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Laboratory and field experiments used to identify *Canis lupus* var. *familiaris* active odor signature chemicals from drugs, explosives, and humans

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Abstract This paper describes the use of headspace solid-phase microextraction (SPME) combined with gas chromatography to identify the signature odors that law enforcement-certified detector dogs alert to when searching for drugs, explosives, and humans. Background information is provided on the many types of detector dog available and specific samples highlighted in this paper are the drugs cocaine and 3,4-methylenedioxy-*N*-methylamphetamine (MDMA or Ecstasy), the explosives TNT and C4, and human remains. Studies include the analysis and identification of the headspace "fingerprint" of a variety of samples, followed by completion of double-blind dog trials of the individual components in an attempt to isolate and understand the target compounds that dogs alert to. SPME–GC/MS has been demonstrated to have a unique capability for the extraction of volatiles from the headspace of forensic specimens including drugs and explosives and shows great potential to aid in the investigation and understanding of the complicated process of canine odor detection. Major variables evaluated for the headspace SPME included fiber chemistry and a variety of sampling times ranging from several hours to several seconds and the resultant effect on ratios of isolated volatile components. For the drug odor studies, the CW/DVB and PDMS SPME fibers proved to be the optimal fiber types. For explosives, the results demonstrated that the best fibers in field and laboratory applications were PDMS and CW/DVB, respectively. Gas chromatography with electron capture detector (GC/ECD) and mass spectrometry (GC/MS) was better for analysis of nitromethane and TNT odors, and C-4 odors, respectively. Field studies with detector dogs have demonstrated possible candidates for new pseudo scents as well as the potential use of controlled permeation devices as non-hazardous training aids providing consistent permeation of target odors.

Keywords Explosives · Drugs · Human remains · Canine detection · SPME

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Introduction

Even with technological advances in instruments, detector dogs still represent one of the most reliable real time detectors of contraband. Unfortunately, to date, there have been limited peer-reviewed published scientific studies demonstrating exactly how these biological detectors work so efficiently. Dogs (*Canis familiaris* or *Canis lupus* var *familiaris*) have been used as chemical detectors dating back to their use as hunting dogs some 12,000 years ago through medieval times and the 1800s including their use as human trackers. Detector dogs have been used in warfare and, in particular, during and after World War II dog-handler teams have been used extensively to locate explosives. The civilian use of dogs began with their use as drug dogs and bomb dogs and has expanded to dozens of uses, including those listed in Table 1. With the recent worldwide emphasis on antiterrorism since the September 11, 2001 attacks in the United States, the use of canines for explosives, drugs and human detection have dramatically increased. In this paper, we highlight recent studies to determine the active odor signature chemicals from illicit drugs, explosives and human remains. A more thorough review of the use of canines as chemical detectors has been described elsewhere [1].

While their use is widely accepted in the forensic and legal community, in recent years the use of detector dogs has come under attack in the courts where the issue of reliability has been challenged. A recent example of the ability and reliability detector dogs being questioned has been in the area of narcotics detection. The use of drug detector dogs alerting to currency associated with drug trafficking has become a point of contention due to reports that most money in circulation is tainted with trace

Table 1 Some different detector dog types

1	Abalone (endangered mollusk poaching) detector dog
2	Agricultural product (importation) detector dog
3	Arson (accelerant) detector dog
4	Brown tree snake (pest species) detector dog
5	Airport/runway detector dog
6	Cadaver (human remains) detector dog
7	Chemical weapon detector dog
8	Citrus canker detector dog
9	Concealed person detector dog
10	Currency detector dog
11	Drug (narcotic) detector dog
12	Explosives (bomb) detector dog
13	Gas leak detector dog
14	Gold ore detector dog
15	Gun/ammunition detector dog
16	GYPSY moth larvae detector dog
17	Land mine trip wire detector dog
18	Melanoma detector dog
19	Missing person detector dog
20	Rotten power pole detector dog
21	Scent line-up detector dog
22	Screw worm detector dog
23	Seal detector dog
24	Search and rescue (warm blood) detector dog
25	Syringe needle (dried blood) detector dog
26	Termite detector dog
27	Tracking (fleeing suspect) detector dog
28	Truffles detector dog
29	Water search detector dog
30	Wildlife detector dog

levels of cocaine [2, 3, 4]. These reports have resulted in contaminated money theories purporting that, due to this widespread contamination, any person carrying currency could potentially initiate a drug dog alert. The questions raised are the same for any forensic specimens, including exactly what chemicals are certified detector dogs being trained to alert to and what is their sensitivity and specificity. It is believed that canines often alert to a scent associated with forensic specimens rather than the specimen itself. The scent is often composed of volatile compounds or classes of compounds that are detected by the canine in the gaseous state. Headspace SPME has been demonstrated to be advantageous in identifying trace volatile components from forensic specimens without having to resort to long extraction times, heating of samples or using dynamic flow (headspace stripping) which can dramatically alter ratios of odor signature chemicals recovered. In the studies reported here, rapid SPME sampling of the headspace above the samples at room temperature (25 °C) is performed to closely simulate conditions commonly encountered by canines. In addition to the increased sensitivity, simplicity, rapid analysis and solvent free nature of SPME compared to other extraction techniques, there are field portable samplers available that allow for convenient on-site sampling and subsequent analysis. Determining exactly which odor chemicals are available and which are used for canine detection is important for understanding the basic science of canine olfaction and is also useful in improving performance, training aids, and improved targets for developing more reliable instrumental methods.

MDMA Detection

While there are dozens of drugs that dogs could be trained on most law enforcement detector dogs are trained to alert to the most common illicit drugs which include marijuana, cocaine, heroin and methamphetamine. Due to the large increases in the consumption and distribution of MDMA (now the fifth most identified non prescription controlled substance in U.S. crime labs) many canines have recently been certified to detect MDMA, including the U.S. Customs Service Canine Enforcement Program and the Florida Highway Patrol (Florida, USA) who participated in this study. Previous studies with narcotics detector dogs have shown that dogs alert to volatile odor chemicals associated with drugs rather that the parent drug itself. For example, in the case of cocaine, field tests simulating actual search scenarios have demonstrated that law enforcement trained narcotics detector dogs detect methyl benzoate, a cocaine decomposition product, as the dominant cocaine odor chemical and at thresholds which indicate that cocaine contamination on currency is not sufficient to alert law enforcement detector dogs [5, 6, 7]. In fact, the threshold detection levels for law enforcement trained detector dogs and humans are similar as seen in Fig. 1. Figure 1 demonstrates the sigmoid curve characteristic of biological dose–response curves with the amount of methyl benzoate plotted against the behavioral response of a drug dog, that is, the dog alerting. The results suggest that a dose–response relationship exists between methyl benzoate

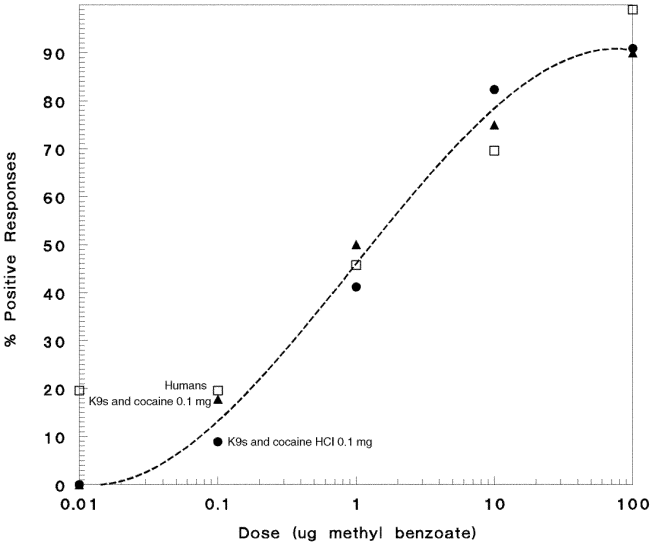

Fig. 1 Percent of tested law enforcement detector dogs and human subjects responding positively to various levels of methyl benzoate spiked on to US paper currency alone and in the presence of 0.1 mg of cocaine and cocaine HCl

and humans and drug dogs tested eliciting a positive response, and that the effective dose for 50% of the canines and humans tested is approximately 1 µg of methyl benzoate spiked onto currency. These results are the averages for 46 human tests, 104 canine tests with cocaine base and 141 canine tests with cocaine HCl.

MDMA is unique in that this illicit drug is most often encountered as tablets. Early in the MDMA odor studies, it was discovered that many MDMA tablets sampled also contained methamphetamine as a volatile headspace component and thus earlier studies of methamphetamine odor signature chemicals were relevant to these studies [8]. In order to ensure that compounds of interest identified within the drug itself are not commonly used in other tablets as fillers and/or binders, the same extraction procedure was applied to common non-illicit tablets. There are various methods of synthesizing MDMA found in the scientific literature as illustrated in Fig. 2. In all cases, the starting material carries the preformed methylenedioxy ring, in the form of safrole, isosafrole or of the derived aldehyde, piperonal. Safrole could potentially be obtained by distilling sassafras oil and is also found in essential oils [9].The first preparation of MDMA was by Merck in 1914. Here, MDMA was synthesized in two steps from safrole. The addition of aqueous hydrobromic acid provides an impure intermediate (1-methylenedioxyphenyl-2-bromopropane) that is converted with an alcoholic solution of methylamine to MDMA [10].MDMA has also been synthesized from MDA by reaction with ethyl chloroformate, followed by reduction with Red-Al [11]. Similarly, MDA can be converted to the formamide that is reduced with lithium aluminium hydride in tetrahydrofuran [12]. Two procedures exist for the synthesis of MDMA by the reductive amination of piperonyl acetone (MD-P2P) with methylamine. The reducing agents are either sodium cyanoborohydride in methanol, or amalgamated aluminium in aqueous isopropanol [13]. The piperonyl acetone (MD-P2P) required for these syntheses are not commercially available but it can be made either by the reduction of the nitroethane adduct or piperonyl with elemental iron, or the oxidation of isosafrole with hydrogen peroxide in formic acid [10]. Since different synthetic routes can produce different byproducts it is important to test a variety of MDMA samples and it is important to perform ongoing studies of headspace odors in MDMA training aids and confiscated samples.

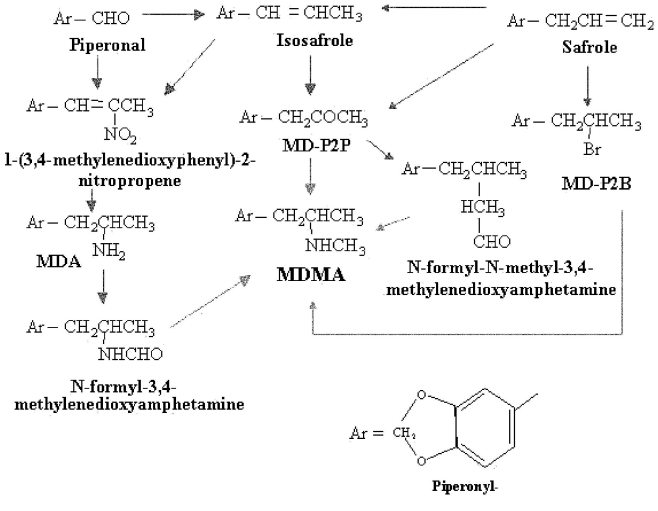

Fig. 2 Different synthesis pathways of MDMA

Profiling of illicit drugs clandestinely manufactured is primarily concerned with the identification of impurities that are derived from specific manufacturing techniques or protocols. Profiling has been done in the past on a variety of drugs including heroin, cocaine, methamphetamine and, most recently, MDMA [14, 15, 16, 17, 18]. This process provides a tool that may allow forensic scientists to relate different street drug seizures to a common source based on differences in isolated chemicals. In contrast to this, for studies of canine odor signatures the main focus is on which chemicals are most common in illicit samples and thus more likely candidates for canine imprinting to target the greatest number of street samples. It has been shown that many compounds are present in the headspace of seized methamphetamine samples with benzaldehyde and the intermediate ketone 1-phenyl-2-propanone (P2P) seen consistently throughout different batches of methamphetamine. The potential of benzaldehyde as a pseudo methamphetamine training aid has been demonstrated [8]. Profiling studies on seized MDMA samples have shown that potential commonly seen compounds in the headspace of MDMA may include: acetic acid, camphor (a flavor additive), piperonal (a starting material), isosafrole (a starting material), the intermediate 3,4-methlenedioxyketone (MD-P2P) and the reduced alcohol form of this ketone, MD-phenyl-2-propanol [16, 17, 18]. While methamphetamine in the headspace of MDMA samples has been reported to be present in some cases, the inconsistency of methamphetamine's presence throughout batches of seized samples that do consistently report the presence of the same starting materials and intermediates, along with the known synthetic mechanisms used to achieve these products, indicates that methamphetamine is likely encountered as an adulterant or contaminant in some MDMA samples rather than a byproduct from a synthetic route [19].

Explosives detection

For explosive detection canines, there are five main compound classes and dozens of explosive compounds which are potential training aids (positive controls) for bomb dogs with common examples as follows. Aliphatic nitro: nitromethane, hydrazine; aromatic nitro (C-NO_2): nitrobenzene (NB); nitrotoluene (NT); dinitrobenzene (DNB); dinitrotoluene (DNT); trinitrobenzene (TNB); 2,4,6-trinitrotoluene (TNT); picric acid. nitrate ester (C-O-NO_2): methyl nitrate; nitroglycerin (NG); ethylene glycol dinitrate (EGDN); diethylene glycol dinitrate (DEGN); pentaerythritol tetranitrate (PETN); nitrocellulose; nitroguanidine. nitramines (C-N-NO_2): methylamine nitrate; tetranitro-*N*-methyaniline (Tetryl); trinitrotriazacylohexane (cyclonite

or RDX); tetranitrotetrazacylooctane (Octogen or HMX); hexanitroisowurztitane (CL20). Acid salts (NH_4^+, NO_3^-): ammonium nitrate; ammonium perchlorate; potassium nitrate (in black powder). The potential odor signature chemicals needed in training can be even more complicated since, in many cases, the major chemical component in explosive mixtures have very low vapor pressures or limited olfactory receptor response making them unlikely odor signature chemicals. For example, single-based smokeless powder contains primarily involatile nitrocellulose but dozens of volatile aromatic organic compounds have been identified including plasticizers (phthalates), stabilizers (including diphenylamine, methylcentralite and ethylcentralite) and nitro and nitroso derivatives of diphenylamine formed by its reaction with the degrading nitrocellulose [20]. Some of the other volatile aromatic organic compounds identified in smokeless powder are cresol, nitrotoluene, carbazole, nitrotoluene, dimethyl phthalate, nitroso diphenylamine, *N*-nitrosodiphenylamine, dinitrocresol, carbanilide, nitrodiphenylamine, diethyl phthalate, trinitrotoluene, dinitrodiphenylamine, dibutyl phthalate, diphenyl phthalate, and triphenylphosphoric acid ester [20]. Obviously, the volatile aromatic organic constituents can be complex and isolating the specific chemical(s) used by dogs to detect an explosive is an equally complex task. Double-based smokeless powder contains added nitroglycerin and triple-based smokeless powder also has added nitroguanidine which themselves may serve as target chemicals for detection. On the other hand, explosive mixtures which have common volatile odor components can reduce the number of training aids needed and in some cases only a representative from each major class is used in training although peer reviewed scientific studies supporting the validity of this approach are lacking.

The most volatile constituents may be the primary odorant signature chemicals but also can contribute to cross contamination issues when explosives are stored together. One study demonstrated that volatile components such as EGDN and DNT can cross contaminate explosives stored nearby resulting in dogs trained to alert to perhaps as few as two of the most volatile explosive odorants rather than the nine parent explosives used in training [21]. A study on the stability of explosive traces on the surface of containers indicates that TNT, PETN and RDX can reside on surfaces for days, with 32% of 2,4,6-TNT remaining on surfaces after 24 h; whereas, the more volatile EGDN, NG and DNT dissipated quicker with 18% of 2,4-DNT remaining after 60 min [22]. Previously, experiments performed with dogs trained and tested under behavioral laboratory conditions with air dilution olfactometry, versus actual law enforcement field trained dogs, showed that signature odor chemicals in Composition C-4 could include cyclohexanone and 2-ethyl-1-hexanol; whereas, signature chemicals in nitroglycerine-based smokeless powder might include acetone, toluene and limonene although they were not the same across all the dogs tested. [23]. Recently, the authors have conducted laboratory and field experiments on certified law enforcement detector dogs under simulated search conditions [24].

Human detection

While dogs have been used extensively for many years in search and rescue and tracking of humans, one controversial area is their use in scent identification lineups of suspects. Recent studies have demonstrated that with a proper experimental protocol, the reliability of canine scent identifications is comparable or superior to human eyewitness identifications and some common laboratory methods including toolmarks and hair analysis [25]. The use of dogs to locate human remains is popular because they are accurate, relatively inexpensive, quick, thorough and can cover large areas functioning during day or night [26, 27]. However, once again, the unique odor signature chemicals used by these dogs have had limited scientific study. Immediately after the biological death of a human, the scent emitted by the body changes and bacteria in the environment quickly cause the degradation of carbohydrates, proteins, and lipids to various acids, gases, and other products which are the basis of color changes, foul odors, and bloating. The unpleasant odors associated with decay come from the anaerobic stage of decomposition known as putrefaction [28]. Compounds identified in the headspace of cadaver samples allowed to decompose for various amounts of time included 1,5-diaminopentane (cadaverine), 1,4-diaminobutane (putrescine), *p*-cresol, benzopyrrole (indole), 3-methyl-1-indole (skatole), dimethyl-sulfides, and organic fatty acids [28]. Cadaver dogs have been trained with a variety of natural and artificial materials. Decaying human flesh and human blood contain a wide range of the by-products of decomposition and putrefaction and provide the most authentic source but involve biological risks. However, these natural materials are not always accessible and putrescine and cadaverine have been used to imprint and reinforce canines for cadaver searches [29]. Cadaverine and putrescine are produced from the decarboxylation of amino acids, lysine and arginine respectively [30]. The analysis of these very polar organic molecules often requires the use of derivatization, specialized injection methods such as cold on-column or HPLC methods [30, 31]. SPME has been applied to the gas-phase analysis of trimethylamine, propionic and butyric acids, and sulfur compounds [32]. In locations where human remains are difficult to access, pigs have been used to train cadaver dogs. However, it has been demonstrated that dogs can differentiate between human and pig remains (Lowy A, Miami-Dade Police Canine Unit, unpublished results). The biological makeup of humans and pigs is very similar and pigs have been used to grow human organs, which implies that the decomposition from pigs and humans may also be very similar. Research to differentiate the odor signatures of human and pig decomposition could create additionally training aids to complement the biohazardous natural decomposition products and could help make the cadaver dog more efficient.

Experimental

All solvents used were Optima grade purchased from Fisher Scientific (Pittsburgh, PA, USA). Compounds used in preparation for the field studies were purchased from Sigma (St. Louis, MO, USA) with the exception of 2,4-dinitrotoluene (99.3% solid) and 2,4,6-trinitrotoluene (1000 μg mL^{-1} in acetonitrile) which were purchased from Ultra Scientific (North Kingstown, RI, USA). DFLEX devices with activated charcoal strip wrapped in Teflon were obtained from Albrayco Laboratories (Cromwell, CT, USA). Solid-phase microextraction (SPME) holders, fibers and portable fibers were obtained from Supelco Company (Bellefonte, PA, USA) and conditioned prior to used according to manufacturer recommendations. The SPME fibers investigated were 100 μm polydimethylsiloxane (PDMS), 65 μm PDMS/divinylbenzene (PDMS/DVB), 85 μm polyacrylate (PA), 65 μm Carbowax/DVB (CW/DVB) and 75 μm Carboxen/PDMS (CAR/PDMS). The polymer bottles used in the permeation studies were low-density polyethylene, high-density polyethylene and polypropylene purchased from Nalgene (Rochester, NY, USA). Electrical metal boxes were purchased from a local hardware store. Custom stainless steel "scratch" boxes were manufactured by American Aluminium (Miami, FL, USA). Helium gas, UHP/Zero Grade, was obtained from Air Product (Allentown, PA, USA). Clear screw top sampling vials (10 mL) with phenolic cap and PTFE/Silicone septa were purchased from Sulpelco. Over the counter tablets sampled were all purchased at a local drug store. Tablets sampled included Advil (Ibuprofen), Motrin (Ibuprofen), Excedrin (aspirin), Tylenol (acetaminophen), Pepcid Complete (antacid), Centrum (vitamin), Dramamine (motion sickness pill), Sominex (sleeping pill), Ex Lax (laxative), Benadryl (anti-histamine), Triaminic (anti-congestive), Certs (breath mint) and Ice Breakers (breath mint). Non-hazardous explosives for security training and testing (NESTT) samples were from XM division Van Aken International (Rancho Cucamonga, CA, USA). Freezer zip lock bags used for sampling large quantities of MDMA and presenting pseudo MDMA were purchased at a local supermarket. A "pseudo" MDMA was prepared from 1 g piperonal (Aldrich, Milwaukee, WI, USA) mixed with 9 g silica gel (Whatman 60A; Clifton, NJ, USA) in a mortar and pestle and shaken for 30 min to insure a complete mixture.

GC/MS analyses were carried out on an HP 6890 series GC system with an HP 5973 Quadrupole Mass Selective Detector. A HP Chemstation was used for instrument control and data analysis. A 30 m×0.25 mm HP-5MS capillary column with a 0.25 μm film thickness and a helium flow rate was 1 mL min^{-1}. The injector port temperature was kept at 250 °C and the runs were done in splitless mode and then split after 2 min. The MS source temperature was set at 230 °C while the MS quad temperature was set at 150 °C. For the explosives studies, an HP5890 Series II gas chromatograph with a ^{63}Ni electron-capture detector (ECD) was employed. The flow rate of He was 1 mL min^{-1} and the solvent delay time was set at 1 min. The injector port and detector was operated at 180 °C and 250 °C, respectively. For the polymer permeation studies, the plots of permeation rate were based on the change of weight of each chemical every one-week with the standard deviation based on triplicate measurements. 1 g of nitromethane, cyclohexanone and 2-ethyl-1-hexanol were placed into three 30 mL bottles each of 0.89 mm thickness and made of high density polyethylene (HDPE), low density polyethylene (LDPE) and polypropylene (PP) with cap closed and kept on the bench at room temperature.

Optimal fiber chemistry selection experiments including recoveries, extraction times and desorption times were performed in triplicate. For MDMA odors the CW/DVB and PDMS fiber proved best. Several of the same tablets (blue spade logo) were extracted after crushing into a powder as well as in whole tablet form using headspace SPME with a CW/DVB fiber for 3 h as well as by liquid–liquid extraction. Liquid–liquid extraction was performed by dissolving 0.01 g of the powder form of the blue spade tablet in 1 mL of a 2 mol L^{-1} NaOH solution extracted with 1 mL of methylene chloride and 1 μL of the resulting mixture was directly injected into the GC/MS. Large quantities of MDMA (>1 kg) were sampled in the Miami-Dade Police Department (MDPD) crime lab using a portable SPME apparatus (Supelco) and compared to analyzing smaller samples down to individual tablets. The single tablet sampled was placed in a 10 mL vial and the headspace compounds were extracted using the CW/DVB fiber for 3 h. These tablets weighed 0.15 g each, were round, yellow in color and had a smiley face logo on one of its faces. The 1 kg sample of MDMA was placed into a freezer zip lock bag sealed and the portable SPME fiber was then introduced into the headspace of the zip lock bag and sampled for 3 h and analyzed by GC/MS.

For the canine field experiments, two different odor delivery devices were employed which enclosed filter papers spiked before each run or permeation bottles containing odorants. Initially, electrical boxes were employed which were round galvanized steel boxes with small-drilled holes on the top to allow diffusion of the compounds into the atmosphere. Later studies employed larger steel "scratch" boxes which also contain drilled holes on one of its faces where a metal box on the opposite side is easily slid in and out as to allow for positioning of the samples or compounds of interest. Prior to any field study experiments implementing the use of the electrical boxes as the sniffing device, all of the boxes used were washed with hot water and soap and rinsed with acetonitrile or acetone and finally with deionized water (DI) water in order to assure cleanliness. Electrical boxes were dried overnight in an oven at 100 °C while scratch boxes were rinsed with water and air dried in the sun prior to any experiments. For the cadaver dog studies, human decomposition fluid used by the Miami-Dade Police Canine Unit was sampled by SPME. Preparation of materials used in field studies and SPME analysis was performed inside a vented biological safety cabinet. Three fibers, PDMS, PDMS/DVB, and CW/DVB, were exposed to an array of adsorption times ranging from 5 to 60 min. Prior to the dog runs, the samples were prepared in PTFE/Silicone septa vials and placed in individual HDPE jars to avoid contamination. Cadaver dog searches were performed to simulate typical search conditions and were performed outdoors in open fields. Previously unused concrete blocks were lined up with at least 10 feet in between each. 250 μL of the liquid standards and 0.25 g of the solid were placed in separated blocks. Each dog was allowed to inspect the field with the empty concrete blocks before the run. After the compounds were randomly placed inside the blocks, the handler would perform a sweeping search of the blocks.

Results and discussion

DFLEX activated charcoal strips were exposed to two different 250 g samples of MDMA tablets, eluted and analyzed by GC/MS. It was determined that none of the compounds identified, with the exception of two, were in concurrence with previous reported SPME results where volatile odor compounds within MDMA were being identified for possible source determination [8, 16, 17, 18]. Additionally, the two compounds of interest that were recovered (piperonal, a starting material for the synthesis of MDMA and 3,4-methylenedioxyketone, also known as MD-P2P, an intermediate in the synthesis) were recovered at very low abundances. Attempts to sample five tablets for up to 1 week in the laboratory were not successful in recovering any odor components. Subsequent experiments focused exclusively on SPME which provided sufficient sensitivity to sample even individual tablets rapidly. A comparison of the SPME headspace and a liquid/liquid solvent extraction of an MDMA tablet are shown in Fig. 3. Headspace SPME recovered methamphetamine, piperanol, MD-P2P and MD-phenyl-2-propanol as major volatile components whereas with methylene chloride/water extrac-

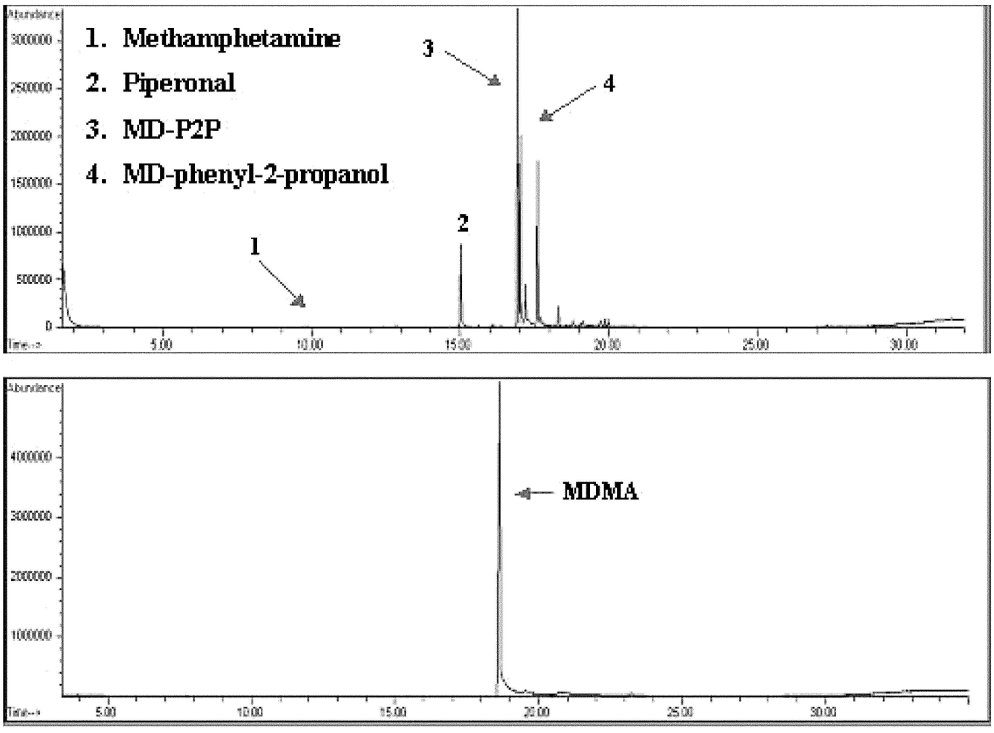

Fig. 3 Comparison of major chemicals extracted from MDMA tablet by direct extraction (*bottom*) versus headspace SPME (*top*)

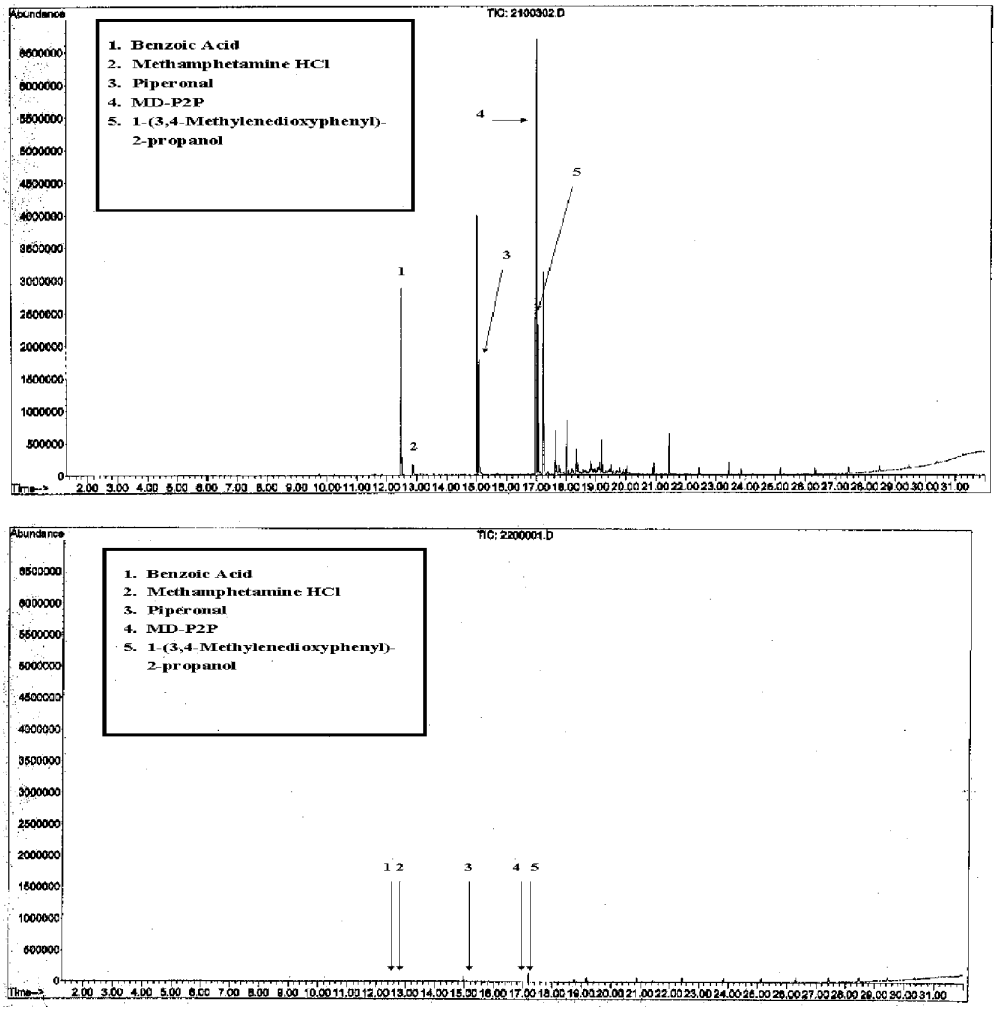

Fig. 4 Solid-phase microextraction (SPME)/gas chromatography–mass spectrometry (GC–MS) of MDMA (*top*) and aspirin (*bottom*) tablets showing no common odor chemicals in the two samples

tion of a MDMA tablet the major peak that was recovered was MDMA itself with a very small peak identified as *N*-formyl-*N*-methyl-3,4-methylenedioxyamphetamine which is another intermediate in the synthesis of MDMA. It was already established from the headspace analysis that the probable synthetic route of synthesis for these tablets were from piperonal to MD-P2P to MDMA. However, as discussed above, MD-P2P may also be reacted with *N*-methylformamide in a Leuckart reaction, and MDMA obtained by the hydrolysis of the intermediate *N*-formyl derivative [10]. These findings indicate that the synthetic route is probably piperonal to MD-P2P to *N*-formyl-*N*-methyl-3,4-methylenedioxy amphetamine to MDMA. In addition to providing useful information regarding synthetic routes, these results provide another example where the target compound, in this cases MDMA, is not available in the headspace and more volatile components serve as odor signature chemicals.

Fiber selection is one of the most important parameters in SPME method development, since it greatly affects the efficiency of extraction. For the MDMA studies the optimal fibers were PDMS and CW/DVB as these fibers yielded the highest recoveries and had optimal extraction times of 3 h above which only modest increases in recoveries were seen. The headspace analysis of street samples of MDMA indicate that there are a variety of odor chemicals commonly seen including benzoic acid, methamphetamine, piperonal (3,4-methylenedioxybenzaldehyde), MD-P2P (3,4-methylenedioxyphenyl-2-propanone) and MD-phenyl-2-propanol (3,4-methylenedioxyphenyl-2-propanol) as seen in Fig. 4. Among the compounds that were discovered to be present in the headspace of the samples, the most abundant compound was the intermediate MD-P2P. Also of interest was the presence of the starting material piperonal and the reduced alcohol form of MD-P2P, 1-(3,4-methylenedioxyphenyl)-2-propanol. Within these samples, the presence of methamphetamine was also of note, although at very low abundances. Various over the counter tablets were sampled in an identical fashion but none of these primary volatile components were identified. Typical mass chromatograms for MDMA and an aspirin tablet extracted by this method are shown in Fig. 4. These are important findings if any or a combination of these primary odor components are the chemicals used by detector dogs to find MDMA. Another potentially important factor is the relative ratios of these chemicals in different samples. The ratios of piperanol, MD-P2P and methamphetamine in the headspace for five different MDMA tablets sampled 3 h with the CW/DVB fiber are shown in Figure 5. The ratio results show that the piperonal abundance relative to the abundance of methamphetamine varied from 16 to 82 times greater, the MD-P2P abundances relative to methamphetamine are 30 to 77 times greater and the MD-P2P abundances relative to the piperonal are from 3 to 7 times greater depending on the tables compared. These results demonstrate that there is great variability between the ratios of odors in MDMA headspace which is useful for profiling applications but may be problematic if multiple odor molecules are used by detector dogs and a simulated odor is required. Interestingly, the headspace SPME (3 h with CW/DVB) of one of the MDMA tablets sampled as a whole tablet and crushed into a powder showed nearly identical odor signature patterns indicating that diffusion of these compounds into the headspace are not impaired by fillers or binders as part of the tablet formation. Also, It was observed that as the sample size was increased, the predominate volatile compound found in the headspace of the sample increasingly became piperonal. Since the canines were trained and reinforced

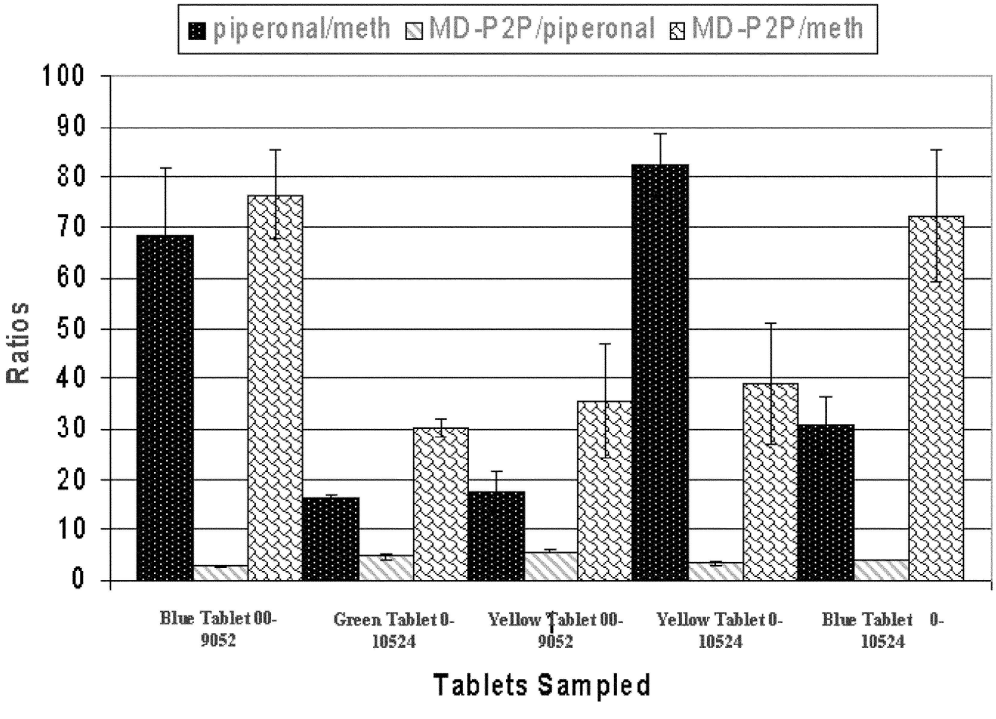

Fig. 5 Comparison of ratios of piperanol, MD-P2P, and methamphetamine in the headspace of five different MDMA tablets

Table 2 Summary of detector dog field tests with various odor chemicals

Chemical	Non alert (N)	Alert (A)
0 mg	30, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, (100%, 23/23)	
Isosafrole, 10 µL	30, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, (100%, 23/23)	
Phorone, 10 µL	30, 32, 33, 34, 35, 36, 37, 38, 39, 40[a], 41[a], 42, 43, 44, 45, 46, 48, 49, 50, 51, 52, 53, (96%, 22/23)	47 (4%, 1/23)
Camphor, 10 mg	30, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, (100%, 23/23)	
Piperonal, 10 mg	32, 33[a], 34[a], 35, 36[a], 37[a], 38[a], 39[a], 41, 42, 43[a], 44, 45, 46, 48, 49, 50, 51, 53, (83%, 19/23)	30, 40, 47, 52 (17%, 4/23)
Safrole, 10 µL	30, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, (100%, 23/23)	
Benzaldehyde 10 µL	30, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, (91%, 21/23)	45, 47 (9%, 2/23)
Acetic acid, 10 µL	30, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41[a], 42, 43, 44, 45, 46, 47, 48[a], 49, 50, 51, 52, 53, (100%, 23/23)	
1-Phenyl-2-propanol (P2P), 10 µL	30[a], 32, 33[a], 34[a], 35[a], 36, 37, 38[a], 39, 40, 41[a], 42[a], 43, 44, 45, 46, 47, 48[a], 49, 50, 51, 52, 53, (91%, 21/23)	51, 52 (9%, 2/23)
Acetophenone, 10 µL	30, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, (100%, 23/23)	

[a]Canine investigated but did not alert

on 35 g of MDMA, it is likely that the dominant signature odor that these dogs were being exposed was piperonal.

Field experiments were conducted with certified law enforcement drug detector dogs using metal electrical boxes containing isolated MDMA and methamphetamine headspace chemicals of varying amounts. One such experiment consisted of 100 µL of methylene chloride added without the addition of any compounds of interest to serve as a blank, and 100 µL of methylene chloride solutions spiked onto a filter paper contained in electrical boxes resulting in the final amounts of odorants listed in Table 2. The boxes were arranged along the wall of a room spaced out 5 feet apart. The dog handlers were not told of the contents in the boxes and were simply instructed to have their canines sweep the boxes for controlled substances. Results from the handlers were recorded as no alert, interest/canine investigated but no alert or alert. The results are summarized in Table 2. Many of the dogs showed interest in piperanol (from MDMA) and P2P (from methamphetamine) with 4 of the 23 dogs (17%) alerting to piperanol and 2 of the 23 dogs (9%) alerting to P2P and benzaldehyde. These later two chemicals have been previously demonstrated to be potential methampetamine signature chemicals [8]. Additional experiments were then conducted with increasing amounts of target compounds and varying ratios for multiple targets compounds. Field tests using different combinations of MD-P2P and piperanol were conducted using scratch boxes shown in Fig. 6 spaced five feet apart in a single file row along a inside hallway. In this experiment the dogs were presented with different ratios of MD-P2P to piperanol representative of those ratios found in the headspace of different MDMA samples in open and closed systems and at high concentrations of the pure compounds. 100 µL of methylene chloride solutions were spiked onto a filter paper resulting in the final amounts and combinations of odorants listed in Table 3. In addition, 5 g of methamphetamine pharmaceutical grade salt

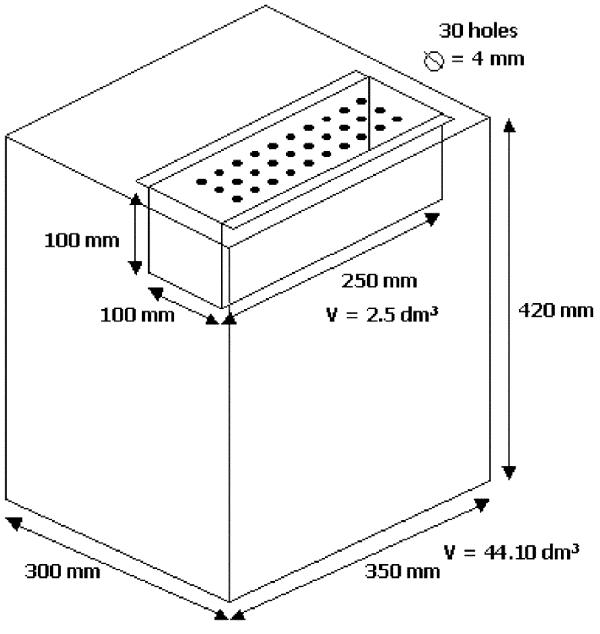

Fig. 6 Schematic diagram of box used in field tests

and 5 g of street methamphetamine were included in the test. In this experiment, the dogs were presented with different ratios of MD-P2P to piperonal representative of those ratios found in the headspace of an open system and in the headspace of a closed system with results summarized in Table 3. 83% of the canines tested alerted to the 10 mg piperonal sample and the one canine that did not alert to this compound showed some interest in it. Also, 17% of the canines alerted to the (1:1) ratio of MD-P2P to piperonal which indicates that piperonal is the primary odor chemical in an open system. None of the canines alerted to 5 g of the pharmaceutical grade methamphetamine while all of the canines in this experiment alert to the 5 g

Table 3 Summary of detector dog field tests with various odor chemicals

Chemical	Non alert (N)	Alert (A)
MD-P2P/Piperonal (1:1) 10000/10000 ppm (1/1 mg)	31[a], 32, 44, 46, 50 (83%, 5/6)	
MD-P2P/Piperoanl (3:1) 30000/10000 ppm (3/1 mg)	31, 32, 44, 46, 50, 53 (100%, 6/6)	
MD-P2P/Piperonal (5:1) 50000/10000 ppm (5/1 mg)	31, 32, 44, 46, 50, 53 (100%, 6/6)	
MD-P2P/Piperonal (10:1) 100000/10000 ppm (10/1 mg)	31, 32, 44, 46, 50, 53 (100%, 6/6)	
MD-P2P/Piperonal (5:1) 250000/50000 ppm (25/5 mg)	31, 32, 44, 46, 50, 53 (100%, 6/6)	
MDMA (bromo method) 100 µg	31, 32, 44, 46, 50, 53 (100%, 6/6)	
MD-P2P 100000 ppm (10 mg)	31, 32, 44, 46, 50, 53 (100%, 6/6)	
Piperonal 100000 ppm (10 mg)	31[a] (17%, 1/6)	32, 44, 46, 50, 53 (83%, 5/6)
Methamphetamine Pharm Grade, 5 g	31, 32, 44, 46, 50, 53 (100%, 6/6)	
Methamphetamine Street Sample, 5 g		31, 32, 44, 46, 50, 53 (100%, 6/6)

[a]Canine investigated but did not alert

Table 4 Results of detector dog field experiments with "pseudo" MDMA

Contain	Not Alert (N)	Alert(A)
Pseudo MDMA 0.1 g in Zip bag	16, 31, 32, 45 (80%, 4/5)	29 (20%, 1/5)
Pseudo MDMA 1 g in Zip bag	31, 32, 45 (60%, 3/5)	16, 29 (40%, 2/5)
Pseudo MDMA 10 g in Zip bag	32 (20%, 1/5)	16, 29, 31, 45 (80%, 4/5)
FHP MDMA tablets (28 g)	29 (20%, 1/5)	16, 31, 32, 45 (80%, 4/5)

street methamphetamine sample. Canine field tests were run with a "pseudo" MDMA prepared from 1 g piperonal (Aldrich, Milwaukee, WI, USA) mixed with 9 g silica gel (Whatman 60A, Clifton, NJ, USA) in a mortar and pestle and shaken for 30 min to insure a complete mixture. Results of a field tests performed with a "pseudo" MDMA containing 10% piperanol are summarized in Table 4. Up to 80% of the dogs certified to detect MDMA alerted to the "pseudo" MDMA and of two dogs trained on the "pseudo" MDMA, one alerted to the 28 g of MDMA whereas the other did not. While these results represent a very limited data set they support the hypothesis that the dominant odor signature chemical in MDMA is piperanol.

Figure 7 compares GC/ECD response of mixture of the TNT odor chemicals 1,3-DNB and 2,4-DNT extracted by different fibers at 5 s and 1 min. The results showed that PDMS was the most sensitive fiber while PDMS/DVB was the least sensitive fiber for extraction of 1,3-DNB and 2,4-DNT at each extraction time. The overall performance of PA and CW/DVB was very close. When the extraction time was shorter, the sensitivity of PA was better; when the extraction time was longer, the sensitivity of CW/DVB was generally better. Also, it was found that as the extraction time increased, the GC/ECD response of CW/DVB increased more quickly than that of other fibers, and it tends to have similar or even larger sensitivity, compared with PDMS when the extraction time is longer. During the study of fiber selection, CAR/PDMS was found unsuitable for extraction of TNT odors and analysis of GC/ECD, since it showed poor desorption efficiency as well as an observed loss of sensitivity of the ECD due to possible contamination from the fiber. The results demonstrate that the choice of the "best" SPME fiber is not always a straightforward decision and depends on various factors. When the sensitivity of fiber is the only factor considered

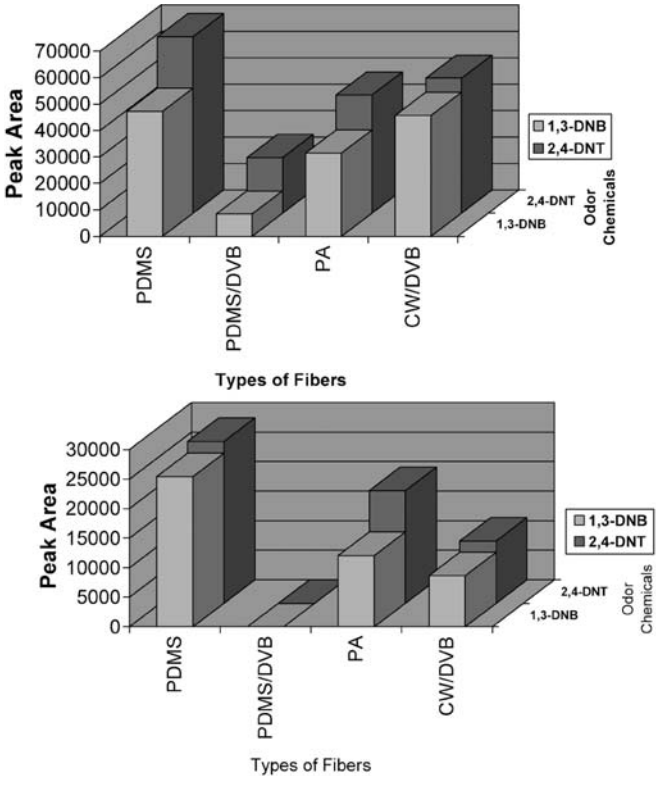

Fig. 7 Comparison of TNT odor chemicals extracted by different fibers for 1 min (*top*) and 5 s (*bottom*)

for selection of fibers, PDMS, PA and CW/DVB are all reasonable fibers for analysis of TNT odor signature chemicals. However, PDMS proved more suitable to extract samples in field, which require fast sampling and rapid desorption. On the other hand, CW/DVB and PA are bet-

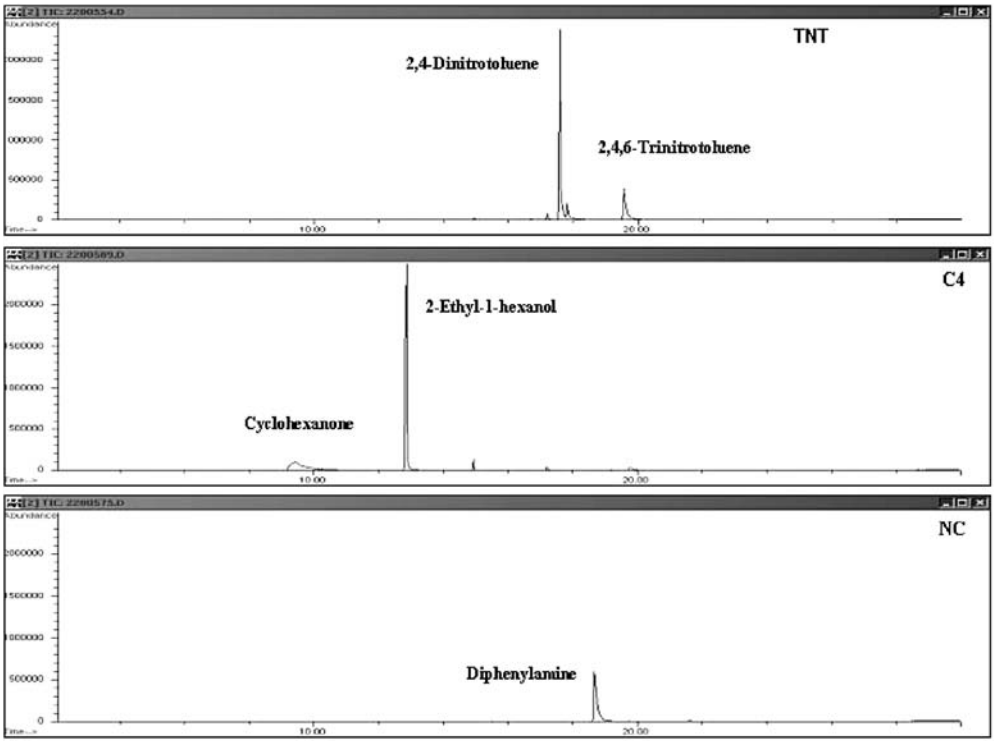

Fig. 8 Comparison of major chemicals isolated from the headspace of TNT, C4, and NC using headspace SPME

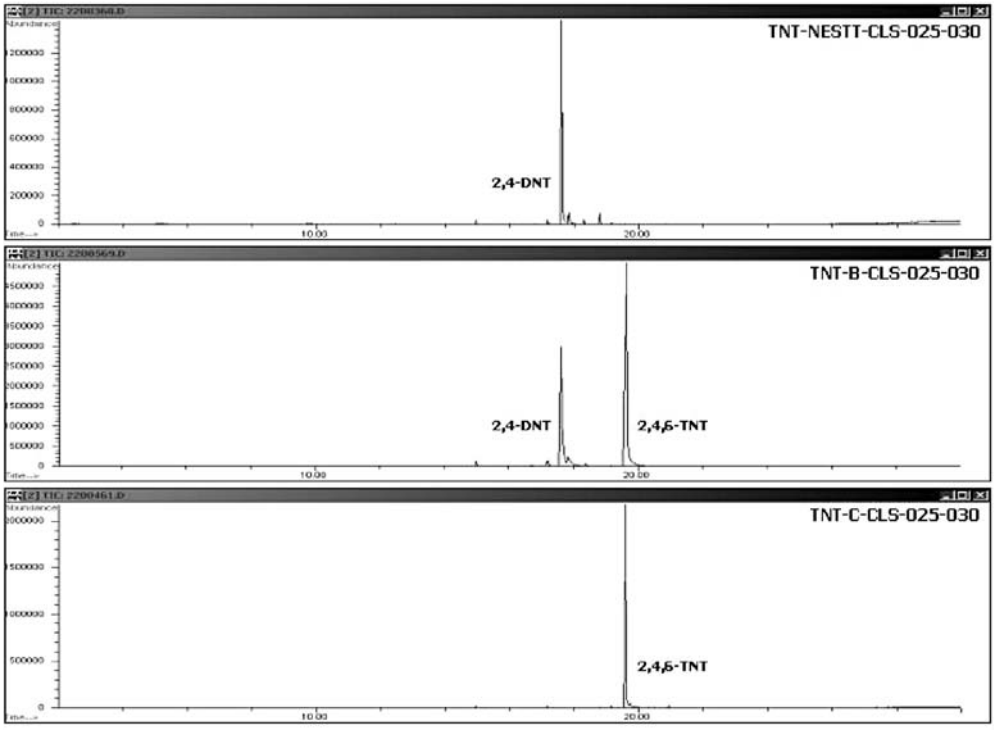

Fig. 9 Comparison of the major chemicals isolated from the headspace of TNT NESTT training aid and two different TNT samples

ter fibers when used in lab analysis with extended adsorption and desorption times. However, for longer extraction studies, CW/DVB was better than PA, and the best overall fiber for long extraction times. Moreover, the conditioning time of PA fibers requires 2 h, which is time-consuming and can significantly increase the analytical time of the SPME method. The time needed to completely desorb the explosives from each fiber demonstrated that complete desorption was achieved after 1 min for PDMS and PA, 2 min for PDMS/DVB and 4 min for CW/DVB. For laboratory analysis purpose, five-minutes desorption time were used to eliminate any possible carry-over from one run to the other. The desorption time profile further proved that PDMS was the best fiber for field applications

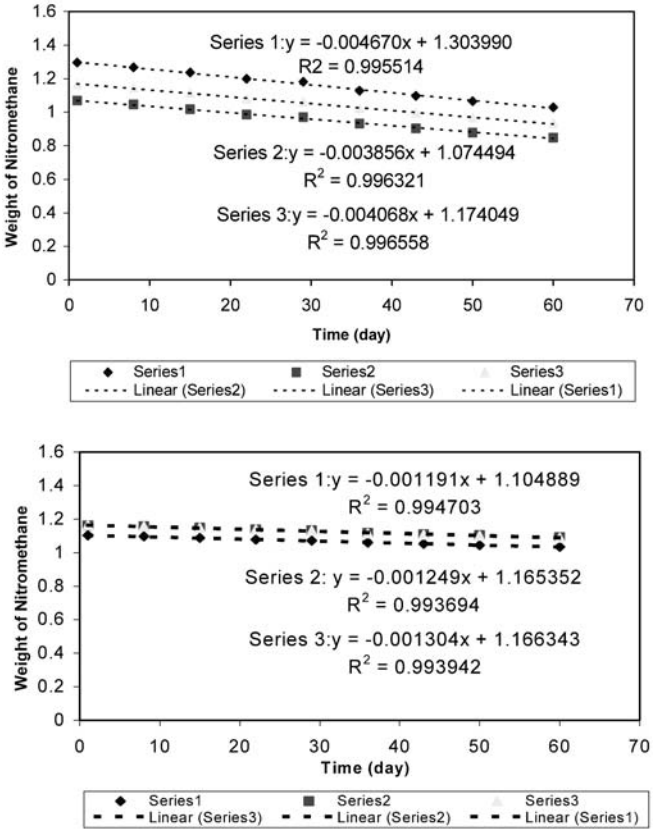

Fig. 10 Permeation of nitromethane from LDPE (*top*) and HDPE (*bottom*) over a two-month period

which required fast sampling and desorption. Overall, the best fiber for field applications was PDMS while that for laboratory analysis was CW/DVB where longer adsorption and desorption times can be employed. Headspace SPME/GC/MS of various actual explosives samples shows 2,4-DNT and 2,4,6-TNT as the primary odor chemicals in TNT samples, cyclohexanone and 2-ethyl-1-hexanol predominant in the headspace of C4 and diphenylamine in the headspace of smokeless powder as shown in Fig. 8. However, cyclohexanone is sometimes missing in more weathered samples studied. Analysis of NESTT material and different TNT samples shows the presence of 2,4-DNT and/or the less volatile 2,4,6-TNT depending on the sample tested as shown in Fig. 9. The NESTT training aid sampled contained primarily DNT with the more weathered TNT sample containing primarily TNT.

Permeation experiments with target explosive odor chemicals demonstrated that the permeation rate of each chemical varied with different polymeric containers, and that the LDPE provided higher permeation rates than HDPE containers and that PP containers had limited permeation and poorer precision. The TNT odors did not permeate the bottles studied to any significant amount and the limited permeation measured was imprecise. Plots of the permeation of nitromethane over a two month period from LDPE and HDPE bottles are shown in Fig. 10 with average permeation rates listed in Table 5 for triplicate measurements.

Table 5 The average permeation rates (standard deviation), in ng s^{-1}, for odor chemicals in different polymer bottles

Odor chemical	Average permeation rate (S.D.) in ng s^{-1}	
	LDPE bottles	HDPE bottles
Nitromethane	53.240 (1.157)	14.232 (0.398)
Cyclohexanone	48.993 (4.819)	5.683 (0.564)
2-Ethyl-1-hexanol	3.472 (1.157)	0.660 (0.082)

LDPE bottles providing the highest permeation rates and best precision and were thus chosen for field testing by placing the bottles containing the odor chemicals within the scratch boxes previously used. The samples were delivered to the test fields and set up into two groups. One was TNT odor chemical that was spiked on filter paper in the field; the other was C-4 odor chemical that were contained in LDPE bottles. Also, TNT and RDX preparations of non-hazardous explosives for security training and testing (NESTT) were used as listed in Table 6. The results indicated that most of the explosive detector dogs tested alert to positive control chemicals, such as TNT (100% alert) and RDX (83.3% alert), but they alert to most chemicals of interest with different sensitivity. Among the odor signature chemicals tested, 2-ethyl-1-hexanol had the highest percentage of alerts followed by cyclohexanone. These field tests as well as additional ongoing field tests indicate that the odor chemical 2,4-DNT is a significant odor signature chemical in TNT, while 2-ethyl-1-hexanol is significant for C-4. These results demonstrate the potential use of these controlled permeation training aids, and may provide valuable information on threshold levels for future studies. Additional tests are underway involving combinations of these and other components as well as for all major classes of explosives.

For the cadaver dog studies, the PDMS/DVB fiber was determined to be the best fiber due to the amount of analytes recovered, the time needed to adsorb analytes and relative ease to work with. Problems encountered included indications of a possible stripping of the fiber by some of the corrosive components studied and the more polar components such as cadaverine and putrescine suffered from poor peak shape and derivatization is currently being investigated. SPME/LC/MS is also being investigated as a complement to these SPME/GC/MS analyses. Compounds isolated by headspace SPME/GC/MS of human materials revealed trimethylamine, 1-pentanol, hexanal, butanoic acid, pentanoic acid, heptanal, benzaldehyde, 2-pentryl furan, dimethyl disulfide, hexanoic acid, heptanoic acid, nonanoic acid, and octanoic acid. Major components seen in the headspace of pig decomposition materials were oleic acid, 2-Anthracenamine, propanoic acid, butanoic acid, and hexadecanoic acid. In field tests, positive cadaver dog responses have been observed with cadaverine, putrescine, indole and skatole. Further analysis and confirmation using additional samples and field tests with additional canine teams are ongoing to contrast the odor signatures of human and pig remains as well as various levels of individual odor components.

Table 6 Summary of canine tests on nine chemicals of interest

Chemical	Description	Non alert (N)[a]	Alert (A)	% Alert
Acetonitrile	Blank, 100 µL	1, 1, 2, 3, 4, 5, 6		0
2-ethyl-1-hexanol	1 g, LDPE bottle	2[b], 6	1, 1, 3, 4, 5	66.7
Nitromethane	1 g, LDPE bottle	1, 2[b], 3[b], 6[b]	1, 4, 5	50
Cyclohexanone	1 g, LDPE bottle	1[b], 1[b], 2[b], 3, 4[b]	5, 6	33.3
RDX NESTT	10 g, positive control	3[b]	1, 1, 2, 4, 5, 6	83.3
Acetonitrile	Blank, 100 µL	1, 2, 3, 4, 5, 6		0
1.3-Dinitrobenzene	100 ppm, 100 µL	2[b], 3[b], 6[b]	1, 4, 5	50
2,4-Dinitrotoluene	100 ppm, 100 µL	1[b], 2[b], 3[b]	4, 5, 6	50
2,4,6-trinitrotoluene	100 ppm, 100 µL	1, 2[b], 3, 6	4, 5	33.3
TNT NESTT	10 g, positive control		1, 2, 3, 4, 5, 6	100

[a]Random detector dog number with repeated number indicating multiple test
[b]Canine investigated but did not alert

Conclusions

Overall, these results demonstrate that SPME/GC/MS combined with field tests using certified detector dogs is an effective method for identifying active odor signature chemicals in forensic specimens. For the drug studies it was found that passive adsorption using DFLEX devices containing activated charcoal was not sensitive enough to recover signature odors from the headspace of MDMA tablets. Only when very large samples (i.e. greater than 250 g) were extracted for extended periods of time (i.e. 1 week) were odors reliably detected. However, with headspace SPME it was found that with the implemented use of the CW/DVB and PDMS fibers with 3 h extraction times it was possible to obtain consistent signature odors from the headspace of a single MDMA tablet. Many compounds of interest were found to be present in the headspace composition of these tablets, including piperonal, MD-P2P and methamphetamine. Through examinations of different tablets, however, it was concluded that the metamphetamine found within certain tablets were present due to its addition as an adulterant or contaminant and not the direct result of synthetic manufacturing and that piperonal and MD-P2P were the common chemicals seen in all samples tested. In studies where different over the counter tablets were analyzed, it was concluded that none of the headspace compounds found within these tablets were present in the headspace of MDMA tablets, therefore negating the possibility of false positive alerts from the canines in association with these commonly encountered tablets. Field studies directly focusing on the signature odor of MDMA have shown that canines are alerting to approximately 10–100 mg of the piperonal compound that is found exclusively in MDMA tablets. These results need further verification through repetitive field studies, but the results to date indicate that piperonal is the dominant odor used by the canines tested when alerting to MDMA samples. Since MDMA manufactured through different synthetic routes can yield different signature chemicals, it is important to perform ongoing studies of headspace odors from current street samples and more than one MDMA training aid may be required for optimal performance in the future.

The SPME/GC/ECD and SPME/GC/MS methods provided rapid (down to seconds) analysis of explosive odors with PDMS the best fiber tested for rapid field methods, due to rapid extraction and desorption process, and CW/DVB showing the greatest potential for laboratory uses employing longer extraction and desorption processes. Initial field tests indicate the potential use of polymeric controlled permeation devices and the effectiveness of RDX and TNT NESTT training aids. The results indicate that 2-ethyl-1-hexanol, and 2,4-DNT are dominant odor signature chemicals in C-4 and TNT, respectively. Additional work is underway to further optimize SPME/GC/ECD and SPME/GC/MS methods for laboratory and field use. Extraction of a larger variety of explosive samples, including under different field conditions, are ongoing and will allow for identification of additional odor signature chemicals. Additional field tests are also underway in order to identify and confirm active explosive odor signature chemicals, thresholds and the utility of a variety of controlled permeation devices and NESTTs. Additional experiments are underway to determine the preferential diffusion of odor signature chemicals under different environmental conditions. These studies should allow for the future development of improved training aids, which are safer to use, easier to acquire, and provide consistent levels of odor signature chemicals. The characterization of the dominant volatile odor signature chemicals in forensic specimens and those chemicals most important for detection by dogs are essential to interpreting and perhaps improving dog performance as well as improving the reliability of electronic vapor detectors.

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References

1. Furton kg, Myers LJ (2001) Talanta 43:487–500
2. Anon (1989) Crime and chemical analysis. In: Res News Sci 3/24:1555
3. Oyler J, Darwin WD, Cone E (1996) J Anal Toxicol 20:213–216

4. Negrusz A, Perry JL, Moore CM (1998) J Forensic Sci 43:626–629
5. Furton kg, Hsu Y-L, Luo T, Alvarez N, Lagos P (1997) In Hicks J, De Forest P, Baylor VM (eds) Forensic evidence analysis and crime scene investigation, Proc SPIE 2941:56–62
6. Furton kg, Hsu Y-L, Luo T, Rose S (1999) In: Higgins K (ed) Investigation and forensic science technologies, Proc SPIE 3576:136–141
7. Furton kg, Hong Y, Hsu Y-L, Luo T, Rose S, Walton J (2002) J Chromatogr Sci 40:147–155
8. Vu DT (2001) J Forensic Sci 46:1014–1024
9. Anon (2001) Drug Identification Bible. Amera-Chem Grand Junction CO
10. Shulgin AT (1986) J Psychoactive Drugs 18:291–304
11. Davis WM, Borne RF (1984) Substance Alcohol Actions/ Misuse 5:105–110
12. O'Brien BA, Bonicamp JM, Jones DW (1982) J Anal Toxicol 6:143–147
13. Braun U, Shulgin AT, Braun G (1980) J Pharm Sci 69:192–195
14. Inoue T, Tanaka K, Ohmori T, Togawa Y, Seta S (1994) Forensic Sci Int 69:97
15. Perkal M, Ng YL, Pearson JR (1994) Forensic Sci Int 69:77–87
16. Verweij A (1990) Forensic Sci Int 45:91–96
17. Renton R (1993) Forensic Sci Int 60:189–202
18. Mas F (1995) Forensic Sci Int 71:225–231
19. Lorenzo N (2002) MS thesis, FIU
20. Fetterolf DD (1995) In: J Yinon (ed) Forensic applications of mass spectrometry. CRC Press, Boca Raton, pp 215–257
21. Hallowell SF, Fisher DS, Brasher JD, Malone RL, Gresham G, Rae C (1997) In: Pilon P, Burmeister S (eds) Chemistry and biology-based technologies for contraband detection, Proc SPIE 2937:227–234
22. Kolla P (1997) In: Pilon P, Burmeister S (eds) Chemistry and biology-based technologies for contraband detection, Proc SPIE, 2937:236–244
23. Williams M, Johnston JM, Cicoria M, Paletz E, Waggoner LP, Edge CC, Hallowell SF (1998) In: DePersia AT, Pennella JJ (eds) Enforcement and securities technologies, Proc SPIE 3575: 291–301
24. Wan T (2002) MS thesis, FIU
25. Schoon GAA (1998) J Forensic Sci 43:70–75
26. Killam EW (1990) The detection of human remains. Thomas
27. Komar D (1999) J Forensic Sci 44:405–408
28. Haglund WD, Sorg MH (1997) Forensic taphonomy. CRC Press, Boca Raton, FL
29. Rebmann A, David E, Sorg MH (2000) Cadaver dog handbook. CRC Press, Boca Raton, FL
30. Tahim NM, Bennett LW, Shellem TA, Doerr JA (2002) J Agric Food Chem 50:5012–5015
31. Bonilla M, Enriquez LG, McNair HM (1997) J Chromatogr Sci 35:53–56
32. Kim H, Nochetto C, McConnell LL (2002) Anal Chem 74: 1054–1060