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A Comparison of Real Versus Simulated Contraband VOCs for Reliable Detector Dog Training Utilizing SPME-GC-MS

Odor detection has become a focused area of research because of its importance to the forensic, law enforcement, and legal communities. Despite the abundance of methods for the detection of these characteristic chemical odors, the use of trained canines as biological detectors remains widely accepted. Thus, detector dog response is one of the major applications involved in odor detection studies, both to determine the chemical signature of individual odors to which the canines are actually alerting, and to discover if there is a common element within different items to support the use of contraband mimics.

Previous research has demonstrated that a compilation of chemical odors can be detected in individual contraband samples, including several common odors as well as uncommon odors.[1,2] Current commercially available pseudo aids contain different amounts of either the actual explosive/narcotic or the chemical compound of suspected interest by canine detectors. The main chemical compound in a substance is not always the dominant volatile compound due to the low vapor pressure or limited olfactory receptor response.[3] In addition, it has been shown that only specific odors are used by canines to detect the various forms of contraband.

Narcotics detection

Detector dog teams are trained to detect most commonly found illicit narcotic substances (i.e., marijuana, heroin, cocaine, and methamphetamines). It has been shown that canines respond to volatile organic compounds (VOCs) in the headspace above the drug instead of the parent compound itself. One case in which this has been proven is for cocaine. Field tests have shown that the trained law enforcement detector dogs respond to the compound methyl benzoate.[3–5] This implies that methyl benzoate must be the dominant odor chemical signature for cocaine.

The headspace above marijuana has been repeatedly sampled and shown to possess a complex array of organic compounds. This list includes α-pinene; β-pinene; myrcene; limonene; and, in many cases, β-caryophyllene. These compounds have been shown to dominate the headspace of marijuana samples (upwards of 85%[6–8]). In a similar manner, it has been conjectured that acetic acid is the dominant odor compound in heroin samples.

Explosives detection

Classification by chemical groups is a common method, especially for research purposes. This is done by classifying explosives into one of the following five groups: organic nitrates (which include aliphatic nitro and aromatic nitro), nitrate esters, nitramines, acid salts, and peroxides.[1,2]

As with drugs, canines respond to VOCs in the headspace above explosives instead of the parent compound itself. An example is single-based smokeless powder, in which the main compound is nitrocellulose, an involatile compound. However, certain common odors, including 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), and diphenylamine (DPA—a stabilizer), and uncommon odors, such as ethyl centralite (a stabilizer), have been found to be present in these smokeless powders.[1,2,9,10] The compound identified as the canine active odor for single-based smokeless powders is 2,4-DNT.

Methodology

All solvents were purchased from **Fisher Scientific** (Pittsburgh, PA). The compounds used to create the field samples were purchased from **Sigma-Aldrich** (St. Louis, MO). A 70-µm StableFlex Carbowax®/

Table 1 Field testing of heroin mimics

Content	No alert	Interest	Alert	% Alert
Pseudo Heroin scent	101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111	112	—	—
Blank gauze	101, 102, 103, 104, 105	—	—	—
Acetic acid, 100 µL on gauze	101, 102, 103, 105, 106, 107, 108, 109, 110, 111, 112	—	104	8%

Table 2 Field testing of marijuana mimics

Content	No alert	Interest	Alert	% Alert
Empty Sigma Pseudo scent cage	106, 107, 108, 109, 110, 111, 112	—	—	—
Sigma Pseudo Marijuana scent	106, 107, 108, 109, 110, 111, 112	—	—	—
Blank gauze	106, 107, 108, 109, 110, 111, 112	—	—	—
Mixture A*, 250 µL on gauze	106, 107, 108, 109, 110, 111, 112	—	—	—
Dichloromethane, 100 µL on gauze	106, 107, 108, 109, 110, 111, 112	—	—	—
Mixture B**, 250 µL on gauze	106, 107, 108, 109, 110, 111, 112	—	—	—

*50 µL at 100 ppm each of α-pinene, β-pinene, myrcene, limonene, and β-caryophyllene.
**50 µL at 50 ppm each of α-pinene, β-pinene, myrcene, limonene, and β-caryophyllene.

divinylbenzene (CW/DVB) solid-phase microextraction (SPME) fiber was purchased from **Supelco** (Bellefonte, PA). The samples were presented using Sigma Pseudo scent cages. The commercial narcotic pseudo scents were Sigma Pseudo Narcotic scents. Nonhazardous explosives for security training and testing (NESTT) samples utilizing the silica form were purchased from **Ray Allen Manufacturing Co.** (Colorado Springs, CO). Headspace vials (40 mL) fitted with phenolic plastic caps and a PTFE/silicon septum were purchased from **Supelco**. Sterile 5.1 × 5.1 cm gauze sponges were obtained from **IMCO (Independent Medical Co-op, Inc.,** Daytona Beach, FL).

The GC-MS analysis was performed on an Agilent 6890 series with HP 5973 quadrupole mass spectrometer (**Agilent Technologies**, Wilmington, DE). An HP5 30 m × 0.25 mm capillary column (**Agilent**) with 25 µm film thickness and a helium flow rate of 1 mL/min was used. The injection port was held at 235 °C with 5-min SPME desorption. The MS temperature was 230 °C. The oven program began with a 40 °C hold for 5 min, followed by a 10 °C/min ramp to 290 °C, and ending with a 1-min hold at 290 °C. A 1.2-min solvent delay was used. Two standard solutions were made for each compound at 100 ppm and 50 ppm with dichloromethane.

For the Sigma Pseudo scents, 5 g was weighed and heat-sealed within 3-mm low-density polyethylene (LDPE) bags. Two spiked gauzes were prepared (mixture A and mixture B) comprised of 50 µL each of five compounds: α-pinene, β-pinene, myrcene, limonene, and β-caryophyllene. Both types of samples were placed in the Sigma Pseudo scent cages on site for testing. For the NESTT canine field trials odor delivery system, 5 g of each sample contained within an open vial was placed inside a sterile quart can.

For the dissipation study, 50 µL of a compound (each in turn) was spiked onto a single piece of gauze. The mass of the gauze was recorded prior to spiking and immediately afterward. The mass was then recorded over a period of 30 min at 0.5-min, 1-min, and 5-min intervals. The process was repeated in triplicate. Statistical analysis was performed, and the results were plotted.

Results

Field experiments were conducted with certified law enforcement drug detector dogs. The scent cages were arranged in a line such that each sample was approximately 1 m apart. Each detector dog team was allowed to walk the line and sample the odor emanating from each cage. The handlers were not informed of the contents of each sample prior to the run. In addition to the two samples, blank gauze sealed in a 3-mm LDPE bag was included as a negative control. As shown in *Table 1*, no canine alerted to the 5-g sample of the Sigma Pseudo Heroin scent. Canine 112 showed interest in the sample. Only one canine alerted (8%) to the acetic acid sample.

A similar setup was used for the marijuana pseudo sampling. Each detector dog team was allowed to walk the line and sample the odor emanating from each cage. In addition to the target odors, empty scent cages, blank gauze sealed in a 3-mm LDPE bag, and a dichloromethane sample were included as negative controls. The results of the marijuana pseudo testing are shown in *Table 2*. None of the detection teams alerted to the Sigma Pseudo Marijuana scent. The mixtures were composed of previously reported headspace components of marijuana samples. None of the canines alerted to either of the mixed spikes. In addition, no false positives can be reported.

For the field tests, the samples were again placed in a line format. Each sample was placed within a quart paint can. In addition to the NESTT aids, blank silica (negative control) and an actual explosive (positive control) were included. A data sheet was used as the positive control and returned a 100% alert response from the canines. In the double-blind studies that followed, none of the detector dog teams alerted to any of the NESTT aids, although canine 516 did show interest in the nitrate and RDX aids. The overall results for these trials can be seen in *Table 3*.

The dissipation study shows the dissipation rate for each of the compounds tested. As each compound slowly

Table 3 Field testing results of NESTT aids

Content	No alert	Interest	Alert	% Alert
Silica: 5 g in open vial	501, 503, 508, 509, 512, 513, 516, 517, 518, 519	—	—	—
Empty quart can	501, 503, 508, 509, 512, 513, 516, 517, 518, 519	—	—	—
NESTT chlorate, 5 g silica in open vial	501, 503, 508, 509, 512, 513, 516, 517, 518, 519	—	—	—
NESTT nitrate, 5 g silica in open vial	501, 503, 508, 509, 512, 513, 517, 518, 519	516	—	—
Empty quart can	501, 503, 508, 509, 512, 513, 517, 518, 519	516	—	—
Deta sheet (½ lb)	—	—	501, 503, 508, 509, 512, 513, 516, 517, 518, 519	100%
Empty quart can	501, 503, 508, 509, 512, 513, 516, 517, 518, 519	—	—	—
NESTT PETN, 5 g silica in open vial	501, 503, 508, 509, 512, 513, 516, 517, 518, 519	—	—	—
Empty quart can	501, 503, 508, 509, 512, 513, 516, 517, 518, 519	—	—	—
NESTT RDX, 5 g silica in open vial	501, 503, 508, 509, 512, 513, 517, 518, 519	516	—	—
Empty quart can	501, 503, 508, 509, 512, 513, 516, 517, 518, 519	—	—	—
NESTT TNT, 5 g silica in open vial	501, 503, 508, 509, 512, 513, 516, 517, 518, 519	—	—	—

evaporated from the gauze, the mass of the gauze could be seen to decrease over time. The results for the dissipation study are shown in *Figure 1*. Both α-pinene and β-pinene dissipated at an exponential rate, with alpha having the more pronounced curve. Limonene and myrcene dissipated at an almost linear rate, with limonene being slightly slower. Beta-caryophyllene dissipated very little over the course of the 30 min, producing a seemingly straight line. To confirm that the headspace intensity changes over the course of time, gauze spiked with each of the five compounds was sampled with SPME. The headspace for the gauze was taken for three samples (immediately, 30 min, and 60 min after solvent drying). These results are shown in *Figure 2*. The intensity of each compound is shown to decrease over time.

Discussion and conclusion

Even though there is sufficient proof to support that SPME helps identify volatile odor compounds from parent contraband, not all the dominant components are the actual identifiers used by detector dogs. This can be seen from the poor alert response found when testing mixtures of five of the major components detected in the headspace of marijuana (α-pinene, β-pinene, myrcene, limonene, and β-caryophyllene). The dissipation study demonstrates that this may be due in part to the short amount of time the compound remains detectable. One relationship that can be drawn from Figures 1 and 2 is that the later the elution time of the compound, the slower the rate of dissipation. The results found with the commercially available products (i.e., the Sigma Pseudo scents and NESTT) were inconsis-

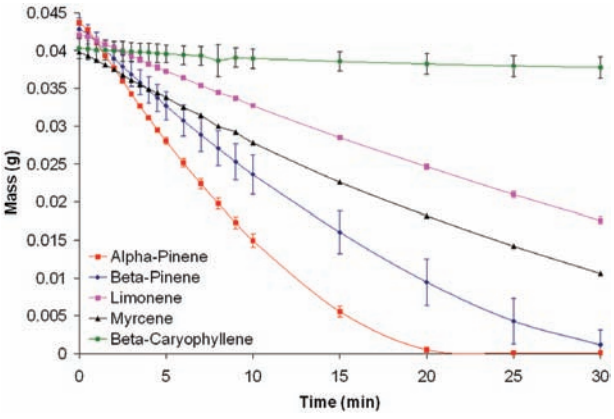

Figure 1 Dissipation study results.

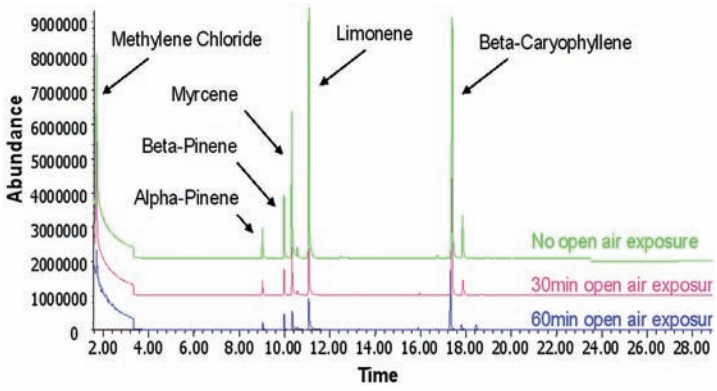

Figure 2 Chromatograms showing decrease in intensity over time of compounds spiked onto gauze.

tent with those of the trained and certified detector dogs. None of the pseudo aids was reliably detected. This may stem from the fact that many of the commercial aids use components that do not create the same volatile odor compounds as the contraband parent compounds.

Further analysis of parent compounds using SPME-GC-MS is taking place to more accurately isolate and identify the volatile odor components used by detector dogs to identify contraband. The applicability of smokeless powders as mimics for high explosives is being investigated. Additional field studies are underway to help improve the permeation devices currently being researched. This should allow for the creation of better training aids that are safer, easier to acquire, and more consistent than those currently available. Overall, this will lead to improvements in the performance and standardization of biological and instrumental standoff detection of targets.

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