

Article

Measuring Odor Transport of Narcotic Substances Using DART-MS

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Abstract: The employment of canines in matters of law enforcement is due to their heightened olfactory senses, which helps in evaluating the presence of illicit substances. However, there have been instances where canines are signaling the presence of narcotics when they are not there. This study aimed to analyze how active odorants transport from one area to another. Direct Analysis in Real-Time coupled to a high-resolution mass spectrometer (DART-MS) was used to analyze, in real-time, the volatile organic compounds (VOCs) of two narcotic substances: cocaine and methamphetamine. This study found that the transfer of VOCs from these narcotics does occur. Methyl benzoate was detected at 39.3 ± 3.2 s after exposure from 3 meters away, whereas benzaldehyde was detected at 43.3 ± 0.6 s from the same distance. The guidelines used for canine certification should be revisited to account for these results to lower or eliminate unconfirmed alerts by canines.

Keywords: canine; direct analysis in real time; mass spectrometry; time of flight; methyl benzoate and benzaldehyde



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1. Introduction

Canines have a highly developed olfactory system. This allows them to be an asset to different organizations [1]. Canines are employed and trained for detection in various capacities, such as the location of human remains, search and rescue missions and detecting illicit materials [1]. The primary focus of this study is illicit substances. It is hypothesized that canines alert to the discharged odor of the illicit substance, and not the physical illicit substance itself—as is the case with cocaine and its active odorant, methyl benzoate [2–5]. Currently, in routine traffic stops, many law enforcement teams have the aid of trained canines to alert if illegal substances are present. The fourth amendment has been brought up many times regarding whether it is an infringement upon an individual's rights for these searches to occur. This has gathered both media attention and the attention of the courts. Several issues have been raised as a result of canines making alerts to areas where narcotic substances were either not present, or were no longer present, and these require further study.

The inspiration behind this study also came from a canine certification session. In Miami, Florida, canines were escorted by handlers through a series of boxes to see if they could indicate which boxes contained illicit substances. In the series, one blank box caused more than half of the training canines to alert to an odor. The canines were alerted by the second-to-last box. The contents of the box should not have caused an alert; however, it was in close proximity to a box that would. The last box contained a kilogram of cocaine. During the certification course, it was only this scenario that an empty box prompted

unconfirmed alerts of that quantity. The hypothesis then was that the odors transported, or travelled, from one box to another, which led to the multiple unconfirmed alerts.

Canine detection has been misinterpreted in regard to routine vehicle stops. The thought is that the illicit substance is being identified by the canines. In actuality, the canine is being alerted to an odorant, or VOC, that is emitted into the surrounding area [6]. For example, the actual cocaine molecule is not causing an alert in the canine. The actual alert is generated by methyl benzoate, a volatile cocaine byproduct [7]. The active odor signature is a chemical within a sample that causes a trained and certified canine to be alerted [8]. Multiple drugs have been recognized and identified this way, including methylenedioxy methamphetamine (MDMA), methamphetamine, and cocaine [3,9–11]. Since these are volatile substances, an attempt should be made to study them in real time using instrumentation that does not require the trapping of said volatiles or the need for a pre-concentration step. Direct Analysis in Real Time coupled to an Accurate Time-of-Flight Mass Spectrometer (DART-MS) is an instrument with ambient, soft ionization that allows for the introduction of samples in many forms (solids, liquids, and gases) directly and with little-to-no sample preparation [12]. It has been validated to analyze inks, explosives, accelerants, fragrances, polymers, and various controlled substances [13–23]. The capability to test samples in real time without pre-concentrating the specimen makes this type of research ideal to test with the DART. When held at a certain distance and sampled directly into the instrument stream, the DART can effectively interpret the headspace of volatile organic compounds (VOCs) [24]. Therefore, the DART could likely interpret these same VOCs when held at various distances. This study focuses on cocaine and methamphetamine, which are two of the narcotics people most often misuse and which are encountered most often by law enforcement [25]. As mentioned before, the active odorant for cocaine is methyl benzoate and the active odorant for methamphetamine is benzaldehyde [7,11].

2. Experimental

Approximately 5 mL of methyl benzoate and benzaldehyde, purchased from Sigma-Aldrich, Inc. (St. Louis, MO, USA), were stored separately in 20 mL disposable scintillation vials (Kimble Chase, Vineland, NJ, USA). The Direct Analysis in Real Time (DART) ion source (IonSense, Inc., Saugus, MA, USA) connected to an AccuTOF™ time-of-flight mass spectrometer (JMS-T100LC, JEOL USA, Peabody, MA, USA). Data collection and analysis were completed using JEOL MassCenter software (v1.3.4m). A 2 mg/mL solution of polyethylene glycol in methanol (PEG 600) was used for exact mass calibration. Calibration was performed by dipping the bottom end of a melting point tube (Kimble Chase) into the PEG 600 solution and “wandering” the bottom end of the melting point tube within the sample gap for a few seconds. Each data file of all samples collected would contain a calibration curve developed from the PEG 600.

First, data analysis occurs with ‘translating’ the data file in TSS Pro 3.0 (Shrader Analytical and Consulting Laboratories, Inc., Detroit, MI, USA). Before the calibration process, the area in the Reconstructed Ion Chromatogram (RIC) before the PEG peaks was completed by selecting the ‘perform background subtraction’ option. Following that, high-quality RIC profiles are extracted by choosing the button above RIC. It will conduct ‘CODA’ (Component Detection Algorithm), which converts complex data sets to a more straightforward interpretation. Next, the total data file was calibrated. This was performed by taking the average of the PEG peaks. After that, the mass spectrum was created. This was completed by recording the intensity and average of every peak in the RIC in a spreadsheet. Each sample and each run went through this exact process. In order to achieve correct identification of every peak in the spectra: the peak must be at or above 5% of relative intensity and the m/z of the analyte of interest must be within ± 5 mDa. Any peaks below 5% in the spectra were not used, and anything exceeding the ± 5 mDa range would not result in a positive identification of the sample of interest. The optimum temperature for the DART gas stream was determined to be 400 °C, and an orifice 1 voltage of 30 V was used for this study.

Two chemical standards were chosen. Each was sampled at 5 distances (0.5 m, 1 m, 1.5 m, 2 m, and 3 m). The objective was to determine the detection of the VOC samples by measuring the time it takes for the odors to transport through the distances. For this reason, during each run, a timer was used to note the moment the vial cap was opened. Each run involved the following steps: (1) begin sample run while simultaneously turning timer on; (2) sample PEG calibrant in triplicate; (3) open vial at specific distance away from the ion source while simultaneously pressing “lap” to mark the exact time the vial was moved; (4) hold vial open for two minutes; (5) cap the vial and simultaneously record moment vial was closed; and (6) directly sample the headspace of the sample vial (positive control). Each sample at each distance was performed in triplicate.

3. Results and Discussion

3.1. Methyl Benzoate

The first trial test of methyl benzoate can be seen in Figure 1. It shows the RIC (after performing CODA) at a distance of 0.5 m.

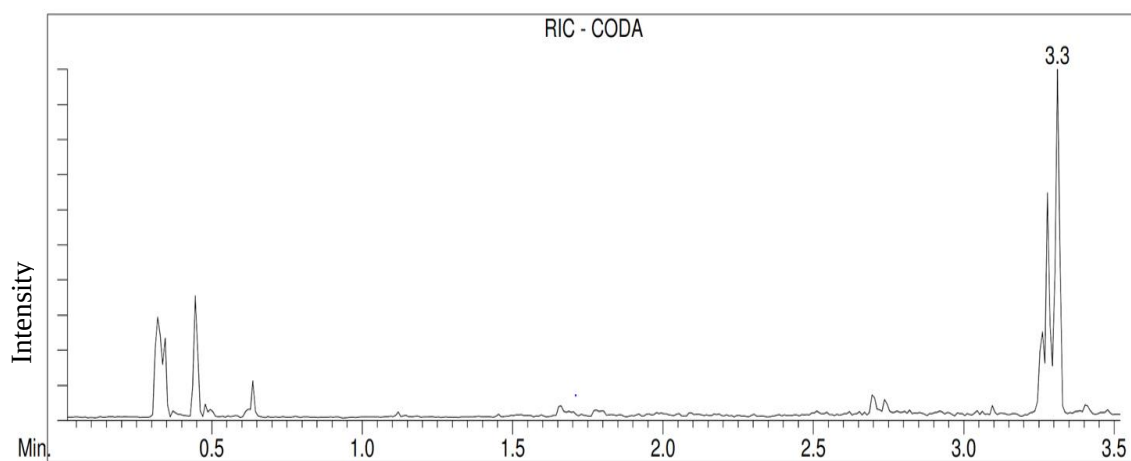


Figure 1. RIC of methyl benzoate (at distance of 0.5 m).

The PEG calibration standard peaks are the first visible peaks observed at the beginning of the RIC. At the end of each run, the positive control is directly sampled and can be seen as the last peaks in the RIC. The first detection of the methyl benzoate VOC is shown in Figure 2. This was completed by choosing the m/z of 137 ($M + H$ of methyl benzoate) then creating a RIC that will only show a response where m/z 137 was detected.

Following the creation of the RIC that shows 137 m/z responses, identifying the moment where the sample was first detected would be the next step. It is important that the observed m/z identified must be within 5 mDa of the theoretical m/z of the sample and the sample peak must not be below 5% in relative intensity.

Figure 3 illustrates the mass spectrum and ‘retention time’ (R.T.) of methyl benzoate when it was first identifiable. In this case, ‘retention time’ is technically incorrect because this is not a chromatographic technique. The software is identifying the moment when a molecule is detected. For trial #1 with methyl benzoate, the vial was opened at the 1:02 (one minute and two seconds) mark and was subsequently identified 5 s later (at 1:07 or 1.12 min). For clarity, please note that the time is both mentioned in (a) minutes and seconds and (b) minutes then fractions of a minute following a period. In trial #2 for methyl benzoate, the RICs are almost identical (Figure 4), and while the cap was opened at the same time (1:02 min), it took 8 s for methyl benzoate to be detected (1:10 or 1.18 min) as detailed in the mass spectrum in Figure 5. For trial #3 of methyl benzoate at the same distance, the cap was opened at 1:03 min and was subsequently detected after five seconds at 1:08 (or 1.13) min.

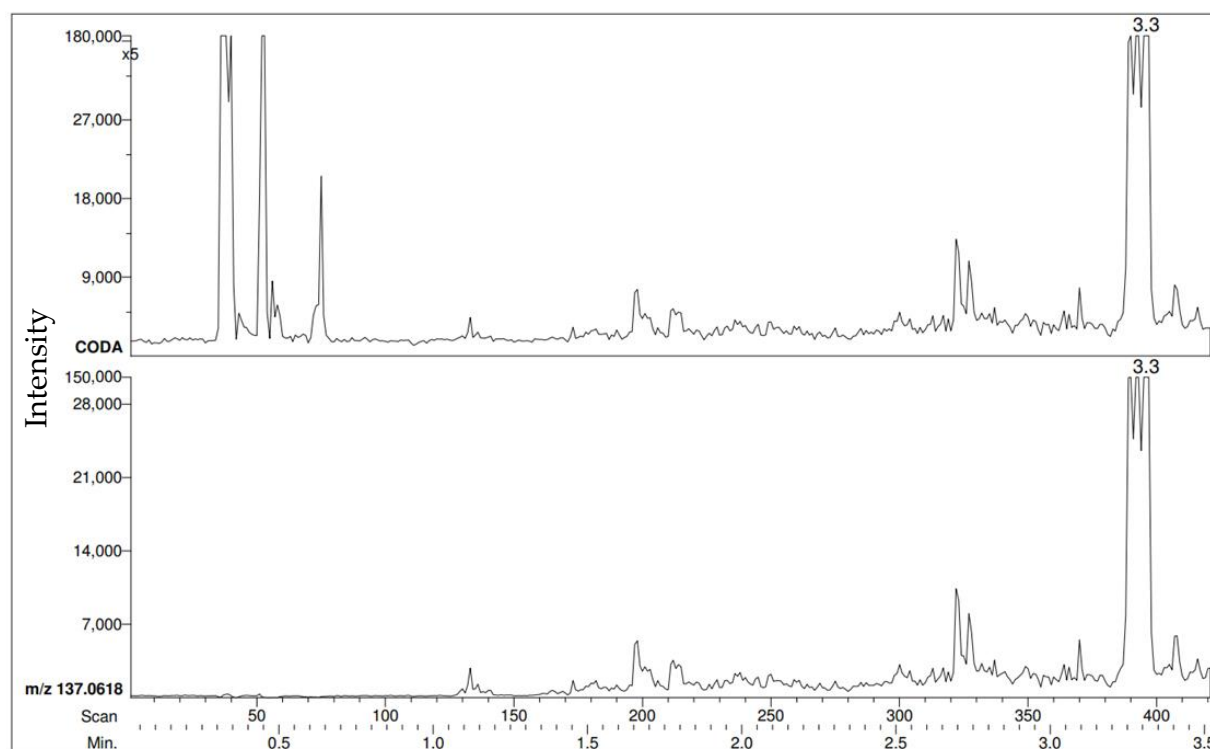


Figure 2. RIC's of methyl benzoate (at distance of 0.5 m). Top: RIC from Figure 1 after performing CODA. Bottom: RIC from Figure 1 only showing peaks where 137 m/z was detected. Cap opened at 1:02 min.

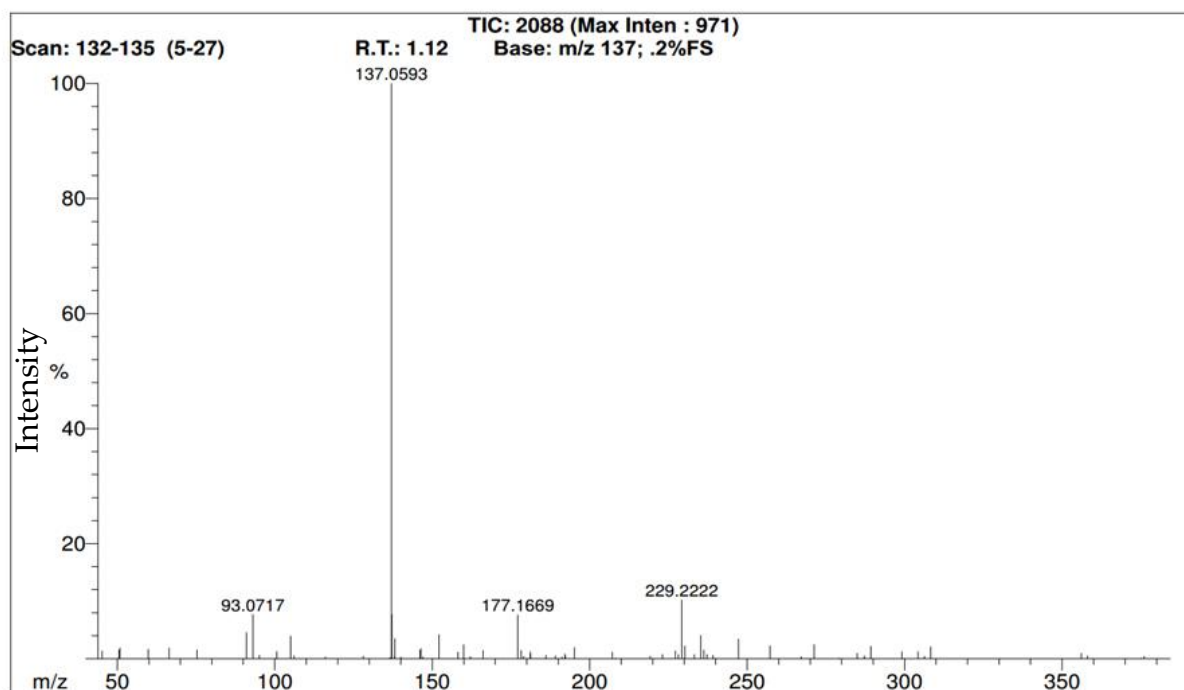


Figure 3. Mass spectrum of methyl benzoate (at distance 0.5 m), detected at (RT) 1.12 min.

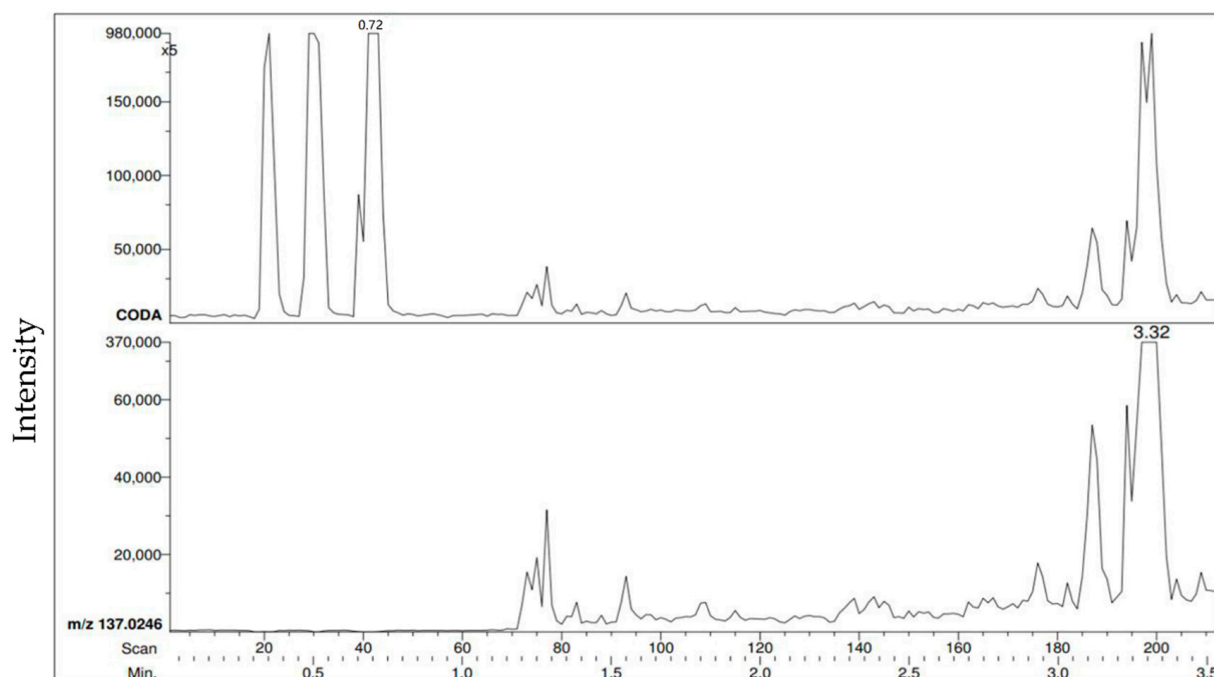


Figure 4. RIC's of methyl benzoate (at distance of 0.5 m, replicate #2). Top: RIC after performing CODA. Bottom: RIC only showing peaks where 137 m/z was detected. Cap opened at 1:02 min.

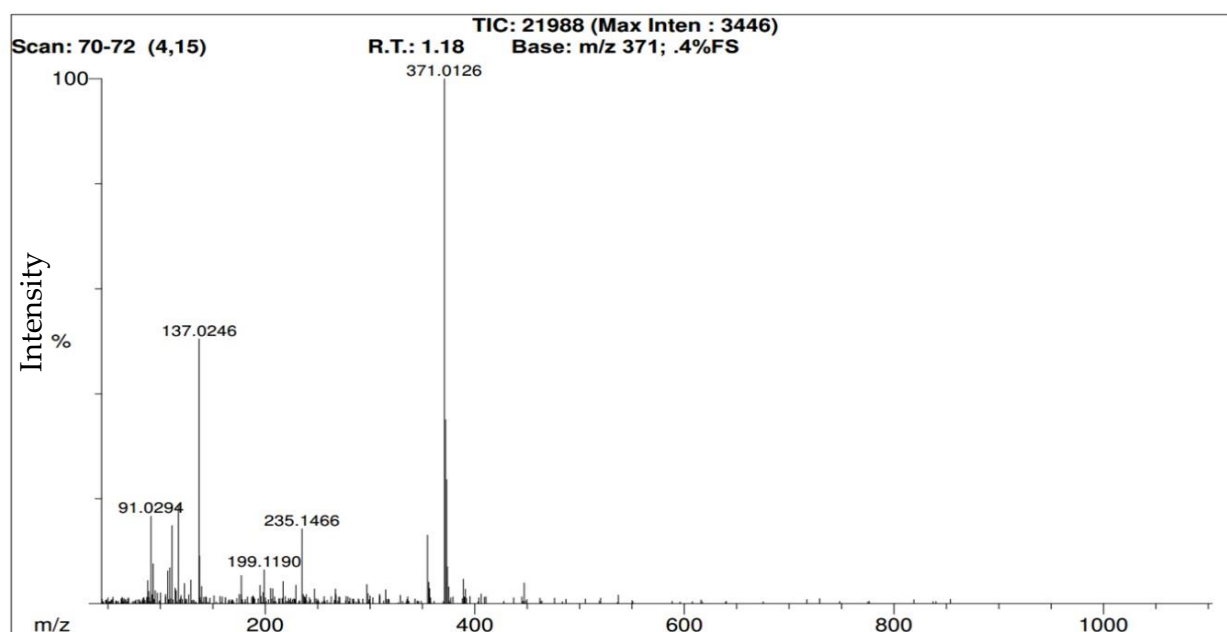


Figure 5. Mass spectrum of methyl benzoate (at distance of 0.5 m, trial #2), detected at 1.18 (1:10) min.

The results from these three trials are summarized in Table 1. Methyl benzoate was then tested at a distance of 1 m. During trial #1, the run was started and the vial cap was opened after 56 s.

Table 1. Methyl benzoate results (distance of 0.5 m).

Methyl Benzoate at Distance of 0.5 m distance of 0.5 m				
Trial	Vial Open (min)	Vial Closed (min)	Detected (min)	Time (s)
#1	1:02	3:08	1:07	5
#2	1:02	3:05	1:10	8
#3	1:03	3:06	1:08	5

The vial cap was opened for trials #2 and #3 after 1 min and 1 min and 1 s, respectively. The summary for the methyl benzoate results at a distance of 1 m is shown in Table 2.

Table 2. Methyl benzoate results (distance of 1 m).

Methyl Benzoate at 1 m				
Trial	Vial Open (min)	Vial Closed (min)	Detected (min)	Time (s)
#1	0:56	3:01	1:11	15
#2	1:00	3:03	1:22	22
#3	1:01	3:04	1:24	23

The remaining results (methyl benzoate tested at distances 1.5 m, 2 m, and 3 m) are summarized in Table 3.

Table 3. Methyl benzoate results at distances of 1.5 m, 2 m, and 3 m, respectively.

Methyl Benzoate at 1.5 m				
Trial	Vial Open (min)	Vial Closed (min)	Detected (min)	Time (s)
#1	1:04	3:08	1:26	22
#2	0:50	2:54	1:14	24
#3	1:32	3:17	1:56	24
Methyl Benzoate at 2 m				
Trial	Vial Open (min)	Vial Closed (min)	Detected (min)	Time (s)
#1	1:10	3:12	1:41	31
#2	1:01	3:04	1:30	29
#3	1:10	3:15	1:43	33
Methyl Benzoate at 3 m				
Trial	Vial Open (min)	Vial Closed (min)	Detected (min)	Time (s)
#1	1:16	3:20	1:53	37
#2	1:31	3:33	2:09	38
#3	1:09	3:12	1:52	43

As shown in Figure 6, methyl benzoate trial results are illustrated at varying distances. Error bars depict the standard deviations, and the averages of all trials were noted by plotting. As the graph shows, as the distance from the ion source increases, the time it takes to detect the sample increases.

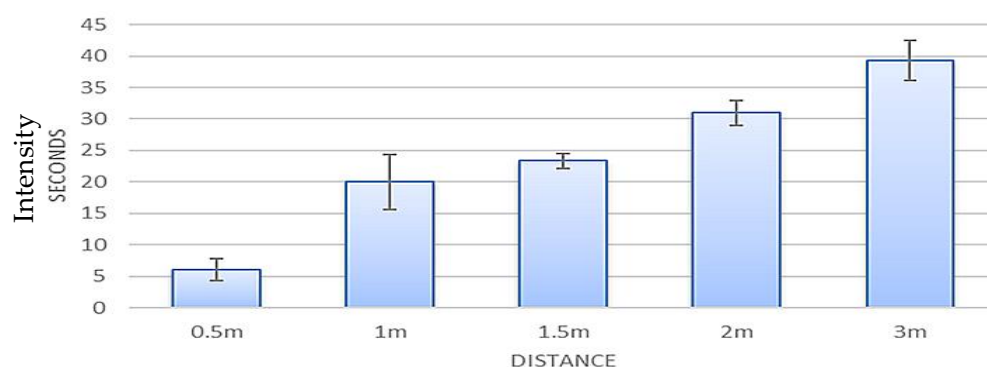


Figure 6. Averaged results ($n = 3$ for each distance) for methyl benzoate at the various distances.

3.2. Benzaldehyde

The results using benzaldehyde were comparable to methyl benzoate. In each of the trials, benzaldehyde was detected. Table 4 shows the data for benzaldehyde at various distances (from 0.5 m through 3 m). Figures 7 and 8 show an example of a benzaldehyde RIC and mass spectrum, respectively, at a distance of 2 m. As stated earlier, Figure 7 illustrates that as the time increased, the intensity of the volatiles detected also increased. In this specific example, it took 44 s for benzaldehyde to be initially detected after the vial cap was opened.

Table 4. Summary of results for Benzaldehyde at all distances.

Benzaldehyde at 0.5 m				
Trial	Vial Open (min)	Vial Closed (min)	Detected (min)	Time (s)
#1	0:57	3:00	1:00	3
#2	1:20	3:23	1:30	10
#3	0:49	2:52	0:58	9
Benzaldehyde at 1 m				
Trial	Vial Open (min)	Vial Closed (min)	Detected (min)	Time (s)
#1	0:58	3:03	1:18	20
#2	1:24	3:30	1:41	17
#3	0:56	2:59	1:20	24
Benzaldehyde at 1.5 m				
Trial	Vial Open (min)	Vial Closed (min)	Detected (min)	Time (s)
#1	1:01	3:09	1:31	30
#2	1:15	3:19	1:46	31
#3	1:21	3:17	1:51	30
Benzaldehyde at 2m (400 °C)				
Trial	Vial Open (min)	Vial Closed (min)	Detected (min)	Time (s)
#1	1:06	3:08	1:42	36
#2	1:06	3:08	1:50	44
#3	1:07	3:15	1:48	41
Benzaldehyde at 3m (400 °C)				
Trial	Vial Open (min)	Vial Closed (min)	Detected (min)	Time (s)
#1	1:13	3:17	1:57	44
#2	1:16	3:19	1:59	43
#3	1:16	3:19	1:59	43

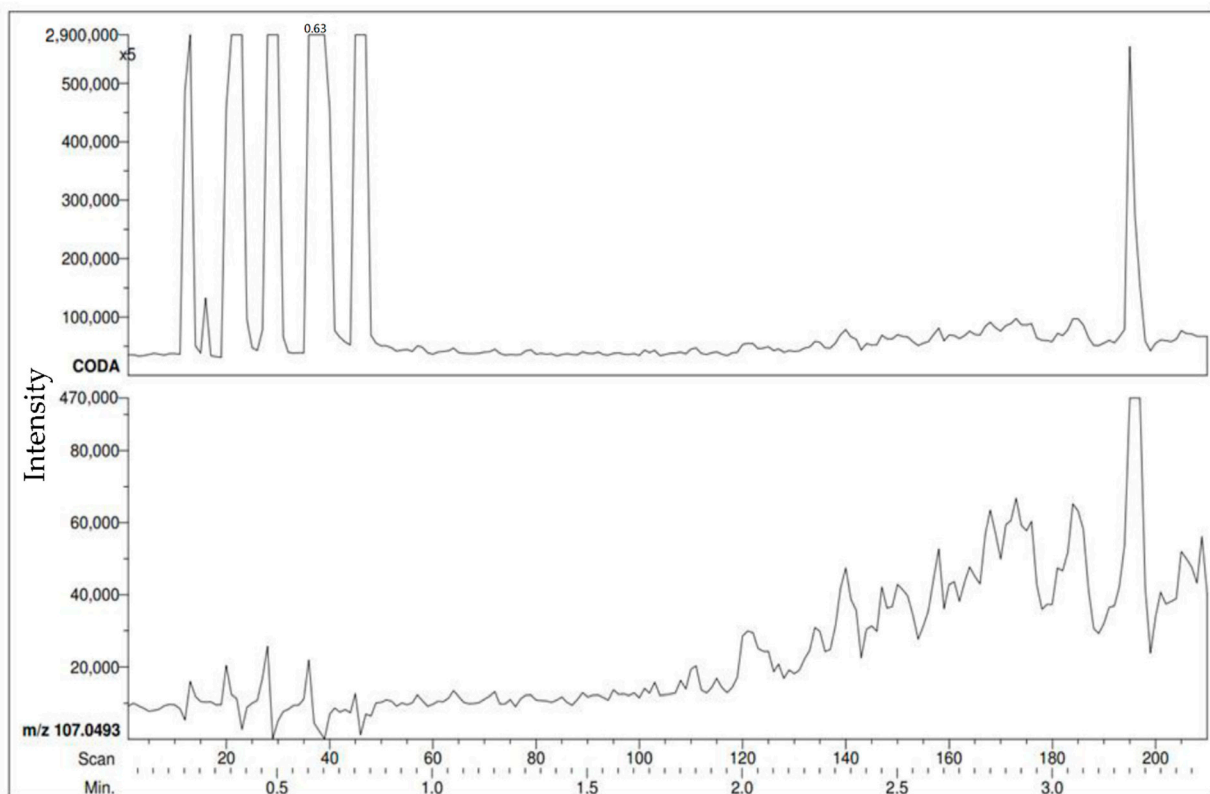


Figure 7. RICs of benzaldehyde (at a distance of 2 m (trial #2)). Top: RIC after performing CODA. Bottom: RIC showing only peaks where 107 m/z was detected. Cap opened at 1 min and 6 s (1:06 min).

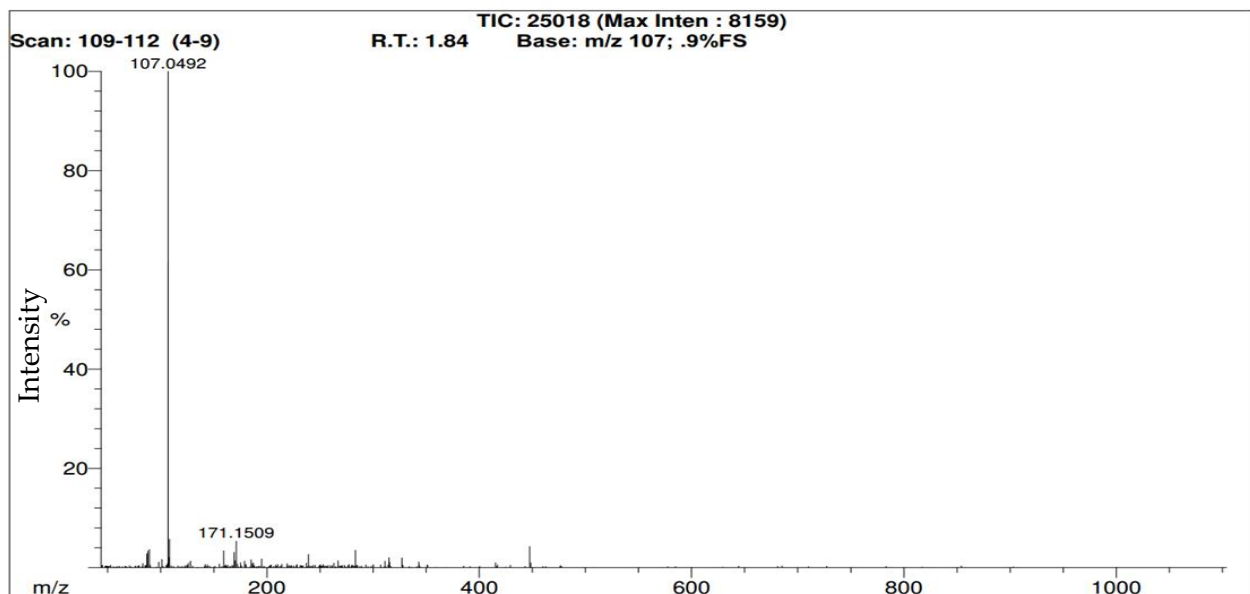


Figure 8. Mass spectrum of benzaldehyde (at distance 2 m, trial #2), detected at 1.84 (1:50) min.

The data from Table 4 was calculated by taking the average at each distance and then calculating the standard deviation, and the data are plotted in Figure 9. At 0.5 m, it took 7.3 ± 3.8 s for benzaldehyde to be initially detected; at 1 m, it took 20.3 ± 3.5 s; at 1.5 m, it took 30.3 ± 0.6 s; at 2 m, it took 40.3 ± 4.0 s; and at 3 m, it took 43.3 ± 0.6 s.

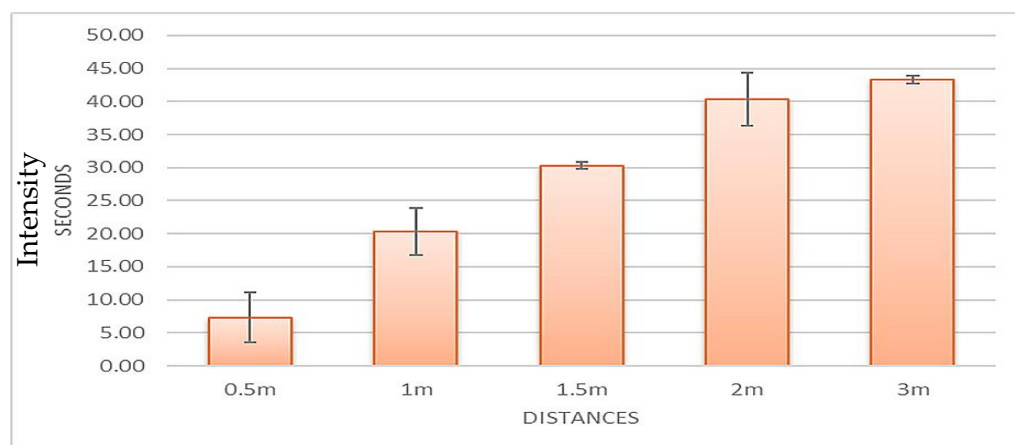


Figure 9. Averaged results for benzaldehyde at the various distances.

4. Conclusions

The primary purpose of this study was to determine if the proximity of illicit substances in an area could prompt unconfirmed alerts made by canines in training. The two narcotic odorants selected for this study were methyl benzoate (cocaine) and benzaldehyde (methamphetamine). The hypothesis of this study was supported in that specific odorants do not need substantial time to travel from one location to another. The time required for methyl benzoate to travel 1.5 m was approximately 23 s on average. Approximately 30 s were needed for benzaldehyde to travel the same distance. It is important to note that the outcomes are based on what the instrument could detect. A canine's ability to smell is more sensitive to these odors, so the values calculated in this study could serve as an upper limit; canines could presumably detect these odors sooner.

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Conflicts of Interest: The authors declare that they have no conflict of interest.

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