A polydimethylsiloxane / divinylbenzene / carboxen (PDMS/DVB/CAR) (Sigma-Aldrich) absorbent fiber polymer was used for the extractions. The SPME fiber was positioned approximately 2 cm above the top of the outlet. Following extraction, the fibers were exposed to an internal standard of 20 ppm methyl benzoate (Sigma-Aldrich) in water, in a 4 mL glass headspace vial (Restek, Inc.), for 30 seconds. The analyte and the internal standard were then thermally desorbed from the fiber in the heated inlet of the Agilent 6890 GC (Agilent Technologies) at 260 ˚C. The temperature program of the GC oven began at 40 ˚C for 1 min, then was increased to to 240 ˚C at 30 ˚C/min, and was held for a final 1 min. A 15 m x 0.32 mm i.d. Rtx-Volatiles column (Restek, Inc.) was used with a column flow of 2 mL/min and an inlet split ratio of 10:1. Analytes in the chromatogram were identified by a mass selective detector (MSD) (Model 5975, Agilent Technologies) with a mass scan range of *m/z* 30-220.

Figure 11 gives the amount of methyl salicylate detected above or across from the sample vial. This amount was normalized to an internal standard to reduce run-to-run variations in the analytical method; however, the errors were greater than desirable. The variations were due to inherent inconsistencies in room airflow due to random fluctuations during the open-atmosphere, static sampling. From Figure 11, there appeared to be some disparity between the amounts of methyl salicylate collected in either position. Using an analysis of variance (ANOVA) statistical test, it was determined that there was not a significant difference between the amounts of vapor detected at either positon indicating sufficient mixing across the LS-MODD outlet. Any difference between the two positions is minimal, thus, in actual training scenarios, where significant airflow across the outlet is highly possible and uncontrollable; these differences are unlikely to affect canine detection. Results of the vapor distribution model and the analytical testing both suggest that the upscaling of the design of the original MODD to that of the LS-MODD did not, qualitatively, affect the vapor distribution at the outlet.
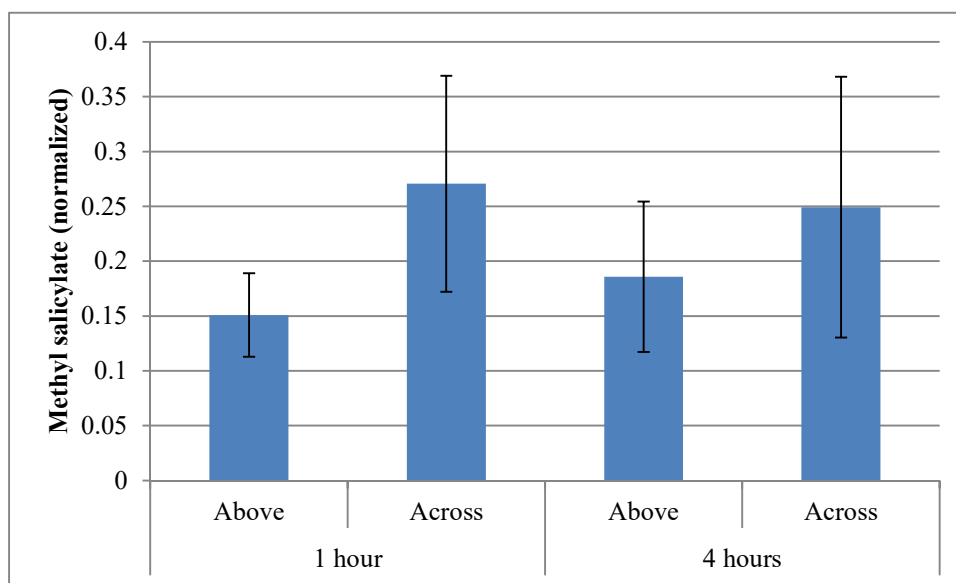
Figure 11. Normalized amount of methyl salicylate vapor detected above or across from vial after 1 and 4 hours in the MODD.

Mixing of component vapor in LS-MODD

Another factor considered in the laboratory evaluations was the mixing of two component vapors placed separately in the LS-MODD. Again, a single jar of methyl salicylate was enclosed in the lower chamber of the device along with a second jar of limonene (Sigma-Aldrich) in a separate location (Figure 12, right). For comparison, a single jar containing both methyl salicylate and

limonene together was placed in the LS-MODD. Using the method described above, the amount of methyl salicylate and limonene vapor at the LS-MODD outlet was measured by SPME with GC/MS. In both scenarios, the SPME fiber was placed approximately 2 cm above the restrictor plug, in the center of the device (Figure 12, left). The ratios of limonene to methyl salicylate determined from both set ups were compared.

Figure 12. Diagram of experimental set-up with two odor sources in the lower portion of the LS-MODD (left) and a single SPME fibers centered at the device outlet (right).

Figure 13 indicates minor differences between the mixed and separated components following equilibration times of both one and four hours. Again, there was no statistical difference between the averaged values, and thus these differences are unlikely to affect olfaction at the LS-MODD. In a similar experiment of the original design of the MODD, the ratio of vapor concentrations at the outlet were also statistically similar comparing mixed and unmixed components [14]. For this mixture, the design of the device does not seem to affect the delivery of the proper vapor mixture.
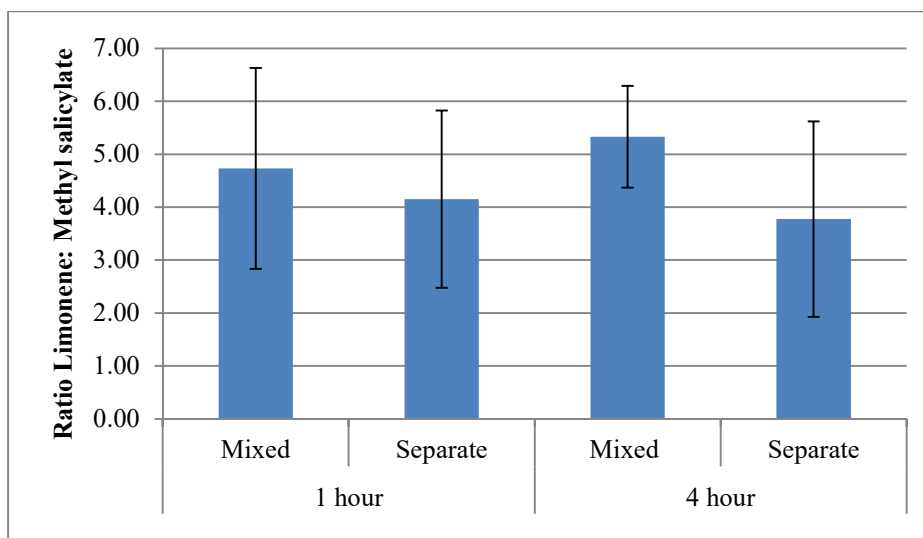
Figure 13. Comparing ratios of limonene to methyl salicylate detected from above the LS-MODD when analytes were mixed or separated in the LS-MODD.

Proof-of-concept

Homemade explosive (HME) materials, ammonium nitrate (AN) and diesel fuel (FO), were used in a final, proof-of-concept, experiment designed to demonstrate the release of an accurate representation of HME vapor at the outlet of the LS-MODD. Three of the same glass jars containing each approximately 10 g of AN (Sigma-Aldrich) and a single jar containing approximately 10 mL of diesel fuel (locally sourced) were enclosed in the device, which was then allowed to equilibrate for five hours. Volatiles in the headspace at the LS-MODD outlet were extracted overnight (approx. 18 hours) by SPME. The SPME fiber was placed approximately 2 cm above the center of the restrictor plug. The same GC/MS method was used as previously described.

The headspace of the LS-MODD containing separated HME components was compared to that of an actual explosive mixture (*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*). Due to mass restrictions when handling actual HMEs in the laboratory, 2.25 g of ammonium nitrate and 0.75 g of diesel fuel were used. The components were mixed in a 28.71 mL, static-dissipative vial (ESD Plastic Containers) 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 of which were disposed in the proper locations.

The overlaid chromatograms below compare the resulting vapor profiles of AN and FO as separate components in the LS-MODD (purple trace) to that of the ANFO mixture (blue trace) (Figure 14). The main vaporous component from AN is ammonia, derived from the dissociation of ammonium and nitrate in ambient humidity [15]. Ammonia cannot be detected using traditional GC/MS methods. Previously, ammonia was detected at the outlet of the original MODD design using an alternative analysis method, in addition to fuel volatiles analyzed by SPME-GC/MS [11]. This testing, however, was out of scope of this research. Characteristic volatile compounds from the fuel oil are labeled in the graph, and were detected at similar ratios in both the LS-MODD and the HME mixture. The presence of the same volatile species at similar ratios from both the HME components in the LS-MODD and actual HME material again suggests an accurate representation of the HME vapor profile from the LS-MODD outlet.
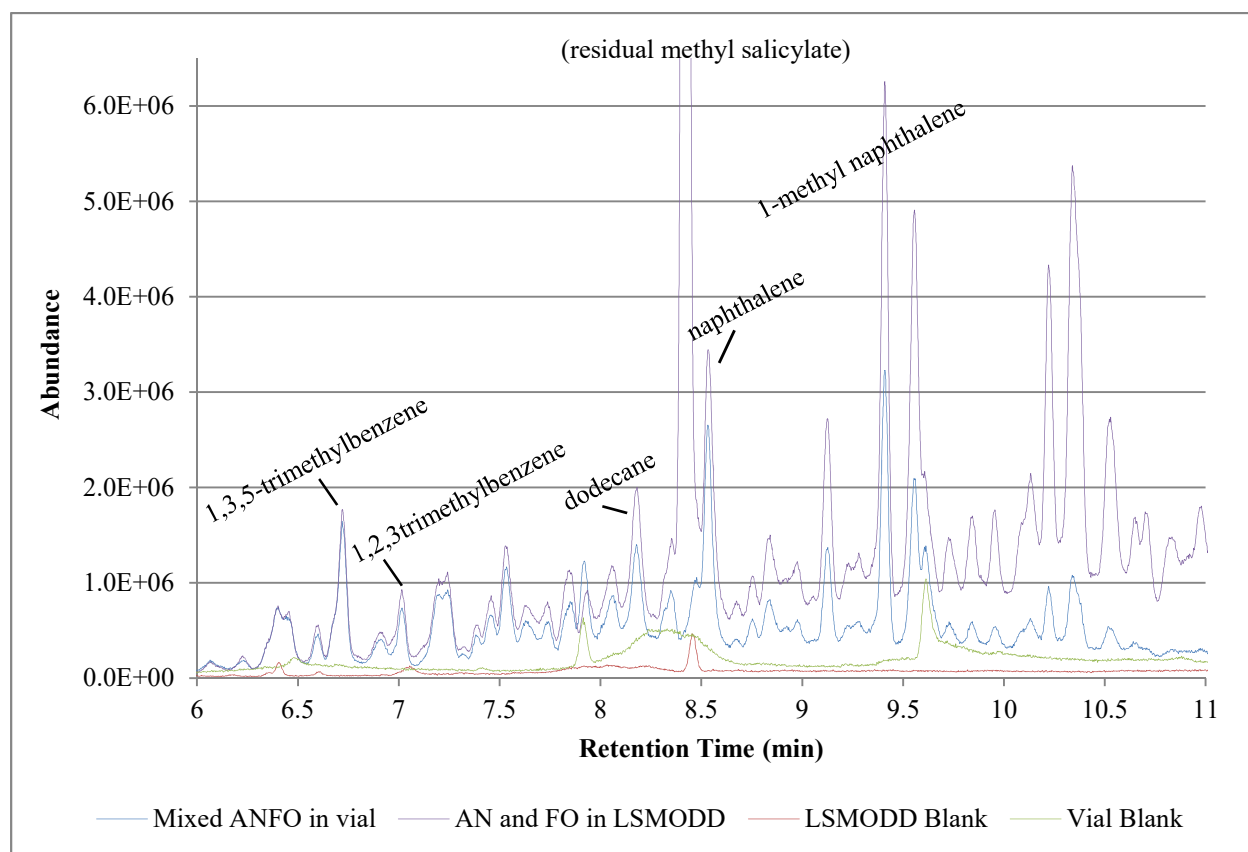

Figure 14. Overlaid chromatograms of ANFO volatiles from the headspace of mixed ANFO in a vial (blue), AN and FO separately at the outlet of the LS-MODD (purple), and blanks of both the LS-MODD (red) and the vial (green).

FIELD EVALUATION WITH CANINES

Following successful laboratory evaluations, four additional LS-MODD prototypes were fabricated in order to conduct field evaluations. Explosive materials or distractor odors were placed separately in the five LS-MODDs labeled M1-M5, as listed in Table 2. M1 and M2 contained target materials (TNT or unmixed AN and FO) and M3-M5 contained distractor odors (nitrile gloves, peanut butter, or dog treats). The MODDs were covered with a lid for a minimum of 3 hours prior to testing.

Table 2. The contents of each LS-MODD used in canine trials.

MODD ID	Components
M1	TNT
M2	Ammonium nitrate/Fuel Oil
M3	Nitrile Gloves
M4	Peanut Butter
M5	Dog Treats

Testing was conducted in the form of "line-ups" of three MODDs each as indicated in Table 3. Testing was carried out with two certified explosives detection canines. These canines were previously shown to be proficient at detecting both target odors. Testing was carried out outdoors at the canine training facility. The experiment was double-blind with both the handler and the assessor unaware of what each MODD contained.

Table 3. LS-MODD lineup for canine trials.

Canine	Run Number	MODD lineup		
1	1	M4	M3	M1
	2	M3	M4	M5
	3	M2	M5	M3
2	1	M4	M1	M5
	2	M2	M4	M3
	3	M4	M5	M3

Both canines accurately alerted to the TNT as well as the AN and FO in the LS-MODD on the first pass through the line-ups. There were no false alerts to distractor material by either canine. Results indicate that the component vapors emitted by the LS-MODD were sufficiently recognizable by the canines. It should also be noted that these canines do not alert to FO alone, thus it can be assumed that ammonia vapor from the AN was present in addition to the FO vapor, though ammonia was not measured in previous laboratory experiments.

CONCLUSIONS

A larger-scale version of the MODD, the LS-MODD, was designed, fabricated, and evaluated. Evaluation methods included computational modeling, headspace analysis, and field-testing with trained canines. The computational modeling of vapor output at the LS-MODD outlet depicted a vapor distribution from separated HME components that distribute symmetrically around the restrictor plug in the outlet. This, thus, implies that when multiple components are placed in the LS-MODD, their vapors will be mixed and the canine detectors will be presented with the vapors as a mixture and not individual components. In addition, the canine will be able to sample the same vapor mixture at any direction from which the device is approached. Headspace measurements taken at the outlet agreed with the predicted model. Further analytical assessments, in combination with canine field-testing, showed that the LS-MODD design accurately portrayed the vapor profile of mixed materials from separated components. The data validated that the upscaling of the original MODD to the LS-MODD did not alter its functionality.

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