TECHNICAL NOTE

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Evaluation of Canines for Accelerant Detection at Fire Scenes

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ABSTRACT: In recent years, canines have been successfully used in fire investigations to detect accelerant residues. We set out to determine the lower limits at which canines could reliably detect potential accelerants. Measured amounts ranging from 10 to as little as 0.01 μL of gasoline, kerosene, and isopars were applied to preselected spots along a continuous sample path (25 to 40 feet long) made out of burned and unburned wood or nylon carpeting strips at the testing site. Two canines were led past this sample path at least three times and positive alerts and negative responses were recorded. Both dogs were generally able to alert on spots containing 0.01 μL or more of all three accelerants, at or beyond the purge and trap recovery and gas chromatographic detection method employed. The canines did alert occasionally on background, especially that containing traces of styrene residues, either purposely added in specific amounts or formed upon partial pyrolysis of carpeting material. The dogs alerted on sites containing 0.1 to 1.0 μL of freshly applied gasoline or kerosene placed at actual heavily damaged fire scenes, but were less successful on samples containing smaller amounts.

KEYWORDS: criminalistics, canines, fire scenes, accelerants

Background

Dogs have been used for some time by law enforcement agencies for detecting drugs and explosives [*1*,*2*]. Their keen sense of smell is legend, leading to their use for many

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other detection purposes as well. Dogs have only been used in helping to detect potential accelerants at fire scenes, however, since the mid 1980s when a group of ATF scientists were able to establish that a canine could be conditioned to respond to odors of petroleum products and could, to some extent, differentiate between these potential accelerants and chemicals arising from background [*3*].

Intensive training of canines (mostly with Labradors) for this purpose was undertaken by the Connecticut State Police Canine unit [*3,4*] the Maryland State Fire Marshall's Office [*5*] the New York State's Office of Fire Prevention and Control [*6*], the Atlantic City Police Department's Arson Detection K-9 Program [*7*] and others. The training programs generally involved teaching the dogs, each of which was paired with an investigator, to recognize the odors of potential accelerants using either play, praise, food, or combinations for reward. The dogs were subjected to determining these odors in the presence of distractions such as burned foam backing, burned Styrofoam cups, burned asphalt siding, and other potential fire scene background under a variety of weather conditions.

Canines have now been successfully used in actual fire investigations in many parts of the country. Trainers have estimated that the dogs have saved many staff hours in fire-scene investigation by accurately pinpointing accelerant residues, which in some cases would not have readily been found. A number of reports have suggested that the dogs noses are anywhere from 200 to a billion times more sensitive than the human nose [*2*] and equal or superior to electronic sniffers [*3,6,7*] and even laboratory gas chromatographs [*4,8*]. This latter claim seems to be a point of contention among investigators and forensic scientists. Furthermore, even though canines supposedly are trained to discriminate between background substances and petroleum products, some dogs in this area have been indicating on some samples in which the crime labs have only been able to detect background substances. In light of this, we set out to determine the sensitivity of two canines to petroleum residues (detection limits), and to compare this with the ability of the laboratory to recover and detect petroleum residues by purge and trap and passive diffusion recovery techniques coupled with gas chromatography using a flame ionization detector (GC-FID). In addition we wanted to determine how well canines can distinguish between common petroleum product accelerants and background interference from typically formed pyrolysis products (for example, styrene).

Experimental Procedure

Canine Training

The two dogs used in this study were Watson, a male black Labrador belonging to BG, and Tracer, a female yellow Labrador belonging to DT, both of the Illinois State Fire Marshall's Office. They were trained by the Maine State Police using a combination of food and praise reward for each positive response. Verbal correction was given in lieu of food and praise for incorrect responses. On a day to day basis each positive alert on a petroleum product is rewarded by two to three kiblets of food until the dog's full food supply for the day is accomplished. Scent discrimination training is also part of this program, as the dogs were trained to ignore odors from polystyrenes, nylon, food, foam backed carpeting (burnt and unburned), pine, spruce, and hemlock wood (burnt and unburned). Once a year, the dogs and their trainers returned to Maine for testing and recertification. In addition, some scent discrimination testing was carried out by the trainers with their dogs at least once a month.

Field Testing

Two types of field testing procedures are described. The first consisted of using carpet squares (burnt and unburned) doped with various amounts (from 0.25 to 25.00 μL) of accelerant. In one set of tests, accelerants in carbon disulfide solutions were used to dope samples, but this method was eliminated when it was found that the solvent alone could elicit a positive response from the dogs. In some cases, carpeting treated with larger amounts of accelerant was partially burned and then allowed to sit open in the laboratory until just trace levels of hydrocarbons remained (as determined by processing and GC analysis of a portion of the carpeting). Both types of samples, along with unburned and burnt carpet square controls containing no accelerant but some detectable background, were then sealed in metal cans and transported to the field testing site. At the testing site, the samples (including some blanks) were removed from the cans and placed in front of them. The canines were led near the samples and commanded to "seek" by their trainers, who were not aware of which samples contained petroleum products. If the dogs alerted by sitting and pointing to the sample, they were rewarded with food, and a positive response was recorded. If they ignored the sample, a negative response was recorded. The dogs were led past each carpet square at least three times. The samples were then sealed in cans and returned to the lab for GC analysis.

When it appeared that the canines were becoming conditioned to alert on the carpet squares themselves, including a few blanks and those containing styrene only, a different procedure was developed. This alternate method was employed for the majority of the field testing, primarily that with the lesser amounts of petroleum products. The revised protocol consisted of first assembling a continuous sample path (25 to 40 feet long) of burned and unburned wood and carpeting strips at the testing site. Varying amounts of accelerant were then applied to preselected spots out of sight of the canine and trainer, and the dogs were led along the strip at least three times, with all positive and negative responses recorded as before. At four actual fire scenes, visited five hours to two weeks after fire suppression, measured amounts of 50% evaporated gasoline and kerosene were applied at selected sites, known to be free of accelerants, and the canines were worked over the scene. Samples were cut out from all sites at which the dogs alerted, as well as any other spots at which accelerant was applied. They were sealed in mason jars, and analyzed by GC in the laboratory.

Laboratory Analysis

In the laboratory the carpet or wood samples were first subjected to a purge-trap sampling technique using a heated nitrogen sweep [*9*] to remove any hydrocarbons from the sample matrix and concentrate them onto a small column containing activated charcoal. Earlier testing in our laboratory had shown the recovery by this method on measured small amounts of petroleum products to be virtually the same as the active vacuum purge and trap method [*10*] used by the Illinois State Crime Lab for actual case analyses (Table 6). Alternatively, a small bag containing charcoal was suspended in the sealed sample can for 24 hr, then the charcoal transferred to a small column (tube) [*11*]. (After comparing recovery methods [Table 2] all later testing was done with this passive diffusion headspace technique.) In either case the charcoal-containing tube was then flushed with carbon disulfide and the volume of carbon disulfide eluate adjusted to 0.1 mL. A sample (0.2–1.0 μL) was injected onto a Hewlett-Packard 5840 or 5830 gas chromatograph equipped with flame ionization detectors and Supelco SPB-1 30 m × 0.53 mm fused silica columns, 1.5 μm film thickness. The helium carrier gas flow was set at 20 cc/min and the column oven was programmed at from 50 to 200°C at a rate of 10°/min after an initial time of 3 min. The chromatograms were rated according to the following "semiquantitative" method devised by our group:

GC Analysis of Test Samples—Rating Scale

+++ readily detectable, off scale even at attenuation of 2^6 [corresponds to > 800 ng of petroleum product, actually injected]

++	detectable, main peaks on scale at attenuation of 2^5 or 2^4 [corresponds to about 200 to 800 ng of petroleum product actually injected]
−+	barely detectable, need attenuation of 2^3 to see a minimum of five peaks[a] (or only detectable after concentration of eluate to less than 0.02 mL) [corresponds to about 40 to 200 ng of petroleum product actually injected]
?	inconclusive; either trace levels (less than 40 ng) of petroleum product and/or significant background interference
−	No evidence of accelerant pattern

[a]For example, the five-peak grouping of C_9 alkylbenzenes and a few C_{10} alkylbenzenes had to be discernible for gasoline and at least five consecutive n-alkane peaks between C_{10} and C_{15} had to be seen for kerosene [*12*].

Results

Gasoline (50% evaporated) was applied in amounts ranging from 10 μL down to 0.01 μL to a wide variety of matrices. Generally unburned nylon carpeting was used, but some was applied to fresh wood and some to heavily scorched carpeting or wood. The testing was done in multiple sessions over a 16 month period with a limit of ten samples per session. The dogs were readily able to detect gasoline at levels down to and including 0.01 μL, although in nearly all cases involving samples of less than 1.0 μL gasoline, their responses were not unanimously positive (Table 1). In general, positive GC identification of the petroleum product used in the field exercise samples was successful at levels down to 0.25 μL. At lower levels many of the samples were either questionable or negative upon GC analysis.

Field tests were performed at heavily damaged fire scenes at which petroleum product accelerants had not been used. Partially evaporated gasoline was applied at levels ranging from 0.02 to 1 μL at selected spots at the scene, and the dogs were worked over the general area. The canines had an excellent positive alert record with samples containing as little as 0.1 μL but were not as successful at lower levels (Table 1).

A series of experiments were performed to determine the charcoal adsorption recovery and GC detection limits for this type of sample. Quantities of 50% evaporated gasoline, kerosene or isopars (either neat or as 5% solutions in carbon disulfide) were placed on four small carpet squares. Two were immediately sealed in jars, and processed by the purge and trap and the static headspace diffusion methods, respectively, prior to analysis by GC. The other two were allowed to stand in the open for an hour (to simulate the approximate time of exposure during routine field tests) and then processed in the same fashion as above. The results, shown for gasoline (Table 2), indicate that the limits of detection for samples processed immediately seem to be approximately 0.01 μL using the passive diffusion method with an elution volume of 100 μL and sample injection size of 0.5 μL. (This would correspond to about 50 ng of product injected assuming complete recovery in the sample collection process). A slightly higher amount (0.025 μL) was needed for detection using the purge and trap technique. For samples exposed to the atmosphere for an hour, the minimum detectable levels of gasoline rose to about 0.025 μL in both cases. Similar results were observed with kerosene and isopars.

Kerosene was applied in amounts ranging from 25.0 μL to 0.01 μL in the same manner as gasoline for field testing with the canines (Table 3). Both dogs performed well on all levels tested, maintaining a very high positive alert performance all the way down to 0.01 μL. GC analysis was only consistently successful on samples containing a minimum of 0.5 μL.

A product consisting of isopars was applied in amounts ranging from 5.0 μL to 0.01 μL in a manner similar to the revised protocol. The dogs were able to detect this mixture at levels down to 0.025 μL, but their performance was not as consistent at levels below

TABLE 1—*Gasoline field test results.*

Quantity (μL)	Sterile environments: Trial 1[a] W	T	GC[b]	Trial 2 W	T	GC[b]	Trial 3 W	T	GC[c]	Overall Alerts	Typical GC	Fire scenes: Trial 1 W	T	GC[c]	Trial 2 W	T	GC[c]	Overall Alerts	Typical GC
0.01	+	+	?[c,d]	+	Y	−[c,d]	Y	Y	−	24 of 30	?								
0.02	Y	Y	+[c,e]	−	+	Y[c]	N	N	−	21 of 30	+	−	+	−	N	−	−	4 of 12	−
0.05	Y	Y	−[c]	+	Y	?	+	Y	+	28 of 30	−	+	+	−[d]	N	+	?[d,f]	13 of 25	?
0.10	Y	Y	−[d]	−	Y	?[e]	Y	+	−[g]	25 of 35	?	Y	Y	−[e]	+	+	−[h]	26 of 30	−
0.25	Y	Y	−	+	+	+	+	+	+	14 of 18	+	Y	Y	+[d]	+	+	?[d]	18 of 23	+
0.50	+	+	+	+	Y	+				9 of 12	+	−	+	+	+	+	?	5 of 10	+
1.0	Y	+	+							5 of 6	+	Y	Y	+[b,i]	+	+	+	18 of 20	+
2.0	+	+	+	Y	Y	+				10 of 12	+								
5.0	Y	Y	++							6 of 6	++								
10.0	Y	Y	+++							6 of 6	+++								

[a]Y means unanimous positive responses (for example, three positive alerts on three passes); + means preponderance of positive responses (for example, two positive alerts on three passes); − means preponderance of negative responses (non-alerts); N means unanimous negative responses (nonalerts); W = Watson, T = Tracer.

[b]Used active purge and trap recovery (see GC rating scale and Table 2).

[c]Used passive diffusion recovery (see GC rating scale and Table II).

[d]Same result on two different test samples.

[e]Same result on three different test samples.

[f]Additional test: W−, T−;

[g]Additional tests: W+, T−; W−, T−.

[h]Additional test: W−, T+.

[i]Same results on four different test samples.

TABLE 2—*Recovery and GC detection limits for gasoline.*[a]

		Passive Diffusion Recovery[b]		Active Purge & Trap[b]	
		GC Analysis[c]		GC Analysis[c]	
Amount	Applied	Immediate	1 H Exposure	Immediate	1 H Exposure
0.100 μL	neat	+++[c]		+++	
0.100 μL	CS_2	+++	++	++	++
0.050 μL	neat	++		+	
0.050 μL	CS_2	++	++	+	+
0.025 μL	neat	++		++	
0.025 μL	CS_2	++	+	+	+
0.010 μL	neat	+		+	
0.010 μL	CS_2	+	?	?,+	−
0.0075 μL	CS_2			−	
0.005 μL	CS_2	?	−	−	−
0.001 μL	CS_2	−	−	−	−

[a]Gasoline (50% evaporated) added to pieces of nylon carpeting.
[b]See experimental for details.
[c]See GC Rating Scale in text.

TABLE 3—*Kerosene field test results.*

Sterile Environments								
Quantity (μL)	Trial 1[a] W	Trial 1[a] T	Trial 1[a] GC[b]	Trial 2 W	Trial 2 T	Trial 2 GC[b]	Overall alerts	Typical GC
0.01	Y	Y	?	−	Y	?	10 of 12	?
0.025	+	Y	?	+	Y	?	10 of 12	?
0.10	+	Y	−	+	Y	−	10 of 12	−
0.25	Y	Y	−				6 of 6	−
0.50	−	Y	+	Y	Y	+	10 of 12	+
1.00	−	+	+	Y	Y	+	9 of 12	+
2.00	−	+	++	Y	Y	+	9 of 12	+
5.00	+	+	+	Y	+	++	9 of 12	+
25.00	Y		+++				3 of 3	+++

Fire Scenes								
Quantity (μL)	Trial 1 W	Trial 1 T	Trial 1 GC[c]	Trial 2 W	Trial 2 T	Trial 2 GC[c]	Overall alerts	Typical GC
0.1	N	Y	+	−	Y	−	5 of 8	+
0.25	Y	Y	+	Y	+	+	10 of 11	+
0.5	+	+	+	Y	−	+	6 of 9	+

[a]Y means unanimous positive responses (for example, three positive alerts on three passes); + means preponderance of positive responses (for example, two positive alerts on three passes); − means preponderance of negative responses (nonalerts); N means unanimous negative responses (nonalerts); W = Watson, T = Tracer.
[b]Used purge and trap recovery (see GC rating scale and Table 2).
[c]Used passive diffusion recovery (see GC rating scale and Table 2).

0.01 μL as it was with kerosene (Table 4). Only samples containing at least 0.1 μL of the isopars were consistently detectable during the GC analysis.

A mixture of styrene and methylstyrene, major components typically formed upon pyrolysis of carpeting materials, were also spotted on carpeting materials as before at levels

TABLE 4—*Isopars product field test results.*

Quantity (μL)	Trial 1[a]			Trial 2			Trial 3			Overall Hits	Average GC
	W	T	GC[b]	W	T	GC[b]	W	T	GC[c]		
0.01	–	Y	–	–	Y	–	N	Y	–	11 of 18	–
0.025	Y	Y	–	+		–	+	Y	–	13 of 15	
0.05	+	+	?	+	+	?				8 of 12	?
0.10	+	–	–	+	Y	+	+	Y	–[d]	23 of 30	+
0.25	Y	Y	+	Y	Y	+				12 of 12	+
0.50	+	+	+							4 of 6	+
1.00	+	Y	++	+	+	+				9 of 12	+
2.00	–	–	++	Y	Y	+				8 of 12	+
5.00	Y	Y	+							6 of 6	+

[a]Y means unanimous positive responses (for example, three positive hits on three trials); + means preponderance of positive responses (for example, two positive hits on three trials); – means preponderance of negative responses (nonalerts); N means unanimous negative responses (nonalerts); W = Watson, T = Tracer.
[b]Used purge and trap recovery (see GC rating scale and Table 2).
[c]Used passive diffusion recovery (see GC rating scale and Table 2).
[d]Trial 4: W –, T Y, GC +; Trial 5: W Y, T Y, GC +.

ranging from 10 to 0.01 μL. The canines alerted on these samples in a relatively sporadic fashion (Table 5). This may have been because although both were receiving bimonthly training to ignore the styrene background odor, they still had not perfected this scent discrimination. Both dogs also alerted on about half of six burnt carpeting samples not containing petroleum products, but shown by GC analysis to contain styrene and other background components.

During this time period the fire marshals submitted samples from 10 actual fire scenes on which the two canines had been worked and had positively alerted. These were processed and analyzed at the Crime Lab using a purge and trap method [*10*]. Identifiable petroleum products were detected in approximately 40% of these samples while another 45% gave only background terpenes or substances from partial pyrolysis of polystyrene or polyethylene.

Discussion

The dogs seem to be able to detect gasoline in a majority of the tests performed at levels at and even below the limits of recovery and GC-FID detection for gasoline by our system.

TABLE 5—*Styrene field test results.*

Quantity (μL)	Trial 1[a]			Trial 2			Overall Alerts	Typical GC
	W	T	GC[b]	W	T	GC[b]		
0.01	+	+					4 of 6	–
0.025	–	Y	+	–	Y	+	8 of 12	+
0.10	–	Y	+	–	Y	+	8 of 12	+
0.50	+	Y	++	Y	Y	++	11 of 12	++
1.00	–	+	+++	Y	Y	++	9 of 12	++
5.00	+	Y	+++	N	N	+++	5 of 12	+++
10.00	–	–	+++				2 of 6	+++

[a]Y means unanimous positive responses (for example, three positive alerts on three passes); + means preponderance of positive responses (for example, two positive alerts on three passes); – means preponderance of negative responses (nonalerts); N Means unamimous negative responses (nonalerts); W = Watson, T = Tracer.
[b]Used purge and trap recovery (see GC rating scale and Table 2).

TABLE 6—*Crime lab results on samples from fire scenes on which dogs gave positive alerts.*[a]

Case	Dog	# of exhibits	Types of debris	Lab result
1	T	1	Burned wood & debris	Inconclusive
2	?	4	Burned wood	Terpenes present
		1	Liquid	HPD[b] present
3	T	1	Unidentified debris	HPD[b] present
4	?	1	Burned foam rubber padding	Gasoline present
5	?	3	All burned carpeting & padding	3 styrene & terpenes present
6	T	1	Burned carpeting & padding	Gasoline present
7	W	2	Both burned wood	Terpenes present
8	W	1	Burned, melted plastic	Gasoline present
9	?	3	Unidentified burned debris	1 toluene 1 styrene 1 polyethylene
10	W	5	All burned carpeting	4 HPD[b] present 1 inconclusive

[a]These 10 cases were processed between 6/92 and 3/93.
[b]HPD = heavy petroleum distillates.

This level was as low as 10^{-2} μL (about 10 μg) of gasoline under pristine conditions, but higher under more realistic fire scene conditions (0.1 μL). The dogs were nearly as sensitive to kerosene and isopar residues (10^{-2} μL with pristine samples), even though they have been primarily trained on gasoline.

Extension of this study to even lower levels of accelerant is difficult to accomplish without using solutions of the accelerant. However, application of petroleum products in a solvent would introduce further complications (that is, the dilemma of whether the dogs alerted on the solvent or the petroleum product therein). Furthermore, most of the common solvents can be potentially harmful for the canines [*13,14*]. An earlier study reported that their canine could detect as little as 10^{-6} μL (about 1 ng) of gasoline, but these samples were applied as solutions in carbon disulfide [*8*]. While we cannot rule this out, we feel that a more realistic, practical lower detection limit on which the canines can alert most of the time is on the order of 0.01 to 0.1 μL of accelerant. From a practical standpoint, this small amount represents levels that lead to inconclusive findings by laboratories and questions about the possibility of cross- or other contamination being responsible for their presence; accelerants found at most scenes are usually present in significantly greater quantities.

The canines successfully alerted on a substantial number of samples, subsequently shown to contain petroleum products by the State Crime Lab. However they also hit on a fair number of samples on which only background components were detected. While this could be because the dog's detection limits may exceed that of the recovery-gas chromatographic analysis method, it may also be due to some problems in being able to distinguish accelerants from certain types of background. During our control studies we found that the canines alerted on a few samples of charred carpeting, which contained low levels of pyrolysis products only. They also hit quite frequently on samples spiked with styrene, one of the more commonly found, major components of partial pyrolysis of many household materials. While this was particularly true in the earlier stages of the study, it should be noted that the dogs actually improved with respect to ignoring styrene later on, as their handlers redoubled their efforts to train them off of that substance.

Finally, a few cautions are in order concerning the reliability of the quantitative aspects of this study, which involved using animal responses.

1. This type of study required subjective judgments as to what constituted a positive alert. Though most canine alerts on materials spiked with petroleum products were very solid, some were half hearted, as the dogs had some days on which their performance was not up to par. On occasion, the dogs would seem to alert on samples that were blanks, but could be called off some of them by their trainer. On warm days, the dogs became less effective as they started panting.

2. The results of the field tests can be influenced by the sampling protocol. There was an observed tendency on the part of the dogs to alert on nearly all isolated, widely separated samples, once they became conditioned to this earlier field testing method. This problem was largely corrected by making the application sites less obvious.

3. Not all canines are equally adept. Certainly there are some canines who exhibit greater sensitivity and/or discriminatory powers than the pair involved in this study, just as there are canines with lesser capabilities. Though the dogs in this study appeared to be very typical and representative based on their performances at annual certification exercises conducted by their trainer in Maine, caution should be exercised in extrapolations of these results to other canines in the field.

Even with some tendency hit on background materials, canines are most decidedly a welcome addition to fire investigators for simplifying accelerant detection at fire scenes. Those dogs with better discriminatory powers will prove to be even more valuable. Nonetheless, gas chromatographic analysis by the laboratory of samples on which canines alert should still be an important part of the overall investigation, even if the lab tests do not always confirm what the canines indicate.

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