Measurements of vapor capture-and-release behavior of PDMS-based canine training aids for explosive odorants

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HIGHLIGHTS

- PDMS is a useful material for the capture-and release of volatile compounds.
- SPME vapor-time measurements characterize the behavior of 2 explosives odorants.
- Time-course measurements evaluate the potential as canine training aids.
- A layered two-component training aid design provides an extended vapor-time profile.

ABSTRACT

Novel solid-phase microextraction with externally-sampled internal standard (SPME-ESIS) vapor-time measurements of two volatile compounds associated with canine detection of plastic explosives, 2-ethyl-1-hexanol and cyclohexanone, are studied to characterize polydimethylsiloxane (PDMS)-based odor capture-and-release materials for use as canine training aids. Diffusion coefficients of these 2 compounds are estimated to be in the 10^{-7} cm^2/s range in PDMS, facilitating vapor collection and subsequent release processes. The vapor release of these compounds from PDMS under continuous and simulated use as canine training aids is evaluated. The effect of mixed vapor capture and the vapor-time behavior of an aid with two layers of different composition are also studied.

1. Introduction

Canines are highly sensitive, selective, and mobile detection systems. With an estimated 5000 olfactory receptors and a purpose-specific transport [1] and olfactory detection system, dogs can detect incredibly small amounts of substance. One of the dilemmas in the initial and maintenance training of 'substance' dogs is the availability of reliable training aid materials [2,3]. In many applications of canine detection, the goal is to provide reliable canine detection of contraband substances such as explosives and drugs. However, because of the strict regulation of such substances, using 'real' materials as training aids has numerous disadvantages: they are difficult to obtain, require recording of the chain-of-custody, need safe and secure storage, require periodic replacement once the material's odor is *considered* spent, and finally require documented destruction. Thus, particularly for explosives, several approaches have been developed to provide 'pseudo', 'mimic', or 'simulant' canine training aids. Approaches to non-hazardous training aids for explosives include (but are not limited to) dilution of the real explosives with an inerting material such as silica [2,4,5] or petrolatum [2], presentation of neat non-explosive volatile components associated with explosives formulations [2], adsorption of volatile triacetone triperoxide (TATP) onto cotton balls [6] and polymer microspheres [7], multiple chamber vapor mixers [8–10] and permeation devices that substitute a less hazardous substance for the target explosive – yet release a scent considered to be associated with the target explosive [5].

Currently, there seems to be little consensus on what materials and candidate odorant(s) are required for the reliable training of the canine to detect the true target materials. One of the difficulties in designing and validating training materials to substitute for hazardous explosives is the challenge of determining the *required* odor profile for canine training to provide an 'alert' response to the target materials. A limited number of key volatile components of explosives have been identified [2,5,11–19] although it is not clear what combinations and proportions of multiple odorants [20] are required to maximize the reliability of alerts [21–23]. In canine evaluation using individual odorants associated with the plastic explosive C-4, these materials were found to be largely ineffective canine training to detect C-4 [13,21].

In general, to decipher the required odor profile for a canine olfactory response, a single analysis of an explosive's vapor components is performed by a technique such as SPME-GC MS followed by odor

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recognition testing of these components with canines [13]. A more direct assessment of the olfactory response to odorants has been based on the excision of living olfactory tissue from dogs or rats and measuring the intensity of the electrical "olfactogram" patch clamp response of neurons when exposed to selected odorants [24,25]. A particularly powerful approach to assessing the nature of the entire canine olfactory response is based on dogs trained to hold their head still for functional magnetic resonance imaging (fMRI) and determining the 3-dimensional volume of neural response (measured in voxels) and intensity (false color) when exposed to selected odorants [26]. The ideal training aid would capture and subsequently release the salient odor 'notes' [27] required to be characteristic of the target explosive in a non-explosive form. This is the primary goal we have pursued in the development of capture-and-release training aids based on the use of polydimethylsiloxane (PDMS) polymer [28–30].

To characterize target and training aid volatile components, rather than making a single 'snapshot' analytical measurement of an explosive's or candidate training aid's vapor profile, we have developed a reproducible analytical measurement of the vapors as a *function of time*. This temporal evaluation provides an analytical path to reliably evaluating when a training aid has lost its effectiveness with use or age. These vapor-time measurements are made using SPME-ESIS (solid-phase microextraction with an externally-sampled internal standard) [28–30]. The experimental set up for SPME-ESIS is pictured in Supplemental Fig. 1. In this variation of "in-fiber standardization," the SPME fiber is first fully extended (1 cm) into the analytical sample for vapor collection. After retraction into the fiber housing, the fiber is moved for a brief exposure of the end-face of the fiber tip to a vapor-saturated internal standard. The use of the end-face minimizes competition of the internal standard with the analyte(s) accumulated in the initial exposure. The measured output, the A/E ratio, is the peak area of the analyte(s) divided by the area of the internal standard. This A/E ratio is proportional to concentration, corrects for variability in the absorbtivity of the SPME fiber, and even allows the fiber to be exchanged while still providing consistent long-term measurements.

To understand the requirements for the development of training aid materials, the SPME-ESIS vapor-time measurements are used to evaluate the effectiveness of various vapor capture approaches and then study the vapor release profile as a function of time. This study focuses on measuring the behavior of prototype canine training aids based on PDMS as a capture-and-release medium using two previously-identified explosives-related odorants: 2-ethyl-1-hexanol (2-EH) and cyclohexanone (CyHO).

2. Experimental[2]

2.1. Materials

Cyclohexanone (Sigma-Aldrich, 99% ACS Reagent) and 2-ethyl-1-hexanol (Aldrich Eastman Chemical Company ≥ 99.6%) were chosen as representative volatiles associated with plastic explosives. The isotope-labeled internal standard used for 2-EH and CyHO measurements was d_{17}-2-ethyl-1-hexanol (Cambridge Isotope Labs, Inc., 98%).

For static headspace analysis, one-gallon metal paint cans were each fitted with a PTFE/Silicone septum in the center of the can lid. The cans were rinsed with pentane (J. T. Baker, Baker analyzed HPLC solvent) and baked in an oven at 180 °C for 2 h prior to use.

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[2] Certain commercial equipment, instruments, or materials are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best for the purpose.

2.2. Capture-and-release training aids

Steel cans "2 oz", 6 cm by 2 cm or "4 oz" 8 cm by 2.8 cm (Paper Mart, Orange, CA) with 6 2-mm holes in the top forming a 3.5 cm circle and 6 evenly spaced 2-mm holes in the vertical center of the side of the can were used to prepare what we term non-explosive alternative training aids (ATAs). This hole pattern was chosen for two reasons: 1) to provide at least two outlet holes in the top that are approximately in line with the laminar inspiration zone of a large dog [31,32] and 2) to allow these heavier-than-air target molecules to leak out the sides of the can to create a vapor plume with greater dispersion, potentially allowing canine detection from a longer distance. The cans were cleaned by soaking and wiping off the anticorrosion coating with ethyl acetate followed by pentane. For storage of the fabricated ATAs, they were enclosed in the "10 oz" steel can enclosure tins and the friction-fit metal lid was further sealed with a single layer of thread-seal Teflon™ tape to minimize vapor transfer.

The absorbent phase for the ATAs was space-grade encapsulant polydimethylsiloxane (PDMS, Dow Corning 93-500 Midland, MI). These 2-part materials were thoroughly mixed and cast into the receiving training aid can, typically adding 5.5 g for the 2 oz cans and 11 g for the 4 oz cans providing ≈ 2 mm depth of PDMS. Additionally, four PDMS training aids of varying thickness were prepared gravimetrically, adding 1.5 g, 7.5 g, and 10 g into the metal can housing resulting with thicknesses of 0.5 mm, 2.4 mm, and 3.2 cm, respectively. In all cases, the PDMS was polymerized for 24 h at room temperature.

After the initial polymerization, the training aids were baked at 150 °C for 2 h to remove volatile siloxanes and the ethyl benzene solvent (71 g/L) present in the polymerization catalyst (≈ 6.4 g/L in the final polymer prior to baking).

The PDMS training aid captured either single or mixed odors by weighing the target odorant in a 5 cm diameter Pyrex™ crystallizing dish, and placing it in the bottom of a 10 oz can enclosure. The training aid (lid removed) was turned upside down, held to the top of the can by a strong neodymium magnet over the odorant, and the steel enclosure was then closed, see Fig. 1. Teflon tape was wrapped around the lid to minimize odor loss. Vapor capture experiments were done at room temperature (≈ 23 °C) for a predetermined amount of time. Accumulation of the 2-EH and CyHO odorant(s) into the training aid PDMS was determined gravimetrically.

2.3. Automated SPME-ESIS GC MS vapor-time measurements

Vapor-time analyses were performed with a Gerstel GC autosampler (Model MPS2, Linthicum, MD) using the SPME autosampling capability. For the accumulated vapor determination, the fiber was inserted into the heated inlet of a capillary GC (Agilent Technologies 6890, Santa Clara, CA) with a single quadrupole mass selective detector (Agilent 5973). The mass spectrometer was operated in scan mode from a low mass of 40 *m/z* to 400 *m/z* at an electron multiplier voltage of 2082 V. The mass spectrometer was autotuned daily using perfluorotributylamine (PFTBA). The source and analyzer temperatures were set at 230 °C and 150 °C, respectively.

A short, non-polar DB5-MS column (15 m, 0.25 mm i.d., 0.25 μm film thickness (Agilent)) was used. The GC method for analysis used helium as the carrier gas at a constant flow of 1 mL/min and a split/splitless injector either in the splitless mode or split mode. The split ratio was typically 5:1 but adjusted for different studies to prevent instrument contamination and/or saturation. The GC oven was programmed from an initial temperature of 50 °C (hold for 3 min) to 180 °C at 10 °C/min, followed by an increase to 280 °C (hold 1 min) at 20 °C/min. For vapor-time profiles studies, the GC oven was programmed similarly, but reached a maximum temperature of 180 °C.

Vapor-time profile studies were conducted using solid-phase microextraction (SPME) and performed at room temperature (≈ 23 °C). The SPME fibers (23 Ga. 100 μm fused silica coated with PDMS) were