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Criminalistics

Characterization of an odor permeable membrane device for the storage of explosives and use as canine training aids

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Abstract

The storage and use of explosives is regulated at the state and federal level, with a particular focus on physical security and rigorous accounting of the explosive inventory. For those working with explosives for the training and testing of explosive-detecting canines, cross-contamination is an important concern. Hence, explosives intended for use with canine teams must be placed into secondary storage containers that are new, clean, and airtight. A variety of containers meet these requirements and include screw-top glass jars (e.g., mason jars). However, an additional need from the explosive-detecting canine community is secondary containers that can also be used as training aids whereby the volatiles emitted by explosives are emitted in a predictable and stable manner. Currently, a generally accepted method for the storage of explosives and controlled emission of explosive vapor for canine detection does not exist. Ideally, such containers should allow odor to escape from the training aid but block external contaminates such as particulates or other volatiles. One method in use places the explosive inside a permeable cotton bag when in use for training and then stores the cotton bag inside an impermeable nylon bag for long-term storage. This paper describes the testing of an odor permeable membrane device (OPMD) as a new way to store and deploy training aids. We measured the evaporation rate and flux of various liquid explosives and volatile compounds that have been identified in the headspace of actual explosives. OPMDs were used in addition to traditional storage containers to monitor the contamination and degradation of 14 explosives used as canine training aids. Explosives were stored individually using traditional storage bags or inside an OPMD at two locations, one of which actively used the training aids. Samples from each storage type at both locations were collected at 0, 3, 6, and 9 months and analyzed using Fourier Transform Infrared (FTIR) Spectroscopy and Gas Chromatography–Mass Spectrometry (GC–MS) with Solid-Phase Microextraction (SPME). FTIR analyses showed no signs of degradation. GC–MS identified cross-contamination from ethylene glycol dinitrate (EGDN) and/or 2,3-dimethyl-2,3-dinitrobutane (DMNB) across almost all samples regardless of storage condition. The contamination was found to

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be higher among training aids that were stored in traditional ways and that were in active use by canine teams.

KEYWORDS
explosive contamination, explosive training aids, explosive-detecting canines, explosives, Fourier transform infrared spectroscopy, gas chromatography–mass spectrometry (GC–MS)

Highlights

- Evaluated odor permeable membrane devices (OPMD) for the storage of explosives.
- Characterized OPMD in terms of the evaporation rate and flux of explosives in the vapor phase.
- OPMDs protect against cross-contamination under realistic conditions such as canine trainings.
- Explosives intended for canine training have significant amounts of contamination upon delivery.

1 | INTRODUCTION

Despite advances in chemical instrumentation, properly trained canines remain one of the most sensitive, portable, and real-time detectors of explosives that are available. In fact, explosive-detecting canines (EDCs) can play a crucial role in the first stages of an explosive investigation, as shown in Figure 1 below:

EDCs excel at locating potential evidence as well as providing a presumptive test for chemical explosives (see Figure 1). This ultimately results in the submission of items to a forensic laboratory where the explosives (intact or as postblast debris) can be identified and confirmed. The use of canines to detect explosives via characteristic volatile compounds also presents several practical advantages. This form of detection is inherently noninvasive and very low levels of explosive can be detected. The volatile species emitted by explosive materials can also be tracked to the source location.

However, the effectiveness of EDCs relies strongly on their successful imprinting on the scent of actual explosives as well as rigorous training under various detection scenarios. The explosive materials used for training should exhibit minimal contamination and degradation to ensure that canines are imprinted on and trained with authentic odors. Explosives intended for use with canine teams must be placed into secondary storage containers that are new, clean, and airtight. A variety of potential containers meet these requirements and include screw-top glass jars (e.g., mason jars). When explosives are placed in containers that are designed to allow vapor to escape into the surroundings and used as a part of canine training and testing, they are considered “training aids,” which are defined as “target odor/scent sources used for training” [1].

The physical form of training aids has differed widely over the years, although all forms feature some way for volatiles from the explosive to escape its container to be detected by the canine. For

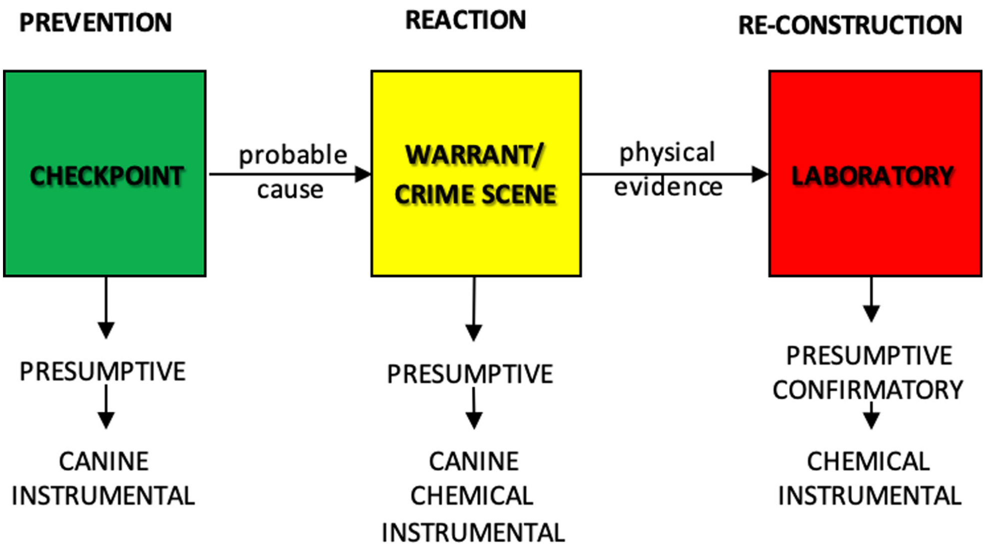

FIGURE 1 Schematic of the three stages of an explosive investigation (prevention, reaction, and reconstruction), the locations where these stages occur (checkpoint, search warrant/crime scene, or laboratory) as well as the presumptive or confirmatory testing that can be accomplished in that stage.

example, the Bureau of Alcohol, Tobacco, Firearms, and Explosives developed a simple apparatus composed of nested paint cans for canine testing (see Figure 2). In this apparatus, a small (2 ounce) sniffer tin with a perforated lid would house the explosive training aid. Then, the sniffer tin was placed inside a quart-sized paint can, which was then placed in a gallon-sized paint can [2].

Other government agencies such as the Federal Aviation Administration (FAA) have used scent boxes for testing and training with an analogous design whereby the aid is concealed inside a box with an opening so that canines could sample the air inside [3].

Further developments in the same time frame as the ATF and FAA containers included explosive vapor generators that were based upon a tube packed with silica particles that had been coated in pure explosive. A carrier gas and applied heat was used to modulate the amount of explosive vapor that was generated [4–6]. In general, these generators were designed for testing and calibration of instruments rather than K9s. A review article published in 2012 describes the state of the art (at that time) for both continuous or pulsed vapor generators [7].

Based on their work in identifying the volatile compounds that are emitted from explosives, Furton et al. introduced COMPS (Controlled Odor Mimic Permeation System) [8–11]. This system was based on diffusion/permeation of volatiles through heat-sealed low-density polyethylene bags. More recently, MacCrehan et al. have introduced a method to monitor the evolution of odors in real time and developed a training aid based on poly(dimethyl silicone) (PDMS) that has been impregnated with explosive vapor [12–16]. A recent (2020) and excellent review of canine training aids has been published by Simon et al. [17]

Currently, there are no generally accepted methods for the storage of canine training aids that allow for convenience but also minimize possible cross-contamination between the different explosives. The ANSI/ASB Standard 092 for the training of explosive-detecting canines recommends training aids be stored individually in containers that minimize odor transport between explosives [1]. The UK government has also published guidelines to safeguard against contamination [18]. The research described in this paper focuses on the use of an odor permeable membrane device (OPMD) as a new way to use and store explosive training aids to minimize cross-contamination and to train canines for explosive detection via odor delivery.

2 | MATERIALS AND METHODS

2.1 | Chemicals

The materials studied in this paper were selected as they are either known liquid explosives, odor compounds produced by explosive formulations, or standard compounds that can be used to calculate relative evaporation rates (Table 1).

Nitropropane was purchased from Tokyo Chemical Industry (Portland, OR). Nitroethane and 2-ethyl-1-hexanol were purchased from Sigma–Aldrich. R-limonene was purchased from Alfa Aesar. Toluene, nitromethane, chloroform, and 1,4-dinitrobenzene (DNB) were purchased from Fisher Scientific Company. All chemicals had a purity of at least 99%.

2.2 | Acquisition and storage of explosives

Explosives were acquired using a Bureau of Alcohol, Tobacco, Firearms, and Explosives (ATF) User of explosives license issued to the corresponding author. The explosives A5, safety fuse, C-4, composition B, cast booster, 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX), 2,4,6-trinitrotololuene (TNT), pentaerythritol tetranitrate (PETN) sheet explosive, PETN detonating cord, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) detonating cord, black powder, single base smokeless powder, and dynamite were purchased from Omni Explosives in two separate batches. Urea nitrate was purchased from TCI Chemicals. It was noted that the age of explosives varied widely, as shown in Table 2. The potential impact of sample age on inherent contamination will be discussed further below.

The explosives were broken up into four identical sets and stored in four Type II Explosive Magazines, with two located at the

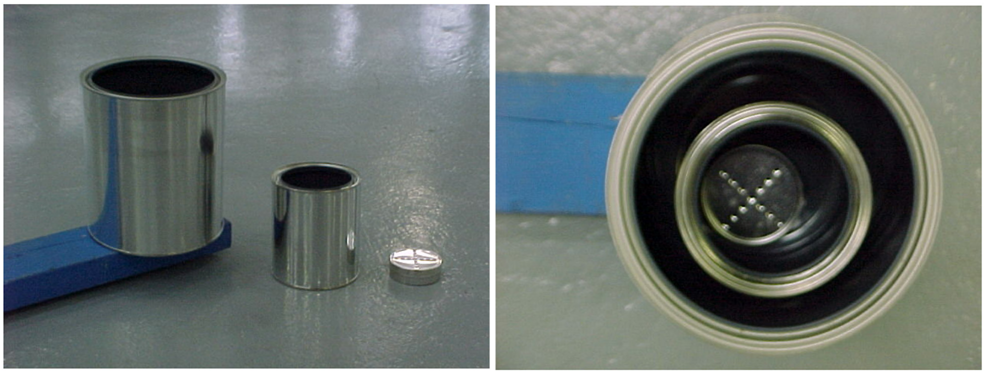

FIGURE 2 Image of an explosives training aid container established by the Bureau of Alcohol, Tobacco, Firearms, and Explosives (ATF). The same container can be used mounted on a rotating wheel as shown or each training aid can be placed independently.

TABLE 1 Enthalpy of vaporization, boiling point, molecular weight, and (when applicable) the type of explosive in which the compound is found.

Compound	Enthalpy of vaporization (kJ/mol) (from NIST webbook)	Boiling point (°C)	Molecular weight (amu)	Emitted by
Nitromethane	38 ± 3	101	61	Binary High Explosives [24]
Toluene	37 ± 3	111	92	Smokeless Powder [10]
Nitroethane	41.6 ± 0.42	114	75	Binary High Explosives [24]
n-butyl acetate	43 ± 4	126	116	Standard Compound
Nitropropane	43.39 ± 0.42	132	89	Binary High Explosives [24]
Limonene	45.9	178	136	Smokeless Powder [10]
2-ethyl-1-hexanol	68.5 ± 0.2	182	130	Composition C-4 [11, 26]

Goodpaster Laboratory at Indiana University – Purdue University Indianapolis (IUPUI) and two located at the Indianapolis Metropolitan Police Department (IMPD). These magazines were registered with both the ATF and the Indiana Department of Homeland Security. The magazines were top-loading, had an all-steel casing, a hardwood non-sparking interior, a double lock system with "¼" steel lock covers, two ATF-approved padlocks, and a red exterior finish. The two sets of explosives stored at the IMPD were incorporated into the regular training regimen of the canine unit and were freely accessible – although each use of the training aids was recorded by IMPD. The two sets of explosives stored at IUPUI remained in the magazines, except when they were removed for sampling and analysis.

The two sets of magazines used two different methods for storage. One magazine contained the explosives using traditional storage methods that reflect common practice of canine handlers as articulated by the sponsor of the project. This approach uses nested bags, where the innermost bag is permeable, allowing vapor to escape into the surroundings. A5 and C-4 were each stored in a Velcro bag. Urea nitrate, black powder, composition B, cast booster, TNT, and smokeless powder were each stored in a nylon cloth draw sting bag and a Velcro bag. Safety fuse, HMX, PETN sheet explosive, PETN detonating cord, RDX detonating cord, and dynamite were stored in a plastic zip bag. All explosives were then stored in a plastic ammo can. Each bag contained approximately 25 g of the explosive sample. Approximately 25 g of each explosive sample was also placed into OPMDs. Both lids of the OPMD were sealed and were only opened during the sampling of the IUPUI explosives and during training and sampling of the IMPD explosives.

2.3 | Odor permeable membrane devices

The OPMD, shown in Figure 3, consists of a glass jar, a membrane holder, and a gas-tight lid. The glass jar is approximately 2.5 inches tall. The membrane holder is housed between the glass jar and gas-tight lid. It contains the odor permeable membrane which is sealed by a gasket.

2.4 | Evaporation rate experiments

Although the process of evaporation is a seemingly simple process, it is actually a highly complex phenomenon that depends on several physical and chemical properties of the compound concerned. These properties include vapor pressure (as reflected in boiling point), specific heat, enthalpy of vaporization, the rate of heat supply, the surface tension of the liquid, and the rate of air movement above the liquid surface [20]. Therefore, some selected compounds have been used for the calculation of relative evaporation rates which equates to the measured evaporation rate of a substance divided by the evaporation rate of a standard material. In the U.S., n-butyl acetate is used as the standard material. These relative evaporation rates are also categorized as either rapid (>3), moderate (0.8–3), or slow (<0.8) [20].

In this study, the baseline evaporation rate of the various liquid compounds was first established under unconfined conditions. The bottom half of a metal sniffer tin was used. The sniffer tin was filled with 30 mL of the compound of interest and was placed on a Fisher Scientific accuSeries balance. The mass of the sniffer tin was recorded manually every 60 s for 10 min. The evaporation of n-butyl acetate was also measured each day to serve as a comparison sample. All evaporation rates were determined in triplicate.

To measure the evaporation rate of the compounds of interest in OPMDs, the OPMD was filled with 30 mL of sample, and the membrane holder and gas-tight lid were sealed. The gas-tight lid was then removed before the OPMD was placed on a Mettler Toledo XPR205DR high-precision analytical balance. The mass of the OPMD and its contents was recorded automatically every 60 s for 60 min. An additional set of measurements were conducted with the same liquids, but the filter membrane was removed from the OPMD. To test the effect of sample volume on evaporation rate, a series of

TABLE 2 Sample name, date received (if known), date of manufacture (if known), age, and storage location.

Sample	Received	Date of manufacture	Age (months)	Location
Urea nitrate	8/1/20	Unknown	Unknown	IUPUI/IMPD
Safety fuse	9/1/20	2/4/20	7	IUPUI
Black powder	9/1/20	9/19/17	35	IUPUI
Smokeless powder	9/1/20	Unknown	Unknown	IUPUI
Dynamite	9/1/20	4/8/20	5	IUPUI/IMPD
TNT	9/1/20	3/4/14	78	IUPUI
Composition B	9/1/20	5/18/17	39	IUPUI
A5	9/1/20	6/14/16	50	IUPUI
C-4	9/1/20	Unknown	36	IUPUI
RDX detonating cord	9/1/20	7/1/18	26	IUPUI
HMX	9/1/20	5/2/18	28	IUPUI
PETN sheet explosive	9/1/20	10/10/18	23	IUPUI
PETN detonating cord	9/1/20	10/10/19	11	IUPUI
Cast booster	9/1/20	9/8/18	23	IUPUI/IMPD
Safety fuse	2/9/21	2/4/20	12	IMPD
Black powder	2/9/21	9/19/17	40	IMPD
Smokeless powder	2/9/21	Unknown	Unknown	IMPD
TNT	2/9/21	1/27/20	11	IMPD
Composition B	2/9/21	4/26/18	33	IMPD
A5	2/9/21	6/14/16	55	IMPD
C-4	2/9/21	Unknown	Unknown	IMPD
RDX detonating cord	2/9/21	7/4/18	31	IMPD
HMX	2/9/21	5/14/20	8	IMPD
PETN sheet explosive	2/9/21	7/23/20	6	IMPD
PETN detonating cord	2/9/21	10/10/19	15	IMPD

OPMDs were filled with 100, 1000, and 10,000 microliters of nitromethane, and the evaporation rate was determined. All evaporation rates were determined in triplicate.

2.5 | Analysis of evaporation data

All evaporation data were exported into Excel and plotted to generate a graph of mass as a function of time for each compound. Linear regression was performed to obtain values used to calculate the evaporation rate of the compound. Relative evaporation rates were determined by dividing the evaporation rate of a compound by the evaporation rate of n-butyl acetate, which has a known and standardized rate of evaporation [21]. Flux (J), Equation 1, was determined by dividing the calculated evaporation rate (F) by the cross-sectional area (A) of the opening of the container (either the OPMD or the sniffer tin). The cross-sectional area of the openings of the containers was calculated using measurements of the diameter. For example, the cross-sectional area of the exposed membrane in the OPMD is 15.52 cm^2. The cross-sectional area of the opening in the sniffer tin is 25.65 cm^2.

$$J = \frac{F}{A} = \frac{F}{\pi r^2} \tag{1}$$

Flow through a membrane can be driven by a difference in pressure (ΔP) and/or in concentration (ΔC). The relationship between flux and characteristics of the solute (diffusion coefficient, D) and membrane (permeability, P and thickness, δ) is shown in Equation 2:

$$J = -P\frac{\Delta p}{\delta} = -D\frac{\Delta C}{\delta} \tag{2}$$

2.6 | Effect of membrane type

The odor permeable membrane in an OPMD consists of a membrane layer, a support layer, and pores. Five different membranes were tested in which the pore size and support layer material varied. The support layer in membranes C, E, and H was polyester. The support layer in membranes A and D was polypropylene. Filters A, C, D, E, and H have pore sizes of 0.45, 0.45, 1.0, 3.0, and 0.2 µm, respectively (see Table 3, below). For each experiment, the membrane was changed by hand with the membrane layer facing the inside of the jar and the support layer facing the gas-tight lid. The evaporation rate was measured the same way as previously stated for confined evaporation.

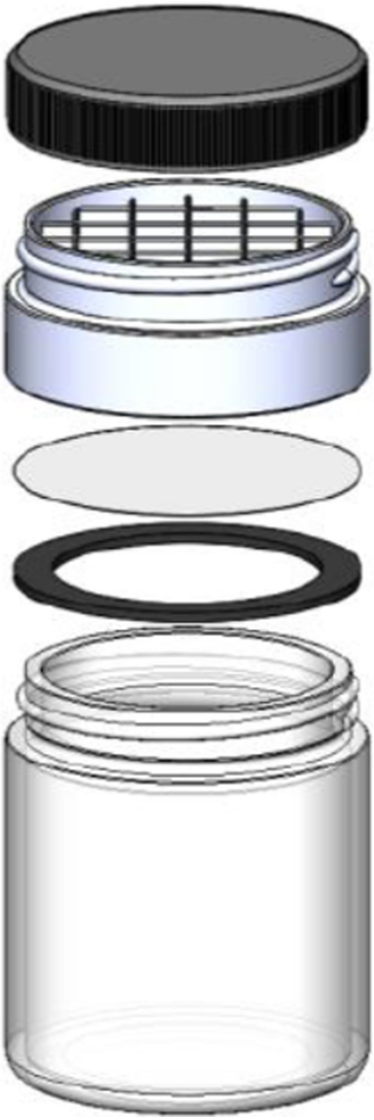

FIGURE 3 Illustration of the OPMD [19]. From top to bottom, the illustration shows the lid, membrane holder, odor permeable membrane, gasket, and glass jar.

2.7 | Membrane "memory" effects

An Agilent Cary 630 FTIR Spectrometer with an attenuated total reflectance (ATR) system was utilized to examine the surfaces of the membranes after exposure to a representative volatile compound (toluene). The filters were removed from the OPMD at various time points after exposure to toluene and placed under a diamond ATR for analysis. The FTIR spectral range is 4000 to 650 cm^{-1}. For each run, 8 background and 16 sample scans were taken. Spectra of both the membrane layer and the support layer were obtained for each filter before they were exposed to the compounds. Spectra of the post-exposure membranes were then compared to the pre-exposure membranes to see if the surface of the filter changed post-exposure.

2.8 | Monitoring contamination

An Agilent 7890B GC in negative chemical ionization mode coupled to an Agilent 5977B Mass Selective Detector with an attached PAL RTC 120 autosampler was used for all contamination experiments. The GC column was an Agilent Technologies HP-1MS Ultra Inert column with a length of 15 m, a 0.250 mm inner diameter, and a 0.25 μm film thickness. Straight inlet liners of 1.8 mm inner diameter from Restek were used for the SPME analyses and straight inlet liners of 4.0 mm inner diameter from Restek were used for the liquid injection analyses. Polydimethylsiloxane SPME arrow fibers were purchased from PAL System. Activated charcoal strips were purchased from Albrayco Technologies, INC. These strips are widely used in the analysis of fire debris given their ability to adsorb volatile compounds from the surrounding air.

Medium odor permeable membrane devices with a glass jar and plastic lid (TADD™) were purchased from SciK9 (www.scik9.com). Polypropylene mini ammo cans were purchased from MTM Case-Gard. Nylon Velcro (Cordura) cloth bags (5″ × 8″) were purchased from EliteK9. Cotton/poly blend cloth drawstring bags (5″ × 8″) were purchased from Grainger.

A sample of explosive material from each storage method at each location was collected at 0, 3, 6, and 9 months. The month 0 samples were analyzed before the preparation of the OPMD and bagged storage methods. Three samples for each type of storage method were prepared and one of these would be sampled from at each time

TABLE 3 Manufacturer's information about the support material and pore size used in odor permeable membranes A, C, D, E, and H.

Membrane	Support material	Pore size (μm)	Permeability range (ft^3/min*ft^2 at 125 Pa)	Nominal thickness (mm)	Measured thickness (mm)
A	Polypropylene	0.45	0.30–0.65	0.102–0.103	0.17 ± 0.005
C	Polyester	0.45	0.20–0.80	0.102–0.178	0.13 ± 0.01
D	Polypropylene	1.0	0.20–0.60	0.152–0.254	0.19 ± 0.01
E	Polyester	3	3.0–5.0	0.152–0.381	0.22 ± 0.01
H	Polyester	0.2	0.09–0.5	0.076–0.178	0.13 ± 0.01

Note: The average thickness of the filters (as measured in triplicate using digital calipers) is also shown.

point and analyzed via GC–MS with SPME. DNB was used as the externally sampled internal standard for all GC–MS SPME analyses and as the internal standard for the liquid injection analyses. Efforts taken to prevent cross-contamination during sampling included cleaning all tools used to sample or cut the explosives, using new gloves for each sample, and cleaning the sampling surface before and in-between each sample.

For the SPME analyses of solid explosive samples, approximately 1-g samples were analyzed in 20 mL headspace vials. The incubation temperature was 60°C and the incubation time was 2 min. The sample extraction and desorption times were 1 min. Note that the relatively short sorption times are due to the use of SPME Arrow™ fibers, which have a much higher volume of the absorbent phase as compared to conventional SPME fibers. The inlet temperature was set to 220°C and was operated with a 20:1 split ratio. The initial oven temperature was 40°C was held for 1 min, then the temperature was ramped at 20°C/min to 300°C where it was held for 1 min. The transfer line was set to 250°C. The source and the quadrupoles were kept at 150°C. A scan range of *m/z* 40–*m/z* 400 was used, with no solvent delay. Compounds were identified based on the retention time and Chemical Ionization (CI) mass spectra of previously analyzed explosive standards (e.g., EGDN, DMNB, NG, TNT).

Four activated charcoal strips were suspended in the explosive storage room and the two magazines at IUPUI, as well as in the explosive storage room and the two magazines at IMPD at the beginning of the study to monitor the air contamination. One of these strips from each location was collected at 0, 3, 6, and 9 months and analyzed by suspending the strips in chloroform with the internal standard and injecting the extracts into the GC–MS via liquid injection.

For the liquid injection analyses, 1 μL of the sample was injected into the GC–MS. A multimode inlet was used, and the initial inlet temperature was set to 40°C and was ramped at 900°C/min to 250°C and operated with a 20:1 split ratio injection. The initial oven temperature of 40°C and was held for 1 minute, then the temperature was ramped at 20°C/min to 250°C. The transfer line was set to 250°C. The source and the quadrupoles were kept at 150°C. A scan range of *m/z* 40 – *m/z* 400 was used, with a solvent delay of 1.50 min.

2.9 | Monitoring degradation

FTIR has previously been used to monitor the biodegradation of nitroaromatic compounds [22]. A Thermo Scientific Nicolet iN10 FTIR spectrometer with a germanium attenuated total reflectance (ATR) attachment was used for analyses of the explosives to screen for chemical degradation by comparing the spectra for chemical changes from each time point. A small sample (i.e., several milligrams) of the solid explosive material was placed onto a glass slide and analyzed using 128 scans with a cooled detector. The safety fuse was analyzed with medium pressure and all other samples were analyzed with standard pressure.

3 | RESULTS AND DISCUSSION

3.1 | Evaporation and flux measurements

The results from the unconfined evaporation rate experiments are shown in Figure 4A,B, below. The evaporation rates (in units of mmol/sec) are plotted as a function of boiling point, which serves as a convenient proxy for vapor pressure (which in turn depends upon the enthalpy of vaporization via the Clausius-Clapeyron Equation). The relative evaporation rates were calculated by dividing the evaporation rate of the compound by the evaporation rate of n-butyl acetate measured on the same day (both in units of mmol/s).

The fact that the evaporation rate declines with increasing boiling point is expected. The exact dependence, however, was not fully known. What is clear is that the data in Figure 4A,B fit very well to an exponential function ($R^2 = 0.98$). As discussed above, many factors play a role in evaporation. To our knowledge, there is not a single equation that, from the first principles, can predict the evaporation rate. The relative evaporation rates span several orders of magnitude and include compounds that evaporate rapidly ($R > 3$), moderately ($3 < R < 0.8$), and slowly ($r < 0.3$) according to the benchmarks which appear as horizontal lines.

The data shown in Figure 5 are the flux of several compounds from a confined container (i.e., an OPMD with a filter in place). As was seen above, the data for confined containers fit an exponential well ($R^2 = 0.94$). Note that, as per Equation 2, in systems where a concentration gradient exists across a membrane, the diffusion coefficient of the material has an impact on flux. Incorporating diffusion coefficients into the model and data presented here is made difficult as diffusion coefficients are generally not widely available in the literature (with the notable exception of TNT, PETN, and RDX [23]). The fact that the OPMDs yield a flux that is largely predictable based upon the boiling point of material is an asset, however.

3.2 | Effect of membrane type on evaporation rate

The five different membranes tested varied in support layer material, thickness, and pore size (see Table 3). Notably, values for the permeability and thickness of the membranes were available (as broad ranges) from the manufacturer. In future work, it would be advantageous to experimentally determine membrane permeability. The compounds used for these experiments were nitromethane, toluene, and limonene. The results from these experiments are shown in Figure 6.

A series of Students' t tests were performed to determine if any of the differences in flux were statistically significant (at the 95% confidence level). For all three compounds, the membranes that allowed for the largest flux of material were membranes A and H. Although membrane H possesses the smallest pores and is the thinnest membrane, its flux was statistically indistinguishable from

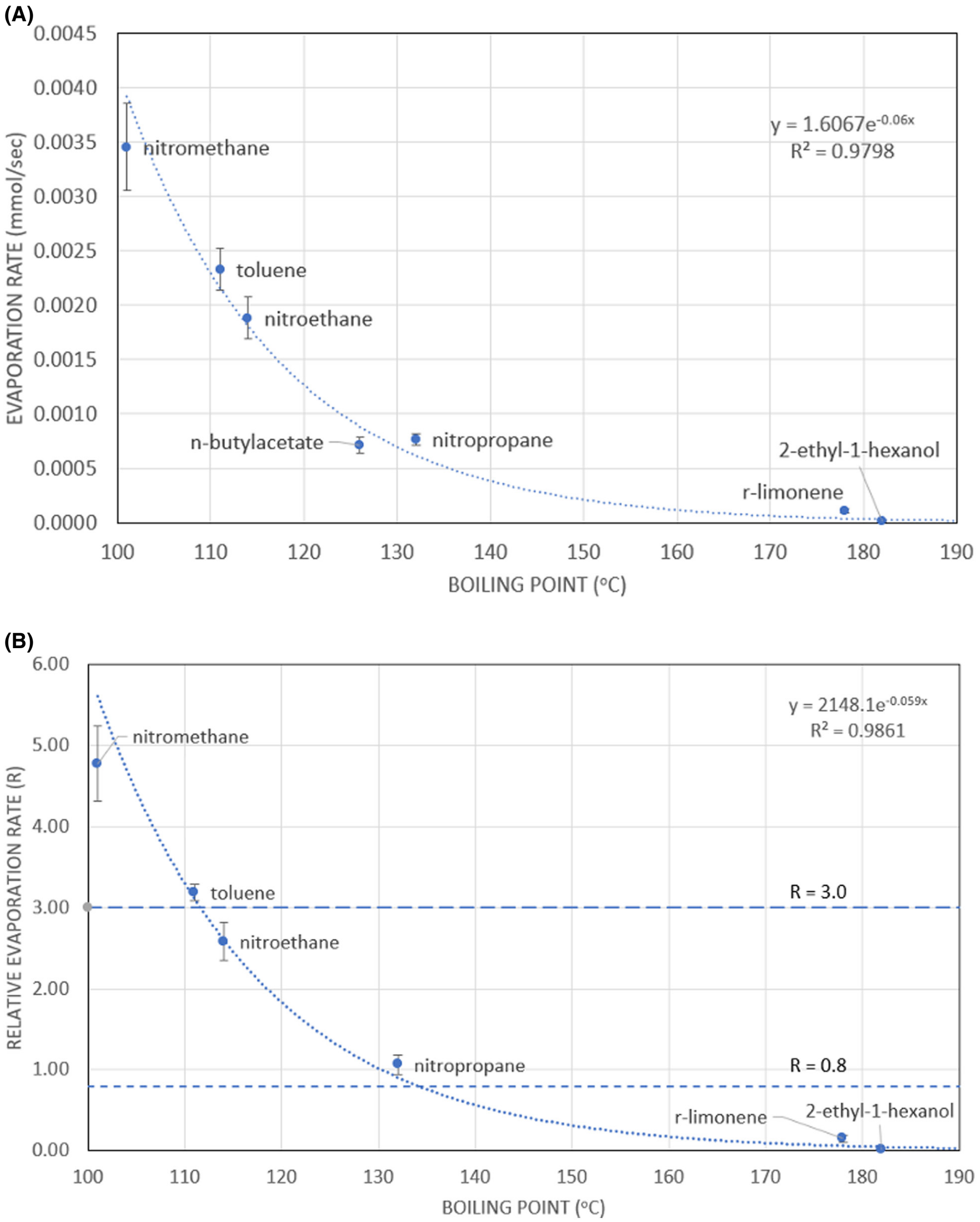

FIGURE 4 Graphs showing changes in (A) evaporation rate and (B) relative evaporation rate as a function of boiling point from unconfined sniffer tins (see Table 1 for details). The relative evaporation rates in B) include the boundaries between rapid ($R > 3.0$), moderate ($0.8 > R > 3.0$), and slow ($R < 0.8$) evaporators. The error bars represent one standard deviation of the average ($n = 3$).

filter A. The only statistically significant differences involving membranes C, D, and E are between membranes D and E for limonene and membranes C and D for toluene. This lack of statistical significance was relatively surprising because of the wide range of pore sizes and thicknesses tested. Furthermore, when the correlation between flux and membrane properties such as pore size and thickness were calculated, essentially no correlation was found between the measured flux of the odor compounds and the membrane's physical properties. Ultimately, for K9 training purposes, it is advantageous to use the membrane that allows for the largest flux of material, which means that there is an increased odor availability for the canine [24].

3.3 | Effect of sample volume

As shown in Figure 7, when the volume of nitromethane placed inside an OPMD is increased by a factor of 100, the flow of nitromethane from the container increases only moderately (from 2.2×10^{-5} g/s to 3.1×10^{-5} g/s). With a pure substance in a closed system, we have shown that the phase ratio (the ratio of headspace volume to sample volume) does not affect the concentration of vapor in the headspace [24]. This, in turn, should create the same concentration gradient across the membrane and, hence, the same flux and flow rate, as per Equation 2. The fact that there is a modest increase implies that a steady state, rather than a true equilibrium, may exist inside the

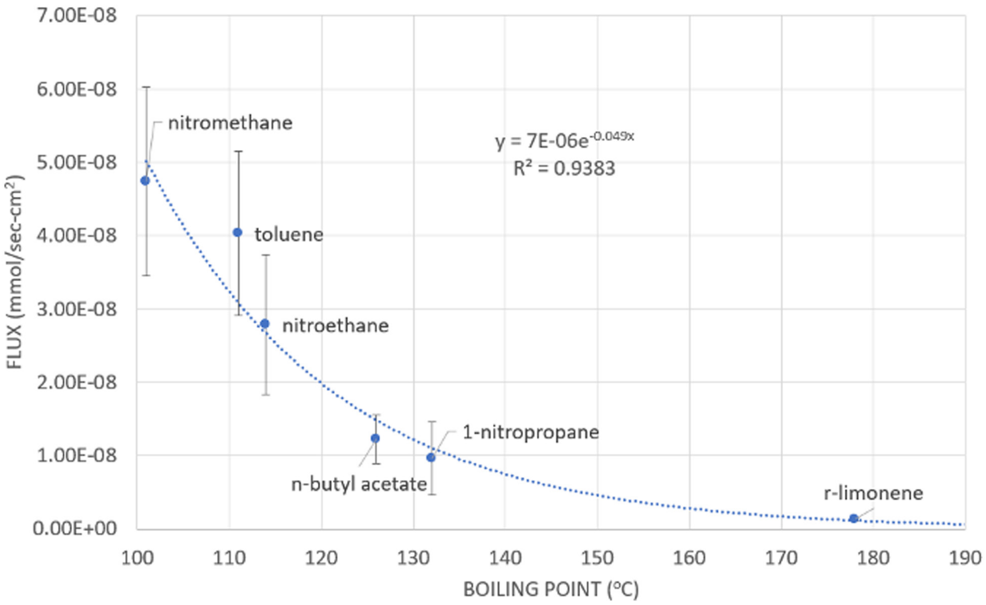

FIGURE 5 Graph showing changes in flux from OPMDs using a 0.2 μm filter as a function of boiling point. The error bars represent one standard deviation of the average ($n = 3$).

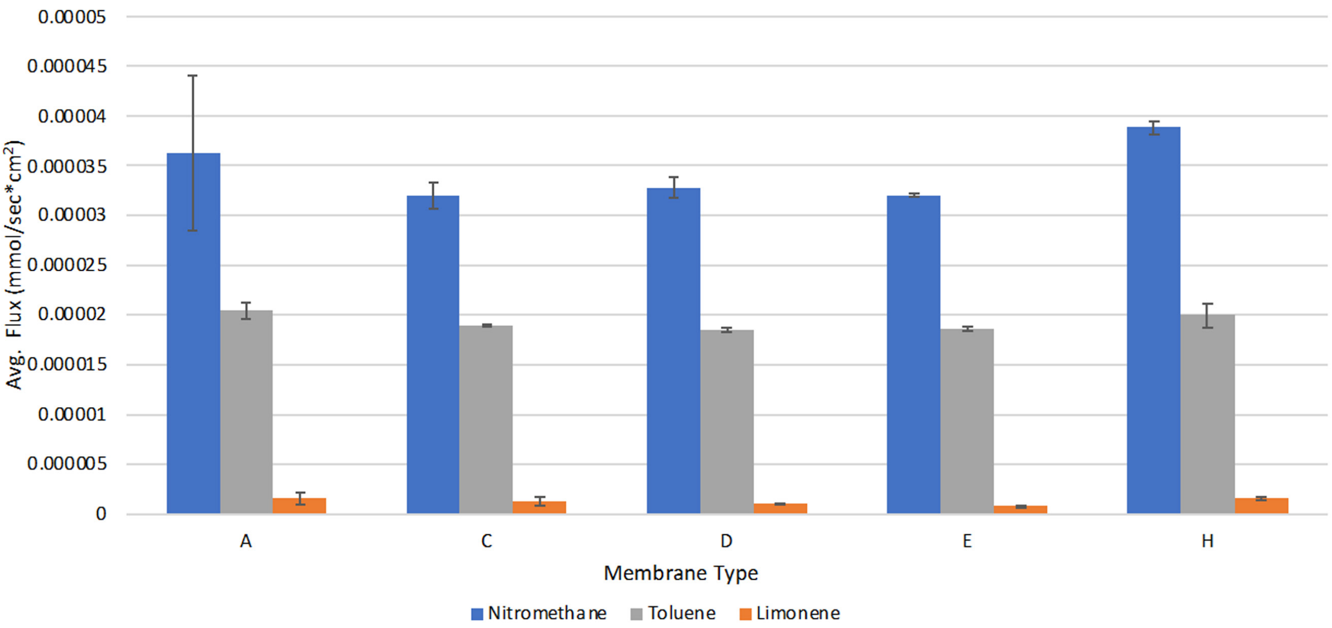

FIGURE 6 Graph illustrating changes in flux as a function of membrane type for nitromethane (left column), toluene (middle column), and limonene (right column) using filters A, C, D, E, and H. The error bars represent one standard deviation of the average, $n = 3$).

OPMDs. The consistency of the resultant flow rates (as reflected in their high precision) is promising as these devices will need to supply a steady supply of vapor for canines to detect.

3.4 | Membrane “memory effects”

FTIR spectra of each membrane's support layer and membrane layer were obtained before and after exposure to toluene to ensure that the membrane is chemically inert after exposure to the training aids. Toluene was chosen due to its relatively high evaporation rate and its specific FTIR spectrum. For example, peaks present in the spectrum at ~3000, 2800, 1600, 1500, 1100, 1050, and 650 cm^{-1} were indicative of toluene on the surface of the membrane. After the membrane was exposed to the air for 10 min, these peaks disappeared from the spectrum and the surface of the membrane is the same as it was pre-exposure. After 90 days, the membrane behaved identically.

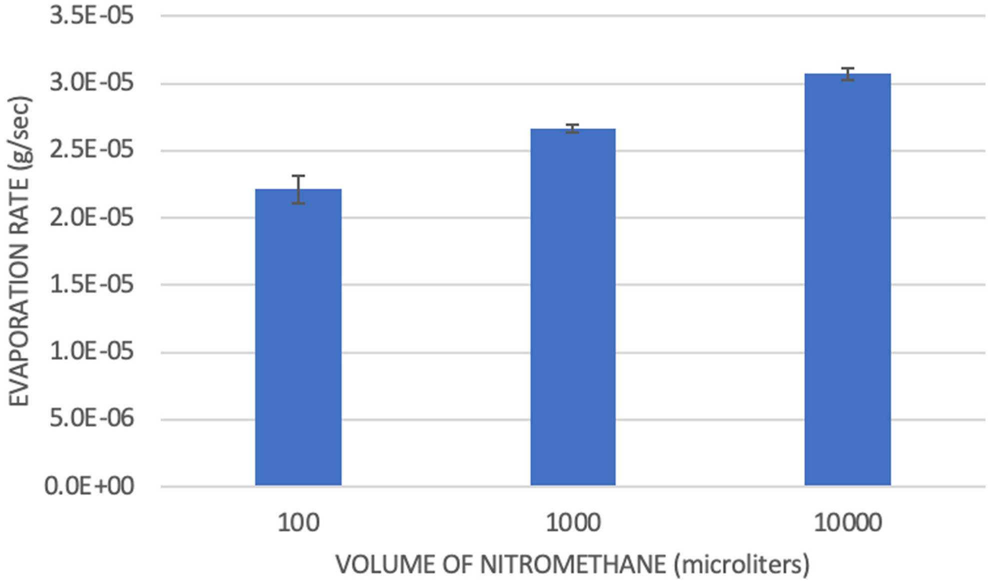

FIGURE 7 Graph showing changes in flow rate of nitromethane from OPMDs containing differing amounts of the compound. The error bars represent one standard deviation of the average, $n = 3$.

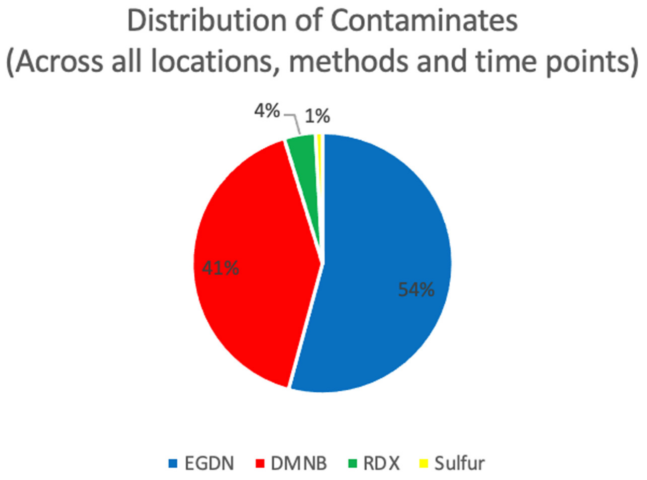

FIGURE 8 Contamination values for each location, storage method, and time point.

3.5 | Cross-contamination

Explosive samples were collected and analyzed via headspace SPME and GC–MS. The volatile compounds that were identified as contaminants over the course of the study were 2,3-dimethyl-2,3-dinitrobutane (DMNB), ethylene glycol dinitrate (EGDN), RDX, and sulfur. The distribution of contaminates for all locations and time points is shown in Figure 8. DMNB is a taggant intentionally added to explosives such as Composition C-4 and PETN Sheet Explosive [25]. EGDN is an energetic component of dynamite. Sulfur is a component of black powder (as well as safety fuse) and RDX is a component of Composition C-4 and A5. A sample was considered contaminated if it contained a volatile compound not originating from the explosive sample. For example, any sample other than dynamite that contained EGDN was considered contaminated.

The IMPD samples were utilized in canine training an average of 1.9 times each over the 9-month study. The number of times a training aid was used did not affect the overall contamination value of the sample. For example, the correlation coefficient for the number of training sessions per sample and contamination values was −0.17 indicating essentially no correlation between the two.

The relative amounts of the contaminates were determined by taking the ratio of the analyte peak to that of the internal standard. A graph of the comparison of the overall contamination levels of each storage location and method is shown in Figure 9. Month 0 had the highest levels of EGDN and DMNB contamination of all time points indicating that explosive training aids are received from the supplier contaminated. This does not invalidate the other measurements, however. It does mean that there was a systematic difference in samples removed from the original packaging of the explosives versus the smaller samples that were segregated into either bag (traditional) versus OPMDs. Future studies of the extent of contamination that exists upon receiving explosives (even those that are specifically marketed to canine teams) are planned.

The number of contaminated samples and the extent of the contamination was compared across sampling locations and methods of storage. At IUPUI, there were 20 instances of contamination for the OPMD samples and 22 for the traditional samples. For IMPD, there were 14 for OPMD and 18 for traditional. The increase in the frequency of contamination between storage methods is to be noted, but the relative severity is also important. The IMPD traditional storage samples had the highest levels of contamination as

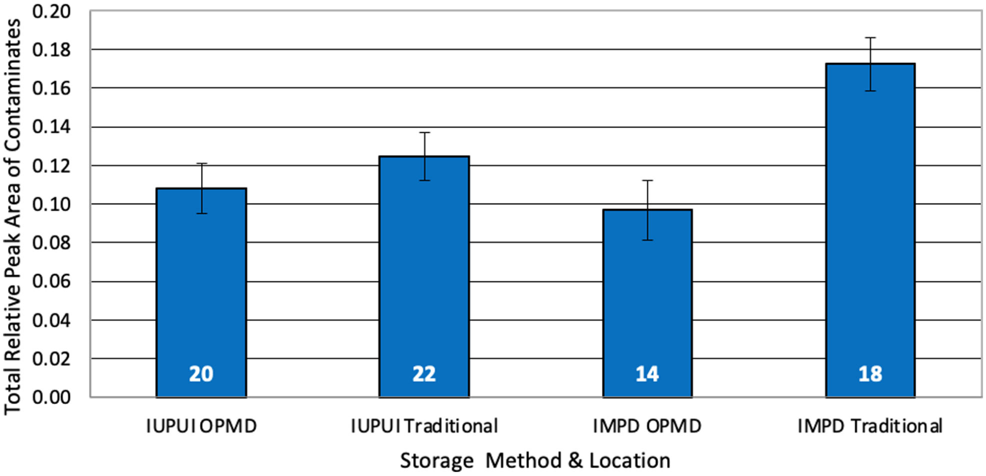

FIGURE 9 Graph of the comparison of overall contamination levels by storage location and method across all time points. Plotted are the sums of all the relative amounts of contaminates. The total number of instances of contamination (out of a maximum possible of 64) is reported at the bottom of each column.

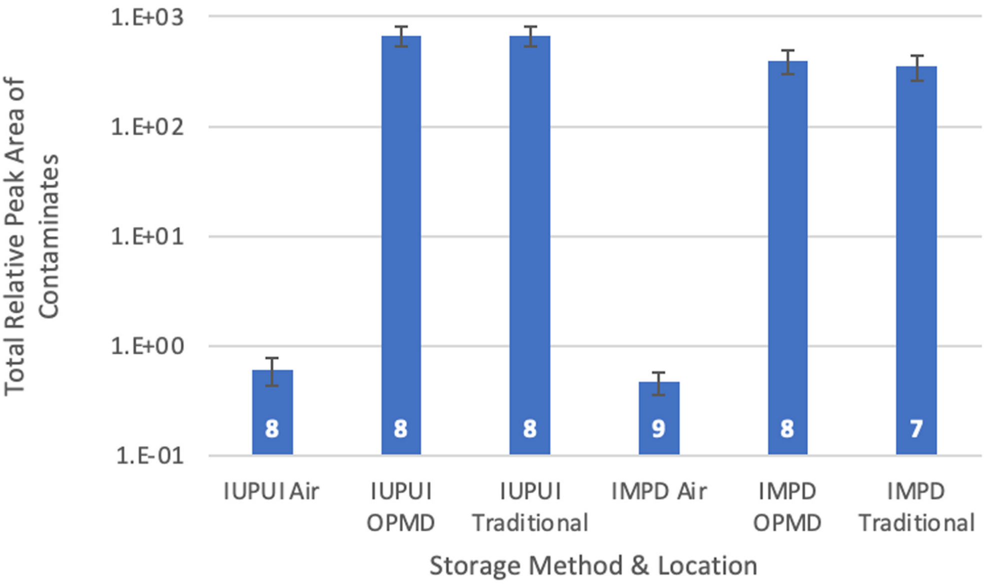

FIGURE 10 Graph of the comparison of air contamination levels in room air (IUPUI Air and IMPD Air) and inside of the explosive magazines by storage location and method (IUPUI OPMD and Traditional/IMPD OPMD and Traditional). Plotted are the sums of all the relative amounts of contaminates. The number of incidents of contamination is listed at the base of each column.

shown in Figure 9. The IMPD OPMD samples had the lowest levels of contamination of all storage methods and locations. Followed closely to this, were the IUPUI OPMD storage samples. For both IMPD and IUPUI, the OPMD storage methods had a lower level of contamination overall than the traditional storage methods.

3.6 | Air contamination

An ACS was used to sample the air at IMPD and IUPUI in the rooms and in the storage magazines. After exposure, the charcoal strips were suspended in chloroform and analyzed via GC–MS by liquid injection. Compounds were identified by their retention time and mass spectral information based on previously analyzed standards. Air sampling revealed the presence of the same types of volatile contaminants as were found on the training aids themselves. These included EGDN, DMNB, sulfur, and nitroglycerin. The IMPD room air sample had nine instances of contamination, the IMPD traditional magazine had seven instances of contamination, and all other samples had eight instances of contamination. So, the frequency with which contamination was observed was largely the same as can be seen in Figure 10. However, the severity of the contamination was much higher inside the magazines. This indicates that the explosive magazines were retaining and concentrating the volatile contaminants. The magazines housed at Indiana University Purdue University Indianapolis (IUPUI) had very similar contamination values. The IMPD magazines also had very similar contamination values but were slightly lower than the IUPUI values. This difference was small but found to be statistically significant. This may be due to how often the magazines were opened. Generally, the magazines stayed closed at the IUPUI location but were frequently opened at the IMPD location to choose training aids for use with the canines. This could result in the release of volatile compounds. Overall, there does not appear to be much difference in air contamination between the OPMD magazines and the traditional storage magazines by location and only a slight difference between the two locations.

3.7 | Monitoring chemical degradation

For most explosives analyzed via FTIR, no degradation was identified as most spectra were visually indistinguishable. Physical differences were seen in the FTIR spectrum for urea nitrate as the sample became dehydrated over time. At month 0, the urea nitrate was about 25% water. This water would gradually evaporate off evidenced by the peaks around 1600 and 3500 wavenumbers. Additionally, differences were also seen in the FTIR spectrum for the cast booster sample with the most noticeable change around 2800 wavenumbers. These differences are likely due to the heterogeneity of the sample and not from degradation or contamination. No contaminates were found by GC–MS in any of the cast booster samples. All other explosive samples analyzed showed very similar or identical spectra to their previous time points.

4 | CONCLUSIONS

Evaporation rate studies demonstrated that nitromethane, nitroethane, nitropropane, toluene, and limonene reliably and reproducibly evaporate from the OPMD. An exponential relationship between boiling point and evaporation rate was observed. It was found that the flux of the material emanating from the OPMD was several orders of magnitude less than that of the flux of the material escaping an unconfined OPMD. It was also determined that in general, the support layer material and pore size of the membrane do not result in statistically significant changes in flux. Future work includes determining a theoretical equation that dictates the exponential relationship between evaporation rate and boiling point, calculating the permeability of the membranes, and testing different known odor compounds.

In terms of contamination, the air contamination data showed that the contaminates in the air of the magazines were relatively similar between the two storage methods. The most common contaminate was the taggant DMNB followed by EGDN. The GC–MS data show cross-contamination from EGDN or DMNB or both across almost all samples regardless of storage type, however, the IMPD OPMD samples had the least amount of contamination followed by the IUPUI OPMD samples. The FTIR analyses showed no signs of degradation in any of the samples except for the loss of water in the urea nitrate samples. Based on these studies, it appears that OPMDs may help to reduce the levels of cross-contamination during the storage of explosive canine training aids. Further studies should be performed on multiple lots and ages of canine training aids to determine if the manufacturer or the age of the sample causes an increase in contamination values.

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CONFLICT OF INTEREST STATEMENT

The authors have no conflict of interest to declare.

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