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Headspace sampling of smokeless powder odor in a dynamic airflow context

Shawna F. Gallegos [a], Edgar O. Aviles-Rosa [b], Nathaniel J. Hall [b], Paola A. Prada-Tiedemann [a,*]

[a] Forensic Analytical Chemistry and Odor Profiling Laboratory, Department of Environmental Toxicology, Texas Tech University, Lubbock, TX, USA
[b] Department of Animal & Food Sciences, Texas Tech University, Lubbock, TX, USA

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ABSTRACT

Biological detection is leveraged within the fields of security screening and criminal investigations. Military and law enforcement personnel utilize canine teams in a range of different applications to detect explosives and narcotics. Due to the ever-changing materials encountered during routine field operations, it is imperative to have an optimal training regimen reflective of current target odor needs. Hence, the chemical understanding of target odor concentrations and subsequent means of odor delivery are essential in canine team training. Using double base smokeless powder as the target odor, this study evaluates the feasibility of presenting an explosive odor using an olfactometer. Furthermore, this study bridges instrumental validation for confirmation and understanding of odor chemical composition as well as persistence of odor over time. Instrumental parameter optimization included analysis of optimal solid phase microextraction fiber chemistry of target odor as a function of peak area response using gas chromatography-mass spectrometry (GC–MS). Studies were conducted directly over the headspace of the target odor and using the olfactometer as the dynamic airflow device for comparison purposes. Previously established volatile organic compounds from smokeless powders were detected, and comparison between non-airflow vs. airflow sampling was achieved. Results indicate a polyacrylate (PA) SPME fiber is optimal for specific detection of diphenylamine when subjected to dynamic airflow. Furthermore, sampling of "blank" trials following an odor trial indicated no residual contamination via instrumental verification. Persistence of odor volatile over a nine-week period of active olfactometer sampling showed decrease concentration, thus the need for consistent monitoring for optimal canine use.

Introduction

The use of biological detection is a common practice within the fields of security screening and criminal investigation [1]. Military and law enforcement personnel utilize canine teams in a range of different applications. These various applications are important for homeland security purposes including that of explosive and narcotics detection[1–6]. To effectively use canine olfactory capabilities as a biological sensor, canines must be constantly trained to relevant targets [7]. Due to the ever changing explosive and narcotic materials encountered during routine field operations, dogs need an adequate training regimen that is reflective of current target odors. Understanding the chemical odor profile of the target odors used in routine canine training is also needed to better inform canine training and for the development of field portable techniques.

In terms of explosive odor signature characterization, research has identified common dominant odor chemicals emanating from explosives that have been utilized in canine testing [8–14]. Studies have highlighted numerous volatiles of importance including plasticizers, phthalates (such as dimethyl phthalate, diphenyl phthalate, dibutyl phthalate, and diethyl phthalate), 2,4,6 trinitrotoluene (TNT), 2-ethyl-1hexanol (2E1H), and stabilizers (including diphenylamine, methylcentralite and ethylcentralite)[14–19]. Another aspect to understand is that of odor availability which relies on properties such as vapor pressure, environmental conditions, age, storage, containment system and surface area [20–22]. Furthermore, accurate and efficient odor delivery and presentation methods are important variables to understand and fully leverage canine detection capabilities.

Odor presentation methods can be direct, wherein the actual target odor material is presented directly to the canine[23]. Some examples

* Corresponding author at: Texas Tech University, Forensic Analytical Chemistry and Odor Profiling Laboratory, Department of Environmental Toxicology, 1207 S. Gilbert Drive, Bldg. 555 Office 110E, Lubbock, TX 79416, USA.
E-mail address: paola.tiedemann@ttu.edu (P.A. Prada-Tiedemann).

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include confiscated narcotics such as cocaine or a sample of C-4 explosive. Pseudo odor training materials are also a means of direct odor presentation[23]. Pseudo materials are created by identifying the chemical components in the headspace of the true material, then creating a physical mixture of those components as a method of presentation. A thorough understanding of the chemical makeup of the specific compound(s) the canine is being trained to is critical to create pseudo training aids that present a realistic representation of the odor of the real material and to understand canine generalization or discrimination of the pseudo relative to the real material [24,25]. There are also indirect methods for odor presentation such as passive headspace absorption, where an absorber such as a gauze pad is placed in a container with the target odor material[26–28]. The gauze pad is then used to present the odor to the canine. Additionally, there is dynamic airflow presentation where air is drawn from the target material through a sampling tube [29]. Some examples of dynamic odor presentation are olfactometers as well as vacuum type devices such as scent transfer units [27,30–32]. Recently, a modified trace vapor generator (TV-Gen) was utilized to quantitatively deliver three target analytes for canine threshold testing through the use of a large muzzle-shaped sampling port thereby highlighting the potential for an alternative vapor delivery system. [33].

For olfactory related studies, olfactometers have been widely used to understand complex odor mixtures by delivering a target odor via a controlled airstream system [34–40]. The olfactometer is not only used to measure and deliver odors but also allows for investigation and understanding of odor dilutions [37,41]. Olfactometers are ideal to use during canine training as they produce stable and predictable odors and have the capability to change concentrations by just manipulating the airflow [37,42].

Most relevant target odors for canine detection are not of pure substances but are a general mixture of several volatiles. Therefore, the challenge in canine detection lies in understanding the individual components of the mixture and the concentration of each volatile within the mixture [3,12,24,25,35,38,40,43,44]. While olfactory training using dynamic airflow sampling has been actively implemented, a current gap in this research area is the lack of knowledge on odor availability and concentration during dynamic-flow delivery processes. While known concentrations of odors can be prepared, there is no instrumental verification of quality of delivered odor during dynamic airflow animal testing. Thus, there is a need to instrumentally verify target odor volatile presence and quality when subjected to dynamic airflow.

The current study focuses on the use of an in-house olfactometer to test a double base smokeless powder as the target odor. Previous work has identified derivatives of smokeless powder additives to include the stabilizer diphenylamine that is used to prevent degradation of the powder materials such as nitroglycerine and nitrocellulose as the powder ages [15,16,45]. Using this volatile as the target odor for analysis, the aim of the study is to provide an instrumental evaluation to confirm volatile odor presence during active olfactometer use. Evaluation of the vapor odor profile was conducted directly over the headspace of the target odor for comparison purposes. Variables such as absence of target odor for contamination purposes and longevity of odor volatile over time were also investigated.

Materials and methods

In-house olfactometer

A schematic representation of the olfactometer is shown in Fig. 1. Construction, electronics, building information, and canine training data of the olfactometer is fully described by Aviles-Rosa et al[46]. In brief, an oilless electromagnetic air pump served as the air source, compressing room air. The air from the pump passed through an activated charcoal filter to remove environmental volatiles. The filtered air is then split and goes into two rotameters which regulate two independent flow paths. One line (dilution flow path) was used as a continuous airflow and was directly connected to the odor mixing Teflon (PTFE) manifold, which delivered the odor dilution directly to the odor port. This path was set to 2 standard liters per minute (SLPM) throughout the duration of the experiment. The second line is denoted as the odor line. This carries the filtered air to a six-channel solenoid valve manifold (see yellow valves in Fig. 2) and was set to 1 SLPM for the duration of the experiment.

A 1/8″ OD PTFE tube connected each valve of the manifold to a glass VOC vial with a septa lid (PTFE, silicone, PTFE septa). Using a needle,

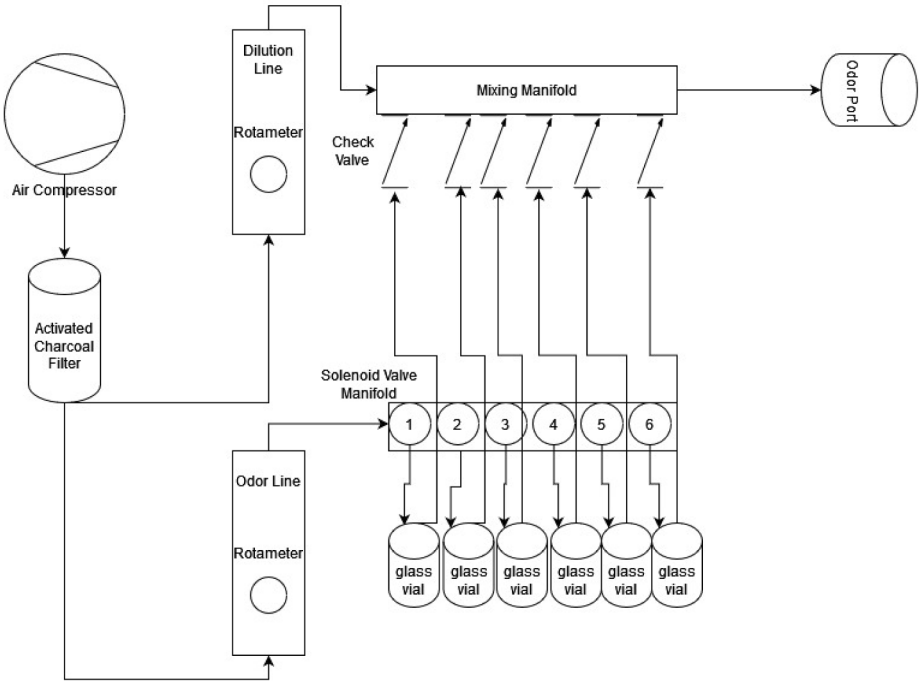

Fig. 1. Schematic of olfactometer depicting overall airflow design.

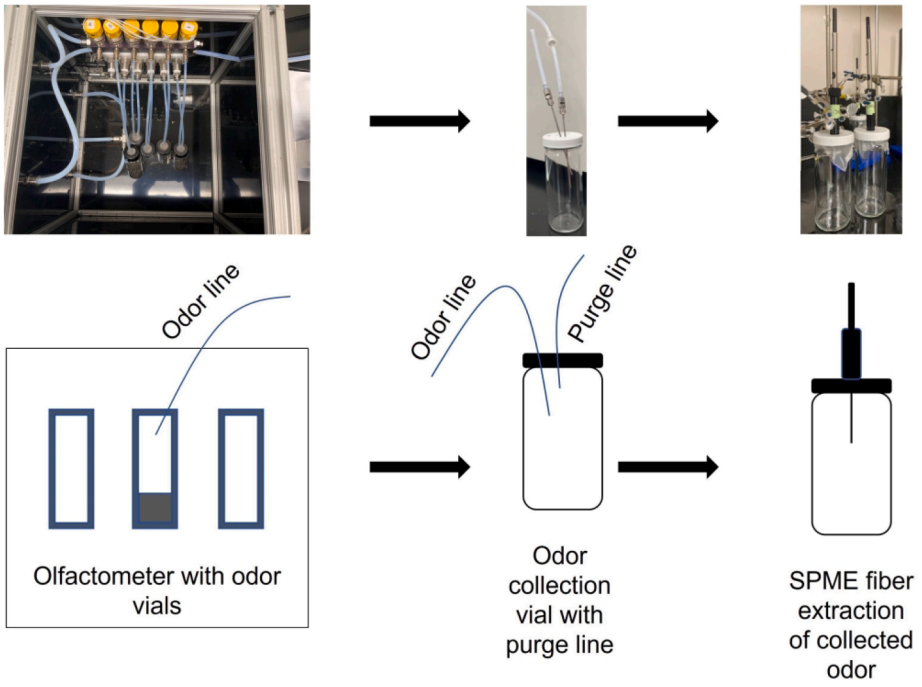

Fig. 2. Sample Vials containing Double base Smokeless Powder (left), Odor Collection Vial (middle), SPME Fiber Extraction (right).

the PTFE tube was inserted through the septa into the jar. When the computer program activated a solenoid valve, clean air from that valve entered to the jar connected to it . A second 1/8″ PTFE tube inserted through the septa carried the headspace of the jar into the PTFE odor mixing manifold. This line was connected to a stainless steel (SS 316 grade) check valve to prevent reverse flow from the mixing manifold to the jar. In the mixing manifold, the headspace of the jar was mixed and diluted with the air from the continuous line. This produced a 33 % air dilution of the odorant. The diluted odorant was carried from the mixing manifold to the odor port trough a final PTFE tube to the canine sampling port. The odor valve to be activated was controlled through the olfactometer computer program . To ensure a consistent airflow was presented, one valve was always active for a sampling period. The valve maybe connected to a "blank" cleaned vial or a vial containing 10 g of double-base smokeless powder, the odor under investigation.

Solid phase microextraction (SPME) sampling procedures

SPME fiber optimization

To identify the target odor volatile emitted from the smokeless powder samples and from the exit ports of the olfactometer device, analysis was completed via SPME GC–MS. All samples were analyzed in 40 mL glass vials with a screw cap and PTFE/silicone septa (Supelco, Sigma Aldrich) throughout the study phase. Prior to any headspace or olfactometer sampling, the glass vials were sterilized by methanol solvent (Fisher Scientific) rinsing followed by a heating period in a 105 °C oven for 2 h, and the septa and caps were sterilized via the same method for 15 min. This cleaning procedure was performed to remove any volatile contamination prior to use as it has been previously established that biological sterile does not equate to analytically clean [47]. For dynamic odor sampling, 236.5 mL collection vials with a screw cap and PTFE/silicone septa (QEC, Beaver WV) were used and prepared in the same manner as the smaller 40 mL vials. For sampling purposes, ten (10) grams of double base smokeless powder (H335 rifle powder, Hodgdon Powder Company, Batch#1020221) were used.

A 3-hour headspace extraction period was utilized to evaluate an assortment of SPME fiber coatings. This extraction time was deemed optimal as it provided with the shortest extraction time for the successful detection of target odor volatile (Diphenylamine). A total of five different commercially available fiber types were tested for the extraction of the primary target compound – diphenylamine. These included polyacrylate (PA), polydimethylsiloxane/divinylbenzene (PDMS/DVB), polydimethylsiloxane (PDMS), divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) and carboxen/polydimethylsiloxane (CAR/PDMS) (Supelco, Sigma Aldrich). Each SPME fiber was conditioned for three 30-minute sessions at an oven temperature of 250 °C to guarantee each fiber was clean and ready to be used prior to sampling procedures. A blank fiber instrument run was then performed to ensure no contaminants or lingering volatiles remained on the fiber. Each fiber was exposed to the headspace of the smokeless powder from the determined optimal extraction time of 3 h, followed by the gas chromatography-mass spectrometry method.

Six extraction replicates were tested with each fiber to obtain a measurable average peak area response for the diphenylamine target volatile, to provide a comparison of chromatogram resolutions and to further evaluate the GC–MS method chosen for the study.

Fiber optimization was also conducted with the olfactometer device to verify fiber chemistry selection under the dynamic airflow sampling conditions. At completion of a 1-hour equilibration, the sample vials containing the smokeless powder were connected to the odor ports of the olfactometer. An odor collection vial (236.5 mL) was pierced with two needles, the first of which was connected to the olfactometer and would transfer the odor from the mixing manifold to the odor collection vial and the second to vent the air pressure so as to prevent damage to the collection vial. The olfactometer was activated for 30 s at an airflow ratio of 2:1 (2 L/min of clean air with 1 L/min of odor). In an effort to prevent the loss of the collected odor volatiles, the airflow needles were removed, and the odor collection vial immediately sealed with parafilm. The SPME fibers were then inserted for an optimized extraction time of 3 h (Fig. 2).

Upon completion of the 3-hour extraction time, fibers were run with the developed GC–MS method.

Olfactometer blank sampling – Contamination evaluation

Blank sampling experiments were conducted to determine if any potential contamination existed in the olfactometer between routine use

[46]. Variations of length of tubing, from 1 foot (short line) to 3 feet (long line) were tested as well as the application of heat tape to the shorter line to evaluate if added heat could reduce any potential contaminants present in the system. Six replicates were performed for each variation of the blank sampling trials.

Forty (40)mL glass SPME vials with a screw cap and PTFE/silicone septa (SUPELCO/Sigma Aldrich) were used in experimentation. The glass vials were sterilized by methanol solvent rinsing followed by a heating period in a 105 °C oven for 2 h, and the septa and caps were sterilized via the same method for 15 min. As with previous experiments, ten (10) grams of double base smokeless powder (H335 rifle powder obtained from Hodgodon Powder Company) was used as the odor sample for olfactometer testing, and an empty sterile vial was used for the blank odor collection.

A 40 mL odor collection vial was pierced with two needles, the first of which was connected to the olfactometer and would transfer the odor from the blank vial to the odor collection vial and the second to vent the air pressure so as to prevent damage to the collection vial. The sample vial containing the smokeless powder was activated for 30 s at an airflow ratio of 2:1 (2 L/min of air with 1 L/min of odor), this odor was not collected. Another 30 s interval was allowed to pass to mimic the time between canine searches. During this time only the continuous line was activated to clear any remaining odor residue. At the conclusion of the 30 s clearing interval, the valve connected to the sterile/clean vial was activated for another 30 s interval. This blank sample was collected in the 40 mL collection vial. In an effort to prevent the loss of potential contaminant odor volatiles, the airflow needles were removed, and the odor collection vial immediately sealed with parafilm. The SPME fibers were then inserted for a 3-hour extraction period. Upon completion of the 3-hour extraction time, the fibers were run with the established GC–MS method to analyze any potential contaminants that may be carried over from the active odor vial and to confirm that the target odor, diphenylamine was not remaining in the olfactometer between active trials.

Longevity and persistence of target odor volatile

Longevity experimentation was conducted to instrumentally monitor the quality of target odor (diphenylamine) from the smokeless powder as measured by the detector response over a nine (9) week period. Three sterile forty (40) mL glass SPME vials with a screw cap and PTFE/silicone septa (SUPELCO/Sigma Aldrich) were prepared with 10 g of double base smokeless powder (H335 rifle powder obtained from Hodgdon Powder Company). Two vials were connected to the olfactometer and subjected to active canine testing for a nine-week period, while the third vial was kept at laboratory conditions and not subjected to dynamic airflow as a means of control. Weekly headspace SPME extractions were performed on the two vials being routinely used for canine training as well as the control vial for a four-week period. In week five, headspace extractions were increased to bi-weekly to monitor the quality of target odor more closely. Temperature and humidity were also monitored and recorded at the beginning and end of the three-hour extraction period at each sample point.

Gas Chromatography-Mass spectrometry analysis (GC–MS)

GC–MS was used as the confirmatory technique for the presence of the target odor volatile in the headspace of all collected samples. An Agilent Technologies GC 7890A with an Agilent Technologies 5975C inert XL MSD with triple-axis detector (Agilent Technologies, Santa Clara, CA) was used to separate and analyze the compounds extracted on the SPME fibers. A Rtx®-5 capillary 30 m × 250 μm × 0.25 μm column (Restek Corporation, Bellefonte, PA, USA) was used. Helium was used as a carrier gas at a flow rate of 1.0 mL/min. The temperature ramp was programmed from 40 °C to 280 °C beginning with a 1-minute hold at 40 °C and then increasing the temperature to 200 °C at 15 °C minute with a 1 min hold at 200 °C. The temperature was then increased to 240 °C at 15 °C minute and held for 6.50 min at that temperature. From 240 °C the temperature was increased at 25 °C minute to 270 °C. The final temperature of 280 °C was reached by ramping the temperature at 5 °C minute and holding for 4 min. The injector temperature was set at 280 °C in split mode at a split ratio of 5:1 as this ratio has been previously utilized in the literature for smokeless powder headspace analysis [15]. The split ratio allowed for enhanced target odor chromatographic resolution when compared to splitless method procedures.

The total run time for analysis was 29.033 min. Mass spectra were repeatedly scanned from 45 to 550 amu. Target compound was identified using the National Institute of Standards and Technology (NIST) (2017) mass spectral reference library and verified with external standard chemical calibration. A calibration curve was generated so that peak area responses could be correlated to the amount of diphenylamine extracted by the SPME fibers. The external calibration was performed using direct injections of 5, 10, 20, 30, 40, 60 and 80 ppm DPA standard solutions in methylene chloride solvent. The response factor across all concentrations yielded an R^2 value of 0.9735 for diphenylamine. The average response factor for diphenylamine was then used to calculate the concentration of target odor present in collected samples in milligrams/liter (mg/L). The criteria for the compounds identified were those with detected peaks greater than or equal to a match quality of 90% or above. All generated data was analyzed using Chemstation software (Agilent Technologies, Santa Clara, CA). Compounds known to be products of the column or sampling process were not included in the analysis.

Results

Fiber chemistry optimization – Direct powder sampling

Headspace vapor odor profiles were evaluated using each fiber chemistry type to monitor peak area responses of the target odor volatile – diphenylamine. A total of six replicates were conducted per fiber type using 10 g of double base smokeless powder sample. While each fiber extracted the target compound of diphenylamine, as seen in Fig. 3, there were considerable variations in average peak area response across the fiber chemistries utilized. The results depicted the polydimethylsiloxane/divinylbenzene (PDMS/DVB) yielding the highest average peak area response across all replicates conducted followed by the polyacrylate (PA), polydimethylsiloxane PDMS, divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) and finally the carboxen/polydimethylsiloxane (CAR/PDMS) obtaining the lowest peak area response signal.

Fiber chemistry optimization – Dynamic airflow sampling

Fiber chemistry optimization was also conducted on samples obtained from the olfactometer device used for odor delivery purposes. Peak area response of the primary odor volatile (diphenylamine) was monitored via SPME-GC–MS methodology. As performed with the pure powder headspace sampling described in Section 3.1, there were five fiber types that were tested which included: polyacrylate (white), polydimethylsiloxane/divinylbenzene (blue), polydimethylsiloxane (red), DVB/CAR/PDMS (gray) and carboxen/polydimethylsiloxane (black). These fibers have all been previously tested with direct headspace analysis of the double base smokeless powder, with the Polyacrylate fiber determined as the optimal fiber. While all five fiber types were tested, only the Polyacrylate (PA) fiber and Polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber were considered as they were the only fibers that consistently detected the target compound. The Polydimethylsiloxane (PDMS) fiber only detected the target compound in two of the six replicates, while the DVB/CAR/PDMS and CAR/PDMS fibers did not detect the target volatile in any of the replicates.

As seen in Fig. 4, the PA fiber proved most successful with the target compound being detected in all six of the replicates during airflow

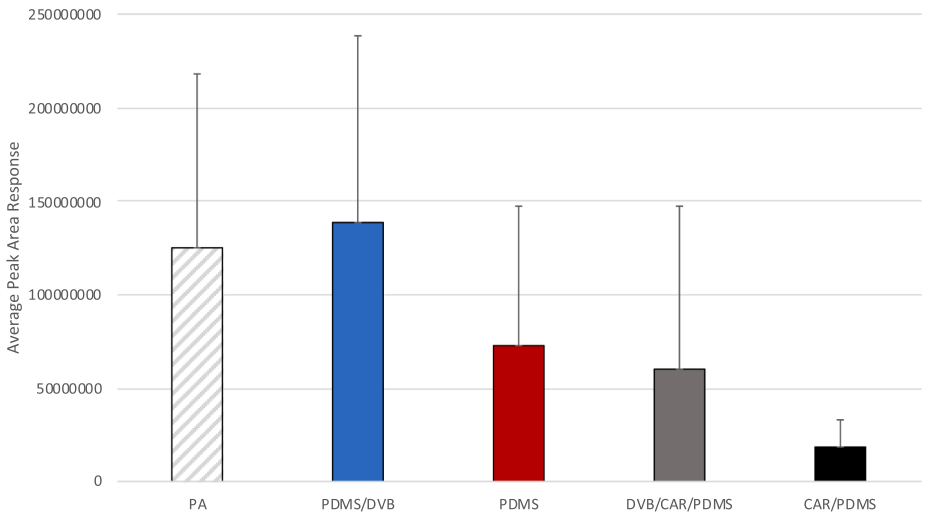

Fig. 3. Diphenylamine Peak Area Response of powder headspace as a function of SPME Fiber Chemistry (bars represent mean of replicates per fiber coating N = 6, error bars indicate standard error of the mean).

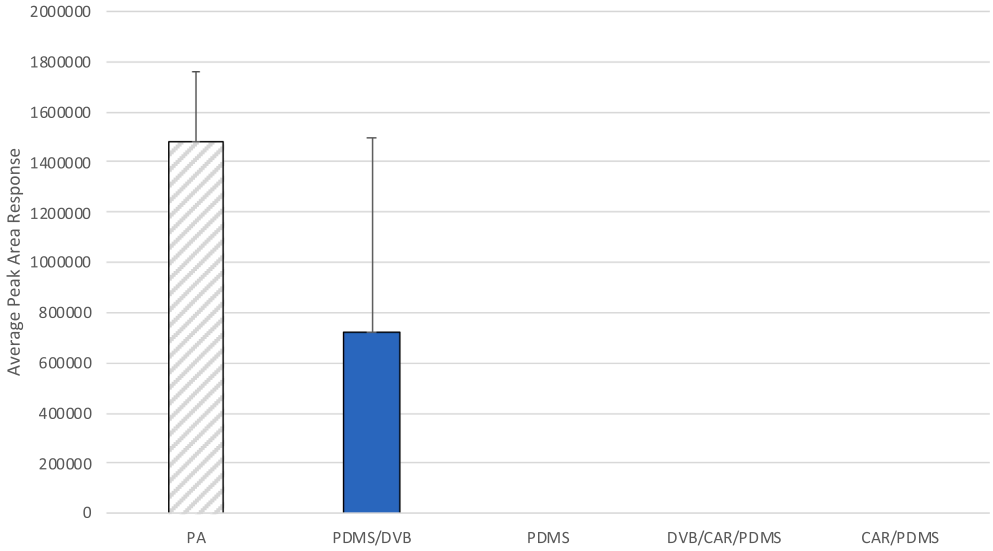

Fig. 4. Diphenylamine Peak Area Response of dynamic airflow collection vials as a function of SPME Fiber Chemistry (bars represent mean of replicates per fiber coating N = 6, error bars indicate standard error of the mean).

sampling. The PDMS/DVB fiber provided a comparable average peak area response; however, the target compound was only detected in three of the six replicates indicating a lack of extraction reproducibility.

Olfactometer blank sampling – Contamination evaluation

To instrumentally verify the clearance of odor volatile from the olfactometer line, blank samplings were performed to evaluate odor cross contamination from run to run. A total of 18 blank replicate samples were taken, 6 foreach tubing variation (i.e. short line, heated tape, longer line). Diphenylamine was not detected in any of the replicate samples. As can be seen from Fig. 5, there is only one compound 2,4-diisocyanato-1-methyl-Benzene that was detected across all 18 samples. This compound is considered an environmental contaminant and can thereby be disregarded as an active volatile originating from the target odor.

Only one other compound, Ethyl 4-ethoxybenzoate was detected in two of the eighteen samples and can be attributed to the PTFE tubing used in the olfactometer. The two samples where Ethyl 4-ethoxybenzoate was detected were in the experimental sampling group that used heat tape. The addition of heat tape to the design could have enhanced the concentration of tubing volatile components due to increased temperature, resulting in detection of this background compound.

Direct powder headspace sampling vs. Dynamic airflow sampling

As expected, when comparing the direct powder headspace sampling with the dynamic airflow sampling, the latter yielded a lower peak area response for the target odor volatile, diphenylamine. This was an expected result with the introduction of direct airflow sampling from the olfactometer. Fig. 6 shows a comparison of the diphenylamine peak detected a) extraction over pure powder headspace ~ 3800 mg/L and b) extraction of collected odor after dynamic airflow sampling ~ 120 mg/L. As can be observed, the peak area was reduced by almost 32X, but nevertheless confirms the detection of the target volatile with an air dilution of 3 L/min which is the amount of air introduced during routine canine testing procedures.

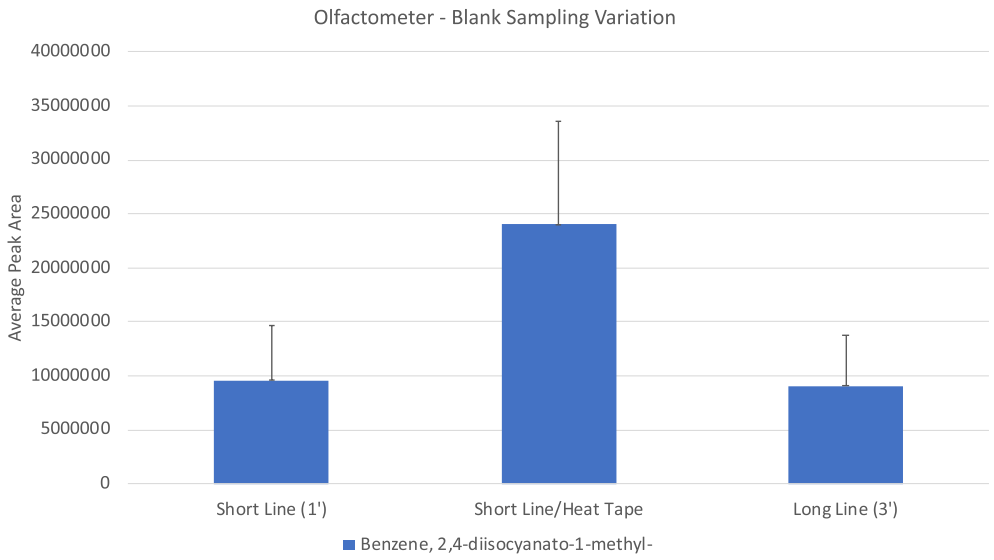

Fig. 5. Blank Sampling Variations with Olfactometer (bars represent mean of replicates per blank design N = 6, error bars indicate standard error of the mean).

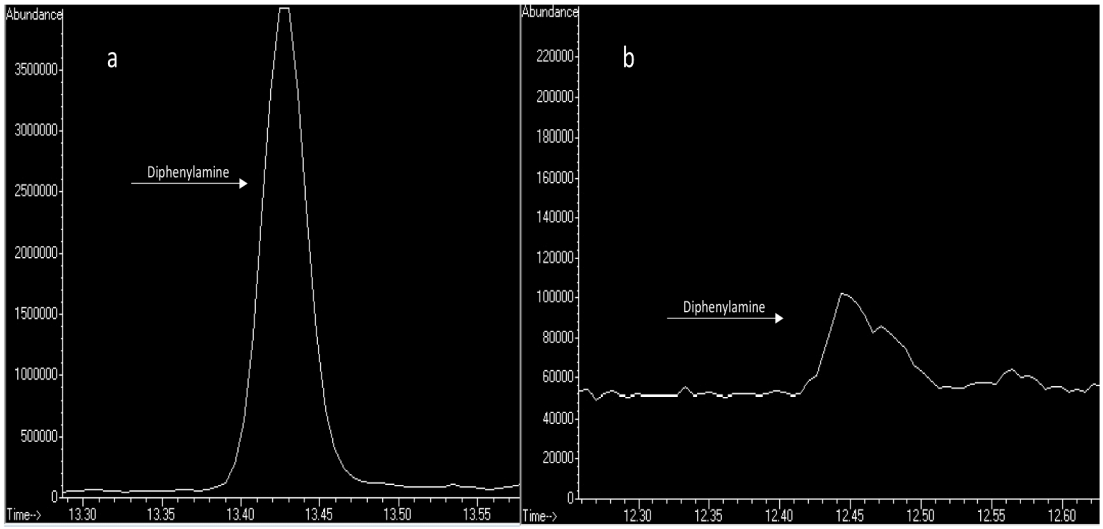

Fig. 6. a) Diphenylamine Peak Over Pure Powder Headspace, b) Diphenylamine Peak After Dynamic Airflow Sampling.

Longevity and persistence of diphenylamine

In order to monitor target odor presence over time, experiments were conducted to evaluate diphenylamine abundance after continued olfactometer use. Samples were taken once weekly through week five, and increased to twice weekly in week 6. The mean temperature was 20.1 °C (high 24.0°C, low 16.0°C) and the mean humidity was 38% (high 61.0%, low 27.0%).

As seen in Fig. 7, the amount of diphenylamine present in week one was ~ 3600 mg/L for all samples. As the weeks progressed, there was a steady variation in the amount of diphenylamine available during sampling. For example, in week two there was a slight increase between 3900 mg/L and 5300 mg/L among the active sample vials followed by a decrease in week 3 to between 3500 mg/L and 3900 mg/L. Even though the control vial had the smokeless powder as a control with no airflow disturbance, the responses fluctuated on a parallel level as the dynamic airflow vials, dropping by 47% in the control vial in the final week of sampling (week 9). An average decrease among all sample vials indicates of almost 56% in the final week of sampling.

Fig. 8 shows the average concentration distribution per vial across the sampling period. A one-way ANOVA did not highlight a statistical significance of diphenylamine concentration among the 3 sampling vials tested. This further confirms the significance of the steady decrease of the target odor as time progresses whether the sample is subjected to dynamic airflow or not.

Discussion

The main objective of this study was to instrumentally evaluate the use of smokeless powder as a target odor in an olfactometer . We selected double base smokeless powder as it is a common explosive detection dogs are trained to find. Due to the increasing use of olfactometers in detection dog research, it is important to monitor and verify quality of odor delivery via an analytical chemistry approach. Thus, to bridge this gap in research between odor delivery devices and instrumental analysis, the study performed a SPME fiber chemistry optimization to validate the optimal detection of diphenylamine, a previously reported component of smokeless powders.

Diphenylamine has been shown to be a key target odor being present in numerous studies evaluating multiple smokeless powder manufacturers and from both burned and unburned conditions [15,16,48]. The study highlighted the polyacrylate SPME fiber as the optimal fiber for

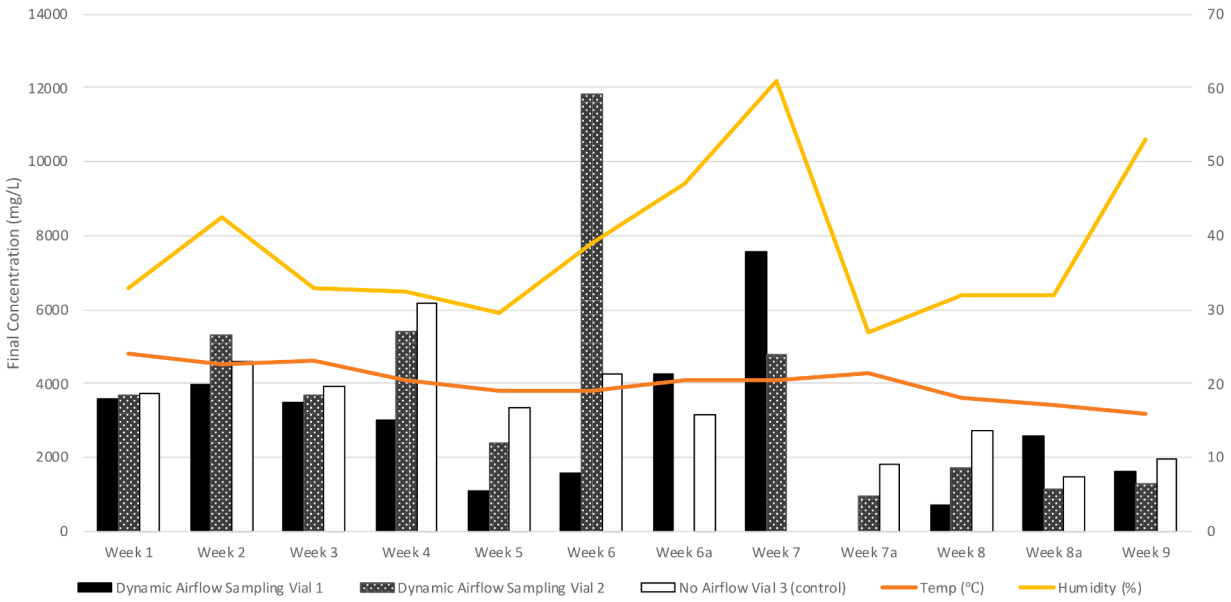

Fig. 7. 9 Week Diphenylamine Vapor Odor Profile Persistence.

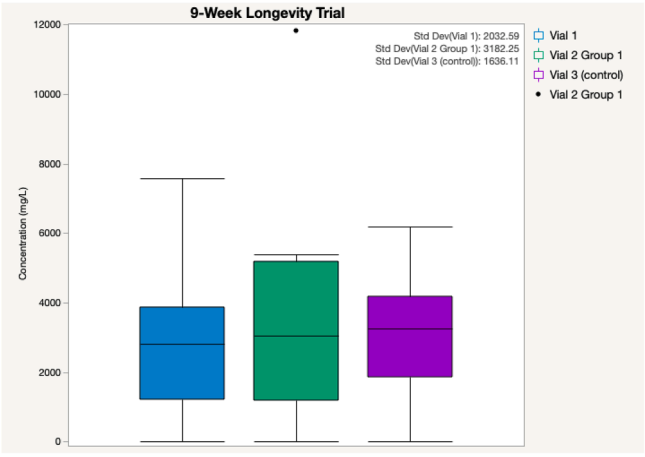

Fig. 8. Diphenylamine concentration distribution across dynamic collection and control replicates (bars represent mean of sample replicates N = 6, error bars indicate standard error of the mean).

the extraction of the diphenylamine odor during dynamic airflow processes. These results are not in accordance with previous work conducted in the extraction of volatile odor signatures from smokeless powders achieved by Joshi et al., [15] as that work highlighted the PDMS fiber chemistry as the selected type for the study. However, the authors in that study did emphasize the need to exploit other fiber chemistries which could lead to more efficient extractions. Furthermore, this study provided the novel SPME extraction from an olfactometer device depicting the polyacrylate fiber as the optimal fiber type for vials containing dynamic airflow content and not necessarily pure substance as has been performed in other studies. When comparing headspace samples from both pure substance and dynamic airflow collection vials, a decrease in odor concentration was observed as it was hypothetically expected with the introduction of air in the olfactometer device. These results confirm that although lower amounts are present, odor volatile can still be detected. Similar results have been previously established with human scent samples where airflow dynamic devices yield lower volatile abundances[28] when comparing static equilibrium vs airflow sampling methodologies.

Sampling of the olfactometer device during blank odor runs also depicted that the target odor was not instrumentally detected, thereby confirming that there is no detectable cross contamination of odor in between odor delivery sessions. This instrumental verification is important for animal training to ensure a clean background for non-target trials.

In terms of the longevity/persistence experiment performed, there was noticeable decrease in week seven going forward through week nine, which may be contributed to increased utilization of target odor material during animal testing procedures. There was also a drop in temperature conditions which again could affect the extraction process and thus the response of target odor. These variations were expected as canine testing varied from week to week, and as can be seen from Fig. 7, there was a drop in humidity from Week 2 to Week 3 of 9.5% which can affect the amount of volatile available for sampling. The results highlight that as was to be expected there is a gradual decrease of odor over time, with fluctuations in temperature and humidity possibly affecting the final instrumental response. It is important to note that stabilizers such as diphenylamine are added into smokeless powders to neutralize decomposition products of nitroglycerin and nitrocellulose. The manufacturing process of each powder ultimately dictate how each of these is incorporated into the final powder product[49]. Thus, when a smokeless powder is allowed to stand, nitroglycerin and nitrocellulose can release nitrogen oxides that affect the stabilizers (i.e. diphenylamine). Thus, the stabilizer may undergo a chemical reaction and produce nitrogen derivatives[48]. In turn, this reaction can reduce the amount of available diphenylamine available in the headspace. Hence, the decrease of diphenylamine recovery as a function of time in both active olfactometer sampling vials and powder control can be expected.

Conclusions

Headspace analysis via SPME-GC/MS was implemented to provide an instrumental validation approach to double base smokeless powder odor volatile in both direct and olfactometer sampling approaches. Polyacrylate fiber chemistry was the optimal fiber for extraction of the target odor diphenylamine. Dynamic airflow sampling yielded a successful detection of the target odor (Diphenylamine). There was a decrease of 32X target odor as expected with introduced airflow. Over a nine-week period of active olfactometer sampling for canine training, there was a decrease in detected target of 60% in the dynamic airflow vials, which did not differ statistically from the decrease observed with a

control (unused) sample (40% decrease). These results highlight that both direct and indirect methods undergo a decrease of diphenylamine concentration across time, therefore highlighting the importance of consistent monitoring for optimal canine training. The need for enhanced olfactory-based behavioral tools is essential for optimal applications of biological detectors. This study evaluates the feasibility of presenting target explosive odor using an olfactometer. Furthermore, this study bridges instrumental validation for confirmation of odor presence and persistence of the odor volatile over time.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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